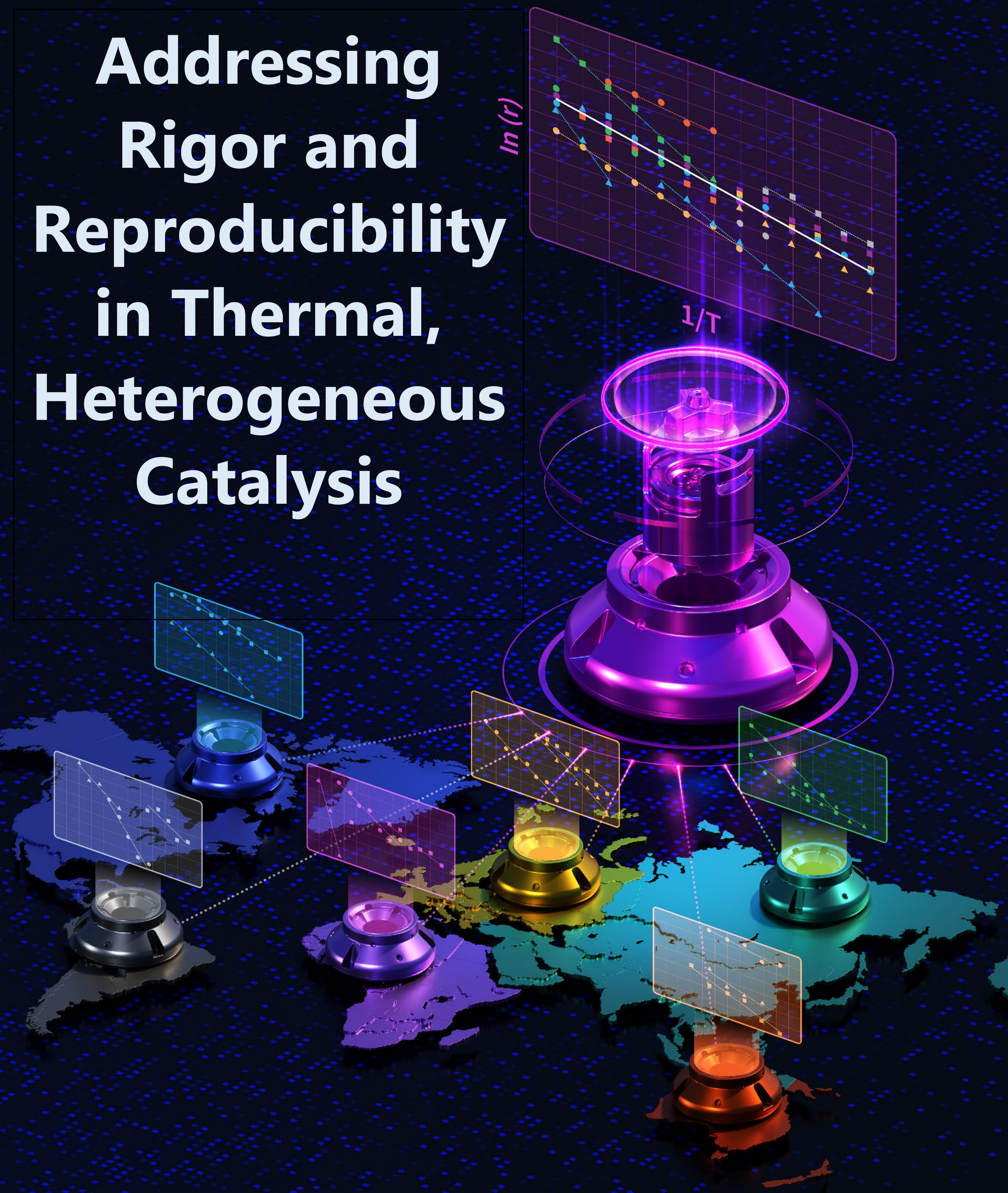
Addressing Rigor and Reproducibility in Thermal, Heterogeneous Catalysis



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Workshop Report on Addressing Rigor and Reproducibility in Thermal, Heterogeneous Catalysis

A National Science Foundation Sponsored Workshop

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Forward

On July 21-22, 2022 in Rosemont, Illinois, an NSF- and DOE-sponsored workshop was held on the topic of rigor and reproducibility (R&R) in thermal, heterogeneous catalysis. The focus of this workshop was to discuss the state of these issues in the field, develop recommendations that can enhance the rigor and reproducibility of data reported in the literature, and to compile collective knowledge about best practices for common methods of study in the field and current knowledge about the availability of benchmark materials. This report documents the collective effort of this workshop.

The root cause of R&R issues in any specific scientific field are systemic in nature and require fundamental change in the way scientific research is performed in academic institutions – issues that are far beyond the ability of a few catalysis researchers to change. Therefore, the purpose of this effort is to provide the community with non-prescriptive guidelines for improving basic methodologies used in our field. However, without the power to enforce these recommendations, it is up to collective action of individuals to choose to use these recommendations. Improvements in R&R in our field will occur gradually, and only if we come together as a community and adopt best practices in how research is performed and reported. For this reason, it was important that this effort be the collective action of a large portion of the community. Many people must be acknowledged for this effort.

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The workshop committee dedicated significant effort in organizing topic areas, working with participants, and overseeing breakout group discussions at the workshop. They were also responsible for writing the technical sections of this report.

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The workshop had over 70 participants, most of which participated in-person, to discuss the topics of this effort. We acknowledge their contributions to the collective knowledge contained in this document, and their feedback on ideas for future collective community action.

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Table of Contents

Executive Summary *1*

1. Introduction
- *The "Reproducibility Crisis"* *2*
- *Definitions: reproducibility, replicability, rigor* *3*
- *R&R case studies in related scientific fields* *4*
- *R&R case studies in thermal, heterogeneous catalysis* *6*

2. Setting the Stage
- *Workshop vision and goals* *16*
- *Layout of the report* *17*
- *Establishing definitions for ambiguous terms* *18*

3. Recommendations for materials synthesis and benchmarking
- *A. General recommendations for catalyst synthesis* *21*
- *B. Specific recommendations for deposition synthesis methods* *27*
- *Recommendations for material synthesis and benchmarking*
  - *C. Supported and bulk metal oxides* *39*
  - *D. Supported metal nanoparticles* *50*
  - *E. Single-atom catalysts* *55*
  - *F. Zeolites* *66*
  - *G. Metal organic frameworks* *74*
  - *H. Bifunctional, multifunctional, and cooperative catalysts* *81*

4. Recommendations for catalyst characterization
- *A. Recommendations for catalyst bulk characterization methods* *86*
  - *Elemental composition*
  - *Crystal structure*
  - *Oxidation state of specific atoms*
  - *Coordination environment of specific atoms*
  - *Surface area and porosity*
  - *Particle size distributions of supported metals*
- *B. Recommendations for site specific characterization methods* *106*
  - *Fourier transform infrared spectroscopy of adsorbates*
  - *Uptake and temperature programmed desorption of adsorbates*
  - *In-Situ titration of active sites*
  - *H_2/D_2 scrambling*
  - *Nuclear magnetic resonance spectroscopy*
  - *Catalytic probe reactions*
  - *In situ and operando Raman spectroscopy*
- *C. Recommendations for catalyst characterization by transmission electron microscopy* *121*
- *D. Recommendations for catalyst characterization by x-ray absorption spectroscopy* *128*

5. Recommendations for catalyst testing **135**

6. Recommendations for collective, community actions to improve rigor and reproducibility **147**

Appendices
- *A. Workshop structure and agenda* *154*
- *B. Workshop keynote talk abstracts* *159*
- *C. Community feedback on issues in R&R* *161*

Executive summary

Heterogeneous catalysis has long served as the bedrock of the manufacturing of energy carriers, fuels and chemicals, and various technologies for pollution abatement. The significant complexity and variability spanning the entire breadth of catalyst material properties, synthesis methods, characterization techniques, and evaluation procedures, has focused attention on the need to establish community-accepted best practices for ensuring high-quality, benchmarked, and reproducible data. In addition, increased societal urgency to transition to clean energy and reduce greenhouse gas concentrations has incentivized interdisciplinary, convergent, and translational approaches to catalysis research in recent years. Research engineers and scientists with expertise cutting broadly across materials science, chemical synthesis, interfacial science, spectroscopy, and methods of data science and computational simulation, all bring diverse and important perspectives to catalysis research, but often with little awareness of the complexity of catalytic systems, especially in their working environment. As has already occurred in other scientific fields, there has been growing recognition and consensus in the heterogeneous catalysis research community that mechanisms are needed to improve the rigor and reproducibility (R&R) of experimental measurements, to ensure alignment of the broader research community with a common core of best practices specific to the realization of high-quality catalysis research. Similarly, the field is moving rapidly toward computationally informed and data science-driven catalyst design, but the success of implementing such predictive tools hinges on model training and validation rooted in rigorously obtained and reproducible experimental data that are benchmarked to common specifications.

As such, this workshop was convened to prepare a report summarizing best practices for reporting data and performing experiments that researchers can use to benchmark, validate, and reproduce data in specific sub-fields of thermal, heterogeneous catalysis. Additionally, we discussed recommendations for future actions that may improve R&R in this field. The workshop organizers and participants include a diverse range of catalysis researchers from various employment sectors (e.g., academia, industry, national laboratory), institutional mission and resources (e.g., PhD-granting research universities, non-PhD-granting teaching universities), career stage (e.g., early, mid and late-career), technical expertise, and demographic background. This diverse group was involved in the discussion of workshop agenda items, writing this report, and discussing possible future action items for the community to consider, which helped ensure that a broad range of perspectives were captured in the description of the problems at hand and the creation of actionable solutions that may be effectively adopted by the diverse practitioners in catalysis research. Importantly, this group of workshop participants also included very early career researchers (e.g., senior PhD students, postdoctoral scholars) who will become the next generation of scientific leaders in various sectors, thus capturing emerging perspectives of newcomers to the field to shape its future while positively impacting the development of its future workforce.

We envision that this effort will help advance the field of catalysis science by improving the rigor and reproducibility of experimental data collected by current researchers and future newcomers to the field, which is of broad importance to health and vitality of any scientific discipline. Therefore, best practices identified in this endeavor for thermal heterogeneous catalysis can be translated to such efforts in other areas of catalysis and other scientific fields involving the study of materials, and vice versa. We also envision this to be an ongoing effort, with future workshops that are convened to discuss issues of rigor and reproducibility on technical topics that were unable to be covered in this workshop due to its scope limitations, and as emerging methods and materials become more prevalent in the research community.

Introduction

The "Reproducibility Crisis"

For roughly 400 years following the formulation of the scientific method in the 17th century, science had been regarded as a stalwart for the advancement of humankind. Motivated by various social factors–including raising the standard of living, pursuit of economic gain, administration of warfare, or just plain human curiosity–science has driven technological advances, both beneficial and detrimental, that have indelibly shaped the course of human history and our planet.

However, science experiences a perception problem that is driven by a "reproducibility crisis"– the assertion that a large percentage of data reported in scientific literature cannot be reproduced. Especially over the last two decades, facilitated by our current culture of rapid information access and news cycles, this perception of scientific irreproducibility has been bolstered in the public by several high-profile failures, [1] popular books, [2] provocatively titled perspective articles, [3–5] and even a Wikipedia page. [6]

Although the issue of reproducibility has been discussed in most scientific fields for decades or centuries, this recently growing external pressure has prompted some interesting perspectives discussing the nature of the crisis itself [7–12] and how the current academic environment exerts pressures on researchers that may influence how they prioritize best practices. [13–18] Various government and funding agencies have also been prompted to take action to study issues related to reproducibility problems in science. Such actions have resulted in significant reforms in proposal submission processes for the National Institute of Health (NIH) [19] and in the commissioning of several National Academy of Sciences (NAS), Alfred P. Sloan Foundation, and the National Science Foundation (NSF) funded workshops and reports:

- *Social, Behavioral, and Economic Sciences Perspectives on Robust and Reliable Science, Report of the Subcommittee on Replicability in Science Advisory Committee to the National Science Foundation Directorate for Social, Behavioral, and Economic Sciences* [20]
- *Statistical Challenges in Assessing and Fostering the Reproducibility of Scientific Results: Summary of a Workshop* [21]
- *Data Science: Opportunities to Transform Chemical Sciences and Engineering: Proceedings of a Workshop in Brief* [22]
- *Reproducibility and Replicability in Science* [23]

Our effort will focus on examining this problem through the lens of materials chemistry, and more specifically, thermal, heterogeneous catalysis. However, one of the difficulties in discussing reproducibility issues in science is the lack of universal, standard definitions for reproducibility and related terms (e.g., replicability). Some fields have established meanings for these terms that directly contradict the meaning established in other fields. [23] For the purpose of this report, we will adopt the definitions put forth by the *Reproducibility and Replicability in Science* report, [23] which represents the consensus of a large number of researchers from a wide range of scientific disciplines.

Definitions: reproducibility, replicability, rigor

- "***Reproducibility*** is obtaining consistent results using the same input data; computational steps, methods, and code; and conditions of analysis." [23] In the context of catalysis research, we interpret this definition to specifically refer to the ability of a researcher to reproduce a result given a detailed procedure to follow. In this context, the researcher reproducing the procedure may be within the same or different research group than where the original procedure was developed. For example, if a new report is published that describes the synthesis and characterization of a new material, can another researcher follow the methods used to effectively synthesize the same material and effectively obtain the same characterization results (e.g., X-ray diffraction patterns, surface area measurements) within reasonable statistical uncertainty? ***Critically, reproducibility depends on the original researchers' ability to both report data on all influencing factors of a measurement or method and report all important details of a procedure.*** Oftentimes, it is the case that the researcher is not aware of all the influencing factors of a measurement/method or which details are important to report. The focus of this report is to provide information on both aspects.

  Regarding reproducibility, an open question for any particular measurement is – What is a statistically significant difference? If two researchers measure a catalytic rate under identical conditions, and the result is different by a factor of two, is this significantly different or statistically similar? There are two general strategies employed by different fields to determine the acceptable variance of a measurements – interlaboratory studies (ILS, also referred to as round robin studies) and meta-analysis of literature.

  ILS studies require the coordinated effort of several independent laboratories to perform a specific measurement using identical conditions and samples. In the case of catalysis, samples may even be from the same synthesis batch. The reasonable expected variance of a particular measurement can be determined from the statistical analysis of the results. Interlaboratory studies are a common method for understanding the expected variability of a scientific measurement that is frequently used by the National Institute of Standards (NIST), [24–26] ASTM International [27], the International Organization for Standardization, and International Zeolite Association (IZA) synthesis commission. [28] As described below, there are also numerous reports in the literature of coalitions of academic groups performing interlaboratory studies.

  In many fields, meta-analysis of literature data [29,30] using machine learning methods has become a useful tool for quantitatively evaluating a hypothesis over a wide range of individual studies that may demonstrate a large variance in data. [31–33] The use of meta-analysis has now advanced to the point that many authors have established best practices for ensuring the reproducibility of meta-analyses. [34–36] Likewise, meta-science, meta-research, or "the science of science" [37] is an emerging field using meta-analysis of literature citation records to understand the publication behaviors of scientists and how these behaviors influence the quality of science being reported. [38]

- "***Replicability*** is obtaining consistent results across studies aimed at answering the same scientific question, each of which has obtained its own data." [23] For example, can two separate researchers agree on the effects of a high-temperature oxidation pre-treatment on the particle size distribution of platinum nanoparticles supported on silica? Each researcher may synthesize the materials a different way and characterize the particle size distribution in a different way (e.g., transmission electron microscopy vs. CO pulse chemisorption), but do they arrive at the same conclusion?

  The distinction between the concepts (if not the specific terms themselves) of reproducibility and replicability is important for framing an analysis of the current state of a field. For example, in several fields (particularly psychology, economics, and medicinal sciences) there is ongoing debate on the extent of the "reproducibility crisis". Some argue that there is no crisis at all, and that separate research groups reporting results that are seemingly at odds is a fundamental aspect of the scientific process. Since the scientific process is self-correcting, such data will become resolved or obsolete with time. This argument has merit when viewed from the perspective of replicability. Replicability is qualitative and, if need be, amenable to correction by the scientific method. However, science cannot self-correct if conclusions being debated are supported by data that are not reproducible. The focus of this report is to discuss how to enhance reproducibility of reported data.

- ***Rigor*** is not defined in reference [23], and to our knowledge, has not been defined before. For the purpose of this report, we define it as a researcher's adherence to best practices. From the perspective of the researcher, there are two implications of this definition. First, the researcher needs to be educated about the best practices concerning the specific procedure being performed. Second, the researcher must demonstrate the diligence required to adhere to these best practices.

R&R case studies in related scientific fields

Although reproducibility has been discussed internally within most subfields of chemical sciences for decades, there has been less action taken towards correcting potential issues than in the fields discussed above (outside of medicinal chemistry). Perhaps this is because failures of reproducibility in the chemical sciences [39,40] are not as well-publicized as those referenced above, and also because the impact of technologies from basic research performed in the chemical sciences is not at the forefront of the consciousness of the general population. Regardless, there is evidence of the perception of a major reproducibility crisis among scientists within chemical sciences. In 2016, survey results published by *Nature* [41] indicated that about 90% of participants self-identified as researchers in the field of chemistry could not reproduce someone else's experiment at some point in their career, and roughly 65% could not replicate one of their own experiments. Further, approximately 20% of chemistry researchers believe that at least 50% of published literature is not reproducible, and roughly half of participants believe that 25% of literature is not reproducible. It is fair to argue that the numbers presented in this survey are inflated due to participant self-selection–researchers that already think there is a problem with reproducibility in science are more likely to respond to an open call for this type of survey than researchers that do not perceive a problem–but the high numbers are quite concerning.

In a slightly more quantitative perspective, Bergman and Danheiser [42] reported that 7.5% of papers submitted to *Organic Synthesis*, [43] a unique journal in which experimental methods are required to be highly specific and all procedures and chemical yields must be reproduced in the lab of one of the editors, were rejected because the results were not reproducible. This high rejection rate was not due to a lack of rigor on the part of the submitting authors as the journal editors work directly with the authors to attempt to figure out the root causes underlying why the results were not reproducible. This is an example of unknown factors contributing to irreproducibility.

Although demonstrated to be useful tool for gauging the reproducibility of measurements in other fields, to our knowledge there has been little meta-analysis work done to better quantify the extent of the reproducibility problem in the chemical sciences. One recent example is in the area of gas adsorption organized by David Sholl and colleagues, specifically examining the reproducibility of metal organic framework (MOF) materials in gas adsorption applications. [44–49]. There are two concerning findings from these studies: 1) relatively routine measurements reproduced in the literature have a high variance across researchers, and 2) there are very few documented attempts to reproduce previously reported values, particularly from different research groups. The left panel of figure 1.1 shows CO_2 adsorption isotherms for the metal organic framework (MOF) HKUST-1 reported 18 times in the source database - the NIST Standard Reference Database Number 205. According to their analysis, 20% of the reported isotherms are outliers, and the remaining isotherms have a very large variance. To some degree, this is not unexpected because HKUST-1 is known to be highly sensitive to moisture and variations in pretreatment procedures. The right panel of figure 1.1 shows reported ranges of CO_2 adsorption values for nine different MOF materials as a function of the number of replicates found in the database (excluding outliers determined by the authors). According to the authors' analysis, the database contains 211 measured CO_2 isotherms from 27 MOF's that have been repeated at least once. Of these, only nine (see figure 1.1) have been reported more than 4 times.

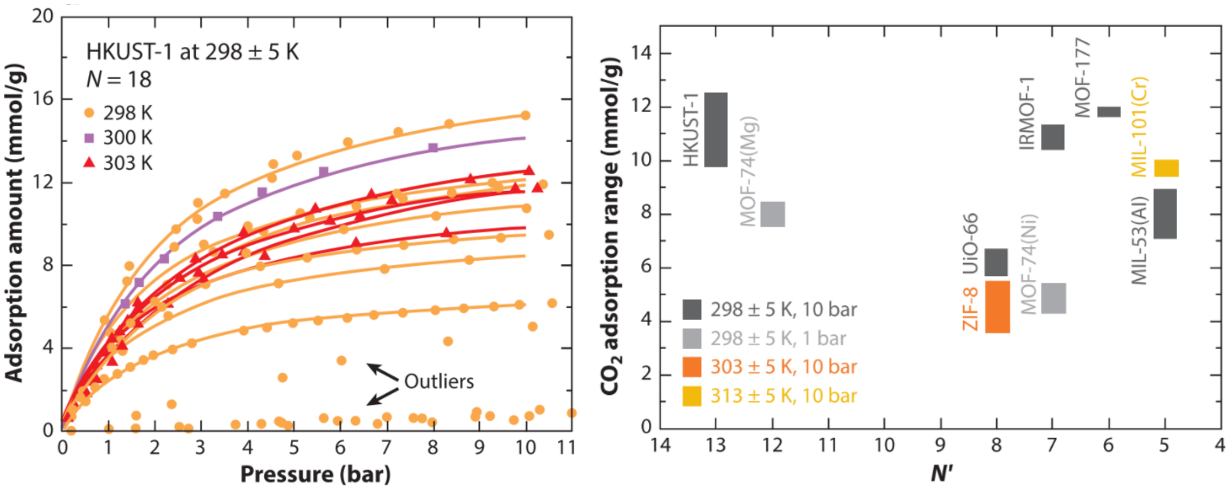


Figure 1.1. *left:* reported isotherms for CO_2 adsorption on metal organic framework HKUST-1 reported by 18 different research articles, *right:* variance of CO_2 adsorption capacity reported in the literature for materials that were reported by more than four research articles. The x-axis indicates the number of references that reported the value. Reprinted with permission from [47]. Copyright 2017 American Chemical Society.

As described above, interlaboratory studies are frequently used in various chemical fields to determine the reasonable variance or important types of measurements. In addition to NIST, ASTM, and ISO, several academic coalitions have formed and published results. Some examples involving techniques typically used in catalysis research include gas adsorption isotherm measurement, [25,26,50] gas chromatography-mass spectrometry (GC-MS) isotopic analysis, [51] particle size analysis by transmission electron microscopy (TEM), [52] surface enhanced Raman spectroscopy (SERS), [53] X-ray photoelectron spectroscopy (XPS), [54], elemental analysis of organic compounds by commercial laboratories, [55] and a comparison of home-built, gas permeation systems by ten labs comparing results for a commercially available membrane materials. [56] A powerful outcome of these types of studies is to quantitatively determine what a reasonable variance is among different laboratories performing common experimental measurements. For example, Kuveke et al. determined that typical journal requirements for elemental analysis to determine compound purity (typically ±0.4%) is not reasonable based on their finding that, in many cases, independent, commercial labs could not reproduce the analysis of the same material within this uncertainty range. [55]

Perhaps one of the most shocking recent reports, Fairen-Jimenez et al. [57] found that calculated Brunauer-Emmett-Teller (BET) surface areas for a range of metal-organic framework (MOF) materials could vary drastically between different laboratories, even when analyzing the same data set! In this study, the authors sent 61 different laboratories the same gas adsorption data for 18 different materials. In the best cases, BET surface areas varied by 300 m^2/g. For the most complex isotherm, the range of reported surface areas varied from 9341 m^2/g to 1757 m^2/g. This study demonstrates that, even for an analysis as "routine" as surface area measurements, the specific protocols used to analyze data can have a significant influence on data reproducibility, and thus, should be rigorously reported in literature.

R&R case studies in thermal, heterogeneous catalysis

Like in other fields, difficulties associated with independent reproduction of important measurements in heterogeneous catalysis, like turnover frequencies (TOF), have been discussed for decades. [58] However, the recent "reproducibility crisis" has once again brought these issues to the forefront of the field. In 2016, the current state of these issues was summarized by a discussion at a Department of Energy (DOE) Basic Energy Sciences (BES) Contractor's Meeting in Catalysis Science, as documented in an article focused on recommendations for benchmarking and best practices in thermal-, electro- and theoretical catalysis by a group of prominent researchers in the field. [59] In 2019, a conference-wide panel discussion preceded the 26th Meeting of the North American Catalysis Society in Chicago focusing on best practices for conceiving, planning, and executing catalysis research. [60] These discussions have prompted several important editorial and perspective articles in thermal [61–67], photochemical [68–70], and electrochemical [69,71–75] catalysis to describe best practices and suggest benchmarking experimental measurements and theoretical calculations. However, outside of these publications, actionable changes and efforts to better understand the extent of the problem in the catalysis community have not materialized.

Unlike in the other fields described above, to our knowledge there have been no meta-analysis studies performed to quantitatively assess the reproducibility of reported and published catalysis data, such as reaction rates. In fact, to our knowledge, there only a few attempts to use data mining techniques and machine learning methods to analyze reported catalytic rates of specific systems, but none of these studies report an analysis of the reproducibility of compiled dataset that were used. [76–80] The overall lack of meta-analysis studies involving catalytic data may be due to 1) a lack of uniformity of data reporting in the literature, and 2) a lack of formatting consistency, which makes it difficult for computers to read data. [81] In Europe, there has been a substantial recent effort to develop methodologies for standardizing data reporting for this purpose. [82–84]

There are literature reviews and interlaboratory studies that have directly or indirectly reported on the variance associated with catalytic rate measurements, but data from these reports represents a very small portion of the research community. Nevertheless, there are important lessons to be learned from them. Somorjai et al. [58] performed an analysis of available literature data and found that reproducibility could depend on the nature of the system being studied. For example, The authors analyzed reported data for ethylene hydrogenation rates on several different types of Pt catalysts. Being a "structure insensitive" reaction (i.e., the site time yield (STY) is independent of the arrangement of surface atoms of the catalyst nanoparticles [58]), the different catalysts show a variance in rate of no more than an order of magnitude. However, the variance of a "structure-sensitive" reaction (i.e. the STY is dependent on the structural arrangement of the surface atoms [58]) such as ethane hydrogenolysis can vary significantly. Somorjai et al. offer a useful, semi-quantitative assessment of how several different factors contribute to the reproducibility of TOFs and STY. Although a myriad of factors can influence the order of magnitude of an observed rate, they identify transport disguises in catalytic rate measurements as the main contributor to differences in observed activities. Effects such as differences reactant and product partial pressures, product inhibition, and potential poisoning or alloying effects of impurities or carbon deposition can also play a large role in observed differences in catalytic rate from nominally, similar materials.

Another recent example comes from a review of vanadium catalyzed propane oxidative dehydrogenation, in which Carrero et al. [85] performed a quantitative assessment of catalysts synthesized and tested by different groups. The authors made extensive efforts to rigorously examine the available literature and parse down their references to studies that presented the most complete and reliable data sets. Specifically, they compared the kinetic rates of TiO_2, ZrO_2, Al_2O_3, and SiO_2 supported vanadium catalysts. The comparison of TOFs for the V/TiO_2 and V/SiO_2 catalysts at 400°C as a function of submonolayer V surface coverage is presented in figure 1.2. These cases represent the class of materials with the smallest (TiO_2) and largest (SiO_2) variance in the data. There are two notable features of this data. The first is that, because of a lack of standardization for catalyst testing and reporting, the TOF values for most of the references had to be extrapolated to a single set of conditions using the kinetic data (apparent activation energies and reaction orders) provided within the references. The second, perhaps more concerning feature, is that the reported (or calculated) TOFs can span over two orders-of-magnitude. Likewise, the range of apparent activation energies were reported to be 60 ± 12 kJ/mol for the TiO_2 samples and 117 ± 28 kJ/mol for the SiO_2 samples. The error on this value was smaller within a given reference, but the variation among different reports was substantial. This example emphasizes the importance that variances in surface impurities, synthesis method, precursor sources, pretreatments, and testing conditions can have on the reproducibility of nominally similar materials. The significant influence of surface impurities on the reproducibility of characterization and catalyst testing measurements has been specifically emphasized by works from Wachs and collaborators. [86,87] The large variance both in testing conditions and kinetic data seems to be persistent across many chemistries and materials that have been studied by the community and presents a challenge for the use of machine learning applications through data mining. [81]

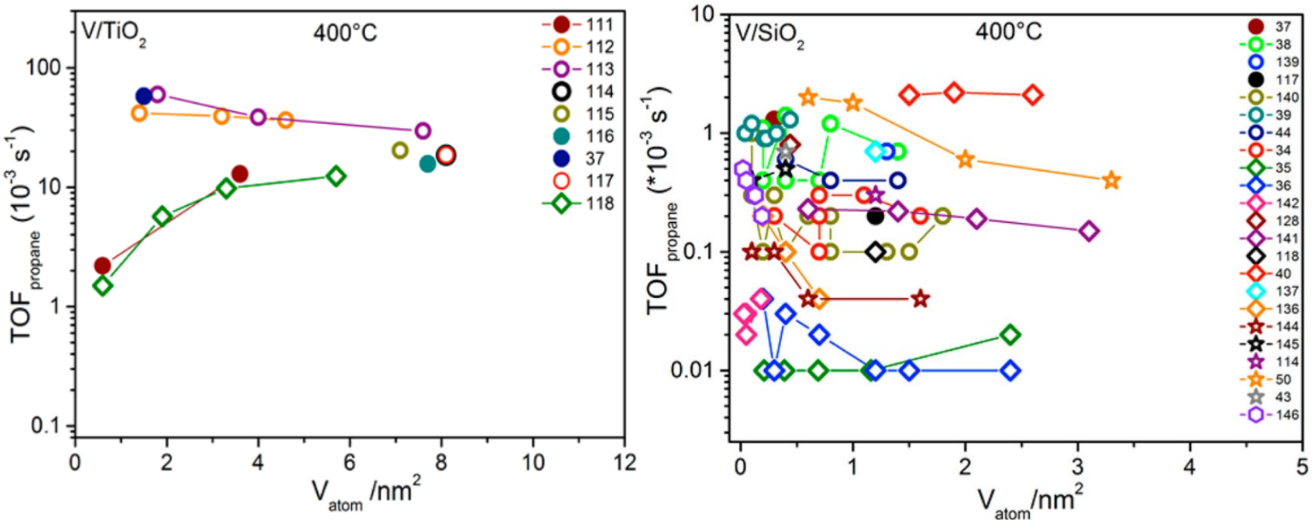
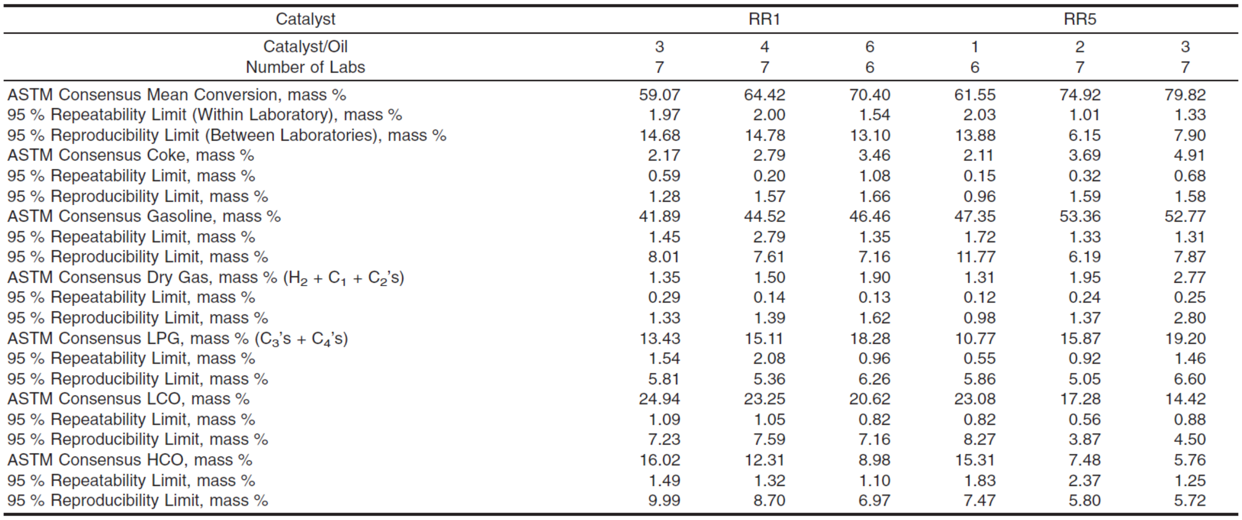


Figure 1.2. Propane ODH rates on V/TiO_2 (*left*) and V/SiO_2 (*right*) catalysts as a function of vanadium loading. Numbers in the legend refer to specific references within Carrero et al. Filled symbols are taken directly from the indicated reference. Open symbols were calculated using kinetic parameters in the cited reference so all values could be compared at similar conditions. Reprinted with permission from [85]. Copyright 2014 American Chemical Society.

A series of interlaboratory studies in the 1970's and 1980's helped establish important information about metal catalysis that is widely known and accepted today. This study focused on a catalyst named EUROPT-1, a nominally 6 wt% Pt/SiO_2 catalyst that was produced at a large scale by Johnson Matthey. [88–90] Samples distributed to several European research groups provided the community with valuable insight into different common characterization methods. For example, the community learned several important lessons on the application of static adsorption of H_2, O_2, and CO for the measurement of metal dispersion and how these measurements relate to particle size analysis via TEM. [88] The evaluation of EUROPT-1 was the first in a series of different interlaboratory studies on various catalysts, although to our knowledge, there has not been a wide interlaboratory study specifically dedicated to measuring catalytic rates.

ASTM International also performs interlaboratory studies as a standard practice for establishing standardized protocols. The subcommittee on catalysis, D.32, has over 40 published standards, some that would be of particular interest to academic researchers in the field of catalysis. [91] Most of these standards include quantitative results of interlaboratory studies, including comparing intralaboratory and interlaboratory repeatability. One example for the *Standard Test Method for Determining Activity and Selectivity of Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test* is presented in Table 1.1. [92] The data represented in this figure show, consistently, that the variance of measurements between labs is larger than the variance of repeated measurements within a single lab.

Table 1.1. Results of an interlaboratory study performed for the verification of ASTM method D5154 *Standard Test Method for Determining Activity and Selectivity of Fluid Catalytic Cracking (FCC) Catalysts by Microactivity.* The data represents gasoline conversion and several different product selectivities collected for two different reference materials (RR1 and RR5) with varying catalyst to oil ratios recorded in 6-7 independent laboratories. [92]



Catalyst	RR1			RR5		
Catalyst/Oil	3	4	6	1	2	3
Number of Labs	7	7	6	6	7	7
ASTM Consensus Mean Conversion, mass %	59.07	64.42	70.40	61.55	74.92	79.82
95 % Repeatability Limit (Within Laboratory), mass %	1.97	2.00	1.54	2.03	1.01	1.33
95 % Reproducibility Limit (Between Laboratories), mass %	14.68	14.78	13.10	13.88	6.15	7.90
ASTM Consensus Coke, mass %	2.17	2.79	3.46	2.11	3.69	4.91
95 % Repeatability Limit, mass %	0.59	0.20	1.08	0.15	0.32	0.68
95 % Reproducibility Limit, mass %	1.28	1.57	1.66	0.96	1.59	1.58
ASTM Consensus Gasoline, mass %	41.89	44.52	46.46	47.35	53.36	52.77
95 % Repeatability Limit, mass %	1.45	2.79	1.35	1.72	1.33	1.31
95 % Reproducibility Limit, mass %	8.01	7.61	7.16	11.77	6.19	7.87
ASTM Consensus Dry Gas, mass % (H_2 + C_1 + C_2's)	1.35	1.50	1.90	1.31	1.95	2.77
95 % Repeatability Limit, mass %	0.29	0.14	0.13	0.12	0.24	0.25
95 % Reproducibility Limit, mass %	1.33	1.39	1.62	0.98	1.37	2.80
ASTM Consensus LPG, mass % (C_3's + C_4's)	13.43	15.11	18.28	10.77	15.87	19.20
95 % Repeatability Limit, mass %	1.54	2.08	0.96	0.55	0.92	1.46
95 % Reproducibility Limit, mass %	5.81	5.36	6.26	5.86	5.05	6.60
ASTM Consensus LCO, mass %	24.94	23.25	20.62	23.08	17.28	14.42
95 % Repeatability Limit, mass %	1.09	1.05	0.82	0.82	0.56	0.88
95 % Reproducibility Limit, mass %	7.23	7.59	7.16	8.27	3.87	4.50
ASTM Consensus HCO, mass %	16.02	12.31	8.98	15.31	7.48	5.76
95 % Repeatability Limit, mass %	1.49	1.32	1.10	1.83	2.37	1.25
95 % Reproducibility Limit, mass %	9.99	8.70	6.97	7.47	5.80	5.72

Conclusions

In conclusion, in conversations the chair and co-chairs have had with members of our community, there is a consensus that mechanisms are needed to enhance the reliability of reported catalyst characterization and thermal catalytic measurements. For the most part, this perspective stems from the anecdotal experiences of individual scientists serving as reviewers for journals and funding agencies. There is a general sense that many scientific studies make strong claims that are not fundamentally supported by the reported data. These assertions are buttressed by a general acceptance that it is very difficult to reproduce catalytic measurements in separate labs. By our definitions, these are problems of rigor and reproducibility, respectively. As demonstrated above, there are several factors that probably contribute to this discontent: 1) The field of catalysis is behind other scientific fields at using well established tools (e.g., literature meta-analysis and interlaboratory studies) to quantitate what constitutes a reasonable variance for a common measurement, 2) reasonable variances may be different for different catalyst systems or different chemistries, and 3) measurements of rates can depend strongly on every step of catalyst formulation and testing (e.g. synthesis procedure, sample aging, sample pretreatment, and testing conditions). These claims do not even consider if researchers are using best practices for conducting experiments.

The purpose of this report is to provide the community with recommendations for best practices of common methods used in the field, help establish suitable benchmark materials for specific material classes and chemistries, and provide direction for future activities that can help alleviate the stresses described above.

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Setting the stage

Workshop vision and goals

This workshop was organized to build upon the momentum and growing recognition in the catalysis research community for the need to improve the rigor and reproducibility (R&R) of catalysis research and translate this groundswell into a set of individual and collective actions that can be implemented by the researchers in this field. Importantly, this workshop was organized with the explicit purpose of discussing strategies to develop and implement mechanisms to improve R&R and how to incentivize the broader community to adopt them. Enacting change at the institutional or societal level is beyond the scope of this workshop; rather, we aim to effect change by creating solutions within the current research environment. Specifically, we aim to address these issues from the perspective of researchers and reviewers, who serve at the front line to maintain the standards of rigor and reproducibility in any scientific field.

For researchers and reviewers, our goal is to provide guidelines for evaluating the rigor and reproducibility of measurements performed in one's own laboratory and in other research laboratories. It is important to emphasize that this report does not provide prescriptive advice, nor the creation of strict rules or methods which every researcher must follow in every circumstance. Innovation is at the core of research activities, which oftentimes requires straying from conventional approaches. Therefore, strict guidelines for certain measurements or analyses in some circumstances may stifle innovation. That being said, our viewpoint is that minimum standards, both in methodology and in reporting, should be upheld to demonstrate the reproducibility and significance of new types of measurements. Benchmarking and control experiments should also be performed to calibrate instruments and evaluate the behavior of new catalytic materials.

The scope of this workshop was limited to thermal, heterogeneous catalysis, given that R&R issues in other sub-disciplines of catalysis (e.g., homogenous catalysis, electrocatalysis, photocatalysis) are complex topics unto themselves that warrant focused workshops dedicated to these specific areas. The scope was further limited to experimental measurements in thermal, heterogeneous catalysis, given that R&R issues in theoretical simulations and modeling are also sufficiently complex to warrant a focused effort in this area. Finally, given the finite scope of this workshop, only a subset of technical topics among the broad array of materials and methods relevant to research in experimental, thermal, heterogeneous catalysis were chosen as topics for discussion. We envision this effort to be ongoing and "evergreen", such that topics that are not covered in this report can be addressed in the future editions, while also encompassing emerging materials and methods that become more widespread or newly introduced to the field in the future. Currently, we plan to convene a group of editors every two years (at each NAM meeting) to update this report document by adding additional detail to current sections and adding new sections where appropriate.

The purpose of this report is to provide the reader with:

1. *Guidelines and resources for improving the rigor of their work* – There exist ample resources for new researchers in the field of thermal heterogeneous catalysis to learn best practices for a variety of methods and data analysis that are common to the field. However, much of this information is only available in publications that are difficult to obtain, [1] expensive, or have limited access. [2] Further, it may be difficult for researchers to find necessary information through accessible journals or search platforms like *Web of Science* if the researcher does not know appropriate keywords to search. ***For researchers**, t**he purpose of the technical portion of this report is to provide guidelines for best practices and a list of readily available resources for deeper learning***. This report is not meant to replace the valuable and extensive resources described above, but rather to simply provide the reader with a roadmap to find critical information. ***For reviewers**, these recommendations can serve as a basis to help establish consistent grounds of*

acceptance or rejection of proposals and manuscripts across journals and agencies, establishing a more predictable and equitable submission process. Overall, we hope this report is a useful resource to help the community improve both the rigor of how experiments are performed and the rigor of how data are analyzed and reported.

2. *Potential future directions for the field to better evaluate reasonable reproducibility limits of specific measurements* – Rigor and reproducibility are intrinsically linked. Assuming all researchers follow best practices for making measurements and reporting data, external researchers should be able to reproduce their data with low variability. However, it is often the case that unknown or unexpected factors contribute to problems with reproducibility, even if known best practices are followed. Therefore, it is important for research communities to quantitatively evaluate reasonable variances for broadly used measurements in order to be able to benchmark measurements and more confidently evaluate the differences between the catalytic properties of different materials. In the latter portion of this report, we discuss recommendations for future activities that will both help evaluate the inherent variance of different measures and help enhance the reproducibility of measurements in the community more broadly.

Layout of the report

This report is divided among sections that align with the focused topics of breakout group discussions during the in-person workshop.

Section 3 focuses on specific material classes. It starts with two subsections on catalyst synthesis: "General recommendations for catalyst synthesis" and "Specific recommendations for deposition synthesis methods." These are followed by sections focused on a specific material classes - detailing information about common synthesis strategies, recommended characterization, and potential, available benchmark materials. During the workshop, breakout group leaders focused the discussion based on the report template below:

Report Template for "Recommendations for materials synthesis and benchmarking" subsections

- Introduction and Applications
- Common Synthesis Methods and Reporting Recommendations
- Recommendations for Standardized Characterization
- Recommendations for Benchmarking Properties and Performance

Sections 4 and 5 focus on best practices for catalyst characterization and reactivity testing, respectively. For the purpose of organizing breakout group discussion topics, characterization methods were broken down into general categories: bulk characterization, site specific characterization, and advanced characterization methods. *For each specific technique discussed*, groups were asked to focus the discussion based on the following report template:

Report Template for "Recommendations for Catalysts Characterization and Testing"

- Common Applications
- Known Limitations
- Specific Recommendations for reporting data in literature
- References for Best practices

Section 6 contains recommendations for future actions that can be taken by the community to improve R&R, and potential advances and challenges associated with each action.

Establishing definitions for ambiguous terms

In this section, we will define often ambiguous or misused terms in our field. The purpose of these definitions is not to establish hard definitions that should be used by researchers, but to establish definitions for the sake of uniform use and understanding throughout this report. Although the chair and co-chairs of this report support the use of these terms broadly, it is not our intent to establish these terms as a prescriptive requirement. For publication purposes, researchers are reminded to always define the terms they are using, even relatively simple, well-known terms such as conversion and selectivity, to ensure that readers can comprehend your results and scientific arguments.

Turnover frequency, turnover rate, and site time yield

Turnover frequency (TOF), which is equivalent to turnover rate (TOR) is a relatively simple concept to understand, but incredibly difficult to apply to real systems. The term has been defined by many authors, [3–7] and we will adopt a similar definition for this report. Turnover frequency is defined as the number of reaction events occurring at a reactive site of a catalyst per unit time (overall formal units are s^{-1}). Importantly, as this definition depends on the number of reaction events, it does not depend on the stoichiometry of the reaction. That is, if $A \rightarrow B$ and $2A \rightarrow B$ have the same TOF, then the second reaction will consume A twice as fast as the first reaction. This example shows how TOF relates to reactant consumption rates or product formation rates.

The greatest complexity with the term TOF comes from the definition of the active site, [4] because it often is very difficult to identify and quantify the true active site of a material. In fact, it is more likely that there are several different active sites that work in parallel or in concert to give rise to the reactant consumption rates and product formation rates that are macroscopically observed. In this case, best research practices are to measure a proxy for the putative active site, such as the total surface area of an active material (e.g., the total number of exposed metal sites via CO chemisorption), and to explain the sufficient details needed for an independent researcher to reproduce this characterization measurement. When rates are normalized to a "total number of putative reactive sites," we will use the term *site time yield (STY)*. At worst, STY represents a minimum value of the true TOF of a material, but it is a metric that is more useful than a mass-normalized rate to compare the reactivity of different catalysts (see Section 4 of this report) and to assess the reproducibility of a rate measurement.

Operando versus in situ measurements

The terms in situ and operando are used extensively in this report. The terms refer to a modality of performing a characterization measurement. Operando measurements are conducted while the material is actively performing a catalytic function. That is, the characterization measurement occurs while the catalyst is under relevant reaction conditions (at the temperature, pressure, reagent composition, and space velocity of the reaction of interest). Operando measurements, by definition, include an analysis of the reaction product stream to show that the measured rates and selectivities are statistically the same as those recorded in a separate batch or plug flow reactor system of well-controlled hydrodynamics.

In situ characterization measurements refer to cases in which the material is exposed to the reaction environment, but without simultaneous measurement of the catalytic function (e.g., rates, selectivities) to verify the catalyst is operating as intended. Additionally, in situ measurements can refer to cases wherein the material has undergone a specific treatment, or has been tested under specific reaction conditions, but the characterization measurement is then performed under different conditions that are more well-suited for the characterization (e.g., under high vacuum for an XPS measurement). In this case, the use of the term in situ implies that the material was never exposed to ambient environment between the treatment or reaction step and the characterization measurement.

Finally, an ex situ measurement implies that after the material has been exposed to a treatment or reaction environment, it has then been exposed to a very different environment (e.g., ambient air) prior to the characterization measurement. In some cases, exposure of catalytic materials to ambient air does not have a strong role in the outcome of a characterization measurement, such as quantification of coke formation on a spent catalyst via thermogravimetric analysis.

Since operando and in situ measurements can require complex instrumentation, researchers with limited resources may have difficulty performing such experiments. Thus, the merit of scientific products (articles and proposals) should be judged based on: 1) what measurements researchers can perform, not on measurements that they could not perform, and 2) whether the conclusions are justified by the data and analysis presented. From the standpoint of rigor and reproducibility, however the experiments may be performed, it is important that researchers report the conditions of all their measurements and the full history of their samples during the course of these measurements. Generally speaking, operando measurements will have the highest likelihood of being reproduced, followed by in situ measurements, followed by ex situ measurements.

Benchmark materials and chemistries

The benefits of the potential widespread use of benchmark materials in our field has been heavily discussed recently. [8,9] For the purpose of this report, we propose that a useful benchmark is any material that can be acquired by the general community with properties that are relatively straightforward to test. These materials could be available via large scale production and distribution (e.g., available through an established vendor or supplier) or could be made available through the distribution of known, verified synthesis methods. [10] In either case, the materials should have known properties that are relatively simple to verify upon receiving. These properties may include but are not limited to elemental composition (including quantification of known impurities), surface area and porosity, site density of reactive sites, and catalytic properties relating to a specific, benchmark chemistry.

The widespread use of these materials would have several benefits for individual researchers and the community. For researchers, these materials would be useful to verify the proper operation of their instrumentation. Since these types of materials are provided by instrument manufacturers, this type of verification is already common for commercial physisorption/chemisorption types of instrumentation. We would argue that the use of benchmark materials is even more important for catalyst testing instrumentation, which is often not standardized and commercially available units, but rather “home built” apparatuses.

It would also benefit the community if these materials were more broadly used to benchmark catalyst testing by individual researchers. If these materials were always used by researchers as control measurements and reported in their publications, it would be 1) easier for the community to judge the quality of the data, and 2) compare results of different materials across different laboratories. Section 5 of this report expands on these ideas and proposes strategies for future incentivization and implementation of the use of benchmark materials.

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General recommendations for catalyst synthesis

Introduction and summary

Despite the wide range of material classes that are studied in catalysis research, there are several common aspects of the procedural methods used to synthesize these materials that greatly influence the outcomes of the product properties. The outcomes are critical for catalytic reactivity, and therefore the methods need to be described in explicit detail to ensure the reproducibility of reactivity measurements. In this section, we focus on the synthesis of bulk materials. Bulk catalyst materials are broadly defined here as those that are unsupported or serve as nanoparticle supports; mainly bulk oxides, metal organic frameworks (MOF), zeolites, clays, and colloidal nanoparticles. For the most part, the synthesis of all these materials involves the crystallization of mono- or polycrystalline powders out of a liquid solution. Together, these bulk materials present challenges to rigor and reproducibility in catalysis research. For example, bulk catalysts frequently are difficult to fully characterize because the properties of bulk materials can differ from the surfaces and exposed atoms involved in chemistry. This, in turn, poses challenges to determining catalytic structure-function relationships. [1]

Regardless of materials class, each individual laboratory will invariably have a set of specific procedures they use to synthesize their catalytic materials. Typically, these procedures are generally adapted from a set of steps previously reported in the literature; [2] however, experimental nuances and unreported adjustments made by specific researchers to the method will ultimately become procedures unique to each lab, and in turn differences in both the physical and chemical properties of the materials such as purity, size, surface area etc. (Figure 3.A.1). The differences in properties are an intrinsic function of the complexity of these heterogeneous materials and are likely to be affected by variables such as temperature, concentrations, and mixing or stirring protocols used during synthesis. Treatments of samples after their synthesis—such as heating rate and hold times during drying procedures and/or oxidation/reduction treatments, as well as static or dynamic pre-treatment atmospheres to obtain the final active material—will also affect the properties of the material obtained. [3] Although these variables are important, they are often unreported.

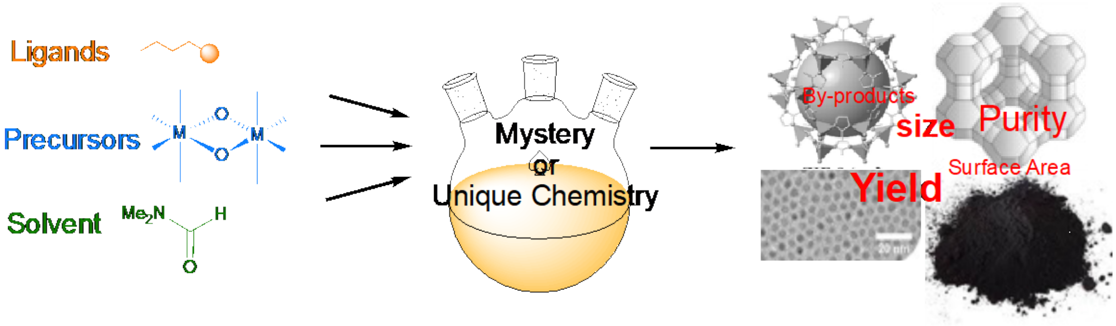

Figure 3.A.1. Illustration of a typical bulk synthesis route and the possible variable outcomes. Adapted with permission from [4]. Copyright 2022 American Chemical Society.

In this section, we provide recommendations for best practices in the reporting of syntheses for bulk materials. These guidelines are primarily focused on how to improve the description of synthetic methods in the literature to ensure that they are comprehensive, thereby enabling reproducible materials synthesis. Some guidance is also provided regarding how to increase rigor in the characterization of these materials to meet minimum standards and to ensure that the material synthesized has similar characteristics to previously reported samples. This section is focused on recommendations for the general steps in synthetic procedures that are commonly unreported (or reported in insufficient detail) and suggestions for details to be included that will better facilitate reproducible outcomes. We also address the necessity of reporting specifics such as precursor purity (with characterization of known impurities) and batch-to-batch variation, as well as any other "tips and tricks" that are critical to the success of a particular synthesis. We make suggestions for detailed reporting in supplementary information of journal publications. Following this section focused on synthetic parameters that are common across material types, the subsequent sections of this report describe sensitivities that are unique to certain materials classes and provide specific references for specific synthesis procedures.

Known limitations and recommendations for reporting of synthesis procedures

Although differences exist in the specific synthetic protocols for different materials classes, there are common trends regarding experimental parameters that could benefit from more thorough, detailed reporting in the literature to facilitate reproducible synthesis outcomes across different laboratories and within a given laboratory. [5] For solution-based synthesis, these parameters can be classified into five general categories: (1) preparation of reagents, (2) synthesis procedure, (3) post-treatment/characterization, (4) storage, and (5) activation and pre-treatment prior to use in chemical reactions. In Table 3.A.1, each of these categories is listed along with examples of specific parameters that can be critical to reproducible synthesis, but which are commonly not reported.

Table 3.A.1. Examples of parameters where increased reporting is necessary to improve reproducibility in materials synthesis.

Category	Example Parameters
Preparation of reagents	purity (and known contaminants), lot number, purification procedures used (e.g., distillation, drying)
Synthesis procedure	pH, mixing protocols, stir rate (type and size), vessel size, reaction scale, vessel headspace, cleaning procedures of the equipment and glassware (acid or base bath wash)
Post-treatment/characterization	aging, thermal treatment conditions: ramp rates, hold times, atmospheres (e.g., gas compositions, purity, flow rates), thermal batch size: crucible size, with amount of powder, accounting for mass/heat transfer.
Storage	storage environment (e.g., desiccator or "ambient" conditions), notes regarding protection from ambient light, length of storage, state of material prior to storage, vessel/vial type
Activation and pre-treatment	environment for activation (e.g., temperature ramp, holds, atmospheres), pre-washing volumes (e.g., number of cycles, preparation of solvents)

Preparation of reagents and reaction vessels

Most synthesis procedures found in the literature indicate the source of the chemical precursors used in the synthesis and often also include the gases used and their purity. However, in many cases, more detail is needed to reproducibly obtain the same material. For example, in some syntheses of colloidal metal nanoparticles, the purity of a reagent can vary between different batch and lot numbers from the same supplier and therefore this information (or awareness of this sensitivity) is critical to successfully repeating the reaction (Figure 3.A.2). [4,6–12] In zeolite synthesis, the method used to clean the vessel where the materials synthesis takes place is important (base bath or acid wash). [13] Consequently, we recommend reporting in detail the following parameters for the preparation of reagents:

- Scale of the synthesis reaction and type of reaction vessel used (including any cleaning procedures and volume capacity)
- Specific reagent and precursor details (including manufacturer, type, and purity for all reagents and precursors; including lot number if it is sensitive for the reaction). State known synthetic sensitivities.
- Purity of inert gases (if relevant)
- Distillation, drying, or other purification steps done to the precursors prior to use in synthesis.

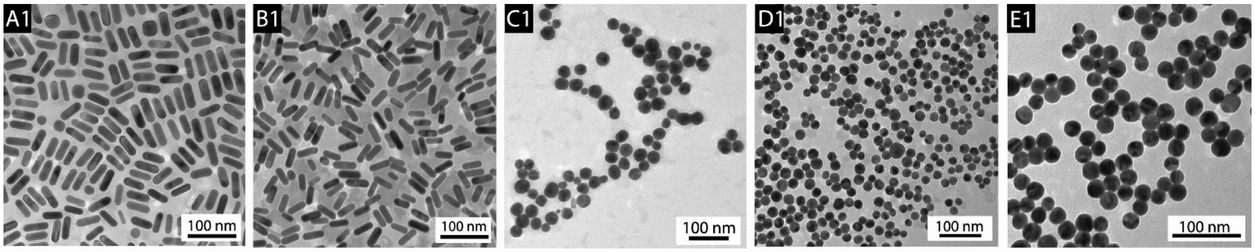

Figure 3.A.2. Illustration of the importance of known and unknown trace impurities in materials synthesis. Transmission electron microscopy images of Au "nanorods" synthesized via the same protocol but with the surfactant cetyltrimethylammonium bromide (CTAB) originating from different commercial suppliers. The same chemical, CTAB, can result in difference in catalyst structure—here rods vs. spheres—due to trace impurities not provided in manufacturer specifications. Reprinted with permission from [8]. Copyright 2008 American Chemical Society."

Synthesis Procedure

While synthesis procedures generally include what reagents are needed and their concentrations or volumes, there is not a standardized method of describing synthesis experiments that outlines what information should be included. Consequently, critical information often goes unreported, affecting the reproducibility of the synthesis method. For example, normally the volumes of ligand and metal precursor solutions for MOF synthesis are listed, but not the order of addition or rate of addition required to ensure crystallization. Additionally, stir rates and how heating is carried out are often not reported for metal oxides. We recommend the following specifics be included at a minimum in the reporting of the synthesis procedure:

- Parameters required for success in the reaction setup including the size of the reaction vessel, the stir rate with stirrer type and size for stirred reactions, the type of heating used (water bath vs. hot plate)
- Concentration of the precursors, precipitation agent and starting pH and scale of the synthesis
- Scale of the synthesis, and any added reagents (precipitation, structuring, etc.)
- Measured pH of the reaction solution (in addition to reporting the volume of acid or base added)
- Order of addition and timescale of addition (including targeted pH and deviation if applicable), and other mixing protocols used
- Color changes or aspect changes such as turbidity, bubbling or precipitation, and other observable parameters that indicate successful or failed reactions
- For colloidal suspensions: the stability of the suspension and directions for suitable storage

Post-treatment/characterization

After synthesis of these bulk materials, they are often prepared with additional steps, or post-treatments for characterization, or stored until further use. This is often the part of a synthesis that is reported in the least detail. It is customary to report washing or purification steps and the solvent used for a treatment prior to a characterization, but not the volumes and purity of the washing solvent or the number of times the purification was carried out. It is also common to read that a material was filtered, but the sensitivity of the filtration procedure to solvent purity or water content is not reported. For sol-gel syntheses, how long the sol-gel was stirred (or if it was stirred), and the evaporation rates of the solvent are often not detailed specifically. We recommend the following specifics (when relevant) be included at a minimum in the reporting of the post-treatment for storage and treatment steps prior to characterization of a synthesized material:

- Detailed instructions for rinsing, centrifugal separation, and/or ligand exchange procedures—including the number of times the procedure was repeated
- Detailed aging time and temperature—including stir bar size and rate of stirring
- Drying time and temperature with ramp rates and hold times (as well as vessel, type of oven, type of environment)
- Calcination ramp rate and final temperature and time
- Precise thermal pretreatment of the samples prior to any characterization (e.g., dehydration at specified temperatures and time intervals)

Storage

Bulk catalysts are often metastable materials subject to changing surface and even bulk composition over time—such as hydroxyl concentrations on the surface, oxidation state, and alloying. However, the way materials are stored after synthesis and how they might be expected to change and/or degrade over time are generally not reported, even though this information can be critical to reproducing catalyst performance. It is also not common to report how soon the material must be used after synthesis or, conversely, the period of time that must pass before using the material to achieve reproducible behavior. Additionally, it is important to report on what form the catalyst is stored in (passivated carbide/nitride, colloidal suspension versus dried powder, unactivated MOF). Any storage conditions for reagents/materials should be reasonably described in situations where there is a possibility, they could be relevant to reproducible synthesis. If any storage dependencies are observed, this should be specifically noted and reported, as well as if material performance changes over time or with aging. It is particularly important to be aware of any such changes in material composition or quality if catalytic experiments are conducted over a large time range. We recommend the following specifics be included at a minimum in reporting the storage conditions for a synthesized material:

- Storage environment (bench vs. refrigerator vs. desiccator vs. glove box)
- Relative humidity and room temperature if unstable or high/low
- Time the material was left at each condition
- Length of time of stored sample before use
- Necessity of protection from ambient light

Activation and pre-treatment

Before use in a catalytic reaction, it is likely that a material that has been stored in a solution or has residual capping agents from synthesis must then be treated to decompose or remove adsorbed molecules as part of a pre-treatment and activation procedure. In addition, clear procedures need to be reported for any hygroscopic or easily oxidized material, including the time taken from the storage (oven or desiccator) to the scale and to the reactor. Notes regarding the quickness in this transition to avoid mass water uptake and oxidation of the surface material need to be reported to reproducibly use these materials after storage. We recommend as a standard practice explicitly describing any activation process that is carried out after synthesis (e.g., solvent exchange, ligand removal, combustion, calcination), recognizing that some in situ treatments may be described as part of the synthesis procedure.

Other recommendations for best practices

In many cases, reproducibility can be improved by better reporting of observations made during synthesis (Figure 3.A.3). It is important to train all new students and researchers in the field that extra details recorded in lab notebooks—such as noted observations of color, precipitation, etc.; the speed of these observable changes; reagent lot numbers; and deviations from procedure—are critical to ensuring synthesis reproducibility. In this section we list a few more recommendations regarding batch size, replicates, reporting of negative results, and characterization.

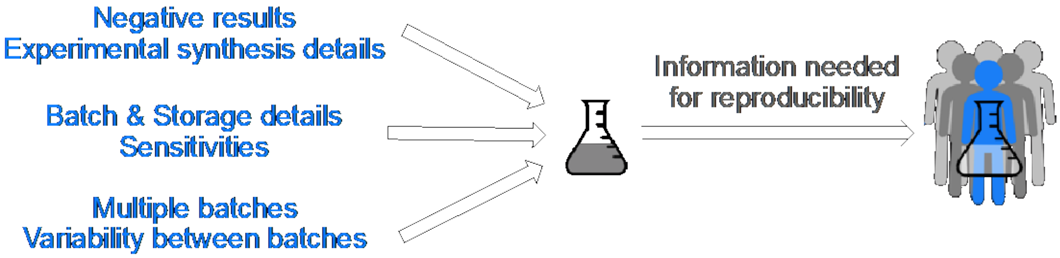

Figure 3.A.3. Often unreported variables that when reported would lead to improved reproducible materials within and among laboratories.

In general, issues with batch-to-batch variability can be eliminated by using the material from a single batch, though this is not always feasible depending on batch size and scalability. However, even studies performed with materials from a single batch should include information about how the material changes with time during storage or use, and if any pre-treatment is needed to return the catalyst to a state of reproducible reactivity (if degraded or modified by aging). It is important to be aware that materials storage can influence reactivity, and we recommend regularly repeating a selected control experiment to test for effects of aging or storage on reactivity when conducting experiments over an extended period of time. Additionally, reporting of materials syntheses should include how many batches of material were made and how often/well the product was reproducible. If the synthesis was not repeated, it should be explicitly stated that a statistical measure of reproducibility from batch-to-batch was too prohibitive in terms of time or cost. *Multiple batches should be synthesized if the manuscript is the first reported synthesis of a particular material.* It is common to carry out a series of small batch syntheses of a new material before scaling up, but information about these experiments and their reproducibility is rarely reported.

We also suggest an *increase in the reporting of negative results and sensitivities in the description of the synthesis*. For example: “this order of addition did not yield crystalline material,” or “oxidation in air leads to an inactive catalyst, therefore activation must occur under nitrogen,” or “carrying out solvent exchange in a different way leads to…,” or “closely following this procedure was found to be necessary to ensure good yield.” If a specific step of the procedure is important to successful synthesis, including phrases such as “these are the sensitive parts of the synthesis” may be informative to a new researcher in the field. Common pitfalls should also be mentioned in the synthesis procedures, such as that MgO picks up CO_2 from the atmosphere, and that the carbide passivation rate matters. Lot numbers need to be reported if a sensitivity is found. All of these statements signal to the reader that sensitivities and reproducibility information can be found in the experimental section or supporting information. *A material synthesis that is not sensitive for reproducibility can be indicated by stating “no known sensitivities” in order to help future scientists have confidence in the method.*

We recommend including the full synthesis details in the supporting information even if it appears in the main text because the supporting information is freely available, thus ensuring that resources are accessible to a variety of researchers. The full experimental procedure should be listed in every publication, even if it is a previously published synthesis, in order to avoid long or broken citation trails. *To facilitate this, we recommend that editors relax rules around self-plagiarism for experimental sections of manuscripts, especially for detailed descriptions that can be included in the supporting information document.* It is also important to point out any deviations, however slight, from a previously published synthesis.

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Specific recommendations for deposition synthesis methods

Defining the material class and challenges

Deposited catalysts are defined here as those in which a pre-synthesized support is placed in contact with a precursor in a fluid phase to react, be adsorbed, or otherwise be deposited, followed by a pre-treatment to form the active phase. Examples of deposition methods include wet/dry (incipient wetness) impregnation, ion exchange, strong electrostatic adsorption, atomic layer deposition, grafting of organometallic precursors, and others. Our focus is on transition metals with structures ranging from atomically dispersed species to larger nanoparticles. The process of deposition can influence the distribution of structural features of the active phase, as well as the incorporation of other species onto the catalyst from the deposition source (e.g., counter ion or ligands). Once the active phase is produced, the storage and treatment of the material can significantly influence the resulting reactivity. Differences in synthetic procedures that appear small can have a significant influence on the structure and reactivity of the deposited active phase. Thus, it is critical to define the necessary information that should be reported during the synthesis, storage, and treatment of deposited catalysts to enable reliable reproducibility. [1]

Regardless of materials class, each lab has a set of standard procedures they use to synthesize catalytic materials. These procedures are generally adapted from a set of steps previously reported in the literature, [2–5] which can result in differences in both the physical and chemical properties of the materials due to experimental nuances and unreported adjustments to the method that are unique to each lab. The differences in properties are an intrinsic function of the complexity of these heterogeneous materials and are likely to be affected by temperature, concentration(s), pH, extent of mixing during synthesis, as well as contamination in reagents, glassware, etc. The use of gloveboxes to control the atmospheric environment during synthesis may also be critical. Treatments after synthesis also affect the properties of the catalyst. [6] These include heating rate and hold times during drying, calcination, and reduction/passivation, as well as static or dynamic pre-treatment atmospheres (where weight hourly space velocity of flowing gases should be reported) for obtaining the final active material. Furthermore, characteristics of the support, including structural features, composition, surface area, pre-treatment, etc., can also influence the resulting deposited species.

In the following sections, guidelines are proposed for reporting synthetic, storage, and pre-treatment methods associated with deposited catalysts to maximize reproducibility. These guidelines result from consideration of the following questions:

> *i*) What steps of the synthesis, storage, and pre-treatment procedures need to be described thoroughly in order to ensure the resulting material properties are reproducible?
>
> *ii*) What synthetic parameters are often unreported that can affect material outcomes? What parameters do we as a community think are important to report for increasing reproducibility?
>
> *iii*) What characterization(s) of the material are needed at a minimum to ensure that the sample is the same as previously reported or to compare to a benchmark?

Motivating examples

A few motivating examples are provided to highlight how synthetic, storage, and pre-treatment conditions can significantly influence the resulting catalyst properties.

1. **The roles of contaminants in the support and pre-treatment conditions:** Commercial alumina is derived from aluminum hydroxides or alumina gels (e.g., *ex* $Al_2(SO_4)_3$ + $NaAlO_2$). The latter can contain residual quantities of sulfur and Na (0.01 – 0.1 wt%). When Pt is deposited via impregnation from H_2PtCl_6 on S-containing Al_2O_3 and reduced in H_2 at temperatures > 573 K, the resulting Pt surfaces can become poisoned with S. The S-poisoned Pt catalysts exhibit different dispersions that depend on both the S content and dispersion measurement technique when analyzed by chemisorption (hydrogen chemisorption, oxygen chemisorption, hydrogen-oxygen titration) due to specific interaction of the probing molecules with surface-bound S on Pt.

Further, depending on the technique used for surface area measurements, the resulting TOFs for the probe reaction hydrogenation of cyclohexene can vary significantly. [7]

Additionally, impurities in the support can dramatically affect metal dispersion. For example, different NiO dispersions were obtained on alumina supports with different Na contents. [8] This highlights the importance of washing the supports to remove contaminants. For example, as high pHs are used for cation exchange, low pHs should be used for washing cationic impurities. Other important examples exist on the general issue of contamination caused by the synthesis apparatus, or the materials and supplies used during synthesis. [9,10]

2. **The role of mixing time during deposition precipitation:** Although Au/TiO_2, Au/Al_2O_3, and Au/CeO_2 catalysts prepared by deposition precipitation show rapid and complete metal uptake, smaller particle sizes are obtained when using longer contact times. This is attributed to the fast precipitation of large Au aggregates followed by increased pH due to urea decomposition resulting in the fragmentation and redispersion of the active phase. [11,12] In general, the mixing time can dictate whether slow reactions associated with metal precursors (e.g., aquation or speciation) or support (oxidation or hydroxylation) proceed that could influence the nature of the deposited species.
3. **The role of activation procedure:** The Phillips catalyst (Cr/SiO_2) is widely used to produce high-density polyethylene. If activated in a fluidized bed with dry air, all particles are exposed to a similar concentration of water vapor, uniformly forming the desired Cr(VI) species. However, if the activation is performed in a fixed bed, this leads to a gradient from Cr(VI) to Cr(III) down the bed as water vapor builds up (Figure 3.B.1). [13] As a result, the commercial activation is performed in a fluidized bed to minimize the exposure of the catalyst to water at high temperatures.

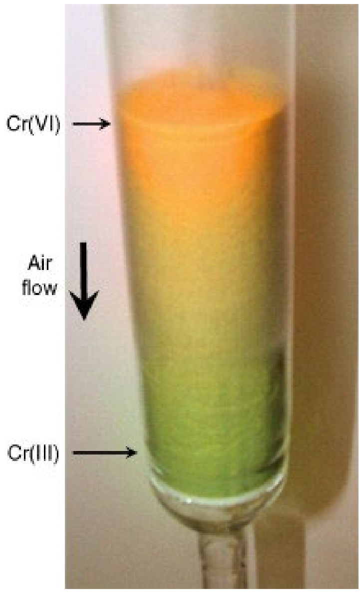

Figure 3.B.1. Cr(VI) to Cr(III) gradient as a result of the activation of 1 wt% Cr/SiO_2 in a fixed bed at 800 °C. Reprinted from [13], with permission from Elsevier.

4. **The role of storage environment:** Catalysts are often prepared and then stored in the lab for extended periods of time before use. The conditions of storage and length of time can be important. For example, it was shown via surface science analysis that when TiO_2 is exposed to ambient environments (both in Vienna, Austria, and Ithaca, United States), a complete surface coverage of carboxylic acids forms, even though these species exist in ppb concentrations in the atmosphere. Without proper in-situ cleaning of the TiO_2 surfaces, these adsorbed layers are likely to influence reactivity measurements. [14] Furthermore, it is known that ppb-level exposure of Ni catalysts to H_2S can reduce catalytic rates by an order of magnitude. Given that natural environments can contain H_2S at close to ppb levels, this could certainly influence the results of catalytic materials if not appreciated. [15]

General best practices for reporting synthesis

Regardless of the exact metal deposition procedure, there is common information about synthetic procedures, materials used, apparatus used, and the storage and pre-treatment of materials that are consistent across all deposited catalysts. It is further suggested that information about the support, metal precursors, solvents, gasses, or other chemical species used during synthesis be reported in a table in the supporting information of the paper that include common information. This allows for easy access and comparison across reports.

*Information about the **support** that should be reported*

- Vendor, catalog number, lot number, date purchased, date opened, storage details (how long and in what environment).
- Total surface area, pore volume, and pore size distribution of the support (note whether these were measured or provided by the supplier) and what method was used to make the measurement.
- Known surface functional groups and impurity concentrations (note whether these were measured or provided by the supplier). If the supplier does not supply impurity concentrations, this is a suggested analysis.
- Specific treatment procedures prior to use (e.g., calcination procedures, washing procedures, functionalization procedures, and chronological order of the treatments; see below for suggestions on reporting treatments).
- Surface composition to check for impurities.

*Information about the **metal precursor** that should be reported*

- Vendor, catalog number, lot number, date purchased, date opened, storage details.
- Purity (impurity identities and concentrations if known).
- Precautions to take in case of air- and/or moisture-sensitive metal precursors.
- How the precursor is weighed and transferred (for example, some metal precursors can react with metal spatulas or water in humid air), the range of weights used if multiple catalyst batches are made and compared, and whether electrostatic discharge was required.

*Information about the **solvents** that should be reported*

- Vendor, catalog number, lot number, date purchased, date opened, storage details.
- Purity, known impurities and their concentrations, other known components.

*Information about the **gases** that should be reported*

- Vendor, catalog number, date purchased, purity.
- For CO cylinders, the type of cylinder (Al lined) and if a carbonyl trap is used.
- The use of other traps (O_2, CO_2) to remove contaminants.

*Information about the **synthesis protocol and apparatus used for synthesis** that should be reported*

- Where the synthesis was conducted: location, elevation, lab temperature, and humidity. In cases where syntheses are conducted over multiple days, the general range of laboratory environmental conditions should be reported.
- Glassware dimensions and volume,
- Volumes of solutions,
- Headspace,
- Masses,
- Cleanliness of apparatus,
- Times,
- Rates of addition, adsorption (may be challenging to measure), contact,
- Type of mixing, with relevant parameters provided (e.g., stirring rate),

- Magnetic bar shape and dimensions,
- Atmosphere (open/ closed/ under an inert atmosphere blanket/ vacuum),
- Interaction between precursor and support,
- Ripening of precursor solutions (how long before deposition were solutions prepared),
- Light exposure.

Information about the ***treatment and storing*** *of materials after deposition and before materials become catalysts (regardless of the deposition technique)*

In general, it can be helpful to perform analyses to identify optimal temperatures for drying, precursor decomposition, precursor oxidation, precursor reduction, ion removal, etc. These are often executed using differential scanning calorimetry, temperature-programmed oxidation/reduction, and thermal gravimetric analysis. While not required to promote reproducibility, these analyses are encouraged to provide insights into the choice of pre-treatment conditions and the influence they can have on the resulting deposited species. Regardless of how the conditions are chosen, there is critical information for making the processes reproducible.

Supported pre-catalyst treatment: drying, calcination, reduction, and passivation

- Specific apparatus and method: Treatment reactors are important. We pay great attention to finite rates of transport and gradients in the reactor employed to test catalysts. It would be beneficial to pay comparable attention to the characteristics of the reactor employed to prepare the catalyst, as gradients in temperature and concentrations can cause significant inhomogeneities in the resulting materials. For example, the flow rate of treatment gases can dictate the concentration of volatile species produced (e.g. HCl during H_2 treatment of a catalyst made using Cl based precursor), which can influence the resulting metal dispersion.
- Flow rate and gas space velocity: fixed or fluidized bed and geometry of the reactor bed,
- Gas environment (e.g., air, O_2, N_2, H_2, 1% O_2/N_2),
- Static atmosphere or under gas flow,
- Temperature (including an assessment of gradients),
- Temperature ramp rate(s),
- Hold time(s),
- Cooling method (passive versus active),
- Visual observation of color gradients in the resulting material,
- Transition between the reduction and passivation stages; for example, if H_2 is flushed with inert prior to introduction of passivation agents (and vice versa in calcination-reduction protocols).

Catalyst storage

- Container,
- Atmosphere (air, inert, vacuum),
- Light exposure,
- Presence of potential contaminants in the lab (e.g., sulfur),
- Range of lab temperature and humidity commonly experienced.

There are countless deposition methods discussed in literature. Each method has additional associated details that dictate the structure of deposited catalytic species. It is not feasible to include exhaustive discussions of every method reported in literature. Here, focus is given to some of the most commonly used methods, including incipient wetness impregnation, wet impregnation, strong electrostatic adsorption, deposition precipitation, ion exchange, atomic layer deposition, and air-free deposition methods. Although this list is not exhaustive, the specific information required for consistent reproducibility of these methods highlights a majority of the specifics that should be reported in deposition techniques not commented on. These specific overview sections are accompanied by references that provide more detailed discussions on the synthesis methods and the influence of synthetic parameters on the resulting materials properties.

Best practices for reporting incipient wetness impregnation (IWI)

1. *General description of the approach*

Incipient wetness impregnation (IWI) is one of the most common methods for the synthesis of deposited catalysts. [16–18] IWI is superior to wet impregnation (section below), which makes it the preferred impregnation method. First, it is necessary to measure the incipient volume (pore volume) by addition of small volumes of solvent (generally water) until the material is homogeneously wet without running (saturation). Once known, the specific amount of precursor solution needed to provide the desired weight loading is dissolved into that volume. Then, this solution is added dropwise to the support with intermittent mixing, dried, and subjected to pre-treatment to form the active phase. If the mass of precursor needed is above what can be dissolved in the incipient volume of solvent, successive impregnations with intermediate drying are required. It is worth highlighting that the pore volume obtained from liquid measurement might differ from that obtained in the gas phase (e.g., BET measurements) due to the ability of gas to fill the micropores as well. This causes a difference in the deposition of the active phase and particle size distributions.

2. *Specifics not covered in the general section on reporting the materials and supplies used during synthesis*

- Mass of support used to measure the incipient volume,
- Solvent used to measure the incipient volume,
- Solubility of the precursor in the solvent.

3. *Specifics not covered in the general section on reporting the apparatus used during synthesis*

- Size of the container (e.g., porcelain or crystallization dish) used to measure the incipient volume.

4. *Specifics needed on reporting the synthetic protocol*

- Volumes of solvent used to determine the incipient volume,
- Number of impregnations (if sequential impregnations are needed to meet the target weight loading),
- Drying temperature, time, and environmental characteristics.

5. *Specifics needed on reporting the collection of the material following deposition*

N/A

Best practices for reporting on wet impregnation (WI)

1. *General description of the approach*

Unlike the IWI method, wet impregnation (WI) does not require measurement of the incipient support volume (pore volume), as the total mass of precursor required is dissolved in a specified volume of solvent, which is in excess to fill the pore volume. [18–20] Once the support is put in contact with the precursor solution, these are homogeneously mixed and subjected to a drying protocol, followed by a pre-treatment to form the active catalyst.

2. *Specifics not covered in the general section on reporting the materials and supplies used during synthesis*

N/A

3. *Specifics not covered in the general section on reporting the apparatus used during synthesis*

- How support and precursor solution are homogeneously mixed,
- Apparatus used to dry the material (e.g., rotovap or stirred open flask),
- If using a rotovap to dry the mixture: speed, bath temperature, condenser temperature, and time,
- If using a stirred open flask: flask volume and dimensions, atmosphere (e.g., forced extraction inside fume hood, under flow of inert gas, or under vacuum), stirring rate, and time.

4. *Specifics needed on reporting the synthetic protocol*

N/A

5. *Specifics needed on reporting the collection of the material following deposition*

   N/A

Best practices for reporting on the synthesis of catalysts by strong electrostatic adsorption (SEA)

1. *General description of the approach*

Strong electrostatic adsorption (SEA) of charged species onto oppositely charged support surfaces is frequently used for synthesizing atomically dispersed catalysts and/or supported monometallic/bimetallic nanoparticles with ultra-small sizes. [21–24] To achieve this, metal precursors and synthesis pH are chosen such that the net charge of the support surface is opposite to that of the precursor, in such a way that the precursor electrostatically adsorbs to the support, but repels other precursor molecules (Figure 3.B.2). This creates a situation where metal dispersion is maximized, at least prior to pre-treatment. In principle, the SEA synthesis process is simple and intuitive: oppositely charged species attract each other. In practice, however, complications can arise due to interactions between charged solution species and high surface area supports.

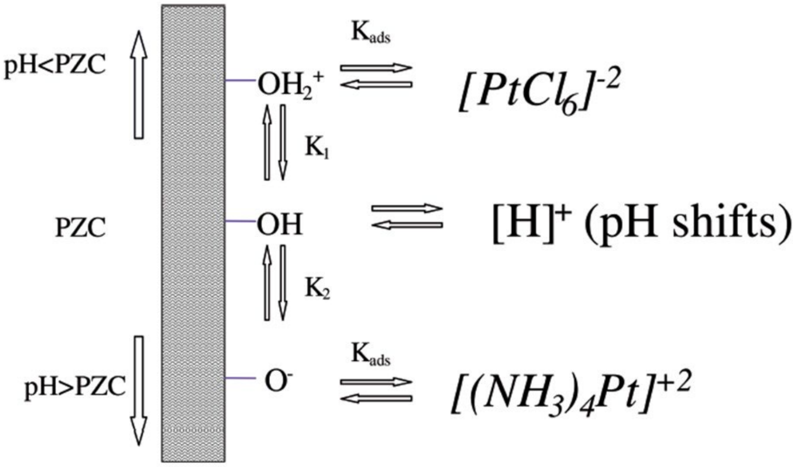

Figure 3.B.2. Strong electrostatic adsorption mechanism. Reprinted with permission from [24] by John Wiley and Sons.

2. *Specifics not covered in the general section on reporting the materials and supplies used during synthesis*
   - Point of zero charge (PZC) of the support material (also how this was measured; pH dependent zeta potential or titration with H^+/OH^-),
   - Speciation of the metal precursor as a function of pH with acid/base used for pH control. Either derived from literature or measured via UV-vis, ESI-MS, XAS, etc.
3. *Specifics not covered in the general section on reporting the apparatus used during synthesis*

   N/A

4. *Specifics needed on reporting the synthetic protocol*
   - Initial concentration and pH of metal solutions, final pH, and metal solution concentration after contacting with support (can close the mass balance with measurement of metal concentration on support),
   - Surface loading used during synthesis (specific surface area of the support times mass of support divided by solution volume, $SL (m^2/L) = [m_{support} (g) \times SA (m^2/g)] / V_{liquid} (L)$),
   - Order of addition of precursors to water, addition of acid or base, mixing of precursor and support solutions, further pH modification, etc.,
   - Contact time (electrostatic adsorption occurs on the order of minutes; no need for hours of contact, which may hydrolyze or dissolve supports).
5. *Specifics needed on reporting the collection of the material following deposition*

- Specific method of filtration,
- Characterization of solution following filtration to quantify metal uptake,
- Volume and temperature of washing solvent, washing method (e.g., ultrasonication, stirring, etc.), washing time, and number of repeated washes.

Best practices for reporting on deposition precipitation (DP)

1. *General description of the approach*

This method consists of the transformation of a precursor into a different compound with lower solubility in the medium, usually through a pH change. In the presence of a support, this results in the deposition and dispersion of the active phase. Frequently, deposition precipitation is carried out in the presence of urea, as its decomposition increases the pH gradually to avoid bulk phases in solution. [25–27] Deposition precipitation can also be conducted by decreasing the pH, using a reducing agent, changing the concentration of a complexing agent, or through a change of the valence state of the precursor via electrochemical reactions. [26]

2. *Specifics not covered in the general section on reporting the materials and supplies used during synthesis*
    - Precipitant used,
    - A plot of pH versus time, as these preparations often occur after a given induction time and then the pH changes rapidly.
3. *Specifics not covered in the general section on reporting the apparatus used during synthesis*

    N/A
4. *Specifics needed on reporting the synthetic protocol*
    - How the precipitant is added to the solution (e.g., syringe pump, increase temperature for decomposition of urea, etc.),
    - Precipitant addition or temperature increase rate.
5. *Specifics needed on reporting the collection of the material following deposition*
    - Specific method of filtration,
    - Volume and temperature of washing solvent, washing method (e.g., ultrasonication, stirring, etc.), washing time, and number of repeated washes.

Best practices for reporting on ion-exchange (IE) methods

1. *General description of the approach*

Ion exchange is typically used to incorporate metal cations into zeolites. The presence of Al^{3+} replacing some Si^{4+} in the structure leads to negative charges that can be counterbalanced by metal cations. [28] Although ion exchange (IE) has been frequently used to refer to strong electrostatic adsorption (SEA), it is worth highlighting that, unlike SEA, IE is pH independent. [24,29] Although IE can also be performed in solid state (e.g., through a grinding process), it is most commonly done in aqueous medium. Due to the reversible nature of the exchange, zeolites are usually put in contact with different fresh solutions of metal cations with intermediate filtering processes to maximize the uptake.

2. *Specifics not covered in the general section on reporting the materials and supplies used during synthesis*
    - Information about the exchange capacity (e.g., Si/Al ratio).
3. *Specifics not covered in the general section on reporting the apparatus used during synthesis*

    N/A
4. *Specifics needed on reporting the synthetic protocol*
    - Concentration of metal precursor used,

- Volume of water used for the slurry,
- Number of fresh solutions used for the exchange.

5. *Specifics needed on reporting the collection of the material following deposition*

- Specific method of filtration,
- Volume and temperature of washing solvent, washing method (e.g., ultrasonication, stirring, etc.), washing time, and number of repeated washes.

Best practices for reporting on atomic layer deposition (ALD)

1. *General description of the approach*

Atomic layer deposition (ALD) is carried out by alternating exposures of metal precursors and a co-reactant to a support surface, often repeatedly. [30,31] This is typically used with the goal of creating conformal, well-defined reactive species. Conformal deposition relies on surface self-limiting reactions between the molecules (precursors and co-reactants) and generated surface intermediates (Figure 3.B.3). Although some liquid-phase ALD methods have been reported, most ALD used for catalyst synthesis is carried out in the gas phase. The structure and composition of active phases prepared by ALD can be tuned by altering the deposition sequence and number of cycles.

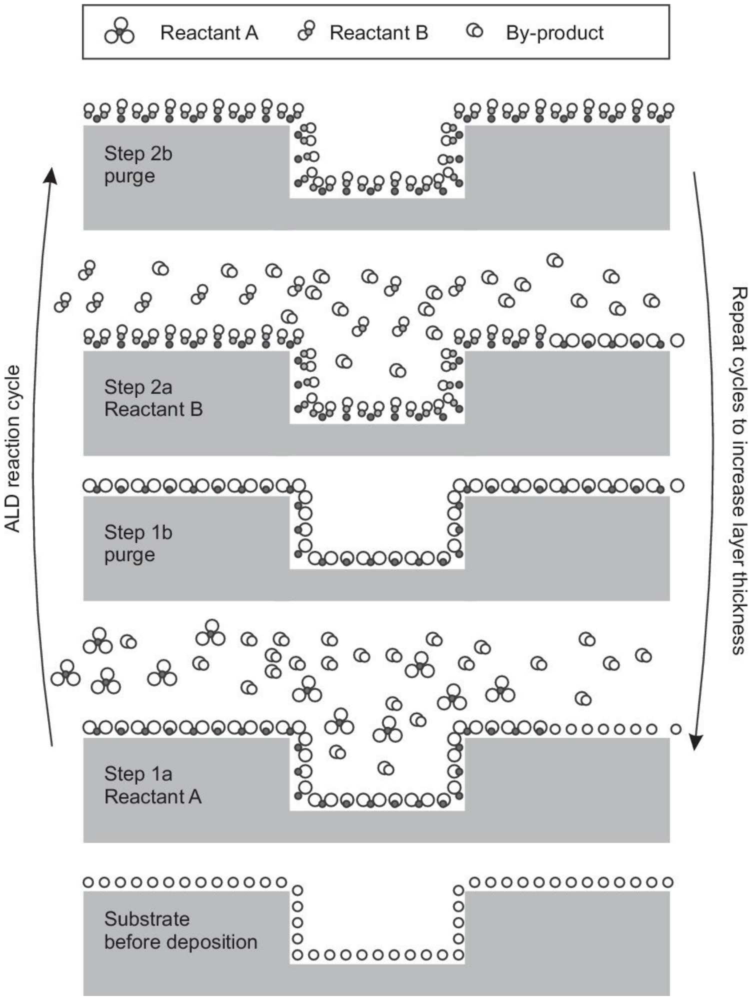

Figure 3.B.3*:* Schematic of atomic layer deposition. Reproduced from [31] , with the permission of AIP Publishing.

2. *Specifics not covered in the general section on reporting the materials and supplies used during synthesis*
   - History of the precursor: Many metal precursors (the source of metal used in the synthesis) can endure multiple heating and cooling cycles, although certain precursors are not stable under repeated thermal cycles.
3. *Specifics not covered in the general section on reporting the apparatus used during synthesis*
   - ALD reactor manufacturer/model if commercial,
   - Detailed reactor geometry/structure if home-built,
   - ALD reactor base pressure, carrier gas purity and flow rate, flow type (report Reynolds number),
   - ALD precursor container temperature and reactor temperature,
   - Type of precursor container: bubbler or cylinder,
   - Exposure time and evacuation time used in each step: was the precursor container pressurized or was the deposition a steady state process.
4. *Specifics needed on reporting the synthetic protocol*
   - Partial pressure/vapor pressure for each gas-phase molecule,
   - The loading of the deposited material (either assumed or measured gravimetrically) should be normalized to the surface area of the support to obtain growth rate per ALD cycle. The growth rate obtained from the high surface-area support should be compared with the growth rate on a 2D support (e.g., silicon wafer) reported in the literature. The growth rate on a high surface area support may be different than the growth rate on 2D supports. This can indicate that local concentration of reactant molecules differs in support pores (mass transport or thermal gradient limitations), that reactions are occurring within pores (either blocking pores or causing continuous surface reaction), or that evacuation is not complete on each cycle.
5. *Specifics needed on reporting the collection of the material following deposition*
   - Weight gain should be reported when possible.

Best practices for reporting on grafting/vacuum or air-free techniques

1. *General description of the approach*

Grafting/vacuum or air-free techniques, also known as surface organometallic chemistry (SOMC) or surface organometallic grafting (SOG), consists of the anchorage of organometallic or gas phase precursors (e.g., metal oxyhalides such as $VOCl_3$) to a support via reaction with surface groups (e.g., silanol). Those anchored species can be directly used as catalysts or can be transformed/modified into others (e.g., metal nanoparticles) through thermal treatments to be used as catalysts or to incorporate new organometallic compounds. [28,32–34] For that reason, it is desirable to use precursors with ligands that can be easily decomposed (e.g., HCl for $VOCl_3$). As most organometallic precursors are air-sensitive and/or moisture-sensitive or have increased sensitivity when supported on high surface area metal oxides, it is critical to perform the grafting under an inert atmosphere using glove boxes and/or Schenk techniques.

2. *Specifics not covered in the general section on reporting the materials and supplies used during synthesis*
   - Information about the sensitivity of the organometallic or gas phase precursor to air and moisture,
   - Characteristics of the support surface groups (e.g., –OH surface density and acidity/basicity),
   - Solvent purities and solvent purification methods.
3. *Specifics not covered in the general section on reporting the apparatus used during synthesis*
   - Air-free synthesis and handling of samples with techniques including Schlenk line, glove box, and sample transfer capabilities. These need to be spelled out in detail, with statements about the water and oxygen contents of the glove boxes.

4. *Specifics needed on reporting the synthetic protocol*
    - Statements about how samples are transferred to spectroscopic cells and reactors.
5. *Specifics needed on reporting the collection of the material following deposition*
    - Specific method for solvent removal,
    - Statement about the chosen temperature for removal of the organometallic precursor ligands (e.g., thermal gravimetric analysis data) and environment (inert, oxidative, reductive).

Recommendations for standardized characterization

A majority of this section on standardizing synthesis and characterization of deposited catalysts has described the information that should be reported during synthesis, pre-treatment, and storage of deposited catalysts to promote reproducibility. This leads to the question of what analyses or characterizations should be performed to justify that a catalyst has been reproducibly prepared.

The most obvious analysis is to compare intrinsic reactivity characteristics between a newly synthesized sample and a reference material. For example, comparisons of turnover frequencies, selectivities, rate constants, apparent activation barriers, and reaction orders for relevant probe reactions would be excellent initial analyses. The use of turnover frequencies as performance metrics would implicitly require characterization to count exposed sites, providing an additional physical parameter for comparisons. Benchmarking of reactivity characteristics should be made in recognition of batch-to-batch variability in the reactivity of the “control” sample. The choice of probe reaction is critical, depending on the information being derived. Different probe reactions have different magnitudes of sensitivities to the distributions of active site structures (structure sensitivity) and different sensitivities to contaminants. Probe reactions that are quite sensitive to characteristics of active sites without inducing significant changes to the material would be best suited. Because deposited catalysts vary significantly in composition, and reactivity, common probe reactions are not suggested.

In addition to reactivity, comparisons of physical characteristics of newly synthesized and control samples are important to substantiate claims of reproducibility. Because certain probe reactions can be less sensitive to certain catalyst characteristics than others, comparing and reporting physical characteristics is quite important. We refer to characterization sections for details on how to perform these analyses, and here simply list representative techniques. It is strongly encouraged to report bulk and surface compositions, including impurities (ICP, EDS, XRF, XPS, LEIS, etc.), fraction of active species exposed (reactive or adsorptive site counting are most common), surface area (BET), active phase and carrier crystal structure (XRD, Raman), and distributions of domain sizes of various species in the catalyst (electron microscopy, UV-vis, SS NMR).

In addition to information about the proposed active domain, information about the physical and chemical interactions between various species in the catalyst (e.g., alloy formation, solid-solution formation, spatial coincidence) can be important for reproducibility. This information can be obtained at small length scales using electron microscopy or spectroscopy techniques, and through sample averaged analysis via X-ray absorption, photo-electron spectroscopies, and probe-molecule spectroscopy, among other approaches.

Finally, formulated catalysts can contain various macroscopic domain structures, for example support domains of varying grain size or the addition of binders. The physical characteristics and reactivity of the active phase can be dependent on the nature of the supporting environment. Thus, reporting how the bulk and surface composition and physical catalyst characteristics change throughout the macroscopic heterogeneity of the support can be important to promote reproducibility.

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Recommendations for material synthesis and benchmarking: Supported and bulk metal oxides

Introduction and applications

Metal oxide catalysts constitute unsupported bulk metal oxides, unsupported polyoxometalates (POMs), unsupported hydrotalcites and layered oxides, and supported metal oxides. Each of these materials can be composed of one or more elements. Zeolites and (alumino)silicate molecular sieves are also oxide catalysts but are covered in a separate section of this report.

Metal oxides have physical and chemical properties (redox, acid and base) that make them widely useful as heterogeneous catalysts. Consequently, metal oxide catalysts find application for selective oxidation, total combustion, acid catalysis, base catalysis, hydrogenation/dehydrogenation, and reactions of syngas (mixture of CO and H_2). Oxidation, reduction, and acid-base catalysis are several of the most prominent reactions for metal oxides due to their efficacy in conversion and selectivity. In the table below (Table 3.C.1) types of reactions catalyzed by metal oxide catalysts with specific examples of each type and a partial list of known reactions for that class of catalyst are listed. Although appearing simple, oxide catalytic surfaces are complex, dynamic systems. For example, many of the elements in an oxide can go through changes in oxidation states as a function of environmental conditions. In some cases, portions of the oxides may be converted to a reduced metal phases (e.g., metallic copper sites for $CuO/ZnO/Al_2O_3$ catalysts during water-gas shift) or carbide phases (e.g., FeC during Fischer-Tropsch synthesis) during reaction.

Metal oxides are also useful supports for other active sites, however, these materials may potentially be non-innocent with many critical interactions taking place at the metal-support interface. [1] For supported metal catalysts, the domain size, geometric configuration and electronic structure of the metal nanoparticle is strongly affected by the oxide support [2–5] For reducible oxide supports, it has been demonstrated that under reducing conditions the oxide support cations can actually migrate onto the surface of the supported metal nanoparticles [6]. For supported metal oxide catalysts, the interaction between the supported metal oxide phase and the oxide support is more pronounced and can result in formation of a surface metal oxide overlayer that contains the catalytic active sites. [7] Furthermore, the support has been shown to greatly influence the activity of the supported oxide overlayer. [8–10]

As the catalysis community puts forth more complex and nuanced metal oxides, it is important to understand the underlying chemical properties that lead to reactivity and selectivity, which demands detailed knowledge about their surface and bulk properties. The availability of spectroscopic techniques has now made it possible to address the complexity of their surfaces by monitoring detailed structural and electronic changes under different environmental conditions (*in situ* and *operando* spectroscopy). Thus, ideally, the determination of the active phases and the active sites often requires characterization of the catalyst under operating conditions (*operando* methodology), including the relevant temperatures and partial pressures. [11–16] At the same time, while operando methodologies are preferred, the complexity and cost of these measurements and the measurement systems can be prohibitive for many investigators, and as such not reliably accessible. This should not be a disqualifying factor when considering quality contribution and work.

Table 3.C.1. Partial list of types of metal oxides and classes of commercial applications in catalysis. [17–19]

Metal Oxide Class	Specific Catalyst	Reaction
Acid Catalysis	Bulk and supported heteropolyacids (polyoxometalates), silica-aluminas, tungstated-zirconia, sulphated zirconia, protonated zeolites, niobic acid	acylation, alkylation, cracking, dehydration of alcohols, esterification, hydration of unsaturated hydrocarbons, rearrangements, isomerization
Ammonia	Potassium-promoted iron oxides	nitrogen plus hydrogen
Base Catalysis	alkaline earth oxides, alumina, basic clays, basic zeolites, hydrotalcites (and derivatives of), layered oxides, zirconia	aldol reactions, aromatic alkylations, condensations, hydrogenation, isomerization, Michael additions
Hydrogenation/ Dehydrogenations	Bulk and supported copper, iron, chromia, other transition metal oxides	alkane and aromatic dehydrogenation, alkene hydrogenation
Selective Oxidation	Bulk mixed metal oxides (vanadium-phosphate, molybdenum-ternary phase oxides), supported mixed oxides (VO_x/TiO_2, VO_x-WO_x/TiO_2, TiO_x/SiO_2 (TS1), promoted silver oxides/Al_2O_3)	oxygenate formation (acids, alcohols, oxynitriles, aldehydes, etc.) through partial oxidation of hydrocarbons, oxidative dehydrogenation, selective catalytic reduction
Syngas Reactions	Bulk and supported iron/chromia and copper/zinc oxides, supported iron and cobalt oxides	high- and low-temperature water gas shift. methanol synthesis, Fischer-Tropsch synthesis
Total Oxidation	hexaaluminates, perovskites, spinels, transition metal oxides (e.g., V, Cu, Cr, Co, Ti, Ag, Mn)	combustion (i.e.: VOC's, CO, methane), pollution remediation (NOx, NH3, urea)
C=C bond reactions	Supported WO_x/SiO_2, MoO_x/SiO_2, MoO_x/Al_2O_3, ReO_x/Al_2O_3, CrO_x/SiO_2	olefin metathesis/oligomerization

Common synthesis methods and reporting recommendations

Unsupported, single component metal oxides can be synthesized using wet chemical synthesis [20,21] (colloidal, sol-gel, co-precipitation, etc.), [22–24] solid-state, or pyrogenic methods. [25] Key metal oxides whose syntheses we have considered include TiO_2, [26] SiO_2, Al_2O_3, MgO, CaO, ZrO_2, HfO_2, Fe_2O_3, CuO, Mn_3O_4, MnO_2, Co_3O_4, ZnO, CeO_2, SnO_2, WO_3. This list of particular oxides were mentioned during the this workshop, but is not meant to be exhaustive. Hard and soft templating are common tools used in some metal oxide syntheses procedures. For example, some syntheses start with a hard template, such as carbon, which can be combusted later to create mesoporous structures in the oxide. Other solvothermal metal oxide syntheses use organic molecules (often surfactants) that serve as structure directing agents. One must ensure that these templates are properly removed. In the past, impurities of these organic molecules have led to problems with reproducibility, and whether they are or not fully removed can also be a problem for catalysis. [27] Metal oxides can also be synthesized to form particular structures (nanorods, nanowires, nanosheets, nanoparticles) [28] whose properties are dictated in part by their structure. [29] Ordered metal oxides form an important category of metal oxides. [30] Pyrogenic or fumed syntheses (combustion of metal chlorides) are commonly carried out by metal oxide synthesis companies. [26] Many such commercial oxides have been well characterized in the literature because of their wide availability. [30] An issue for synthesis of metal oxides is that the intermediate gels lack long range order and thus useful characterization is difficult. Further, the calcination process of the gel can yield very different final products depending on the time, temperature, pressure, environment, ramp rate, etc.

For unsupported bulk mixed metal oxides consisting of two or more metals, co-precipitation is used as a method to mix more than one metal salt precursor in solution. Precipitation is induced by changing the pH or by the addition of other salts, acids, or bases which cause differences in structure or chemical properties but are often unreported. Further steps require the aging of the gel; purification steps to remove undesired salts or solvent; and drying steps and calcination—steps which are often not reported with fine detail. The sol-gel method is another synthesis strategy that allows for highly controlled synthesis of mixed oxides with the use of a complexing agent. Further control of sol-gel (aero-gel) processes can be gained through careful control of the rates of hydrolysis and condensation in addition to solvent removal. However, the many steps to obtain the final bulk mixed metal oxide are often not reported and may result in irreproducibility. [26]

Supported metal oxide catalysts are most commonly synthesized by incipient-wetness impregnation (IWI) of a precursor that is soluble in a suitable solvent to assure optimum contact of the precursor with the surface of the oxide support. Prior to drying, the metal oxide precursor solution is subject to hydrodynamic forces such as capillary action that disperses the precursors in the support pores. The driving force for the anchoring and dispersion of the metal oxide precursors on oxide supports is the reaction of the precursors with the support surface hydroxyls and defects that reduces the surface-free energy of the final catalytic material. The surface diffusion properties of many metal oxides are related to their lower Tammann temperatures and therefore increasing temperatures to a certain degree facilitates this process. The strong interaction between precursors and oxide supports and the surface diffusion propensity of the surface metal oxides means that the final state of the supported metal oxides is not dependent on the precursors and solvents employed. [31–33] The anchoring of metal salts during aqueous dispersion may occur at elevated temperatures during drying/calcination. It is at that point that the driving force for wetting of the oxide support by the oxide overlayer operates. Although the IWI method is a straightforward method to yield fully dispersed surface metal oxides on an oxide support when conducted properly, some reported studies do not perform the IWI method very well and produce non-uniform catalysts. Non-uniform catalysts with metal oxide nanoparticles are formed when (1) the wet precursor solution is not intimately stirred with the oxide support powder, (2) the precursor has low solubility in the solvent, (3) the impregnated catalyst is insufficiently dried before calcination, and (4) the precursor amount exceeds monolayer surface coverage. The type of stirring and interaction for the solution with the support necessitates a reporting of scale and method for stirring or mixing. The cleanliness of the oxide support must also be confirmed since surface impurities are common and depend on the source of the support. [33] Fumed metal oxide supports tend to be freer of impurities than supports prepared by wet methods. Furthermore, exposing the oxide supports to high calcination temperatures (>600 ^{0}C) may surface segregate trace bulk impurities that will interact with the active sites and alter their structures and catalytic activity/selectivity. [34]

Common deficiencies when reporting synthesis details in the literature:

Possibly because co-precipitation of unsupported bulk mixed metal oxides is such a widely used method, the complete list of specific details often go unreported, which sometimes may make reproducible synthesis of the bulk mixed metal oxide materials challenging. The precursor solutions and the precipitation agent solutions or pH are often described, but the concentrations and the volume of these are unreported. Sometimes the pH is reported, but often within a range and not with a measure of acceptable deviation. Details regarding the order of addition or the time of addition (dropwise) are also neglected. With regards to aging, often the time is given, or the temperature is given, but rarely both. Very little is reported regarding the scale of the precipitation or stirring rates. Analogous to the co-precipitation method, details must be noted for the sol-gel synthesis of oxides. The details regarding the quantity and quality of precursors used, pH of solution, volume, heating rate of the solution, gel aging, and dry rates must be reported as significant deviance from the reported procedure can result in irreproducible oxides with differences in acid-base characteristics. Details regarding purification steps such as how much solvent was used to wash, centrifugation parameters, and evaporation of solvent are also sparsely reported. For drying conditions, temperature and time are often reported, as well as the time and temperature for calcination, but rarely is the ramp rate reported.

In an effort to increase transparency and synthetic reproducibility of our metal oxide catalyst materials reported in the literature, we have the following recommendations. While this list represents significant effort to write down in detail, only by collective commitment to reporting can we increase our reproducibility rigor between investigators and their locations.

Summary of synthesis information that should be included in publications:

- The brand and purity of all chemicals and gases must be reported.
- The exact synthesis steps must be reported in great detail such as volume, scale, temperature, order of addition, etc.
- Pre-treatment of supports undertaken before synthesis must be reported. Care must be taken to distinguish between incipient-wetness and wet impregnation methods; these are different i.e.: in case of incipient-wet, pore volume must be reported. Incipient-wetness impregnation method is the preferred method over wetness impregnation methods for reproducible results.
- For syntheses involving temperature treatments, temperature ramp rate, temperature holds, and cooling steps must be mentioned clearly.
- Storage of the material whether in atmosphere or in a desiccator must also be reported.
- Aside from the specifics listed above for synthesis, it is also helpful to report all color changes, evaporations, etc.
- Citation trails are common but should be avoided. Readers may not always have access to previous publications. Details regarding methods should always be reported in every paper.

There has been no widespread adoption of a forum or medium to discuss or adopted reproducible synthesis methodology of the broad family of metal oxides, and this is something that could generate value in the community. The International Zeolite Association has founded a Synthesis Commission to help this process within the zeolite community. [35]

Recommendations for standardized characterization

Due to the inherent complexity of the metal oxide materials described above, the properties that are important to reactivity vary depending on the material and the specific application. Necessary properties to consider are surface hydroxyl density, facet density, crystallinity, surface defect density, surface impurities, particle size, morphology, acid/base site density/strength, and redox properties, which could all be relevant or irrelevant for specific studies. For example, if only surface defect sites in a metal oxide are active, then the reporting of the entire BET surface area may not be relevant to the report discussion.

However, there is some minimum information that can help set comparisons that help in the first level of rigor and reproducibility evaluation. Many other sections of this report detail these best practices in reporting methods for synthesis, characterization, and reaction. For oxides, surface area and XRD measurements should be strongly considered for inclusion as surface area provides a simple understanding of the materials micro(nano) structure and XRD provides an initial discussion of the structure of bulk phases and their domain size and orientation for non-amorphous materials. If a catalytic conclusion depends on the levels of an intentional dopant in the materials, bulk and surface compositional analysis should be performed and reported. Impurities as provided from the vendor of raw materials should be noted, and we emphasize the importance of including lot numbers and vendors in experimental writing and documentation. Common elemental impurities in metal oxides from the original raw material sourcing should be understood so that observed differences in performance between laboratories, and accessible books exist that can detail the ores and sources for the elements that begin this conversation. [36] Characterization of a catalyst's properties described above under *in situ*/*operando* conditions is highly desirable. Many labs, however, do not have access to *in situ* or *operando* instrumentation, so this cannot be required, but collaborators with such instrumental capabilities should be sought out. However, in the case that *in situ* and *operando* characterization are not available, it is highly recommended that the catalysts be characterized post-reaction in order to understand deactivation or structural evolution with the understanding that things may have changed after reaction. Characterization of spent catalysts should be accomplished while minimizing exposure to ambient conditions (e.g., molecular oxygen and moisture) by executing sample transfers in an air-free environment (e.g., glovebox). The community must learn to understand the limitations of some investigators and their ability to reduce exposure, and therefore not judge, with the trade-off of better transparency regarding the conditions of characterization. With full disclosure comes not judgement, but the basis for scientific discussion on noted variation in findings and what that might means for active site interpretation and description.

For comparison of the reactivity of unsupported *bulk mixed metal oxides*, we suggest that the following measurements are considered:

- Details of sample pretreatment before any characterization technique must be reported.
- Physical properties of the catalyst powder, such as surface area measurements (e.g., N_2 physisorption), porosity characteristics, and particle size of the mixed metal oxide phase.
- Crystalline phases of the material are also necessary to determine if one or multiple bulk phases are present and confirm that the synthesis of the desired bulk phase was achieved (e.g., XRD or Raman).
- TEM analysis to determine if the bulk crystalline phase is encapsulated by a thin amorphous phase.
- Surface analysis of the bulk mixed metal oxide phase to examine for surface impurities and elemental composition of the outermost surface layer(s). While XPS is commonly available, other techniques such as LEIS, SIMS and DRIFTS may provide better sensitivity for common surface impurities.
- The entry for characterizing chemical properties includes measurements of redox/acidity/basicity (adsorption of chemical probe molecules (e.g., NH_3, CO_2, CH_3OH, TPD, TPSR and TPR with DRIFTS). The best chemical probe molecule is usually one of the reactants that will be used in the reaction (e.g., CH_3OH for methanol oxidation, etc.).
- It is important to quantify the number of active sites (e.g., titration with a suitable chemical probe molecule or isotopic labeling) because it is critical for the determination of the TOF value.

For comparison of the reactivity of *supported metal oxides*, we suggest that the following measurements are considered in addition to the ones listed above:

- Chemical analysis of the catalyst to examine for surface impurities (e.g., XPS, LEIS, low temperature CO DRIFTS). [34,37] XPS "survey spectra," where all energies are scanned, should be reported to account for the possibility of unexpected impurities.

- Confirmation that a surface metal oxide phase was achieved (e.g., *in situ* Raman, $CO/CO_2/CH_3OH$ DRIFTS).
- The entry for characterizing chemical properties includes measurements of redox/acidity/basicity. Although H_2-TPR is most commonly employed to probe the redox character of metal oxides, H_2 is not representative of many reactions since the reactions don't involve breaking H-H bonds (typically O-H, C-H, C-C, C=C, etc.) and, therefore, may give misleading reducibility information.
- It is important to quantify the number of active sites for the determination of the TOF value. The number of surface metal oxides species is typically also used for determining TOF values since they should be 100% dispersed below monolayer coverage or maximum dispersion.
- Characterization of a catalyst's properties described above under *in situ*/*operando* conditions is highly desirable.

Use of characterization data of previously published materials within the same research group

While previously published materials can sometimes be referenced, they must be referenced with caution. Some information is likely to be relevant from publication to publication while others will be different. For example, the following information can likely be referenced from previous publications if the *exact* synthesis procedure is followed:

- For unsupported bulk mixed metal oxides: crystal structure/surface composition/active site(s).
- For supported metal oxides containing only surface metal oxide species: properties of the oxide support/monolayer surface coverage/molecular structure/active site(s).
- Chemical properties: Relative acidity/basicity/redox for similar types of catalysts.
- Well-characterized model materials are useful for spectroscopic assignments, especially when supported by theoretical calculations.

However, the following properties should be tested and reported in every publication:

- Surface impurities: Oxide supports if supported metal oxides and all catalysts before and after reaction.
- Structure: To assure that the synthesis is reproducible, each time the details have to be reported (including methods, solvents or even bulk oxide support with significant difference in particle size, exposed facets etc.).
- TOF: It is highly recommended that rates be reported as normalized to a relevant catalytic property for the metal oxide. In this respect, the mass of material is not sufficient. While a turnover frequency is preferred (turnovers per active site per unit time, e.g., molecules/site-s), it is recognized that there may be considerable disagreement as to the exact chemical structure on a metal oxide that comprises an active site since the whole of a metal oxide surface need not be active for a particular chemistry. However, some well-reasoned and documented methods of site normalization by reporting areal rates (limit to unsupported bulk metal oxides), rates per measured redox/acid/base site, or other metric, is preferred for discussion with the expectation that sufficient information is provided that any subsequent reader of the publication may recast the TOF into another site comparison for their work and subsequent discussion.
- For new catalysts: all chemical and physical properties

Recommendations for benchmarking properties and performance

In benchmarking the reactivity of metal oxide catalysts, experiments are not difficult to reproduce when good characterization is available or good synthesis methods are adopted. Providing an explanation about the rationale behind the measurement will provide better papers with specific details for a measurement collected and what conclusion can be obtained from the data. Additionally, both editors and reviewers need to allow or provide equitable access to requests for measurements and experiments needed for publications. For example, surface properties are important to distinguish from bulk properties. The determination of surface impurities, surface composition, and surface density of active sites, defects and oxygen vacancies are important correlations for activity and are demanding to measure since the activity may not directly correlate to these observed properties. This is because when catalyst properties are measured common issues are encountered such that "optimum reaction conditions for one catalyst may be markedly suboptimal for another, and the nature and number of active sites may evolve during the test," or measurement. [38] In addition, the synthesis, storage, and preparation of these materials may also change the property being determined if care is not given to variables that affect metastable metal oxide outcomes (humidity, treatment temperatures, aging). Every publication needs to specifically address conversion, selectivity, apparent barriers, etc. for exact replication of catalyst synthesis and similar reaction conditions. Reproduction of this data from previously published work from the same group is only possible if the tests are done within a short time frame as material metastability may change over time.

From Table 3.C.1, it is clear that metal oxides can do a variety of different catalytic chemistries, that this makes choosing a single benchmark material a difficult task. There was no particular consensus among group discussants about a single metal oxide that exhibits all the characteristics of oxides more broadly, as discussed in the introduction. Our discussion eventually focused on a small set of metal oxides that together might be representative of typical characteristics: SiO_2 (a non-reducible oxide with very weak acid character), a transition Al_2O_3 (non-reducible with strong Lewis acid character), ZrO_2 (weak Lewis acid sites and basic sites) and CeO_2 (a redox basic metal oxide with the ability to form vacancies). With these oxide support materials, if standards could be sourced in the community, they broadly could provide the community with a selection of representative benchmarks across laboratories to compare both characterization and reaction results.

Suggested sources for standards

While any of the metal oxide material in the industrial list of Table 3.C.1 might be available from commercial vendors or other locations, proprietary modification of these materials by individual manufactures to achieve desired performance will likely render the materials unsuitable as collaborative standards. There are "available" and mass-produced metal oxides that can be obtained from commercial sources, national institutes, and companies. Micromeritics Instrument Corporation [39] often offers some sample meant as adsorption standards, but may be applicable for other characterization or simple reaction needs. NIST has standard reference materials such as zeolites, TiO_2, Al_2O_3, and SiO_2 that could serve the same purpose. [40] Available options as of 2023 are the following materials shown in Table 3.C.2:

Table 3.C.2. Standard or certified reference materials with source, processing information, and cost as of spring 2023

Standard/ Certified Reference Material	Description	Qty. (g)	Cert. Date	Material Source	Material Processing	Cost ($)
NIST 423	molybdenum oxide concentrate	50	2012/02/12	Highland Valley Copper (Logan Lake, BC, CA)	dried, acetone washed, sieved, mixed	549
NIST 670	rutile ore	90	1993/01/22	Bethlehem Steel Corporation (Bethlehem, PA, USA)	sieved	441
NIST 676[a]	alumina powder (XRD standard)	20	2015/11/04	Baikowski International Corporation (Charlotte, NC, USA)	N/A	N/A[a]

NIST 691	reduced iron oxide	100	2021/04/21	Allis-Chalmers (Milwaukee, WI, USA)	crushed, ground, sieved, mixed	499
NIST 742	aluminum oxide pyrometric standard	10	1990/07/06	commercial source	calcined	481
NIST 1898	titanium dioxide nanomaterial	15	2020/10/08	Aeroxide TiO_2 P25, Evonik North America (Parsippany, NJ, USA)	homogenized	620
NIST 1979	nano-crystalline zinc oxide (XRD standard)	2x3	2021/06/04	Zinc oxalate 99.999%, Alfa Aesar (Ward Hill, MA, USA)	vacuum annealing, see certificate	970
NIST 2556[b]	used auto catalyst	70	1993/08/24	INCO Ltd. (Copper Cliff, ON, CA)	pulverized, blended	475
NIST 2696	silica fume	70	2017/09/08	Elkem Materials, Inc.	N/A	N/A[a]
NIST 2910b	Hydroxyapatite	2	2015/12/16	NIST and ADAF Volpe Research Center	see certificate	1220
NIST 8850	zeolite Y	35-40	2020/12/11	zeolite-producing company	transferred	441
NIST 8851	Zeolite A	35-40	2020/12/11	zeolite-producing company	transferred	441
NIST 8852	ammonium ZSM-5 zeolite	35-40	2020/11/13	zeolite-producing company	transferred	441
Micromeritics 004-16880-00	alumina, $5m^2/g$	6 vials	N/A	N/A	N/A	950

[a] out of stock at the time of this writing

[b] also available in monolith form (NIST 2557)

Companies that revolve around catalyst property measurement could be seen as logical sources of potential reference metal oxides to the community if it was willing to purchase in significant quantities as to justify the resources required at said companies. While simple metal oxide materials such as alumina, silica, titania, or ZSM-5 are not necessarily the best catalyst for every chemistry, including characterization and catalytic results for simple and available metal oxide standards in archival journal report for everyone’s chemistry provides a common basis between laboratory to question differences in results due individual catalytic and characterization results, assisting interpretation for the whole community.

There are advantages and disadvantages to using any materials selected as a standard. While an available material may have a low cost and be readily available in a few shipping days with the same stated chemical formula and SDS, the chemical impurities, structure, and batch may be different even within a few months if purchased from a company. This can be overcome by using materials from a reference organization, but there is high cost in producing a reference material that can make it expensive for members of our community. More complex metal oxides may be available from vendors, but unless it is a widespread commercial material (e.g., Titania P25) there may be limitations based on what you are allowed to characterize, such as structure but not impurities, physical properties but not chemical properties. Additionally, one can possibly obtain a standard from a larger source such as an industrial standard. In these cases, sometimes a request can result in a kilogram of sample to a person with ties to the network (e.g., via collaboration) while others result in no response to the request. As a result of these thorny issues from commercial sources, it is difficult to bridge the gap for community standards for those with lots of resources and those with little.

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Recommendations for material synthesis and benchmarking: Supported metal nanoparticles

Introduction and applications

This section focuses on the selection of materials, synthetic methods, and characterization methods to enable the benchmarking of model catalytic reactions both within and across laboratories to increase the rigor and reproducibility of reported results for novel materials and chemistries. The intent is that future work includes comparisons of physical properties and catalytic observables on benchmark materials to validate synthesis and characterization methodologies and to add credence to the interpretation of catalytic tests. This benchmarking could include use of commercially available benchmark materials; simple and accessible synthesis methods to create benchmark materials within laboratories or centralized support laboratories; and combinations of physical and catalytic measurements to be made both on benchmark materials and materials of interest for specific catalytic studies. We discuss some challenges with the implementation of commercial benchmark materials and then propose strategies for enabling in-lab synthesis and testing of suitable benchmark materials. In particular, we describe common underlying physical and chemical phenomena that contribute variability in the outcome of certain synthesis methods (e.g., drying rates, thermal treatments, impurities, provenance of supports), identify synthesis methods that seem less sensitive to these variables (e.g., strong electrostatic adsorption in comparison to incipient wetness impregnation), and suggest the development of published text or and video resources that explain common synthesis pitfalls and provide complete descriptions for methods that give reproducible materials. We supplement this discussion by pointing to existing published sources of information on these topics to provide a centralized accounting of these resources.

Common synthesis methods and reporting recommendations

Metal nanoparticles and supported metal nanoparticles used as catalysts may be formed from a variety of methods and chemical precursors. Many different synthesis protocols are reported for even “simple” materials (e.g., Au colloids, Pt nanoparticles on silica), however, physical, chemical, and catalytic characterization of ostensibly similar materials often reveal discrepancies. These discrepancies may originate from use of different components (or apparently identical components but with different provenance) intended to introduce a given element (e.g., metal nitrates or chlorides precursors), provide a specific support, or confer chemical or physical interaction (e.g., ligands) purported to influence the morphology, size, composition, or spatial distribution of elements (e.g., ligands), etc. The intent and manner for combining the components, chemical reductants or oxidants, and the temperature programs may be explicitly (or implicitly) described. Yet, however, unrecognized or non-ideal effects of the chosen synthesis procedure led to differences between the outcome from different research groups or from researchers within a single laboratory may be present. Consequently, reducing the number of these unrecognized and unreported aspects of the synthesis procedures is important.

We recommend standardizing the use of well-documented materials and synthesis procedures when preparing materials for use as benchmark catalysts. In Table 1 below, we outline a few classes of reactions frequently encountered in current literature along with suggested relevant metal nanoparticle catalysts and synthesis methods that can provide reproducible materials while minimizing the presence of potential interfering surface adsorbates. Many of these methods involve chemical processes and interactions between metal precursors and the support during synthesis that improve reproducibility of metal loading, distribution across the support, and consequently the ultimate size and location of metal nanoparticles formed. The guiding principles for a number of these synthesis strategies are described in instructional references that describe monometallic metal nanoparticles and bimetallic nanoparticles. We recommend that readers consult these reviews [1,2] and the primary citation contained within them to familiarize themselves with methods and the intent behind each step of these procedures.

Here we provide a few examples primarily focused upon the synthesis of monometallic metal nanoparticles upon refractory (non-reducible) supports. This broad class of materials can be the basis for useful benchmarks because their preparation and typically monofunctional nature help reduce the sensitivity of catalyst testing results to variations in elemental composition, spatial distribution of the metal atoms, nanoparticle size, and intraparticle transport. Regular synthesis and testing of these "simpler" (but still not simple) materials can serve multiple purposes including (1) providing a useful introductory exercise for new researchers and/or those who are familiarizing themselves with new synthesis and characterization methods and (2) helping to identify errors or inconsistencies in pretreatment, storage, etc. of materials as compared to their standard or best activity.

Table 3.D.1. Common reaction classes and suggested syntheses for suitable benchmark materials

Reaction	Material	Synthesis Methods
Aerobic oxidations	Pt-SiO_2, [3] Au-SiO_2, [4] Au-TiO_2, [5] Pd-SiO_2, [6] Ag-α-Al_2O_3 [7]	Strong electrostatic adsorption of chlorine-free complexes; deposition precipitation; controlled decomposition of Ag-amine-oxalate complexes
(De)hydrogenation	Pt-SiO_2, Pt-Al_2O_3 [3]	Strong electrostatic adsorption of chlorine-free complexes
Hydrogenolysis	Ru-SiO_2, Ir-SiO_2, Rh-SiO_2 [8]	Decomposition of strongly interacting organometallic complexes
Aerobic oxidations, Organic dye degradation	Au colloids, [9] Ag colloids [10]	Reduction of metal salts by sodium citrate in aqueous conditions (modified Turkevich method) followed by (a) mixing with support and (b) ligand removal via thermal, chemical, or UV-ozone treatment [11–13]

When following recommended synthesis procedures, researchers must be aware of best practices for preparation and material synthesis. The starting point is to develop, discuss, and document detailed procedures that address all steps in the process, the intent of each step, and report expected and encountered sensory observations (e.g., color change or warming of solutions indicative of adsorption or ligand exchange processes). The methods utilized within a single laboratory may be inspired or translated from publications, however, the specifics often differ due to resources and supplies available. Consequently, the present mode for each synthesis should be fully documented and reported and not simply referenced to earlier work. Characterization of the materials formed at intermediate steps by accessible methods (e.g., UV-Vis, gravimetry, compositional analysis, temperature programmed reactions, electron microscopy, volumetric adsorption of H_2, O_2, or CO) are useful to test if individual steps in a sequence achieve their intended purpose and to document the outcome of each step in the synthesis. The set of characterization methods accessible for each laboratory inevitably differ, however, the spirit of the recommendation is to invest attention and care to synthesis and characterization for benchmark materials commensurate with the level spent on the catalyst compared to the benchmark material.

These recommendations are given to minimize the likelihood of common pitfalls that cause synthesis procedures to fail or result in a material different from prior attempts. These pitfalls may stem from subtle differences in the chemistry among precursors (e.g., $Pt(NH_3)_4(NO_3)_2$, $Pt(NH_3)_4Cl_2$ versus H_2PtCl_6); structural, textural, and functional properties of common supports with identical chemical formulas (e.g., surface areas and particle diameters of SiO_2, Al_2O_3, TiO_2 supports), and approaches for transforming molecular precursors into nanoparticles with desired attributes (e.g., changes in temperature with time while drying in vacuum or reducing in mixtures of H_2 or other gases). Countless examples demonstrate that seemingly innocuous but *known* variations in the materials or procedures used impact the outcome of synthesis. In addition, less visible or unrecognized differences among purportedly identical materials (e.g., sodium content or chlorine impurities within SiO_2 supports with different provenance or with different lot numbers from the same supplier) may lead to difficulties in reproducing the results from prior syntheses. Consequently, practitioners should report source, purity, and lot numbers of all reagents. Similarly, the particle shape, dimensions, porosity, surface area, and other properties should be reported for formed materials used, because the structure of these materials (e.g., supports) is not captured by their molecular formulas but can directly impact the outcome of catalytic testing. As a final note, accurate measurements of catalytic performance or the quantification of kinetic parameters (e.g., appropriately normalized rates, rate constants, or activation energies) for a benchmark chemistry should be considered as one – and perhaps the most direct – form of characterization to confirm the benchmark catalyst behaves in a manner that resemble prior reports.

Recommendations for benchmarking properties and performance

Benchmarking efforts in catalysis are best served by benchmark materials that (1) can be synthesized reproducibly and (2) are well characterized. One approach to benchmarking of catalytic data is to generate standard benchmark materials that are then distributed to research groups for use in testing and characterization. Such a material would generally be produced by a single source and then shared in a "round robin" fashion where it is sequentially passed between research groups or a "hub and spoke" arrangement where a supplier provides material to each research group. The advantage to this centralized approach is that—in the ideal situation—each sample of the benchmark material is identical, which enables identification of any differences in research groups' characterization and testing protocols, sample treatment, and data analysis as well as providing a point of comparison for testing the performance of novel materials.

A major challenge to this idealized approach is the difficulty of synthesizing the benchmark material(s) reproducibly and at sufficient scale. Inconsistency across batches is a significant concern because even minor differences in structure, size distribution, or the presence of trace contaminants can lead to large differences in catalyst behavior. In addition, identifying a supplier to be responsible for producing such a benchmark material is non-trivial, as the resource and time demand of developing a reproducible process and carrying out thorough characterization is high. Support for the financial costs for the production of the material would need to be identified and guaranteed for a suitably long period of time to motivate the community to adapt to the use of these materials. The source and purity of all precursors would need to be known and a stable supplier of these precursors established. This is too large of an effort for one academic research group to take on for the whole community. The material would also need to be distributed at relatively low cost to make it accessible to researchers at all types of research institutions, and thus the benefit for a commercial supplier to produce such a rigorously controlled and carefully characterized material is low. Likewise, it would be important to know the precise synthesis conditions for the material, which a commercial supplier might be hesitant to provide freely. The production cost and personnel commitment would be similarly challenging for a national lab.

Two previous examples of this type of benchmark material are EUROPT-1 (Pt/SiO_2) and the World Gold Council gold reference catalysts (Au/TiO_2, Au/Fe_2O_3, Au/Fe_2O_3 on alumina beads, and Au/C).

EUROPT-1 was manufactured by Johnson Matthey (UK) under the supervision of Dr. Dennis E. Webster and characterized by the Council of Europe's Research Group on Catalysis, a consortium of academic research groups. The catalyst was provided to the research groups in the consortium with the goal of understanding how to best characterize this type of material. The results of this effort were published in a series of papers in *Applied Catalysis* [14–18] as well as in subsequent studies. [19,20]

The World Gold Council catalysts were manufactured by Süd Chemie (Japan) with supervision by Dr. Masatake Haruta. They were characterized at the National Institute of Advanced Industrial Science and Technology (AIST, Japan) under the supervision of Dr. Susumu Tsubota. The gold catalysts were distributed on request to any researcher with only a charge for handling and administration and were intended to provide a reference for researchers to benchmark their catalyst synthesis and characterization techniques. References to these gold materials being used as benchmarks for comparison appear in numerous publications. [21,22] Neither EUROPT-1 nor the World Gold Council catalysts are readily available at this time, in part due to the effort and cost required to maintain highly reproducible production of these materials. Anecdotally, several participants within the workshop possessed small samples of these original materials within their labs but had not used them in all cases.

Topics for future discussions

The focus of discussion on the synthesis of metal nanoparticles in this workshop focused on educating practitioners in methods, pitfalls, and complete reporting of synthesis procedures and the integration of characterization techniques throughout the synthesis process. The discussion centered around the creation of monometallic metal nanoparticles on less reactive forms of metal oxide supports. While these constraints are useful to initiate a conversation on recommendations for the community, a number of important areas were postponed for future discussions out of necessity. These topics include best practices for reproducible synthesis of multimetallic nanoparticles (e.g., substitutional alloys, intermetallics, high entropy alloys, or single atom alloy structures); the creation of bifunctional materials that possess unique active site functions upon metal nanoparticles but also upon the support (e.g., metal nanoparticles within Bronsted acidic zeolites); methods to control or account for interactions between metal nanoparticles and supports that modify or create distinct active sites (e.g., interfacial site between Au and reducible oxides; the formation of reduced metal oxide overlayers upon noble metal nanoparticles by the strong metal support interactions (SMSI)); and promoted metal nanoparticle catalysts (e.g., partially chlorinated Ag nanoparticles upon α-Al_2O_3), and other complex systems. These classes of metal nanoparticle catalysts frequently involve more components and a larger number of steps, which causes the form of the final material to be highly sensitive to each portion of the synthesis procedures (e.g., methods of contacting metal precursors with support or preexisting nanoparticles); thermal treatments; and catalyst activation procedures. Small variations in early steps of the synthesis are amplified through their impact on subsequent steps. Overall, many recommendations from above (more comprehensive training, reporting, and characterization) will improve reproducibility but a larger number of factors must be carefully controlled and their expected influence on the structure and performance of the active catalyst must be established in order to learn which factors matter most. Hence, recommendations for reproducible synthesis will follow insight to structure-function relationships for each form of catalyst based upon metal nanoparticles.

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Recommendations for material synthesis and benchmarking: Single-atom catalysts

Introduction and applications

We define single-atom catalysts (SAC) as materials in which the predominant species responsible for the observed chemistry are metal atoms (ions) isolated from other metal atoms on a support (i.e., no shared ligands within at least 2 coordination spheres). Although there are recent examples in the literature of metal dimers, trimers or even larger complexes or clusters with atomically precise sites showing unique and interesting catalytic activity, we limit our discussion here to single metal atom centers. One must recognize in all cases that metal atoms possess some ligand environment, even if this is merely M-O bonds with a metal oxide support. Supports can also be non-oxides such as boron nitride, activated carbon, polymers, and metal organic frameworks. There may also be ligands other than those derived from the support bonded to the metal, for example hydroxyls or ligands derived from metal precursors, see Figure 3.E.1. Support heterogeneity can lead to a variety of bonding environments even for completely dispersed metals. Active metal species in supported catalysts therefore frequently possess a variety of structures and coordination environments, and so care must be taken in assigning catalytic activity to any single structure. Our discussion will involve both guidelines on assigning the reactivity of single-atom active sites, as well as the chemistry occurring at these sites.

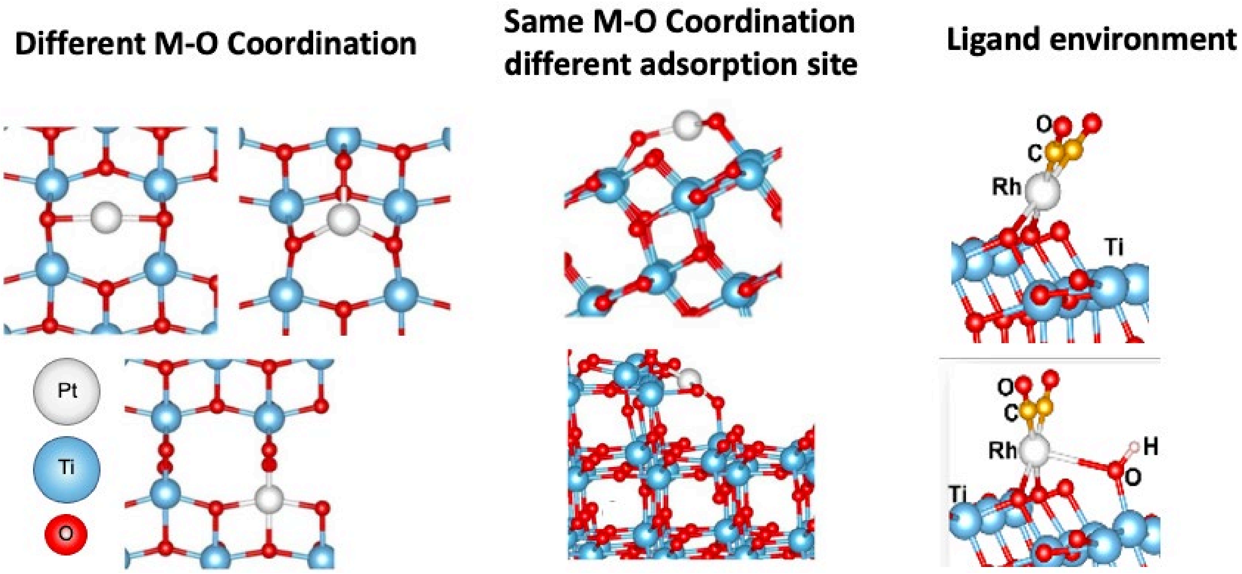

Figure 3.E.1. *left:* Pt atoms adsorbed on an anatase-TiO_2 (101) terrace in different coordination environments between the metal atom (M) and the oxygens derived from TiO_2. *middle:* PtO_2 species bound to anatase TiO_2 (101) and (145) stepped surfaces, showing that the same metal coordination environments can exist at different support sites, which results in different chemical and catalytic properties. *right*: Single atom Rhodium gem-dicarbonyl species, $Rh(CO)_2$, bound to anatase TiO_2 (101) with and without proximal OH species. In all schematics Ti, O, and Pt (Rh) are blue, red, and white spheres, respectively. *left* and *middle*: Reprinted from [1], with permission from Elsevier. *right*: Reproduced from [2] with permission from the Royal Society of Chemistry.

First, it is useful to compare and contrast SAC materials where the single atom is an early transition metal versus a late transition metal. SACs consisting of supported early transition metal active sites are well documented. [3,4] The heterogeneity of the oxide support surface (nature of surface hydroxyls and distribution of surface defects) and its reactivity towards deposited metal species directly affects the metal oxide anchoring site, molecular structure, and reactivity/selectivity. The surface mobility of deposited early transition metal oxides, due to their lower Tammann temperatures, assures that the early transition metal oxides selectively anchor at the more energetic support sites as long as a proper synthesis methods and low active site coverage is used. Once the specific anchoring sites are titrated or saturated by the atomically dispersed early transition metals, oligomers and clusters will begin to nucleate. This knowledge allows control of the distribution of the surface metal oxide sites among the different anchoring sites by surface modification of the oxide supports.

Single late transition metal atoms dispersed on oxide supports are rarely thermodynamically stable endpoints, even more so than the respective nanoparticles of the same elements. Single atoms may be entropically stabilized when surface loadings are low and temperatures high. The thermodynamic landscape that describes the stability of the metal-support combinations is poorly understood, being a function of many variables, including the chemical potential of surface binding sites, temperature, and gas pressure and composition. In particular, the diversity of surface binding sites on supports (facets, edges, steps, defects, surface hydroxyls), the bound ligands on single metal atoms, and the large number of alternative cluster configurations lead to difficulties in theoretically estimating the stability of single atoms.

Commercial single-atom catalysts

Although there has been a surge of interest in single-atom catalysts in the last decade, primarily relating late-transition metal active sites, the distinct activity of single metal atoms on high-surface-area supports has been recognized for more than 50 years. [5] Specifically, atomically dispersed early transition metal species (e.g. ReO_x, TiO_x, ZrO_x, VO_x, NbO_x, TaO_x, CrO_x, MoO_x, WO_x) that exist as stable species in high oxidation states on oxide supports have been studied for many decades. [6,7] Several commercial catalysts use single metal atoms supported on metal oxides. For example, atomically dispersed Re, Mo and W are used commercially for olefin metathesis. [8] Shell employs a single site Ti-silicate catalyst for their propylene oxide/styrene process. [9] Phillips uses a SiO_2-supported atomically dispersed Cr catalyst for polyethylene production. [10] Late d-band transition metal single-atom catalysts have not been commercialized to our knowledge.

Common synthesis methods and recommendations

Synthesis of single-atom catalysts requires kinetic controls to limit clustering and particle formation in the case where energetic support anchoring sites do not allow atomically dispersed species to have a lower overall free energy. This implies that many synthetic details, including the nature of the precursors, the synthesis environment, and the temperature(s) and time(s) employed in the preparation, may play a significant role in determining the final product. Support impurities can drive nucleation and growth behavior of metals, affect diffusion rates, and further complicate the transferability of recipes between research groups. Once formed, single atoms are anchored by ligands and adsorbates directly interacting with them. The resulting ligand environment can have a range of configurations leading to sites with different chemical states and different properties, see Figure 3.E.1.

Recipes for single-atom catalysts have been reported in the literature, but synthetic strategies for producing these materials often depend on the metal atom and support of interest, complicating the applicability and usefulness of benchmark controls. The required synthesis protocols are also markedly different for early and late-transition metal active sites. Representative synthetic approaches may however exist for certain classes of materials. The structure of the support plays an important role in determining the number of single atoms that can be supported. A few synthetic reports are highlighted and are primarily focused on late-transition metals.

Strong electrostatic adsorption [11] provides a relatively simple approach for depositing highly dispersed metal precursors, particularly if low metal weight loadings are used on high surface area supports. [12] If the strong interaction between metal and support is retained after treatment (which may involve reduction, calcination or simply thermal annealing) to modify or remove ligands present during precursor deposition, then single-atom catalysts may result. [13]

Atomic layer deposition (ALD) can also be used for preparation of single-atom catalysts, which involves the controlled self-limiting grafting reactions of well-defined mononuclear metal molecular precursors. Dose rate/time and temperature must be carefully controlled to avoid generation of clusters or nanoparticles; on the other hand, the ability to tune average nuclearity from single atom to larger clusters by varying ALD deposition procedures facilitates comparison studies among catalysts with different fractions of single atoms. [14] Care must be taken when using ALD to deposit metals within a porous support as limited accessibility of metal precursors may result in a non-uniform distribution of metal sites within the pores of the supporting material.

Other liquid phase deposition techniques, such as incipient wetness, have been used for the grafting of well-defined atomically dispersed metal species on oxide surfaces. For example, liquid phase grafting is commonly applied in surface organometallic chemistry, including with thermolytic molecular precursors. [6,15] Different supported metal molecular structures can be formed depending on the degree of dehydroxylation of the support (either silica or alumina) prior to grafting (with air-free conditions maintained). This has been demonstrated on supports beyond silica or alumina. [16]

In the so-called "atom-trapping" synthesis approach, single-atom catalysts of late transition metal elements (e.g., Pt, Rh, Cu) are prepared by in-situ generation of volatile intermediates followed by trapping on a suitable support. [17–20] Initially, metal nanoparticles are formed on a support such as alumina via conventional methods. Thermal treatment drives emission of volatile species (e.g., molecular PtO_2) from these nanoparticles, which may then migrate along the support surface or through the vapor phase to trapping sites on another support. In the presence of a support containing suitable trapping sites (e.g., step edges on ceria, [17] or nitrogen-rich sites on pyrolyzed carbon [19]), these mobile intermediates may become anchored as atomically dispersed species (i.e. single atoms). It has also been shown that the transport of mobile species does not have to be through the vapor phase, for example alternatively diffusion along the support, to utilize the atom-trapping synthetic approach. [21]

These synthetic methods are not the only approaches used for the synthesis of single-atom catalysts; many others have been reported [22]. The reader is encouraged to refer to the “Specific recommendations for deposition synthesis methods” section for more details on these methods.

Recommendations for standardized characterization

As these materials may often be structurally dynamic, it should be expected that the material may evolve over time, with the rates of change and types of changes being dictated by the environmental conditions. Therefore, in situ (or ideally operando) characterization is critical for understanding these catalysts under conditions related to the on-stream performance of the material. Ex-situ characterization may not represent the structure of the active catalyst during operation as exposure to reaction conditions may cause the catalyst to restructure. For example, at high C_2H_4:H_2 ratios, ethylene can cause oxidative fragmentation of Rh clusters supported on HY zeolite, resulting in the presence of single atoms, which catalyze ethylene dimerization. [22] In contrast, hydrogen causes sintering and reduction of Rh atoms on HY zeolite, resulting in the formation of clusters that selectively catalyze the hydrogenation reaction to give ethane. Oftentimes these changes are fully reversible, but in other cases the sample history will be critical to the distribution of catalytic species.

Further, any post-reaction characterization must be done with care to preserve the catalyst structure (and this might not even be possible). Water can have a strong effect on SACs as hydroxylation of oxide supports may facilitate metal sintering or re-dispersion. Water may also strongly adsorb or activate on single metal atoms and restrict their ability to activate other molecules. Given the ubiquitous existence of water vapor, even in “dry” environments, the role of water in dictating the structure and reactivity of single atom catalysts should always be carefully considered.

Various techniques including Scanning Transmission Electron Microscopy (STEM), X-ray Absorption Spectroscopy (XAS), Infrared (IR) of probe molecules, UV-vis spectroscopy, and Raman spectroscopy [7,23] are frequently employed to justify claims of the presence (and importance toward reactivity) of single metal atoms in a catalyst sample. [24] Each of these techniques has its own limitations, and potential users should be aware of them.

Aberration corrected (High Angle Annular Dark Field) AC-HAADF STEM has been the preferred imaging technique for analysis of single atom catalysts, particularly for heavy active elements like Pt and Ir, due to its favorable contrast and direct image interpretation. [25] Routine analysis can be performed on single atom catalysts with high atomic number and supported on light oxides. For some catalysts, the limiting factor for analysis is the image contrast. As the difference between the atomic number of single atom catalysts and oxide support decreases, imaging becomes limited to the thinnest section/fragments of the support. The thinnest fragments may not be representative of the overall support. Single atoms with identical or smaller atomic number as the cations of oxide support cannot be conventionally analyzed. In contrast, nanoparticles of low atomic number metals can often be identified by TEM/STEM. Hence, as a general rule the image of the catalyst after reaction should be reported in addition to the as-prepared catalysts. If initially present single atoms transform into nanoparticles, these will be "easier" to observe. However, the influence of air-exposure should not be discounted as potentially causing structural changes to the metal species since most TEM images are reported from catalysts that have been handled in air. Additionally, researchers should be aware that the meta-stable nature of single-atom catalysts makes them susceptible to beam damage. [26] Finally, this technique also has the disadvantage that it is not a sample averaged measurement, and often only a small portion of the sample is examined.

On the other hand, although EXAFS is a sample averaged measurement, rigorous differentiation of single atom species from the existence of sub-populations of small (often oxidized) clusters is challenging. For example, XAS spectra of Pt samples with 100% single atoms and samples with 75% single atoms and 25% oxidized nanoparticles are virtually indistinguishable. [27] Also, although not commonly discussed in literature, SAC can suffer beam damage from the high X-ray flux used at synchrotron facilities. [28]

IR spectroscopy experiments of CO adsorbed on Al_2O_3-supported Rh atoms were reported by Yang and Garland as early as 1957. [29] Probe molecule IR spectroscopy experiments must be planned with a recognition of the potential for changes in the nature of the catalyst in response to the presence of the probe molecule. Oxidative fragmentation of Rh clusters by CO on hydroxylated supports has been well-established, even at room temperature. [30] Conversely, CO is known to result in sintering of Pd and Pt on Fe_3O_4 [31] The widths of spectroscopic features in IR experiments should be consistent with a single adsorbed species, although broadening is expected depending on the heterogeneity of bonding environments of the single atoms to the support. [12,32] Additionally, for in situ/operando measurements it should be recognized that probe molecules such as CO only capture the sites that bind CO strongly. Furthermore, the IR spectrum is an average of all the intermediate states which can include states with no CO bound to the metal. Therefore, complementary in-situ/operando techniques that probe the metal directly, such as XAS, should be used to capture the ligand environment of all the metal atoms in the catalyst during reaction. [33] For early transition metals present as oxo species in the catalytic or precatalytic state (especially V, Mo), diffuse reflectance UV-visible spectra can reveal the relative contributions of single-site versus oligomeric species. [34,35]

Currently there is a need to further improve tools for characterization of single atoms under operando conditions. As discussed above XAS, IR, SSNMR, EPR, UV-vis, Raman, and TEM can be used under environmentally relevant conditions for the study of single atom catalysts, but limitations exist with each technique that preclude examination of many systems and limit the information that can be gleaned. This will require new efforts by the community to develop new tools for studies at higher temperature, higher pressures, and using high Z oxide supports.

Researchers in the field are also encouraged to explore additional spectroscopy tools such as Electron Paramagnetic Resonance (EPR) and Solid State Nuclear Magnetic Resonance (SSNMR) more widely to provide additional evidence for the state of the catalyst. To date these techniques have been underutilized in the exploration of supported catalysts. However, unique information can be determined with regard to bonding vs. non-bonding interactions between metal atoms and zeolite frameworks via SSNMR spectroscopy. EPR spectroscopy offers the ability to examine oxidation states of metals with extremely high sensitivity, however a select few elements are detectable and quantitative analysis can be challenging.

Recommendations for benchmarking properties and performance

Benchmarks to help guide the field might at first be thought to offer value. However, as the chemistry of each metal/ligand (support) combination is unique, it is not clear how to choose a benchmark that would broadly serve the community, except in cases for which improvements to existing commercial catalysts might emerge. There is no particular benefit to these materials in having a single reactivity benchmark. Of course, benchmarks can be developed specifically for each chemistry to help establish the proper conditions for performance. However, these should be benchmarks for assessing the reactor performance and not necessarily targets to exceed for best catalyst performance.

Molecular organometallic complexes have well-defined structures and generally exhibit similar coordination structures and oxidation states as supported single atom catalysts of the same elements (depending of course on pre-treatment conditions of the supported catalyst). Thus, it is sometimes worthwhile to identify molecular complexes that can serve as well-defined benchmarks for spectroscopic features of single atom catalysts to provide insights into symmetries and ligand environments of the supported species. [6,36]. However, it is important to appreciate that the initially well-defined structure of grafted organometallic complex may transform under relevant reaction conditions, and thus their structures and oxidation states should be assessed through the course of grafting and reaction conditions.

There are developing links between single-atom catalysts on metal oxide supports and those on metal-organic frameworks (MOFs) that incorporate metal oxide clusters as nodes. Metals in MOFs can be located at 3 positions: 1) in the nodes, 2) on the node, and 3) as part of the linkers. Metals bonded to the nodes are akin to SACs on metal oxides and because MOFs are crystalline materials and structurally more nearly uniform than most metal oxide supports, they provide more opportunities to understand the relationship between structure, bonding environment, and observed reactivity of supported metal centers than do metal oxide supports.

Specific Recommendations for reporting the inherent reactivity of SAC active sites in literature

An important goal of fundamental studies involving single-atom catalysts is the identification of the reactivity that can be uniquely ascribed to single-atom active sites. As reaction rates often change substantially with nuclearity, the existence of sub-populations of non-single atom active sites (i.e., clusters) can obfuscate understanding. This complexity suggests that the analysis of the contribution of single atoms to observed reactivity should involve investigations of multiple materials with systematically varied properties. In order to demonstrate this effect, it is necessary to use proper controls (e.g., to avoid comparisons of Pd_1/Fe_3O_4 vs. Pd nanoparticle catalysts supported on Al_2O_3). The comparisons are best done through a series of materials with varying site characteristics from predominantly single atom species to predominantly clustered or nanoparticle forms of the same metal on the same supporting material. Quantitative site counting techniques and site-specific characterization tools that can together estimate the fraction of exposed sites in the form of single atoms and clusters/nanoparticles could then provide information about the inherent reactivity of single atom sites. The series of materials should further be characterized to identify the structure and oxidation states of the metal species (in the best case, before, during, and post-reaction). For example, in Figure 3.E.2(a) it is shown how the turnover frequency (TOF) of Pt/TiO_2 catalysts for the hydrodeoxygenation (HDO) of m-cresol varies with Pt weight loading. By exploring a range of Pt weight loadings that is expected to navigate the Pt structure from primarily single atoms (0.025 wt%) to primarily Pt clusters (> 0.3 wt%), and further by characterizing the distribution of Pt structures via probe molecule IR spectroscopy (Figure 3.E.2(b)), rigorous site-specific assignments of TOF can be made. [37]

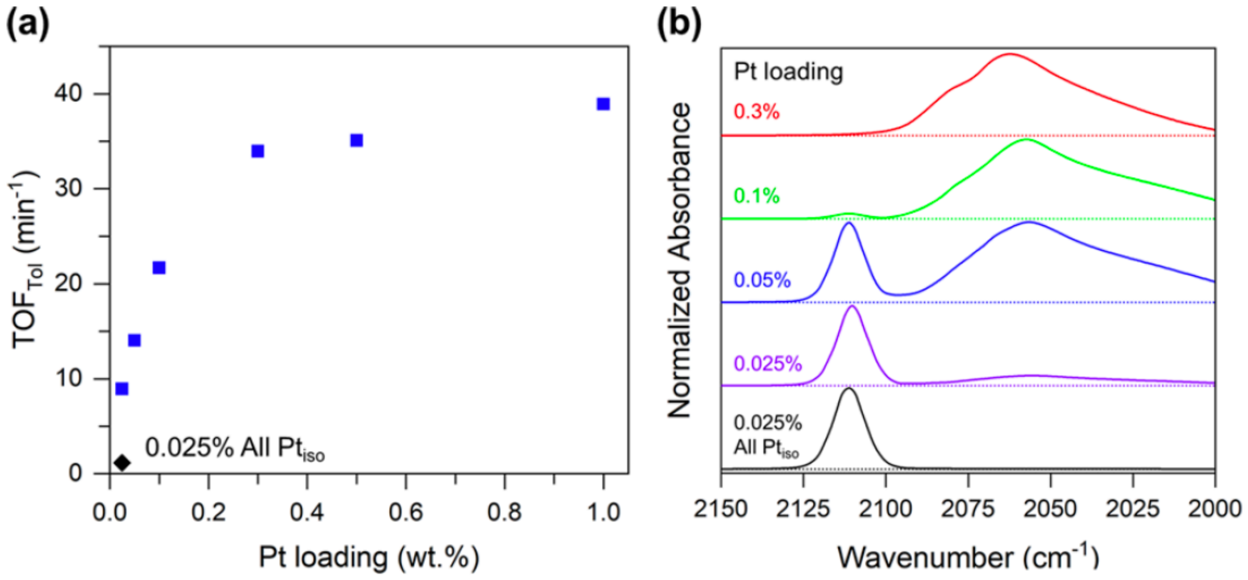

Figure 3.E.2. Activity of catalysts containing both single Pt atoms (Pt$_{iso}$) and Pt clusters for HDO of m-cresol. (a) TOF values (±1 min^{-1}) for deoxygenation of m-cresol to toluene at 350 °C for samples of different weight loadings from 0.025 to 1.0 wt %. TOF for higher Pt loadings is based on number of surface sites counted by CO chemisorption; a dispersion of 100% is assumed for lower weight loadings (<0.10% Pt). TOF of catalyst synthesized on higher surface area support containing exclusively Pt$_{iso}$ shown for comparison. Reaction conditions T = 350 °C; P = 1 atm H_2; TOS = 20 min. Conversion was maintained below 15% by adjusting W/F. (b) CO probe molecule IR spectroscopy of the same catalysts. Data normalized to maximum peak intensity and offset for clarity. Dotted lines are added to make weak features more easily visible. Catalysts were pretreated in situ in 50 sccm of a 10% H_2/Ar at 250 °C for 1 h, prior to exposure to 10% CO in Ar for 10 min at room temperature and subsequent purging in Ar prior to IR collection. Reprinted with permission from [37]. Copyright 2020 American Chemical Society.

Other recent examples have effectively utilized this approach through a combination of techniques for site counting and then examination of the kinetics of test reactions involving the same group of materials to determine the TOF as a function of metal loading. [38] If single-atom active sites have unique activity, then one should expect changes in reactivity as a function of metal loading and the metal nuclearity and oxidation state, such as a shift in the activation energy, [37] a shift in the reaction orders, [39] or changes in selectivity. [22] Researchers may consider how the activity varies with the loading even for clustered materials, following the example of Ribiero and co-workers. [40]

Based upon how the activity on a per site basis varies with metal loading, with a correlated understanding of how weight loading influences the distribution of exposed active site structures, specific hypotheses might be developed. It should not necessarily be expected there will be a linear dependence between loading and activity, even at extreme low loadings where only single atom species are expected, as the nature of the interaction of single atoms with the support may depend on the loading. [3] For example, the first metal atoms may bond to support defects imparting different activities on the single atoms from those supported on defect-free terraces. It may be possible to vary properties of single-atom sites depending on their bonding site to the supporting material. [41] It should be recognized that as the metal loading varies, the distribution of single atom coordination environments and concentration of metal clusters will change, but any catalyst measurement will be assessing the reactivity of an ensemble average of sites. Researchers should be aware of possible changes in the state of the metal that depend on reaction conditions.

Single atoms and nanoparticles of the same metal on a support are often characterized by different kinetics and different catalytic activities. Differences in the apparent kinetic parameters (e.g., apparent activation barriers and reaction orders) for single atoms and active sites on metal clusters can be particularly useful in differentiating the distinct reactivity of these sites. For CO oxidation on Ir/$MgAl_2O_4$, changes in the kinetics as a function of the reactant partial pressures were observed that contrast the single atoms and the nanoparticles. [39] The complexity could be resolved only by investigation of multiple samples with different distributions of single atoms and nanoparticles and the use of multiple tools to count and characterize active site distributions as shown in Figure 3.E.3. Kinetic measurements over a broad range of conditions can help identify contribution from even a minority species such as clusters and/or nanoparticles. [42]

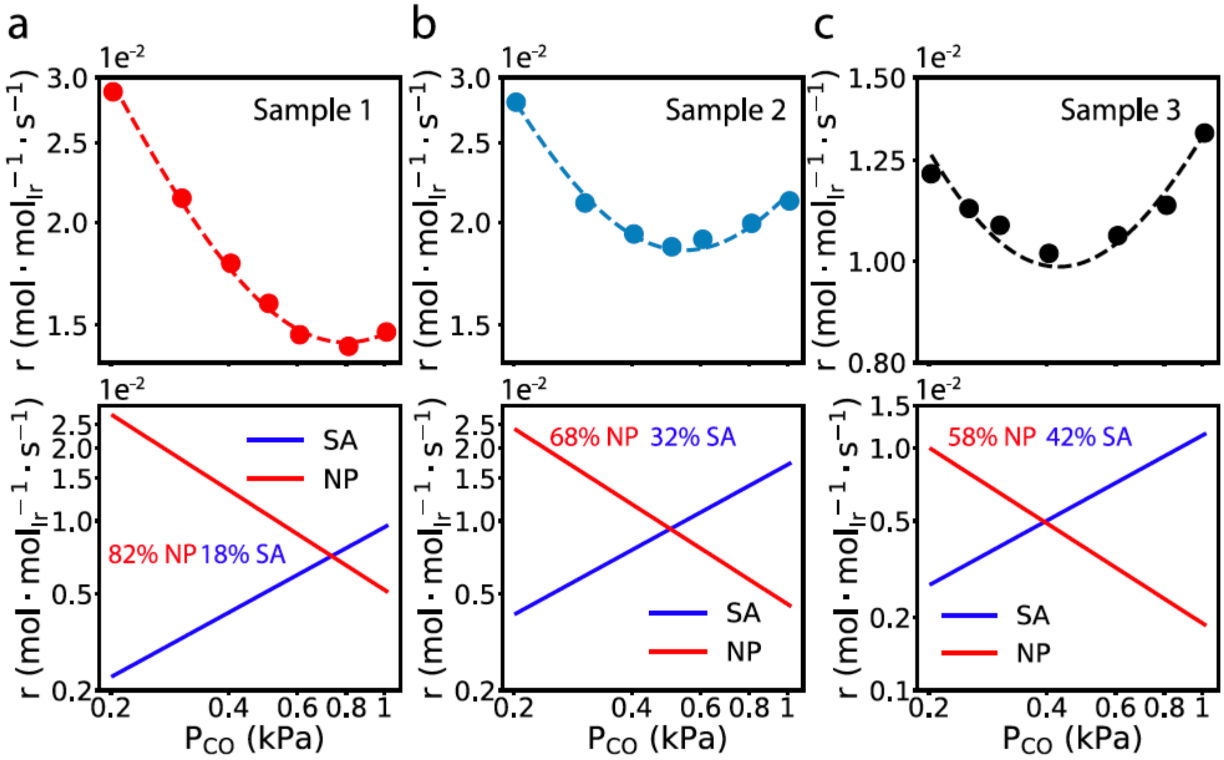

Figure 3.E.3. CO oxidation kinetic measurements (effect of CO partial pressure on reaction rate) on samples 1–3, which contain mixtures of Ir single atoms (SA) and nanoparticles (NP) and the results of fitting the reaction rate with a linear combination of single atoms and nanoparticles. All samples were measured at 155 °C with P_{CO} between 0.2 and 1 kPa and PO_2 at 10 kPa and T = 155 °C. The results were reproducible when the measurements were conducted from low to high P_{CO} or high to low P_{CO} and the catalysts were stable during the entire experiment (<10% deactivation). Top figures are experiments (filled circles) and fits (dashed lines). Bottom figures are the individual contributions of SA ($r_i(Ir_{SA})$ *n_{SA}/n_{Ir} , blue lines) and NP ($r_i(Ir_{NP})$ * n_{NP}/n_{Ir}, red lines) in each sample. (a) 1 wt % Ir on $MgAl_2O_4$ without calcination and reduced at 800 C in H_2 (sample 1); (b) 1 wt % Ir on $MgAl_2O_4$ calcined at 500 °C and reduced at 800 °C (sample 2); (c) 0.05 wt % Ir on $MgAl_2O_4$ calcined at 500 °C and reduced at 500 °C (sample 3). Reaction rate of samples 1–3 were normalized by the total moles of Ir in each sample. The percentage of SA and NP from fitting the reaction rates of samples 1–3 were (a) 18% SA + 82% NP, (b) 32% SA + 68% NP (c) 42% SA + 58% NP, respectively. Reprinted from [39], with permission from Elsevier.

Now that a significant body of recent literature has provided strong evidence that single atoms can be used for many different reactions, and exhibit unique reactivity as compared to metal clusters of the same element, workers in the field should more deeply interrogate the underlying principles that govern their activity. How do the nature of the support (ligand environment) and metal dictate the types of bonds that can be activated? How does support heterogeneity play a role in the dynamic nature of these catalysts (both restructuring broadly, but also during catalytic turnovers)? What parallels can be drawn from organometallic chemistry that provide insight into the optimal choices for metal/support combinations?

The support is not only a means of stabilizing the metal, but the support (ligand) environment can play a key role in the observed activity. Recognizing that the species are dynamic in nature and that the support gives rise to a distribution of species, each with their own unique reactivity, one realizes that reactivity may be governed by a minority of these species. To advance the science in this area, one would like to predict how to choose support materials that will impart the desired activity and which species among the distribution of active sites are responsible for a majority of the catalytic turnovers.

There is a trend in the field to claim that new catalysts are "best performing materials to date," but these comparisons are often reports of data collected under conditions that are not industrially relevant and lack proper context. Researchers are encouraged to focus on a science-based approach and minimize performance metrics unless clear industrial benchmark materials and reaction conditions exist.

Finally, researchers should recognize that it is usually not possible to demonstrate conclusively that single atoms are the sole active site responsible for observed reactivity in a catalyst sample. A realistic goal is to obtain data that is consistent with a hypothesis that only single-atoms are the active sites.

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Recommendations for material synthesis and benchmarking:

Zeolites

Introduction and applications

Zeolites and zeotypes, crystalline and porous silica-based framework materials with uniform pores of molecular dimensions, find applications as heterogeneous catalysts for the synthesis and derivatization of hydrocarbon fuels in petrochemical refining (e.g., fluid catalytic cracking, hydrocracking, reforming, dewaxing, etc.), for pollution abatement (e.g., NOx and unburnt hydrocarbons in automotive exhaust), and for a variety of isomerization and alkylation chemistry of relevance to the petrochemicals sector. [1–5] The remarkable practical successes in this sub-field of catalysis have spurred over the past decades an intense research effort in both academic and industrial laboratories around the world towards the synthesis and characterization of new framework structures. Underpinned by advances in chemical characterization, spectroscopy, and theory, a focal point for the field of zeolite catalysis in recent years has been the control of crystal size and shape to better exploit diffusive properties of these materials and thus expand their range of applications. [6,7] Additional efforts have focused on developing less costly synthesis methods using more diverse and accessible protocols and structure-directing agents. In addition to framework topology (represented by a three-letter code), framework composition (i.e., the atomic Si/Al ratio of the tetrahedra in the framework) and extra-framework cation content, numerous characteristics can be tuned to optimize the performance of a zeolite including crystallographic positions of Si and Al atoms, [8] crystallographic location of extra-framework cations, crystal size and shape, extent of crystallite aggregation comprising a zeolite particle, the presence of mesoporosity, the occurrence and frequency of intergrowths with related framework types, and other types of defects like Si or Al framework extralattice species or vacancies associated with Lewis acid sites [9] and hydroxyl nests [10] (See Figure 3.F.1.). Along with the physical characteristics of the material, this tunability allows for zeolites to be synthesized with varying populations of different catalytic sites including Brønsted acid, Lewis acid, [11] and redox sites, the relative amounts of which can be tailored. Zeolites can also serve as a support for active metal nanoparticles. [12]

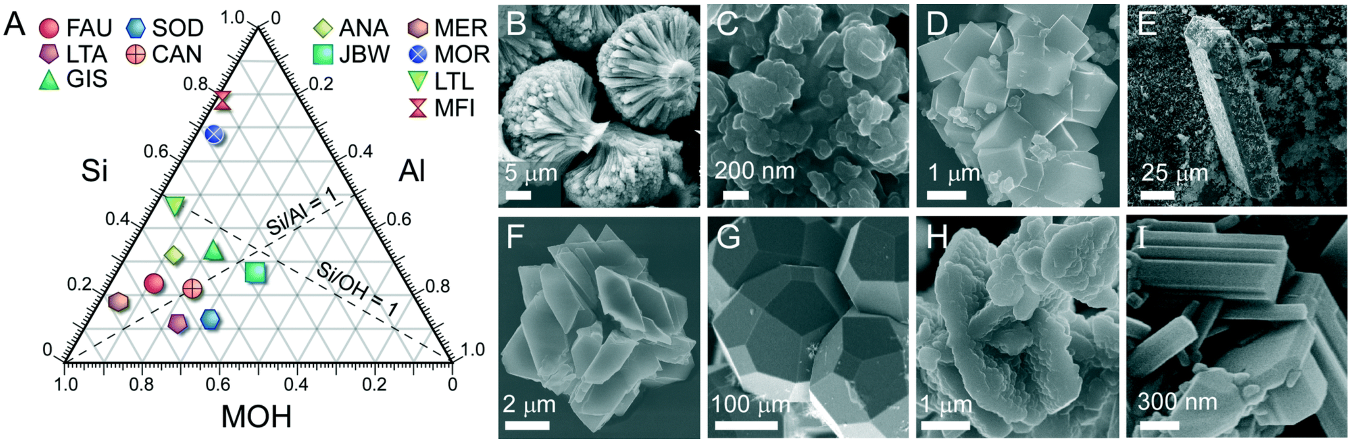


Figure 3.F.1. (A) Kinetic phase diagram highlighting representative molar fractions of zeolites prepared with alkali metals (M+ = Na+ or K+) and without organic structure-directing agents. Scanning electron micrographs of the zeolite crystals (B) K-MER, (C) Na-FAU, (D) Na-LTA, (E) Na-JBW, (F) Na-GIS, (G) Na-ANA, (H) Na-SOD, and (I) Na-CAN. Reproduced from Ref. [13] with permission from the Royal Society of Chemistry

Common synthesis methods and recommendations

Zeolites are most commonly produced by a hydrothermal synthesis approach, [14] wherein a zeolite gel is first made by mixing together raw materials in a prescribed fashion, followed by heating the zeolite gel in an autoclave at elevated temperatures and autogenous pressure to convert it into the desired zeolite phase (Figure 3.F.2). The zeolite is then separated out of the slurry by a method like filtration or centrifugation. In cases where organic structure directing agents (OSDAs) are used to form a particular zeolite structure, the OSDAs are typically removed by a high-temperature oxidation treatment, whereas alkali cations are removed by liquid-phase ion-exchange. Alternate approaches to hydrothermal synthesis include dry gel conversion and other solid state transformation processes.

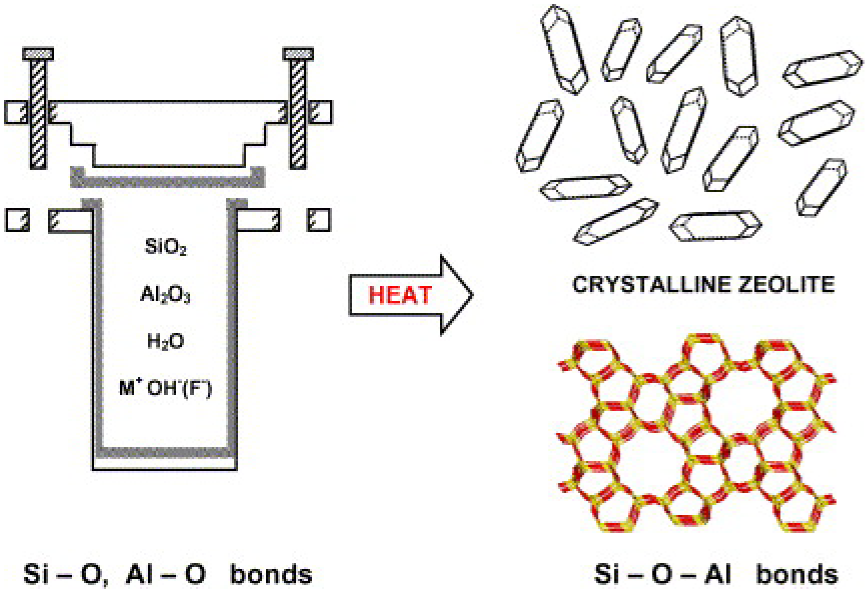


Figure 3.F.2. Hydrothermal zeolite synthesis. The starting materials (Si-O and Al-O bonds) are converted by an aqueous mineralizing medium (OH− and/or F−) into the crystalline product (Si-O-Al bonds) whose microporosity is defined by the crystal structure. Reprinted from [14], with permission from Elsevier.

Potential pitfalls for zeolite synthesis:

- Impurity in precursor source: The precursor chemicals purchased from chemical suppliers can have slight variations in the impurities (e.g. Fe, K, Mg, Ca). The purity can also vary from lot-to-lot since most specialty chemicals are produced in batch operation. These changes in purity can lead to failure in zeolite synthesis or result in batch-to-batch variation. It is recommended that published scientific reports include all particulars of reagents and report syntheses that result in the desired framework material as well as those that result in amorphous materials or in zeolite intergrowths.

- Humidity or air quality depend on geographic location and can impact zeolite synthesis, especially in synthesis approaches that crystallize gel compositions with very low water contents (e.g., “dry-gel” or “solvent-free”). In these cases, the amount of water affects the degree of hydrolysis significantly, which directly determines the degree of crystallization and framework type. These factors can thus impact zeolite syntheses and reproducibility.

- Upon repeated use, zeolite residue can adhere to Teflon liners and magnetic stir bars [15] and act as seeds to induce changes in zeolite topology or crystal habit. Thus, it is recommended that extensive cleaning (e.g., with HF and KOH) is performed before each synthesis.

- To the extent that water or other volatile components can evaporate during the gel preparation leading to a change in the molar composition of the gel, it is also important to know the water content, or H_2O/SiO_2 ratio, of the gel prior to addition into the autoclave. Details such as whether or not a vessel is capped or uncapped, or stirred or not stirred, at various points in the aging of the synthesis gel can lead to unexpected variation in the molar ratios of ingredients present when the gel is loaded into an autoclave for crystallization. It is best to clearly specify whether the vessels are capped or uncapped at all stages in the materials synthesis procedure.

Recommendations for standardized characterization

Structural and chemical characterization will play a key role in facilitating the adoption and use of benchmark zeolite materials. Benchmark data for reference samples provided by NIST and IZA are available as discussed below. This reference data can be leveraged for rigor and reproducibility in zeolite catalysis research if comparable data could be reported in scientific publications and presentations. This data would not only represent a best practice but as part of a centrally archived public resource would also enable inter-laboratory comparison. A hierarchy of protocols would likely be adopted given restraints on time and resources in acquiring these data. A list of relevant and recommended characterization protocols is provided below:

- **Bulk structural characterization:** Bulk elemental composition and powder X-ray diffraction patterns depicting crystalline phases should be mandatory for synthesized zeolites. Pore volume (and pore size distribution) measurements and electron microscopy characterization are recommended to corroborate the crystal structure and morphology, respectively.

  If claims about zeolite crystallization and growth mechanism/kinetics/thermodynamics are reported, then it is recommended that characterization data as a function of time and synthesis gel composition be presented; it is also recommended that researchers analyze composition of both the solid and the synthesis liquor.

- **Acid site characterization:** Acid site density and strength are key parameters in zeolite catalysis and first and foremost it is important to distinguish among them. Equally important is the distinction between Brønsted and Lewis acid sites and the void environment in which these sites are circumscribed. Enumeration of acid site density by chemical or structural characterization to report a specific quantity on a per aluminum basis (e.g., H^+/Al) by either NH_3 thermal desorption, iso-/n-propylamine reactive desorption, probe molecule infrared spectroscopy should be mandatory for zeolite catalysis.

  In situ chemical titrations during catalytic reaction are recommended for accurate enumeration of active site densities under reaction conditions and to distinguish different populations of sites. If catalyst performance is attributed to aluminum arrangement and coordination environment in the framework then it is recommended to validate these claims based on either spectroscopic (e.g., NMR or UV-Vis) or cation titration (e.g., Co^{2+} or Na^+) methods.

- **Porosity and diffusion characteristics:** Porosity measurements by adsorption of inert gases such as N_2 and Ar are strongly recommended with Ar isotherms (measured at liquid argon temperatures) being especially relevant for assessing microporosity characteristics.

  Intracrystalline transport of species plays a key role in determining rate and selectivity characteristics in zeolite catalysis. Thus, it is strongly recommended that probe molecule adsorption and uptake studies report details of pore size distribution and hysteresis phenomena to determine the potential role of mesopores and diffusion characteristics. It is also recommended that researchers report crystallite size distributions and morphology for the samples, such as by using electron microscopy techniques.

- **Local structure and coordination environment:** Solid-state NMR of ^{27}Al (and ^{29}Si) to assess Al, Si coordination environments would augment the detail of local structure and coordination of framework T atoms.
- **Post-reaction characterization:** In scenarios where reactions are liable to cause irreversible changes to catalyst structure and/or when significant catalyst deactivation is observed, it is recommended that post-reaction characteristics of the zeolite material be probed. Thermogravimetric analysis, temperature programmed surface reactions, and ^{1}H and ^{13}C NMR methods can provide information pertaining to the content and speciation of occluded organic species.
- **Other characteristics:** In some cases where hydrophobic and hydrophilic characteristics of the zeolite impact adsorption and reaction, it is recommended that spectroscopic (e.g., infrared spectroscopy) or adsorption measurements (e.g., water or organics) be reported to document these characteristics of material. Along the same lines, in cases where reactions are likely to occur only on the external surface or in a zone of the zeolite crystallite then specialized measurements that provide spatially resolved characteristics of the zeolite at the pellet or crystallite scale can be pursued.
- **In situ characterization:** Structure-function relationships in zeolite catalysis require a combination of precise material synthesis; structural and chemical characterization of the microporous material as-synthesized, post-reaction, and in operando; and rigorous protocols for catalyst testing. Best practices for these are discussed in other sections of the report. Where in situ and operando methods are available and applicable these methods take precedence but, methods most appropriate for assessing changes in structure and function of the zeolite under reaction conditions will depend on the specific catalytic chemistry and process conditions of choice.

Potential pitfalls for zeolite activation and characterization:

- Zeolites are often activated on-stream in dry carrier gas as pretreatment for catalyst testing. The purity of gaseous reagents (e.g., trace amount of water) can be an issue because hydrolysis of Al-O(H)-Si bonds in the zeolite framework can result. [16] Also, incomplete decomposition of organic templates in zeolite synthesis can lead to imprecise measurement of catalytic performance. Thus, it is recommended that researchers report purity of reagents, flow configurations and flow rates of all reagents, sample loading, and thermal treatment protocols (e.g., ramp rates and dwell times) for pretreatment and activation in published reports.
- The measurement of micropore and mesopore volumes can depend on protocols for preparation of the powder samples, such as the pressure and time used to press pellets prior to grinding and loading and thus it is recommended that protocols for preparing powder or pelletized samples be reported.
- In temperature programmed desorption studies, care should be taken to ensure weakly bound, physisorbed titrants are removed prior to temperature ramps and quantification of Lewis acidic sites in zeolites and zeotypes. [17,18]
- Zeolitic materials can evolve at ambient conditions over time by loss of framework integrity, T-atom integrity in the framework. In most cases aluminosilicate materials are shelf stable; however, zeolites in their proton-form (especially at lower Si/Al ratios) can undergo structural degradation upon storage under ambient conditions.

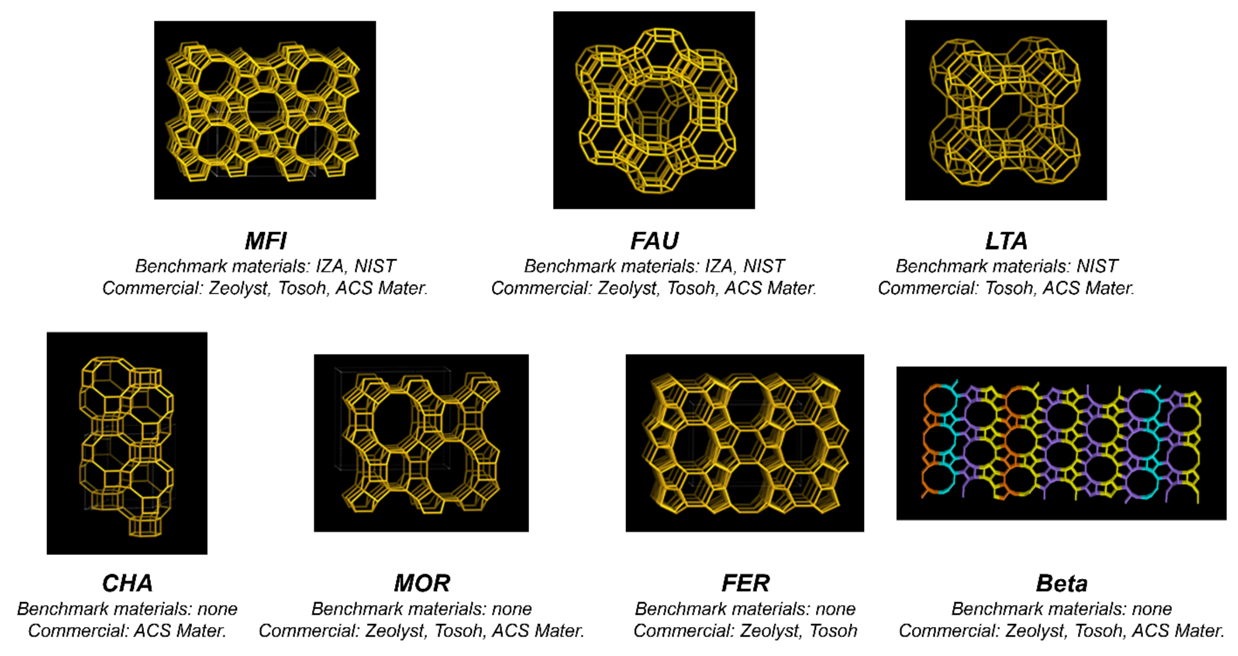
Recommendations for benchmarking properties and performance

Zeolites are adapted for application as catalysts. Frequently, these involve changes in T-atom coordination and location, heteroatom addition, surface functionalization, addition of mechanical binders and other additives, morphological changes, etc. Benchmark materials must be produced in large homogeneous batches and made readily available to the zeolite catalysis community. Thus, it is recommended that these materials be of aluminosilicate form and omit the use of additives or modifiers that could potentially modify stability or reactivity for particular reactions of interest. Aluminosilicates cover the widest scope of materials and catalytic reactions of interest both in industrial applications and in academic research and are thus best suited to serve as benchmark materials.

Prior efforts at benchmarking zeolite catalysts have identified materials that may serve as appropriate benchmarks:

- The catalysis commission of the International Zeolite Association (http://www.iza-online.org/catalysis/) now provides MFI and FAU zeolites for scientific purposes that can be used as reference materials. These samples made available as part of the International Zeolite Reference Project are available worldwide and are intended to serve as a guidepost for advanced research.
- Along the same lines, the National Institute of Standards and Technology (NIST) provides a set of reference materials for FAU, LTA, and MFI topology and has published data reporting X-ray fluorescence, gravimetry, instrumental neutron activation analysis, nuclear magnetic resonance, calorimetry, synchrotron X-ray diffraction, neutron diffraction, laser light extinction, laser light scattering, electric sensing zone, X-ray sedimentation, transmission and scanning electron microscopy and optical microscopy, to establish homogeneity of these materials. [19]
- It is worth noting that the synthesis commission of the International Zeolite Association (http://www.iza-online.org/synthesis/default.htm) provides detailed protocols verified for the syntheses of zeolite materials and that the American Society for Testing and Materials (ASTM; https://www.astm.org/) provides protocols and inter-laboratory comparison data for structural characterization and catalytic evaluation of zeolites for many materials and reactions of common interest.
- Reference samples for various commonly used solid acid zeolites have been available from Zeolyst as part of the CBV series and from Tosoh. These samples have in some manner served as reference materials for the scientific community in the past and both material characteristics and catalytic performance for these samples for a wide variety of reactions have been reported for these samples in scientific publications over the past two decades. Collation of these data from the archival literature in the form of a database would also enable benchmarking and comparison in zeolite catalysis.

These materials and protocols serve as a very valuable starting point in establishing benchmark zeolite materials for catalytic applications (Figure 3.F.3). These efforts should be augmented by the addition of a handful of other zeolite materials deployed in industrial use including Chabazite (CHA) and if feasible Mordenite (MOR), Beta (BEA), and Ferrierite (FER) in aluminosilicate form. As mentioned above, the use of these materials and protocols for zeolite characterization and testing in catalysis research would enable both comparison among samples and laboratories and if data associated with these studies can be archived in the form of a public data repository then these data could both leverage and augment the Research Data Framework (https://www.nist.gov/programs-projects/research-data-framework-rdaf) aimed at providing a structured approach to develop a customizable strategy for the management of research data.



MFI
Benchmark materials: IZA, NIST
Commercial: Zeolyst, Tosoh, ACS Mater.

FAU
Benchmark materials: IZA, NIST
Commercial: Zeolyst, Tosoh, ACS Mater.

LTA
Benchmark materials: NIST
Commercial: Tosoh, ACS Mater.

CHA
Benchmark materials: none
Commercial: ACS Mater.

MOR
Benchmark materials: none
Commercial: Zeolyst, Tosoh, ACS Mater.

FER
Benchmark materials: none
Commercial: Zeolyst, Tosoh

Beta
Benchmark materials: none
Commercial: Zeolyst, Tosoh, ACS Mater.

Figure 3.F.3. Summary of zeolite frameworks available from benchmarking organizations and commercial vendors. ACS Mater. = Advanced Chemicals Supplier Material, and may not be the original manufacturer.

Reporting metadata for zeolite synthesis and characterization

The Synthesis Commission of the International Zeolite Association (http://www.iza-online.org/synthesis/default.htm) provides verified recipes for synthesis of numerous zeolites. However, reproducibility in synthesis and activation of zeolite materials has been a challenge for the zeolite catalysis community. This challenge can be redressed to a large extent by requiring that published reports report all syntheses undertaken, both that resulted in well-defined materials and those that resulted in materials with intergrowths or amorphous material as this would greatly augment methodological development for zeolite formulations. Along the same lines, a metadata template that incorporates all particulars relevant to synthesis of the zeolite material would alleviate to some extent challenges in reproducing zeolite syntheses. A sample metadata template in tabular form is presented below (Table 3.F.1.). Structural and chemical characterization of these samples (see section 3) reported in conjunction with the material synthesis parameters could then be readily linked and archived. Protocols associated with activation of the zeolite sample and catalytic testing of the material can also be archived in a metadata archive.

Table 3.F.1. An illustrative metadata template for zeolite synthesis

Parameter	Units (if applicable)	Value
Gel Composition	molar ratios	
Si source		
Al source		
OSDA(s)		
Acid/base additives		
Other additives		
Order of addition		
Stir bar size, rate of agitation		
Gel aging temperature	°C	
Gel aging time	h	
Crystallization vessel (Materials of construction)		
Vessel size	cm^3	
Crystallization mode	static/rotating (rpm)	
Crystallization temperature	°C	
Crystallization time	d	
Washing solvents (purity, procedure, quantities)		
Solid mass recovered	g	
Methods of solid recovery		
Calcination gas		
Calcination gas flow rate	$cm^3\ min^{-1}$	
Calcination ramp rate	°C/min	
Calcination temperature	°C	
Calcination time	h	
Solid mass recovered	g	
Cleaning Methods for aging and crystallization vessels		

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Recommendations for material synthesis and benchmarking: Metal organic frameworks (MOFs)

Introduction and applications

Metal organic frameworks (MOFs) are materials that are comprised of inorganic nodes interconnected by organic linkers into extended porous structures that are crystalline in nature (Figure 3.G.1). They find applications in a wide range of areas including gas storage (sorption and separation), chemical sensing, [1] and catalysis. [2–4] MOFs are widely applicable due to their high surface area and crystallinity, [5] and high degree of structural tunability for both the metal sites and the pore structure [3] by changing the ligands. [6] MOFs are of interest for catalytic applications [2,7] because of the ability to tune the active site, which provides an analogue that may be compared to the active sites in a homogeneous catalyst. [8] Active sites are found in multiple locations including at metal nodes [9] (specifically the metal sites that have coordinative unsaturation), organic linkers, and functional groups that can be added to the MOF structure. Specifically, MOFs have been used as catalysts [4] for reactions such as CO oxidation, CO_2 cycloaddition with epoxides, Friedel-Crafts alkylations, and Knoevenagel condensations. [2] The applications to thermal catalysis are broadening with the discovery and synthesis of ever more stable MOFs at high temperatures.

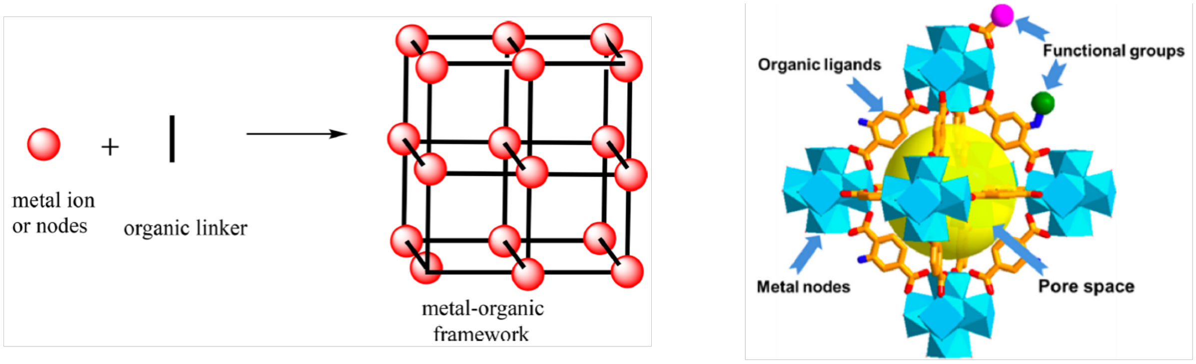

Figure 3.G.1. *left*: Constitution of MOF materials [10] r*ight*: Depiction of various types of active sites that can be hosted by MOF materials. Reprinted from [11], with permission from Elsevier.

Common synthesis methods and recommendations

There are many methods to synthesize MOFs including solvothermal synthesis (which is the most commonly used method), [12] pre-forming metal subunits before framework growth, or employing electrochemical, mechanochemical and microwave assistance. [13] Other methods synthesize the MOFs using different modulators [14] such as acids to keep the metal-ligand bonds dynamic and to allow for structural growth to occur. MOF linkers can also undergo chemical transformations or replacement, allowing for post synthetic modification of the framework. [15] Parameters that are critical to structure, size and purity of the material include the synthesis temperature, time, solvent, and pH. Several additional steps are nominally post-synthetic but are required to activate the MOF for use by removing solvents and weakly coordinating ligands. This is influenced by the temperature, heating rate, and the methods employed, such as freeze drying, dynamic vacuum, or air drying. [12]

Finally, storage can inadvertently alter materials, with materials changing as a function of time stored, temperature of storage, and the atmosphere of storage (e.g., inert atmosphere glovebox vs. desiccator vs. benchtop). Care must be taken that MOFs are not altered by solvents used or stored in the same environment, such as in the same glovebox. In general, it must be recalled that MOFs are neither indefinitely stable, nor arbitrarily stable against chemical attack, and both the treatment of these materials and the documentation of their use should reflect these considerations.

All these steps strongly influence bulk properties such as crystal sizes and habit, total surface area, or stability on storage. Unfortunately, the synthetic metadata listed above are frequently un- or under-reported and have significant impacts on the number and type of defect sites and on the overall reproducibility of results, especially catalytic function. Reproducibility challenges can manifest themselves from individual to individual within a laboratory, or when a new laboratory attempts to enter a research space and repeat a literature result. Poor reproducibility also makes it much more challenging to scale up MOF synthesis and can make it more prone to failure.

These synthetic and post-synthetic steps have a controlling influence on catalytic activity and stability under reaction conditions due, in part, to their role in determining the number and type of structural defects, which can be catalytic active sites or can provide (or block) access to the sites. Defects can arise from the loss of linkers, distortions of the node or its coordination to the linkers, and the absence or presence of additional coordinating solvent, modulator, or solvent decomposition products, such as formate.

Recommendations for standardized characterization

The following practices are recommended to help address concerns related to rigor and reproducibility in MOF catalysis:

- Regardless of the characterization or catalytic testing being carried out, we recommend full documentation of the synthesis conditions, ‘activation’ or pretreatment conditions, and time and manner of storage, as noted in the previous paragraphs. It is the opinion of the authors that incomplete or absent documentation of these metadata is a primary source of failures of reproducibility.

- Powder XRD is standard practice in MOF synthesis and utilization. Researchers are urged to go beyond pattern-matching and to carry out quantitative analysis whenever possible. Electron diffraction [16] is opening up the possibility to routinely interrogate MOFs that do not form relatively large crystallites.

- Physisorption experiments and the resulting surface areas and pore distributions are useful, but limited metrics for evaluating the success of a synthetic protocol or the effect of reaction conditions. Reported surface areas can vary widely for the same material, and they can be very dependent on the sample history, pretreatments, and method of data analysis. [17] When reporting BET surface area, care should be given to the conditions of the analysis and the use of the terminology. [18] Experimental errors can be indicated by adsorption and desorption isotherms that do not overlap at sufficiently low pressures, or artifacts arising from inadequately long equilibration times. [19]

- Quantitative determination of the overall elemental composition of the MOF is strongly encouraged. Methods include 1) combustion thermogravimetric analysis (TGA) to calculate the linker-to-node ratio, 2) digestion and elemental analysis (e.g., ICP-MS) for MOFs with multiple heteroatom types, or 3) digestion and solution NMR analysis to determine the relative amounts of different linkers, remaining modulators, or other coordinating species. A comprehensive comparison of one or more of these analyses against each other and against the composition predicted from the crystal structure will inform the investigator as to the presence of various types of defects, which determine the local structure. The number and type of these defects is strongly dependent on pretreatment conditions, and these defects, in turn, likely play a significant role in catalytic activity. Therefore, these analyses should be carried out, whenever possible, on materials that have been pretreated as if they were to be tested catalytically. Accurate reporting of pretreatment protocols affecting local structure will aid significantly in reproducing measured catalytic data.

- The above-calculated bulk composition should be compared to a technique with lateral resolution (e.g., SEM/EDX) or depth resolution (e.g. XPS, possibly combined with depth profiling). This is especially important for MOFs that underwent steps following framework formation to install or modify potential active sites. This will assess, relatively qualitatively, if the sites are distributed evenly throughout a MOF crystallite. Such techniques generally do not have sufficient resolution to determine, and they should not generally be used to claim that sites are ‘atomically dispersed’ or to verify whether added metals are homogeneously distributed across all nodes.

- It is noted that thermal stability assessed by thermogravimetric analysis or crystallographic stability in various solvents may not be representative of catalyst functional stability under reaction conditions. It is recommended that researchers carry out post-reaction physical and/or spectroscopic characterization, blank reactions in the absence of catalyst, and sufficiently long reactions to note deactivation or approach to a steady state in the case of continuous reactions. In the liquid phase, hot filtration and other tests are recommended to assess contributions of homogeneous (versus heterogeneous) catalysis. [20,21] Researchers are reminded that even in cases where there is not large evidence for catalyst leaching, catalysis can still arise from very small concentrations of very active molecular complexes, including those that may be physically trapped within the MOF pores.
- MOF materials do not, strictly speaking, behave as 'hard' materials, [22] the structures of which remain relatively constrained under activation and reaction conditions. For example, gate-opening phenomena occurring in ZIF-8 materials upon exposure to N_2 even at sub-ambient pressures and temperatures create uncertainty as to its structure under reaction conditions. [23] As such, careful attention and documentation must be paid to effects of particularly energetic physical processes such as stirring, mixing/grinding, and pelletization, which might alter MOF properties. Researchers may wish to avoid some of these actions, such as by shaking reaction vessels or using overhead stirrers rather than using stir bars, which can grind particles.
- Measurements of overall morphology and particle or crystallite size are recommended by SEM and in some cases, sieving to achieve a consistent size. This can monitor for physical changes induced by processing, as mentioned above, and it can alert for potential mass- or heat-transfer artifacts. [24,25] The reader is directed to the report section on reaction kinetics for further recommendations. While we do not wish to comment on the likelihood of mass transfer artifacts in specific MOF-catalyzed reactions, best practices are to have at least an approximate knowledge of particle sizes, allowing for reasonable estimates of mass transfer rates to be made. Furthermore, it is recommended to compare MOF catalysts of similar particle sizes, where possible, to minimize chances of reaching erroneous conclusions based on these artifacts.

Recommendations for benchmarking properties and performance

It is our opinion that there exists a general need in the MOF catalysis community for an enhanced focus on reproducibility of data and reaching rigorously supported conclusions, rather than cross-comparisons seeking superiority in performance, which currently dominate the literature. That being said, a round-robin type exchange of materials does not seem to be viable at this time, given the large variety of MOFs being evaluated. Neither do we recommend specific MOF materials as benchmarks for catalytic studies, at this time. This is in part because MOF catalysts remain highly task-specific, which is both part of their appeal and is in contrast with other classes of catalysts like zeolites in which one zeolite can be applied toward a broad swathe of reactions. Further prerequisites for a benchmark MOF would be 1) commercial availability in large, extensively characterized batches of guaranteed availability, 2) good stability during storage, and 3) a framework structure that is unperturbed by processing, pretreatment, and reaction conditions. At the time of writing, there are not commercially available, catalytically relevant MOFs that meet the conditions of 1) and 2), and the ’soft’ behavior of MOFs that underlies point 3) is somewhat intrinsic to the materials, as discussed above. Finally, materials that are not commercially available could potentially be used as benchmarks if syntheses and precursors are sufficiently reproducible. However, we caution against this approach at this time because minor changes in synthetic protocols can result in significant alterations in catalytic properties, largely due to the controlling influence of defects, as discussed above.

Given the many factors limiting potential use of a single MOF benchmark, we instead recommend ‘internal’ benchmarking of MOF catalysts against other MOFs or other classes of catalyst on a case-specific basis.

Fundamentally, we feel that rigor and reproducibility of *conclusions* can be addressed without necessarily addressing strategies to reach an agreed-upon tolerance for data reproducibility or comparisons to a universal benchmark. Some examples include:

1. In liquid-phase reactions, carefully chosen molecular analogues can be used to benchmark claims about MOF catalysts. Such an approach is most appropriate for cases where discrete molecular entities have been modified to act as native MOF nodes or linkers, or where molecular catalysts have been grafted onto MOF nodes or linkers. These comparisons are especially important to support claims of improved stability or dispersion of a molecular active site. However, when researchers compare molecular catalysts to MOF materials, they must pay close attention to potential mass transport effects associated with the MOFs.

2. Oxide- or polymer-grafted analogues can also be used to benchmark MOF-supported molecular catalysts. In general, claims of a particular role for the pore structure of MOF support should be met by comparisons to molecular catalysts or to materials with a different pore structure. Conversely, node-swapped versions of the same MOF topology can be used as indirect evidence of a pore-confinement hypothesis. For example, if confinement within the pores of UiO-66 is claimed to be the origin of catalytic effect, the results could be benchmarked against use of UiO-66(Hf) as the support. [26] Substantial differences between the two catalysts would imply a role of the MOF structure beyond pore effects and contradict, or at least complicate, the original claim.

3. For metal or oxide catalytic elements grafted to MOF nodes, comparisons can be made to the same elements grafted to bulk oxide analogues. For example, NbOx grafted to the zirconium nodes of NU-1000 can be compared to grafting on ZrO_2 or to MOF-808. Care must be taken to account for large differences in support surface area if bulk oxide supports are used. Researchers are suggested to compare grafted catalysts on the basis of exposed support metal atoms or numbers of exchange sites, if possible, rather than a mass-normalized loading. This is an extension of the common practice of normalizing oxide-supported catalysts by surface density, and accounts for the fact that most of the surface area of a MOF arises from ligands, rather than the nodes. For example, 2 Nb atoms grafted per $Zr_6(\mu_3\text{-}O)_4$ node of NU-1000 is 0.33 Nb atoms per surface Zr atom and 0.75 mmol Nb per gram of NU-1000. For a similar surface density of Nb atoms per surface Zr atom on a typical bulk ZrO_2, the material might possess 4-fold fewer Nb per gram. [27]

4. Benchmarking efforts are more complex where MOF catalysts have active sites derived from the nodes or from missing linker defects ubiquitous within this class of materials. However, supported catalysts can still serve as benchmarks. For example, reactions proposed to be catalyzed by the $Zr_6(\mu_3\text{-}O)_4$ nodes of NU-1000 can be compared to supported zirconia catalysts synthesized by impregnating zirconia precursors onto oxide supports, other MOF topologies, or even to pre-formed nodes tethered to appropriately functionalized supports. (Figure 3.G.2). [28,29] In some cases, this can reveal that activity is primarily driven by the number of exposed metal atoms, with a relatively weak dependance on the nature of the MOF. Conversely, these studies can also reveal interesting and unexpected effects of the immediate coordination environment around the MOF node. [30] It is noted that bulk oxides themselves are infrequently good benchmarks without extensive studies to uncover the intrinsic kinetics of the system. As case in point, the number of undercoordinated Zr atoms on a bulk ZrO_2 surface are so much lower than similar sites on a zirconium-based MOF as to make direct rate comparisons challenging and often largely meaningless.

5. In suggestions 3 and 4, active site counting methods are strongly encouraged (see other sections of this report) in order to compare materials on a reasonable basis or to verify hypotheses.

6. Above, we have made suggestions that may involve comparisons of materials with (potentially very) different pore structures, which invites questions about the importance of mass-transfer artifacts on the conclusions reached. We feel that this can be managed, and we direct the reader to the appropriate section of this report. Further, we feel that 'mass-transfer' is often invoked blindly as a reason to explain

slower than anticipated rates in a MOF, even when conditions (slow reactions, low temperatures, relatively small crystallites, and relatively large pores) might not warrant it.

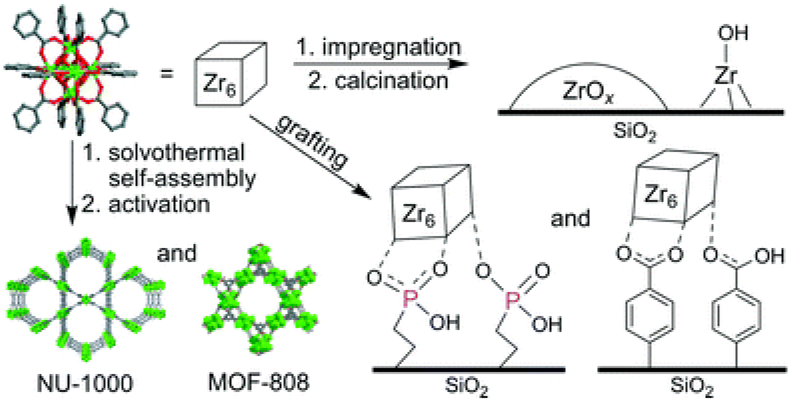

Figure 3.G.2. Materials for comparing epoxide alcoholysis on ZrOx sites found on NU-1000 and MOF-808 nodes, calcined ZrOx-SiO_2, and node-analogues grated to functionalized silica. Reproduced from Ref [28] with permission from the Royal Society of Chemistry.

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Recommendations for material benchmarking: Bifunctional, multifunctional, and cooperative catalysts

To provide recommendations, it is critical to establish common terminology. A well-known definition provided by Burwell and later adopted by IUPAC says "Some heterogeneous catalytic reactions proceed by a sequence of elementary processes certain of which occur at one set of sites while others occur at sites which are of a completely different nature. For example, some of the processes in the reforming reactions of hydrocarbons on platinum/alumina occur at the surface of platinum, others at acidic sites on the alumina. Such catalytic reactions are said to represent *bifunctional catalysis*. The two types of sites are ordinarily intermixed on the same primary particles, but similar reactions may result even when the catalyst is a mixture of particles each containing but one type of site. These ideas could, of course, be extended to create the concept of *polyfunctional catalysis*." [1]

Here, we have broadly defined *bifunctional (and multifunctional)* and *cooperative catalysts* as single materials with at least two types of sites involved in the reaction mechanism. It is necessary to distinguish between (1) two or more sites participating in the rate limiting step of a reaction mechanism (*bifunctional or multifunctional*) *vs.* (2) when different elementary steps of a reaction mechanism occur on different active sites (*cooperative*). In contrast, in the case of *catalytic process intensification*, two or more catalysts are used simultaneously to enable different reactions. To better illustrate this definition, below we identify three classes of materials that are representative of bifunctional and cooperative catalysts (Figure 3.H.1):

a) Bimetallics in which one metal is adding a second function instead of modifying the activity of the first one (including catalysts with a highly reducible metal + oxophilic promoter). [2–4] It is worth noting that this category does not include classic *bimetallic catalysts*, in which the second metal completely modifies the reaction mechanism and the rate limiting step happening on the first one (while not actively participating in the rate limiting step).

b) Metal/oxide and inverse oxide/metal catalysts (i.e., those where catalysis occurs at the interface). [5–7]

c) Catalysts with separated sites (e.g., metal + acid for cracking, including metal on zeolites; redox + acid, redox + base, acid + base sites for multistep and cascade reactions). [8–10]

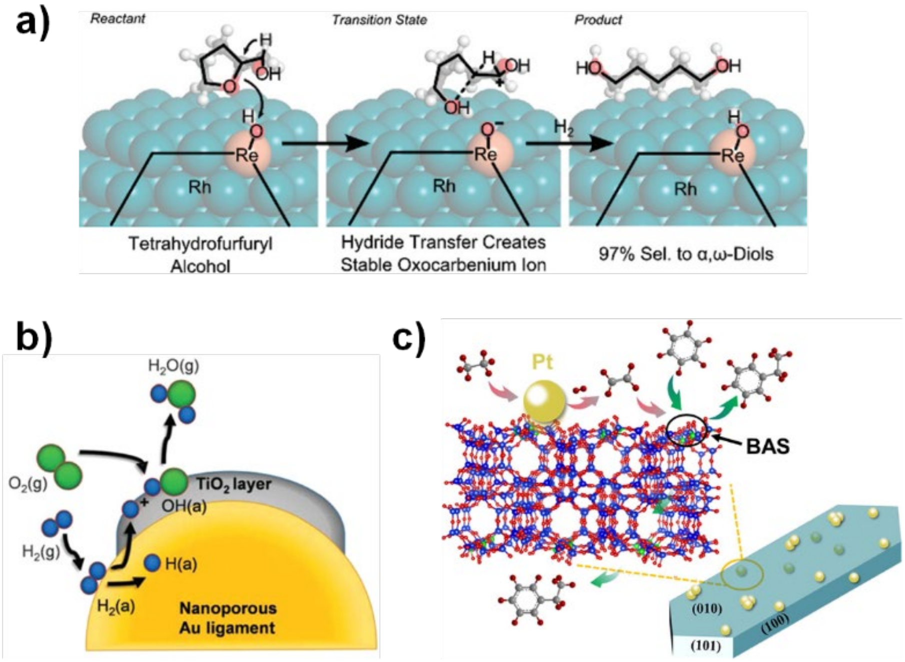

Figure 3.H.1. Illustrations of the three material classes identified above as bifunctional and cooperative catalysts: a) RhRe/C catalyst for acid-catalyzed ring-opening and dehydration reactions coupled with metal-catalyzed

hydrogenation [Reprinted with permission from [3]. Copyright 2011 American Chemical Society], b) inverse TiO_2/Au catalyst for H_2 oxidation at the interfacial perimeter [Reprinted with permission from [6] Copyright 2016 American Chemical Society], and c) Pt/ZSM-5 for the alkylation of benzene with ethane [Reprinted from [11], with permission from Elsevier.].

An example of cooperativity, as seen in simulations, is the proximal Si-OH in the open Sn-OH site of zeolite BEA. [12,13] Another example is a $RhWO_x$ pair catalyst, in which Rh promotes partial WO_3 reduction. Rh can activate an olefin (one site), and the $RhWO_x$ is crucial for splitting H_2 and inserting CO in hydroformylation. This is an example of multifunctionality and cooperativity in the same cycle. [14]

It is worth highlighting that often only a small number of active sites carry out the reaction. Therefore, the mere presence of bifunctionality does not always imply bifunctional catalysis. As a result, the proposed definition of bifunctional catalysis relies on mechanistic insights of how the rate determining step proceeds. As these timescales cannot be accessed by spectroscopy, computational mechanistic investigations can play a critical role in establishing bifunctional catalysis.

In the case of metal-zeolite catalysts (e.g., Figure 3.H.1c), it is unclear whether the metal is separate from the acid site, although this has been commonly reported in the literature. For example, Vlachos et al. found that the proton of the acid site transfers onto the metal and forms a hydride. [15] Even if the metal loading is low, the metal may well coordinate and anchor with the Al of a zeolite. The metal's electronic properties, upon coordinating with the Al or receiving a proton, are not the same as on a siliceous material. [15] Therefore, they believe cooperativity is the rule in bifunctional materials, and the two sites are not just doing their job at a distance from each other on the same scaffold, but they modify each other in important ways. Some of these phenomena and site creation happen dynamically, in situ. For example, in an inverse catalyst, the metal activates H_2, then H spills over and protonates the oxygen of the oxide overlayer, and this now becomes the Brønsted acid site. [16] Hydrogen can also reduce the oxygen creating a redox site in situ again. [16] Therefore, bifunctionality can be dynamic in nature.

Multifunctional catalysts, however, are those involving more than two sites. As an example, a Ru/RuO_2 catalyst presented this multifunctional behavior in biomass conversion, showing metallic sites for dehydrogenation, Lewis acid sites for catalytic transfer hydrogenation (CTH), and redox sites for hydrodeoxygenation. This triplet of sites does *tandem catalysis* where the hydrogen produced in situ on one site reduces the oxide site to drive C-O bond scission, whereas the RuO Lewis center does CTH. [17]

Benchmarking these materials is challenging due to the broad nature of functionalities required for various chemistries. As a result, our core recommendation is that future efforts focus on reporting sufficient information to facilitate comparison of catalysts among laboratories and increasing the rigor in the use of probe reactions and characterization techniques to quantify different sites and study interfaces. It is also recommended to complement experiments with computational studies that may reveal more detailed information on the mechanism, multifunctionality, and cooperativity. The complexity of these phenomena makes detailed studies difficult, as one can easily miss the cooperativity and dynamic aspects of sites.

When evaluating bifunctional and cooperative catalysts, we encourage consideration, measurement, and reporting of the following (not all components are relevant to all catalysts):

- Metal and metal oxide loading
- Site titrations to determine site densities, such as fractional metal exposure/coverage, especially in the case of inverse catalysts
- Differentiating sites through probe reactions when other means of site counting (e.g., titration) are convoluted
- Optimum ratio of sites related to metric of interest (e.g., conversion, product selectivity, turnover frequency)
- Kinetic and/or mechanistic contribution of both types of sites

- To answer the question, “How does the second component affect the activity of the first one?
  - (i) Control experiments with monofunctional materials,
  - (ii) Comparison of bifunctional or cooperative catalysts with physical mixtures of monofunctional materials.

The representative cases presented below are simply provided to exemplify the application of characterization techniques and probe reactions to these materials.

Representative examples of characterization strategies

1. *Fourier-transform infrared spectroscopy (FTIR) of adsorbed CO collected at sub-ambient temperatures:* Common chemisorption techniques are not effective in quantifying metal sites on Au samples. As a result, Au sites are frequently characterized by FTIR of adsorbed CO, especially at sub-ambient temperatures. This technique has been used to estimate the number of interfacial sites on inverse MoO_x-Au/SiO_2 catalysts for the reverse water–gas shift reaction. It was shown that the number of Au sites available for CO adsorption decreased by the addition of MoO_x due to surface coverage, and the number of interfacial sites was estimated from the change in the amount of adsorbed CO with respect to Au/SiO_2. [18]
2. *Analysis of interfacial area on inverse catalysts by scanning transmission electron microscopy/energy dispersive x-ray spectroscopy (STEM/EDS):* The performance of a series of CeO_x-Pd/Carbon catalysts in the hydrogen oxidation reaction (HOR) correlated with the contact area between Pd and cerium oxide. This was estimated by averaging the contact area from multiple STEM/EDS maps for each catalyst. [19]
3. *Titration of H_2-activating sites and NH_3-binding sites to generate a H^*/H^+ ratio for bifunctional metal-acid catalysts:* Different HY zeolites with Si:Al ratios between 3 and 35 and PtHY prepared by ion exchange were used for the hydroisomerization and hydrocracking of n-decane. PtHY catalysts were characterized by H_2-O_2 titration (Pt dispersion) and NH_3 adsorption (number of acid sites) and the H^*/H^+ ratio was correlated with the activity, selectivity, and stability. [20] Other examples in the literature showed a similar approach for the characterization of Pt/SiO_2-Al_2O_3 catalysts. [21,22]
4. *X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES):* Various compositions of Pt_xAu_{100-x} nanoparticles with a similar size (7 nm) were synthesized and their structure was elucidated using X-ray absorption spectroscopy (XAS). The coordination number of Pt and Au was estimated separately, elucidating Au core-Pt shell feature. Pt_4Au_{96} showed Pt single atomic nature with very high activity for electrocatalytic formic acid oxidation. [23]
5. *CH_3OH oxidation steady-state and temperature-programmed surface reaction (CH_3OH-TPSR) spectroscopy studies:* A supported K_2O-V_2O_5/Al_2O_3 catalyst was designed to create surfaces that were 100% acidic, 100% basic, 100% redox, bifunctional redox-acidic, and bifunctional redox-basic. Using CH_3OH oxidation steady-state and CH_3OH-TPSR, it was determined that the formation of dimethoxy methane, $(CH_3O)_2CH_2$, required the presence of dual surface redox-acidic sites, where surface redox sites yielded H_2CO and surface acidic sites inserted the surface methoxy into H_2CO to form $(CH_3O)_2CH_2$. [24]

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Recommendations for catalyst bulk characterization methods

Introduction

Although heterogeneous catalysis is a surface phenomenon, it is critically important to describe the bulk properties of catalytic materials. To a large extent, bulk chemical properties like crystal structure and elemental composition dictate surface composition and electronic structure; as such, variations in bulk properties will frequently impact intrinsic reactivity. In addition, catalytic reactions may be structure-sensitive. [1] In these cases, reaction rates may vary as a function of metal particle size or exposed facets, so obtaining detailed information about bulk properties like shape and particle size distribution can be essential to understanding the macroscale performance of a material. Bulk properties are also important in catalyst synthesis. For example, methods for dispersing metals or metal oxides onto high surface area carriers—such as incipient wetness impregnation—require insight into the surface area, pore volume, crystal structure, and exposed surface facets of that support. Other bulk material properties like porosity and thermal conductivity influence ancillary phenomena, such as rates of heat and mass transfer. Although fluid-phase transport phenomena are not a part of the catalytic cycle, they influence temperature and concentration in the vicinity of the active site. As such, characterizing transport phenomena confers a better understanding of measured catalytic activity. From a qualitative perspective, bulk properties of a material are essentially a fingerprint of that material; thus, bulk characterization facilitates comparison and benchmarking between laboratories and synthetic protocols. For instance, by correctly identifying a TiO_2 sample as anatase, rutile, or a mixture thereof, one can speak to potential sources of observed variation. Finally, from a practical standpoint, bulk characterization techniques are often straightforward and inexpensive. Although they do not generally elucidate an “active site,” they provide a reliable and accessible sense of a material’s aggregate properties. As such, the correct reporting of bulk properties is a first line effort to identify potential origins of inexplicable or irreproducible behaviors observed during catalyst evaluations among different laboratories.

We often dismiss bulk properties as not kinetically relevant, but the above discussion makes clear that proper characterization and reporting of bulk properties is important for understanding material performance and establishing consistent synthesis and testing protocols. Accordingly, this section focuses on describing what bulk properties are the most important in catalysis science, outlining the methods available for their interrogation, enumerating their shortcomings and pitfalls, and establishing best practices in performing and reporting bulk characterization of catalytic materials. We cannot cover every technique available, so we focus on the most useful and widely practiced. We also identify many common themes and build universal insights about improving rigor and reproducibility in catalysis science.

Before proceeding, we note that catalysis books often provide a good introduction to characterization, [2,3] but vendors and longstanding practitioners usually adhere to well-vetted in-house methods that have been established through years of research and accumulated wisdom. [4] Attaining that level of competence is difficult for a single user, and we do not expect to achieve it in this report. Entire volumes can and have been written about the intricacies of each technique described here. [5–7] Excellent overviews of the techniques available for catalyst characterization are available, and readers are encouraged to begin here if they are looking for a more detailed consideration of fundamental principles in bulk characterization. [8–10]

Technical recommendations to improve rigor and reproducibility

Bulk characterization methods help us to understand spatially averaged chemical and physical properties of a material, and both classes of information are important in determining its catalytic performance. From a *chemical* perspective, the most significant bulk properties of a material are elemental composition; crystal structure(s) or lack thereof; coordination environment of specific atoms or “active sites" available for molecular binding; and the oxidation state(s) of elements comprising the material. Although we tend to focus on species intentionally included in a catalyst preparation, such as the amount of aluminum in a zeolite, ***proper reporting of bulk chemical***

properties also requires identification and quantification of potential impurities. This is particularly important in catalysis as minority species can have a significant influence on electronic structure and/or active site distribution, so there is no doubt that they can alter catalyst performance. Within the context of zeolite synthesis, impurity quantification could include determining the atomic percentage of iron unintentionally introduced by using relatively low-grade reagents during the synthesis step. One simple example of why this is important is that Fe^{3+} can substitute into the silica matrix just as Al^{3+} can. Framework incorporation of Fe^{3+} would create a bridging hydroxyl (Fe-OH-Si) with very different Bronsted character than the analogous framework incorporation of Al^{3+} (Al-OH-Si), which would lead to heterogeneity in the acid site population for that zeolite.

Important *physical properties* of a material include specific surface area and porosity; particle size distributions of supported metals; grain sizes (and distributions) of the bulk catalyst; bed density and void volume; and heat and mass transfer characteristics (e.g., diffusion coefficients, thermal conductivity, etc.). We divide subsequent sections into chemical properties and physical properties of a material, and we consider appropriate methods of determination for each property. Before doing so, we emphasize an important consideration that applies to all methods of bulk characterization and, more broadly, to catalysis science in general. The properties of a material and the attributes of that material returned by a characterization method are critically sensitive to the ways in which the sample was prepared, stored, pre-treated, and activated *prior to characterization*. In addition, these properties are critically sensitive to the conditions employed *during characterization*. For these reasons, it is imperative that, regardless of the characterization method or the material considered, materials, methods, and experimental procedures ***must be detailed in publications to the fullest extent possible***.

The goal of the bulk characterization sessions at this workshop was to solicit community feedback in order to define a critical set of important bulk characterization techniques and outline best practices in utilizing them. This was fraught with challenges, and there was consensus that this report should not be prescriptive about bulk characterization. There was also a lengthy discussion of what constitutes a bulk characterization technique and distinguishes it from a method that is “site specific.” We have summarized these conversations in Section 3 of the full report. These challenges notwithstanding, the assembled group agreed on many topics. The main areas of consensus were: (1) the bulk properties of materials that are most important to characterize, (2) the best methods available for doing so, (3) known limitations of these methods, and (4) best practices in reporting characterization data and the methods used to obtain it. In many respects, the final point is the most significant. Regardless of the query or the method, reported procedures must provide the minimum set of information necessary for others to replicate the reported data. Until we adopt better protocols in publishing, it will likely remain impossible to determine if different laboratories are producing different materials. Rigorous reporting is likely an essential precursor to meaningful interpretation of differences in catalyst performance observed across laboratories. While many bulk characterization techniques seem routine and their details unimportant, even methods as ubiquitous as N_2 physisorption for the determination of BET surface area and/or BJH pore volume can generate massive uncertainty when comparing results from different laboratories. [11] With this in mind, for each of the techniques discussed below, we summarize common applications, known limitations, reporting recommendations, and references detailing best practices.

Chemical properties of the catalyst

Chemical properties: Elemental composition

The identity and proportion of elements that comprise a catalyst are of fundamental importance in determining its function. Nearly every physical and chemical property of a material stems from its chemical composition, so it is unreasonable to expect that two materials with different compositions will perform the same in catalytic testing. A detailed analysis of elemental composition and impurity profiles is therefore an essential step in ensuring reproducibility.

The influence of atomic composition is obvious in cases where catalytic function is directly related to a component that is deliberately introduced to the material. As an example, consider the active Pt phase in a supported Pt/SiO_2 catalyst. The atomic percentage of Pt is an important factor in determining the performance of that material. In general, one expects an increase in Pt surface area with an increase in Pt loading, and this manifests in the laboratory as an increase in reaction rate per unit volume of catalyst. If the Pt in this hypothetical catalyst is exchanged with an equimolar quantity of Ir, for example, one should expect entirely different behavior. Alternatively, in aluminosilicates, which are materials comprised of (generally) trace, trivalent aluminum cations incorporated into a SiO_2 matrix, the atomic percentage of aluminum is a critical factor in determining the number of Brønsted acidic bridging hydroxyls (Al-OH-Si) in that material. If instead one substitutes trivalent boron into a silica matrix, the atomic percentage of boron will now determine the number of bridging hydroxyls (B-OH-Si); further, a switch to a boron heteroatom means that these bridging hydroxyls will be far less acidic than they are in the analogous aluminosilicate. Finally, one anticipates that the catalytic performance of a Pt_1Sn_1 alloy may be substantially different from that of a Pt_2Sn_3 alloy. In these cases, it is relatively clear that the performance of a material depends both on the identity and the amounts of the elements that we intentionally add to synthesis media.

Less obvious is the influence of trace elements (impurities) that often silently carry over from catalyst synthesis.[12] As a field, we often fail to consider the role of impurities, and it is common to see the use of “as received” commercial materials reported in catalysis research. It is reasonable to ask what purity level is adequate to ensure that observed phenomena can be attributed to the intended active phases (e.g., Pt dispersed on SiO_2) instead of the impurities that we usually fail to quantify? Laboratory grade reagents are commonly purchased at purity levels between 97.0 and 99.9 wt%, and our intended active phases are typically diluted, especially in fundamental research. Consider a ubiquitous supported metal catalyst, like Pt/SiO_2. One can easily find published kinetic data for Pt/SiO_2 samples that have Pt loadings between 0.1 and 5.0 wt%. [13] One will also likely see that SiO_2 supports used in these studies have purity levels of 95.0 – 99.9 wt%. One should therefore anticipate that contaminants, such as iron oxides and aluminum oxides present in the commercial SiO_2, will carry over between 0.1 – 5.0 wt% into the final Pt/SiO_2 catalyst. [14] Alternatively, MFI is a commonly used high silica zeolite, wherein aluminum is present in trace quantities (Si:Al > 10), [15] so impurities like metal cations and halide anions can easily approach the atomic percentage of aluminum. Such species can impact the state of the material, alter its performance under reaction conditions, and participate directly in the chemistry of interest through alternate pathways from the intended catalyst. We present these cases to highlight the fact that it is not unusual for “trace impurities” to be present in catalytically relevant quantities. This can make it difficult to rigorously attribute macroscale observations to the intended active phase. For example, it was recently reported that both SiO_2 (≥ 99%) and γ-Al_2O_3 (97% - 99.997%) seemingly catalyze minor extents of oxidative ketone scission under a He atmosphere. [16] Under an inert gas, the oxidative scission of ketones can only occur over a reducible solid oxide; as such, it is impossible for either SiO_2 or γ-Al_2O_3 to facilitate oxidative scission at reported temperatures (≈ 200°C). In this case, the observed catalytic activity must be attributed to reducible oxide impurities (e.g., Fe_2O_3) rather than to the dominant solid oxide phases (SiO_2, γ-Al_2O_3). This makes clear that impurities may confer appreciable catalytic activity, which can obscure the intrinsic performance of a material and lead one to report rates or TOFs that are difficult or impossible to reproduce. In the interest of rigorous attributions of catalytic activity, it is important to describe the elemental composition of catalysts in as much detail as possible, noting that it may only take ppm levels of an impurity for it to influence the performance of a catalyst.

A major challenge in providing a definitive elemental composition for a material is that there are no reliably quantitative methods of elemental analysis that will scan across the periodic table with uniform precision for all elements of interest. Methods that are applicable for Li or Na, for example, may not be useful for rare earth or heavy metals, like Pb or Bi. With elemental analysis, one generally needs some insight into species present in a material in order to calibrate methods to obtain precise, quantitative information. That said, some methods allow one to scan for the presence of elements, which can be used for preliminary analysis to determine species present. This can be followed by a more quantitative method designed to probe the composition of specific elements.

The two most common and useful methods of determining the bulk elemental composition of solid materials are X-ray Fluorescence (XRF) and dissolution-based approaches that generally fall under the umbrella of Inductively Coupled Plasma methods (ICP-OES, ICP-MS) or Atomic Absorption Spectroscopy (AAS). No matter the approach, methods of chemical analysis all benefit from prior knowledge about species that are expected to be present in the sample. XRF offers scanning capabilities, and it can be used to detect the presence of multiple elements without specifically tuning the method to those elements. That said, quantitative XRF ultimately requires species-specific calibrations and detection methods. Dissolution-based methods are species-specific, and one typically approaches these methods with significant insight into the specific elements that are present in the sample. One needs these insights for two key reasons. First, specific chemical elements often require unique strategies for dissolution and stabilization in aqueous media. As an example, one can generally dissolve metal cations using low pH treatments in nitric and/or hydrochloric acid, whereas analogous determination of silicon in a zeolite content may require dissolution at low pH in hydrofluoric acid or high pH in a hydroxide solution. Moreover, detector responses in ICP-based methods (e.g., ICP-MS, ICP-OES, etc.) vary with the identity of the matrix (i.e., the solvent and components therein) and species detected, so unique calibration curves must be prepared for each element of interest in a characteristic matrix. Neutron activation analysis (NAA) can also be very useful, albeit rarer in application, for many elements of appropriate neutron adsorption. Finally, other elemental mapping methods are available in conjunction with electron microscopy. More details on these techniques are available in the Electron Microscopy section of this report.

Summary information: composition methods such as ICP-OES/MS, XRF, AAS, NAA

Common applications

- Determination of elemental composition to compare target catalyst synthesis composition versus actual
- Determination of impurity atoms that may influence reactivity/selectivity

Known limitations

- Different techniques are better for different atomic masses (e.g. light element such as Na, Li versus Bi, Pb)
- Many techniques have matrix effects, and element responses may overlap, necessitating careful calibration
- Calibration curves may not be linear over wide ranges
- Poor solubility of some elements after necessary catalyst acid digestion can affect accuracy
- Some methods presented as composition measurement, such as XRD or XPS, are not really meant to serve as quantitative element specific analytical
- Many of elemental sources and calibration standards used in these methods have limited shelf lives and are highly susceptible to contamination when used repeatedly for ICP or AAS. The reproducibly of calibration standards and method blanks must continuously be verified.

Specific recommendations for reporting data in literature

- Report in detail all reagents, their manufacturers, and the manufacturing lot, to provide a record in the literature for potential impurities, compositional variations, etc.
- Report in detail all relevant settings used for each analytical measurement, the calibration methods and levels, digestion methods, and amounts used for each analysis

References for best practice

- Elements and their origins to examine for potential impurities: *Chemistry of the Elements* [17]
- ASTM International Subcommittee D32.03 on Chemical Composition and best practices for certain material therein [18]
- Sample Preparation Guides from Inorganic Ventures [19]
- **HF is extremely hazardous: see the CDC guide for safe handling before use!** [20]
- ASTM UOP961-12 Elemental Composition of Zeolites by ICP-OES [21]

Chemical properties: Crystal structure

The bulk crystal structure of a material provides a reliable fingerprint of (crystalline) materials. Crystallographic characterization is thus a convenient way to compare materials prepared by different syntheses or in different laboratories. Even the lack of crystallinity (when crystallinity is expected) is important to diagnose potential variations between materials. To a good approximation and in the absence of trace impurities described above, two catalysts that have identical crystal structures will have the same spatial arrangement of atoms and degree of long-range order, and one can expect similarity in the surface properties that correlate with these characteristics of a material. In addition, crystallography allows one to distinguish between metals and metal oxides; metal alloys; crystalline phases of metals or metal oxides (e.g., γ-Al_2O_3 vs. α-Al_2O_3); and different framework geometries of crystalline mixed-metal oxides (e.g., an MFI zeolite vs. a BEA zeolite). Furthermore, crystallography can be used to assess the degree of long-range order in a crystalline material and thus give an estimate of crystallite sizes using the appropriate correlations. A good example of this would be the use of the Scherrer equation to estimate the mean crystallite size in polycrystalline powders based on characteristic diffraction peak widths from powder X-ray diffraction patterns.

The crystal structure of a material is important in that the surface properties of that material will directly stem from the bulk crystal structure. For example, the interatomic spacing of Pt atoms in hcp and fcc packing are different, and either can be assessed from the crystal structure of the bulk Pt sample. Alternatively, pore and cavity dimensions of zeolites are well defined within a given framework. Not only will crystallography provide a fingerprint of the zeolite that can be used to identify its morphology—crystallographic data can allow one to distinguish between FAU, BEA, or MFI zeolites—once its morphology is known, one can generally describe its pore structure with reasonable certainty. This is generally possible with materials, like zeolites, that have precisely defined crystal structures. Crystallography is also important in that it allows one to assess the degree of crystallinity in a material, and to determine whether or not amorphous regions are present in that material. [22] This can be critically important in zeolite synthesis. Finally, characterizing the bulk crystallography of a material provides an important way to confirm the phase(s) of the material. For example, crystallographic patterns may reveal the presence of a secondary oxide phase in a bulk oxide (e.g., α-alumina present in a purported γ-alumina catalyst, or rutile present in anatase TiO_2) or even an impurity oxide phase, such as Fe_2O_3 present in SiO_2 or γ-Al_2O_3.

The most common method employed in describing the crystal structure of a material is X-ray diffraction. It has many attractive aspects for characterization of single crystal and powdered materials. It is a straightforward technique, and data acquisition is very fast. Further, sample preparation, especially for powders, is facile: it involves little more than affixing a material to a sample holder. Moreover, X-rays have good penetration depth, and XRD is not a high vacuum method. There are thus no restrictions preventing the use of XRD, for example, to characterize a material suspended in a liquid (including water). Accordingly, XRD is amenable to use under almost any in situ conditions, though there are always engineering considerations in appropriate cell design to allow for operando XRD of samples under reaction conditions. The diffraction patterns obtained from XRD are information rich. In addition to aiding in the resolution of crystal structures, one can extract information about crystal sizes from XRD peak widths. Further, shifts in peak position are informative regarding lattice strain, so they can be helpful in understanding the lattice expansion or contractions that occur upon incorporation of heteroatoms into an otherwise uniform crystalline domain. Finally, XRD can provide quantitative information, and it is commonly employed for assessing the degree of crystallinity in materials, like zeolites, that often have crystalline and amorphous domains whose relative populations are determined by the synthesis method and provide a sense of the “quality” of the material. The International Crystal Database provides a repository of +250k structures with web tools that allow for simulation of powder x-ray diffraction data to assist in assignment and is a tremendous structure resource. [23] Similarly, the International Zeolite Association's Database of Zeolite Structures provides comprehensive structural information on over 250 known zeolite topologies and allows users to directly compared experimental powder data with calculated and measured XRD patterns for each framework. [24]

One limitation of XRD is that peak width scales inversely with the size of the crystalline domain as observed in the Scherrer Equation. For this reason, it becomes challenging to apply XRD for characterizing nanoscale materials. Conventional wisdom states that XRD is useful for probing the structure of crystals that are larger than ~5 nm, but it is worth noting that recent advances in high sensitivity detectors for synchrotron and, in some cases, laboratory-based X-ray sources have made XRD a viable tool for structural characterization of crystals with sufficient metal loading as small as ~1 nm. [25–28] Another challenge with XRD is that it is not an inherently quantitative method in that peak intensity does not necessarily scale only with material quantity. Additionally, as crystallite sizes decrease, diffuse scattering and other nanoscale effects become significant relative to Bragg diffraction and may complicate peak deconvolution. [29] For these and other reasons, quantitative XRD often requires: (1) careful instrument calibration to account for intensity drift and other factors; (2) accurate background subtraction of sample holders, supports, and any non-nanocrystalline material; and (3) and properly accounting for sample effects, such as absorption, finite thickness, surface roughness, and temperature factors.

Summary information: crystal structure methods: XRD

Common applications

- Determination of short- and long-range ordering (or lack thereof) of atoms in the catalyst, from the catalyst support and supported-metal particles to bulk metal oxide materials (i.e., phase identification).
- Determination of an average diameter of sufficiently large crystalline metal nanoparticles or oxide domains, i.e., crystalline grains.
- Quantitative phase amounts after proper calibration

Known limitations

- Broad diffraction for amorphous or small domain phases that make these structures “invisible”
- Long range crystalline order does not necessarily describe active site structure

Specific recommendations for reporting data in literature

- Report instrument type and detector characteristics
- Report sample preparation and the sample holder geometry (e.g., in a sample well, adhered to tape, etc.), and the approximate amount of sample used
- Report calibration procedure for any phase quantitation results and include diffractogram and preferrable the intensity/2Q x-y data so that others may attempt their own fits and reproduction
- Perform and report elemental composition of the catalyst to provide other potential information on impurities
- List reference diffraction patterns and all sources used for peak assignments or diffraction pattern deconvolution
- Prepare figures with sufficient resolution and size to see if small impurity peaks are present.
- Report peak positions to allow direct comparisons with reference peaks.

References for best practice

- J.W. Niemantsverdriet, *Spectroscopy in Catalysis: An Introduction* [8]

Chemical properties: Oxidation state of specific atoms

The reactivity of a catalyst depends on the electronic structure of atoms therein. Electron density in the vicinity of a binding site or active site will determine how strongly that site coordinates reacting species, and it will determine the types of elementary steps that occur at that active site. For example, zerovalent transition or late transition metals (e.g., Ni, Pd, Pd, Ru, Ir) will typically facilitate homolytic bond dissociations and single electron couplings. In contrast, metals in oxide lattices (e.g., Al, Sn, etc.) are cationic. They often behave as Lewis acids, and they can catalyze heterolytic bond dissociations and analogous bond formation steps between ionic species. In defining the electronic structure of an element, it is essential to characterize its oxidation state.

X-ray techniques: Methods like XRD allow one to nominally infer oxidation states from crystallographic data. For example, γ-alumina must contain Al^{3+} cations and O^{2-} anions; however, other methods are more attuned to electronic structure and are therefore able to provide more detail about variations in electron density that can occur within those oxidation states. Such is the case for X-ray Absorption Near Edge Spectroscopy (XANES) and X-ray Photoelectron Spectroscopy (XPS). Generally speaking, XANES provides bulk-averaged information if performed in transmission mode, whereas XPS, by nature of its limited profile depth (which can range from 1-10 nm [30]) will give a picture of surface oxidation states. Comparison of differences between the surface oxidation state (XPS) and bulk oxidation state (XANES) serves as a reminder that bulk and surface properties are often very different, and it is important that one resist the temptation to equate bulk structure with surface structure. Characterization of oxidation states in a catalytically relevant phase becomes increasingly complex when one considers that oxidation states—especially surface oxidation states—may depend strongly on the molecular environment employed within a specific characterization method. For example, XPS spectra obtained under ultra-high vacuum will almost certainly differ from those obtained at near ambient pressure under H_2, O_2, or CO.

Temperature programmed methods: Although they cannot generally be used to definitively assign oxidation states, temperature programmed experiments (TPx) can provide important information, especially if they are used in conjunction with the X-ray methods described above. Some of the most common temperature-programmed techniques are temperature programmed desorption (TPD), temperature programmed reduction (TPR), and temperature programmed oxidation (TPO). Generally speaking, a TPD experiment comprises desorption of a titrant from the surface while heating a catalyst under an inert carrier gas like N_2, He, or Ar; a TPO comprises heating a catalyst sample under an oxidizing gas like air or O_2/He blends; and a TPR comprises heating a catalyst sample under a reducing gas, generally H_2 diluted to 1 – 5% in He or N_2. Regardless of the specific TPx method, it relies on quantifying the generation and/or consumption of one or more gas-phase species within the sample cell—often a differential packed bed for convenience—over the course of a heating ramp. A general challenge is that the gas compositions and flowrates employed must allow for detectable changes in species concentration without inducing substantial gradients in composition or temperature across the reactor. This can be surprisingly challenging. For example, a dilute H_2 stream (e.g., 1% H_2 in He) is attractive in a TPR experiment because it likely ensures that consumption of even small quantities of H_2 will lead to measurable and significant changes in species concentration; however, if the total H_2 flowrate is low relative to the quantity of metal in the cell, one may find that most or all of the bulk H_2 is by metal reduction. This represents a significant change in the bulk gas composition over the course of the temperature ramp, and one expects that it will impact the kinetics of metal reduction and thus the location and shape of reduction peaks in a TPR. Generally speaking, one will need to find a compromise in gas flowrate, gas composition, and catalyst loading that produces detectable responses but does not dramatically alter the composition within the cell.

TPD is generally most useful in the context of active site titration, and it does not provide substantial insights into oxidation states or changes in oxidation states. TPR and TPO are better suited to this task as they can provide information about the total number and quantity of reducible elements in a sample. For instance, the reduction of iron catalysts could proceed as such (with commensurate evolution of water):

$$3Fe_2O_3 + H_2 \rightleftharpoons 2Fe_3O_4 + H_2O$$

$$Fe_3O_4 + H_2 \rightleftharpoons 3FeO + H_2O$$

$$FeO + H_2 \rightleftharpoons Fe + H_2O$$

Reduction events and phase changes in the course of a TPR experiment will generally occur at different temperatures, so appropriate deconvolution of H_2-consumption profiles can, for example, provide insight into iron speciation. A caveat is that specific reduction or oxidation temperatures are sensitive to numerous properties of the material as well as experimental protocols. For example, reduction and oxidation temperatures can change dramatically with metal particle size and shape, degree of support reducibility, concentration gradients, readsorption effects, time delays, and flow and temperature ramp rates used in the experiment. [31] Thus, we advise caution in assigning significance to peaks observed in temperature programmed reduction or oxidation experiments.

Typically, temperature programmed reductions and oxidations rely on monitoring the effluent gas composition as it evolves in real time over the course of the temperature ramp. These changes generally occur on time scales of milliseconds to minutes. Thus, routine chromatographic methods (i.e., those without sample trapping capabilities) have limited utility in a TPx experiment, and one generally must use analytical methods that: (1) allow one to monitor specific species, and (2) have temporal resolutions on the order of 1 second or less. In theory, spectroscopic methods such as FTIR, Raman, and UV-Vis offer adequate time resolution, but these may lack the selectivity to detect species like gas-phase hydrogen or oxygen. In practice, the two most common detectors for monitoring effluent gas composition are mass selective residual gas analyzers (atmospheric pressure sampling mass spectrometer) and thermal conductivity detectors (TCD). Generally speaking, the former offers better resolution for individual species, especially when working with small molecules like H_2 and O_2. That said, mass selective detectors are often subject to drift and/or interferences in fragmentation patterns. Extracting quantitative information from a mass selective detector generally requires frequent calibration and the use of internal standards, such as Ar. [16,32,33] TCD detectors are less prone to drift, and they can be more reliably quantitative. The caveat is that a TCD detector relies on measuring the thermal conductivity of the effluent gas relative to a carrier, which is an average property of the mixture with contributions from all species present. As such, TCD detectors are only useful for binary gas mixtures comprised of an analyte (e.g., H_2) and an appropriate reference/sweep gas (e.g., N_2). For this reason, one must take additional precautions in collecting and interpreting TPx profiles measured with a TCD detector. One common consideration is that TPR experiments will both consume H_2 and generate H_2O. Unless one takes specific precautions to purify the effluent gas, the signal observed in a TCD detector over the course of a TPR is a convolution of H_2 consumption and H_2O generation. A typical resolution is to use a cold trap between the temperature-programmed cell and the TCD detector to condense water and allow one to reliably quantify H_2 consumption. It is also important to outgas the sample properly, so that no adsorbed species is present on the surface before the experiment, otherwise these species can desorb (or react with the H_2 or O_2 gas before desorbing) during the heat ramp and interfere with the signal. Another consideration is that residual carbon species on the catalyst surface, which are difficult to avoid, can react with the H_2 or O_2 and form CH_y or CO_x (or possibly CH_yO_x) which will also interfere with a TCD signal. Users should also generally be aware that the appropriate choice of carrier gas in a TPx experiment will depend both on the type of experiment and the type of detector employed. For example, a N_2 carrier can be problematic when using a mass seletive detector as N_2 ionization reduces detector sensitivity. [34] Moreover, the N_2 fragmentation pattern has peaks at m/z = 28 and 14; the former is prominent and can interfere with some titrants of interest, like CO. In these cases, He is a superior choice of carrier—it improves detector sensitivity, and its mass-to-charge ratio (4) is easily resolved from most species of interest in a TPx experiment. In contrast, if one is monitoring H_2 consumption during a TPR using a TCD detector, He is a poor choice of carrier. Since the thermal conductivities of He and H_2 are relatively similar, a TCD will have poor sensitivity for monitoring H_2 consumption from a blend of H_2/He. In this case, N_2 is a better choice of carrier gas as H_2 and N_2 have substantially different thermal conductivities. For a TPO experiment, the converse will be true – because O_2 and N_2 have similar thermal conductivities, it is usually preferable to employ O_2/He blends for a TPO when using a TCD detector.

The catalyst itself undergoes significant chemical changes during temperature programmed experiments. Unfortunately, effluent gas analysis provides no characterization of the solid material as it evolves over the course of the experiment. It is important to understand that a TPR will generally reduce the oxidation state of metals by removing oxygen atoms from the metal lattice and producing water as a product. Conversely, a TPO will increase the oxidation state of a metal by inserting oxygen atoms into the lattice. Both processes occur with attendant changes in sample mass, so it is useful to combine TPR or TPO studies with gravimetric tracking of changes in catalyst mass. This typically involves using a quartz crystal microbalance as employed in thermogravimetric analysis (TGA), and it allows one to close mass and element balances, which is helpful in spectral deconvolution and resolving specific oxidation or reduction events.

Rigorous interpretation of TPx methods can be challenging. Profiles observed in a TPx experiment will be sensitive to experimental protocols, catalyst properties, and catalyst pretreatment. For example, specific temperatures where reduction and oxidation events are observed—generally evidenced by peaks in the TPx profile-- can change dramatically with metal particle size, degree of support reducibility, and temperature ramp rate. The shape of the TPx profile may also vary considerably with extensive properties of the system, like the total mass of catalyst in the TPx cell, the number of active sites present, and the purge gas flow rate. Thus, we advise caution in assigning significance to peaks in H_2 or O_2 consumption during TPR and TPO experiments, as well as temperature ranges where reduction and oxidation are evidenced by high rates of H_2 and O_2 consumption. As a common example, one might take variation in the temperature range of H_2 uptake in a TPR as evidence of variations in reducibility or H_2-spillover, but this neglects the many confounding artifacts that can influence H_2 uptake rates during a temperature programmed experiment. Although not the focus of this section, these caveats extend to most temperature programmed methods, urging a cautions interpretation. As an example, desorption peaks observed during TPD of ammonia are routinely assigned to Lewis or Bronsted sites of varying "strength," but this practice is questionable unless it can be coupled with spectroscopic tools. In our experience, the most meaningful and reliable metric to report from TPx experiments is the total quantity of evolved or consumed species, which is obtained by integration of the TPx profile.

Summary information: methods for the determination of oxidation state: temperature programmed (TP) methods, thermal gravimetric (TG) methods

Common applications

- Determination of the oxidation state of catalyst components, and their ease of oxidation state changes influenced by local chemical structure, (e.g., O_2 in TP-Oxidation) or reduction (e.g., H_2 in TP-Reduction)
    - While TP methods can require a chemical sensitive analyzer, (e.g., thermal conductivity detector, mass spectrometer), the use of microbalances for TG methods can provide similar information through material mass changes and can be more sensitive and straight-forward for analysis when details of chemical speciation are not required

Known limitations

- Differences in the age and pretreatment of catalyst before analysis can produce wide variability in results
- For methods such as TPR, effective water trapping in cold traps or molecular sieve traps is important for proper signal integrity
- Gas-phase concentration during TPD can be very low and so proper calibration ranges are necessary for quantitative results
- Insufficient ratio of gas flow (concentration) to sample size may result in a high or complete conversion of the reacting gas, giving a non-kinetic and unreproducible response

Specific recommendations for reporting data in literature

- Report instrument type and detector characteristics
- Report sample preparation, age of sample from primary synthesis is known, and the pretreatment conditions performed with any analysis
- Report calibration procedure for the instrument if reporting quantitative analysis (thermocouple, TCD or MS response factor calibration)
- Report all process steps taken, hold times, and ramp rates
- Report gas vendors, lots, and purity levels for all gases. Are they used as bottled or is further pre-treatment performed?
- Perform and report elemental composition to understand what impurities could be present
- Benchmark TPx methods against standard methods for similar catalyst or other materials. Calcium oxalate decomposition [35] and CuO reduction [36] are good selections for instrument calibration.

References for best practice

- J.W. Niematsverdriet, *Spectroscopy in Catalysis: An Introduction* [8]
- *Temperature programmed desorption, reduction, oxidation and flow chemisorption for the characterization of heterogeneous catalysts. Theoretical aspects, instrumentation and applications* [36]
- R.A. Demmin et. Al., *Design parameters for temperature-programmed desorption from a packed bed* [31]
- Scarlett et al., *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density* [37]
- Kanervo et al., *Prerequisites for kinetic modeling of TPD data of porous catalysts—Exemplified by toluene/H-ZSM-5 system* [38]

Chemical properties: Coordination environment of specific atoms

The performance of a catalytic active site is influenced by its local coordination environment. Specifically, the intrinsic activity of a catalytic center is sensitive to both the identity of the species that it is bound to, and the nature of bonds formed with those species. As an example, a Pt atom surrounded by Pt nearest neighbors and next-nearest neighbors can be well-described as having the properties of bulk Pt assuming the Pt cluster is large enough to have sufficient electrons to form a complete metallic band structure. In contrast, a Pt atom in a sub-nanometer cluster supported on ceria, or a Pt atom coordinated only to Sn nearest neighbors in a PtSn alloy will have a significantly different electronic and geometric structure. Alternatively, reducible metal oxides (e.g., oxides of cerium, vanadium, titanium, and molybdenum) are frequently used to facilitate redox chemistries. Often, they are dispersed on high surface area carriers, such as silica or alumina, to compensate for the low surface area of the bulk oxide. The mobility of oxygen atoms in the lattice strongly depends on the identity, electronegativity, and reducibility of the species that oxygen atoms are bound to (e.g., V-O-V vs. V-O-Al). [39] The activity of surface sites on reducible oxides is also sensitive to extended coordination (i.e., the degree of polymerization of the dispersed reducible oxide) as this can significantly impact their electronic structure. Finally, by probing the coordination environment of catalytic centers, one can identify structural defects, which may be important in determining catalyst performance. Bulk characterization of species coordination environment therefore provides an essential description of the physical/chemical structure of the active phase. In doing so, it is important to bear in mind that all methods used for interrogating the bulk coordination environment will be spatially averaged, and the contribution from the surface, where the active sites are located, can vary significantly with particle size and loading of the active phase. Unless they are judiciously combined with titration methods, they provide a "lay of the land" as opposed to specific information about a single active site.

Numerous spectroscopic tools are available for probing coordination environment. Crystal structures inferred from X-ray diffraction provide some information about structures adopted by metal cations present in an oxide lattice or metal atoms present in an intermetallic. However, XRD is only useful if crystalline domains are large enough to provide a meaningful diffraction pattern. X-ray absorption spectroscopy, specifically extended x-ray absorption fine structure (EXAFS), can also be used to probe the local coordination environment of specific atoms present in the catalyst, but one should also be aware that EXAFS is highly dependent on complex deconvolution strategies; as such, it is discussed in a separate section of this report. Solid-state magic-angle spinning NMR (MAS NMR) is frequently used to assess the bulk coordination environment of Al and/or Si in aluminosilicates along with framework connectivity and site proximity in zeolites and microporous materials. Thus, it can be useful in assessing material quality and probing for defects in solid oxides containing NMR-active nuclei. Additionally, MAS NMR can be in conjunction with molecular titrants to distinguish and quantify binding sites based on distinct NMR resonances corresponding to unique chemical environments. [40,41] Vibrational spectroscopies, namely Fourier transform infrared (FTIR) and Raman, provide important information as to the bonding environment and chemical structures present in a specific material. [42] Where possible, it is helpful to use FTIR and Raman in tandem as they are generally suited to probing different bonding environments and so, when coupled, they can provide a more complete picture of the local coordination environment. [43] For example, FTIR spectroscopy can be used to detect hydroxyl species in bulk oxides, which provides insights about surface acidity and structural defects in silicates and aluminosilicates. In contrast, Raman is frequently used to detect M-O and M=O bonds in metal oxides, and metal oxide band locations can be used to distinguish between metal cations in different coordination environments. [32] Moreover, Raman is particularly useful in characterizing carbons as it can distinguish graphitic and amorphous phases. Finally, diffuse reflectance ultraviolet-visible (DRUV-Vis) spectroscopy is often used in characterizing the edge energy (band gap) of solid oxides. As shown extensively by Wachs and others, the edge energy of a solid oxide correlates with its extended coordination environment; as such, one can employ DRUV-Vis to determine the extent of oligomer formation in dispersed solid oxides. [16,44] UV-Vis spectroscopy is also frequently employed to distinguish between framework- and non-framework incorporated heteroatoms in crystalline materials (e.g., Ti-silicalite), [45] but can also be used to assess the size of metallic domains through changes in resonance with the band gap structure of the nanoparticle.

Summary information: methods for the coordination environment of specific atoms: UV-VIS and MAS NMR spectroscopies

Common applications

- Determine the extent of supported metal oxide networks (i.e. isolated, multidentate, polymeric, bulk)
- Through the use of edge energy, determine band gaps of catalytic centers that can correlate to structure/function
- Identify bulk coordination environment, atom presence and concentration, chemical bonding properties, and site proximity in metal oxides, zeolites, and microporous materials

Known limitations

- DRUV-Vis spectra of solid samples are generally broad and complex; while edge energies can be reliably determined, it is difficult to deconvolute spectra or assign specific meaning to a band position.
- Edge energy determination from Ligand-metal charge transfer bands requires assumptions about the type of transition (e.g., spin allowed, spin forbidden, etc.)
- Many NMR-active isotopes have low natural abundance
- MAS NMR requires special techniques for excitation and registration of signals

Specific recommendations for reporting data in literature

- Report instrument type, energy sweep density, and detector characteristics
- Report sample preparation, age of sample from primary synthesis is known, and the pretreatment conditions performed with any analysis
- Report how blank/reference spectrum was measured.
- Include raw x-y data to facilitate for other researchers

References for best practice

- F.C. Jentoft, *Ultraviolet–Visible–Near Infrared Spectroscopy in Catalysis: Theory, Experiment, Analysis, and Application Under Reaction Conditions* [46]
- A.T. Bell, *NMR Techniques in Catalysis* [47]

Physical properties of the catalyst

Because industrial processes must utilize available reactor volume as efficiently as possible, technical catalysts are almost always comprised of an active phase dispersed on high surface area carriers. These carriers are, in general, solid materials with extensive micrometer- and nanometer-scale porosity, and the surfaces of these pores serve as a support for the impregnation or deposition of other catalytic agents: metals, oxide species, organometallics, etc. Assessing the pore volume and pore size distribution, both before and after such deposition, may be necessary to determine how to precisely control the impregnating solution to achieve incipient wetness as well as understand the intra-particle transport properties of the as-prepared catalyst. Moreover, achieving targeted areal loadings (fractions of a monolayer) for dispersed metals or metal oxides requires prior insight into the total accessible surface area of the support. One might also consider the size of catalytic domains—metal nanoparticles or dispersed metal oxides—as a physical property of the catalyst. It is well known that the size of an active domain can substantially impact the activity of a catalyst; accordingly, it is worth a discussion of how one might probe the size of catalytic domains. It is also worth visualizing that the size of the active domain (e.g., a metal nanoparticle) is a different concept from grain size (e.g., a zeolite crystal), which is itself a different concept from the macroscale dimensions of a pelletized material. These various dimensions may influence different aspects of catalyst performance, so they are, at a minimum, worth consideration. Ideally, each of these physical properties would be characterized and described in publications.

Another significant impact of detailed characterization and reporting of bulk properties arises from the need to replicate reactor configurations and reaction conditions in the experimental evaluation of catalyst performance and reaction rates across laboratories. For example, textural properties (surface area, pore volume, pore size distribution, etc.), physical properties (thermal conductivity, bed density, bed dilution), and grain size influence rates of heat and mass transfer and the magnitude of pressure gradients across packed bed. Understanding and manipulating these properties is critically important in evaluating and eliminating transport control in catalytic activity testing (see section 4 of this report).

While experimental methods can help assure the absence of these effects during the interrogation of catalytic rate, complexities, such as rapid deactivation or structure sensitive reactions can confound the use of experimental methods to reveal the extent of transport control. [16] As another example, laboratory-scale reactors are often too small to allow for the placement of thermocouples inside of a catalyst bed, so it can be difficult to monitor temperature gradients and thus eliminate heat transfer effects. In these less straightforward cases, the use of derived correlations—such as the Weisz-Prater Criterion for internal diffusion limitations, the effectiveness factor of a catalyst pellet, or the Mears criteria for heat transfer limitations—are valuable (see section 4 of this report for more details). These correlations invoke numerous physical properties of the catalyst, and they require one to compute a volume-averaged rate of reaction. Accordingly, threshold criteria are heavily dependent on precise determination of catalyst surface area, pore volume, and bulk density. To replicate these results in other laboratories, these bulk characterization attributes need to be reproducibly measured and well-documented.

While some properties of materials—such as their thermal conductivity—are tabulated or can be reliably approximated based on known properties of related materials, others can vary considerably and must be determined experimentally. We subsequently discuss methods available for interrogating physical properties of catalytic materials.

Physical properties: Surface area and porosity

Because heterogeneous catalysis is a surface phenomenon, it is important to quantify the total, accessible surface area of materials used in catalysis. Moreover, pore dimensions are important in that pore diameter and tortuosity determine mass transfer characteristics. Further, at the nanoscale, confinement effects may become significant as the length scale of pores approaches that of reactants, products, and transition states. In addition to (potentially) stabilizing or destabilizing species in the vicinity of the active site, nanoscale porosity can restrict access to the surface and lead to mass transfer limitations. It is also worth considering that solvated ions or complexes may not be able to enter all the microporous spaces of zeolites, carbons, and other microporous materials. This can lead to considerable spatial heterogeneity in the catalyst pellet, and it can be difficult to anticipate without detailed characterization of the pore structure. Finally, specific surface area and porosity can be used as a rough benchmark to assess material quality and whether the material prepared is within spec for the intended class of material. As an example, using the appropriate models and p/p_o regions, one should generally expect to find measured values that align with well-established benchmarks from the literature. For example, HK (Horvath–Kawazoe) analysis of N_2 or Ar adsorption isotherms should return average pore diameters of roughly 0.5 nm for MFI zeolites. [48] In contrast, BET analysis of N_2 uptake isotherms for HMS silicas, like MCM-41, should return a surface area on the order of 1000 m^2/g. The most common technique for interrogating surface area and porosity is inert gas physisorption. A complimentary technique, mercury porosimetry can also be used to interrogate the pore structure of a material especially in the macropore (> 50 nm) regions.

Inert Gas Physisorption

Generally, physisorption experiments involve collecting N_2, Ar, or CO_2 adsorption/desorption isotherms. The choice of adsorbent depends on the material considered and its properties. [49–51] N_2 is the most widely used adsorbent. Through its use in BET and Kelvin pore adsorption theories, N_2 physisorption is a generalizable method for characterizing the specific surface area and porosity of a material. In general, N_2 physisorption provides reasonable determination of surface area, total pore volume, average pore diameter, and pore size distributions for *most materials*, but its polarizability complicates micropore analysis. This makes analysis of N_2 physisorption data challenging for zeolites. As alternatives, either Ar or O_2 (which has a smaller quadrupole moments than N_2) can be used to probe the same material properties, and they are preferred for microporous materials. [52] Although less widely used, there are few drawbacks to Ar physisorption. It can be performed at either liquid nitrogen or liquid argon temperatures, but the use of liquid argon as a cryostat is generally preferred as it will give the same pore distribution coverage as the analogous N_2 physisorption experiment. The only minor drawback here is that liquid Ar is not as ubiquitous as liquid N_2 in most laboratories, but it can generally be sourced at a marginally higher cost. CO_2 is not strictly an inert gas—it has acidic character, and it will bind at basic surface sites like O^{2-} in solid oxides. As such, CO_2 adsorption is less of a general-purpose experiment, but CO_2 physisorption at 273K is available as an alternative for microporous carbons, [53] where the use of N_2 and Ar physisorption at cryogenic temperature results in slow physisorption kinetics and very long overall experiment times. As isotherms are only reliable if data reflect equilibrium uptake at a given titrant pressure, slow physisorption introduces considerable variability of analysis. In these cases, CO_2 physisorption can provide a reliable method for interrogating micropore structures. A general heuristic to bear in mind is that physisorption experiments rely on barometric data—that is, they record the pressure of the gas phase of known volume that is in equilibrium with a solid sample held at a constant temperature. Changes in the gas phase pressure in response to dosing and adsorption of a titrant are then used to determine the molar quantity of gas uptake, and this approach is constrained by our ability to detect changes in pressure that arise from gas adsorption. Total gas uptake scales with surface area, so most instruments have a minimum total required solid surface area on the order of 5 m^2 to allow for detectable pressure changes and reproducible analysis. [54] Sample cells will generally accommodate maximum solid loadings on the order of 1 gram, so it can be challenging to use conventional physisorption of N_2 or Ar to interrogate low surface area materials, i.e., those with specific surface areas below approximately 5 m^2/g. If sample or system properties prevent one from achieving a total surface area of roughly 5 m^2, one should instead consider Kr adsorption at liquid N_2 temperatures for surface area determination.

Physisorption isotherms are most informative when they include uptake data from very low relative pressures ($p/p_o \sim 10^{-6}$ for microporous materials, 10^{-3} for meso- or non-porous samples) up to the saturation pressure of the adsorbate at the temperature where the isotherm is collected ($p/p_o = 1$). Accurate measurement of data at these low pressure ranges require proper degassing of the samples. [55] Furthermore, one can obtain a more complete description of material properties by collecting both adsorption and desorption branches of the isotherm. Specifically, inert gas adsorption and desorption isotherms often show hysteresis—that is to say, the adsorption and desorption processes follow different paths on a graph of gas uptake against relative pressure. Evaluation of hysteresis and other differences in adsorption and desorption branches can reveal important details about the pore structure of a material.

The BET method of isotherm analysis has been the standard for surface area determination for nearly 90 years. While the use of BET and other Kelvin equation-derived theories (e.g. Barrett, Joyner, and Halenda (BJH)) is very commonplace and built into the analysis software of physisorption instruments, significant variation of results from different laboratories is both possible and observed. Users of the BET theory are urged to understand the numerous assumptions that are made, and how to check if the automated fits are appropriate for your data. [50] More modern methods based on nonlocal density functional theory (NLDFT) seek to overcome the limitations of classical theory by using semiempirical models to determine molecular interaction potentials, but they require substantial kernel development. Fortunately, several excellent texts are available for reference. [37,51]

Mercury Intrusion Porosimetry

Mercury porosimetry is an intrusion method govern by the Washburn equation that describes the force required to push a non-wetting fluid into a capillary. [37] Through the Washburn equation, the intrusion into a pore of a given size is inversely proportional to the pressure applied. Unlike gas physisorption that relies on capillary condensation for pore sizing and is therefore limited to micro/mesopore sizes, mercury can directly assess the pore diameter of pores at the macro/meso scale. This makes mercury porosimetry a complimentary technique to that of physisorption to understand a completely developed pore structure of a catalyst material. This macro/meso structure can be especially important for formed catalyst pellets in terms of final industrial catalyst performance. The toxicity of mercury has encouraged research into alternative fluids for analysis; as yet there is no accepted alternative.

Summary Information: methods for the determination of surface area, pore size distribution, and pore volume: Gas Physisorption and Mercury Porosimetry

Common applications

- Determination of material surface area, pore size distribution, bulk density, and pore volumes,
- Determination of material fractal dimensions.

Known limitations

- Results are sensitive to pretreatment conditions. High vacuum (and perhaps high temperature) is required to remove residual gases and solvent from micropore systems and heat treatments that may be detrimental to sample integrity (e.g., MOFs)
- N_2 is the most common and readily available probe molecule, but its polarizability complicates micropore analysis where Ar is preferred.
- While BET or Kelvin theory is easy to use, it is often misused. Strict requirement for use of BET theory have been established and should be utilized.
- Classical adsorption theory is readily available and easy to use, but more modern, but less readily generalizable, NLDFT or molecular dynamics (MD) methods are needed for sophisticated pore size distribution measurement. Pore size results are highly dependent on the chosen model.
- Classical pore size distribution models fail at the capillary limit (for N_2 around $P/P_0 = 0.4$) and this failure can produce artificial pore volume in classical analysis (for N_2 typically at 4 nm).
- Both N_2 and Ar require cryogenic temperatures, and this renders the kinetics of physisorption very slow for microporous materials resulting in variability of analysis.
- During the free space measurement, He can become entrapped in micropores, leading to misinterpretations of isotherm shapes. [56]
- Gas physisorption generally has limitation of pore size ranges from the kinetic diameter of the adsorbate to about 400 nm for cryogenic analysis. For many applications, this 400 nm cutoff is not sufficient for characterization of the complete catalyst pore transport structure and alternative methods are necessary. This is the role of mercury porosimetry.
- While mercury porosimetry can access a broad pore range from tens of nanometers to microns, mercury can alter certain thin-walled pore structures (e.g., carbons) and is often left behind in the sample after analysis making the analysis destructive in contrast to gas physisorption. Mercury toxicity requires precaution during handling, analysis, and material disposal.

Specific recommendations for reporting data in literature

- Report amount of sample used for analysis, the pre-treatment conditions (vacuum level, temperature, time), and sample form (powder or pellet).
- For BET surface area, report the relative pressure range for isotherm linearization and the number of points used (single vs. multipoint).

- For pore size analysis using classical methods (e.g., t-plot, Barrett-Joyner-Halenda (BJH)) report the thickness model and any other corrections used for calculations.
- Report the kernel and its source for NLDFT analysis.
- If full adsorption/desorption isotherms are collected for discussion, they should be included as a plot along with the raw x-y data to show point density used for pore distribution calculations.

References for best practice

- J. Rouquerol et al., *Adsorption by Powders and Porous Solids: Principles, Methodology, and Applications* [51]
- B. Scarlett et al., *Characterization of Porous Solids and Powders: Surface Area, Pore Size, and Density* [37]
- ASTM International: Subcommittee D32.01 on Physical-Chemical Properties [18]
- Hammond and Conner, *Analysis of Catalyst Surface Structure by Physical Sorption* [50]
- C. Orr and P.A. Webb. *Analytical Methods in Fine Particle Technology* [57]
- Zelenka et al., *Artifacts and misinterpretations in gas physisorption measurements and characterization of porous solids* [58]

Physical properties: Particle size distributions of supported metals

Insights from surface science reveal that different metal facets may have very different catalytic functions. Often, activity is associated with rare, high-energy corner, edge, or defect sites as opposed to the low index terrace sites that comprise the majority of metal surfaces in large nanoparticles and bulk structures. Alternatively, some reactions, such as the water-gas-shift, are promoted at metal-metal oxide interfaces. Because interfacial area scales inversely with metal particle size, one might observe that reaction rates are strongly sensitive to particle size in reactions like the water-gas-shift. For these reasons, many reactions should be considered "structure sensitive" and thus dependent on both the shape and size of metal particles. With this in mind, it is important to recognize that the shape and size of metal nanoparticles is almost certainly non-uniform. In the vast majority of catalysts, one expects variations in particle size and structure spatially throughout the catalyst sample. If one accepts that reactions can be size- and structure-sensitive, then one also should expect spatial heterogeneity in reaction rates throughout catalyst pellets. For these reasons, one must not only characterize and report the average size and/or shape of a particle, but also the particle size distribution and heterogeneity in the active phase. As a final note, one generally considers gas titration of metal surfaces—CO or H_2 chemisorption on Pt for example—to be the gold standard for quantitative determination of exposed metal surface area. However, some metal catalysts are not amenable to these straightforward titration methods. In these cases, particle size distributions can be used to estimate the accessible metal surface area. This is common practice for gold catalysts and bimetallic alloys, which either lack a reliable chemisorption method or, especially in the case of alloys, may have a poorly defined active site altogether.

The most common method for obtaining a metal particle size distribution is electron microscopy. For particles at the micron scale, scanning electron microscopy (SEM) and atomic force microscopy (AFM) are possible. That said, metal catalysis generally occurs on particles between 1 and 50 nm, which makes scanning and/or transmission electron microscopies (S/TEM) the methods of choice for quantifying the particle size distributions that are relevant in most catalysis. X-ray diffraction, especially with synchrotron-based methods or modern high sensitivity detectors, is now able to detect crystalline domains down to roughly 1 nm, and peak location/width in diffraction patterns can be used to estimate average metal particle sizes; however, XRD patterns provide no information about particle size distribution and heterogeneity.

Grain sizes (and distributions) of the bulk catalyst

Beyond the size and distribution of the active phase, the dimensions of the bulk catalyst particle (or pellet) are important to consider as they determine the length scales of diffusion/conduction between the bulk fluid and the active material dispersed throughout the catalyst pellet. In general, larger particles will have larger gradients in temperature and/or species concentration between the center of the pellet and the bulk fluid; as such, consideration of the catalyst macrostructure is critical to reproducibility, especially with engineered materials used in industrial practice. Average grain sizes for powders are relatively easy to determine using sieves. These should generally be reported as part of the catalyst synthesis/testing protocols as they aid in assessing the extent of heat and/or mass transfer limitations. Laser techniques are more sophisticated methods can be utilized to determine particle size distributions at the macroscale (i.e., cm). [59]

Summary information: methods for catalyst textural property characterization/particle size distributions: electron microscopies

Common applications

- Macroscopic view of catalyst microstructure
- Particle size distributions of supported metal nanoparticles
- Elemental analysis from different sample spots (Electron Dispersive Spectroscopies)

Known limitations

- Sampling volume is small relative to bulk system (a single grain of sand within a sandy beach analogy)
- User's eye tends to gravitate towards the unique, and not mundane features, resulting in false impression of phenomenon probability
- Focused electron beam techniques can cause localized energy transfer that change structure (e.g., beam-induced particle sintering)
- Small metal nanoparticles or other domains can be limited by Z-contrast to other catalyst or support domains, masking their presence.

Specific recommendations for reporting data in literature

- Sample preparation and mounting
- Instrument and electron beam characteristics
- For metal nanoparticle particle size distribution analysis, report the number of particles collected and a full distribution curve, not merely averaged statistics

References for best practice

- C. N. Satterfield, Heterogeneous Catalysis in Industrial Practice [2]
- P.L. Gai and E.D. Boyes, Electron Microscopy in Heterogeneous Catalysis (Series in Microscopy in Materials Science) [43]
- S.J. Pennycook and P.D. Nellist, Scanning Transmission Electron Microscopy: Imaging and Analysis [44]

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Recommendations for site specific characterization methods

Introduction

Heterogeneous catalysis is a surface phenomenon where reactions occur between reactant molecules and the catalyst at an adsorption site. This adsorption site and the surrounding ensemble of atoms, which can include metal-support interfaces, meso- and micropores, or support modifiers, as shown in Figure 4.B.1, are known as the active site for the reaction. Generally, active sites make up a small portion of the catalyst surface. Catalysts may contain a collection of different active sites, each with their own unique activity and selectivity, which may evolve during reaction. This concept, originally formulated by Taylor, is foundational in the field of catalysis. [1] In some cases, the observed catalytic activity is dominated by a small fraction of the identified active sites, a concept known as structure-sensitivity. [2,3] For instance, it has been shown that Cu step edges in the presence of Zn atoms are much more active for methanol synthesis than all other Cu sites. [4] Catalytic mechanisms may also rely on distinct active site types acting in tandem. [5] It is therefore of great importance for catalyst researchers to not only quantify the number of active sites within a catalyst but to also understand their geometric and chemical makeup. Site quantification allows for the calculation of reaction rates normalized by the number of putative active sites in the catalyst, defined as a site-time yield (STY). [6] Transforming catalytic performance into STYs enables comparisons between catalysts on a putative active site basis. Furthermore, site structural information and normalized catalytic performance can provide insight into how different site types confer catalytic activity.

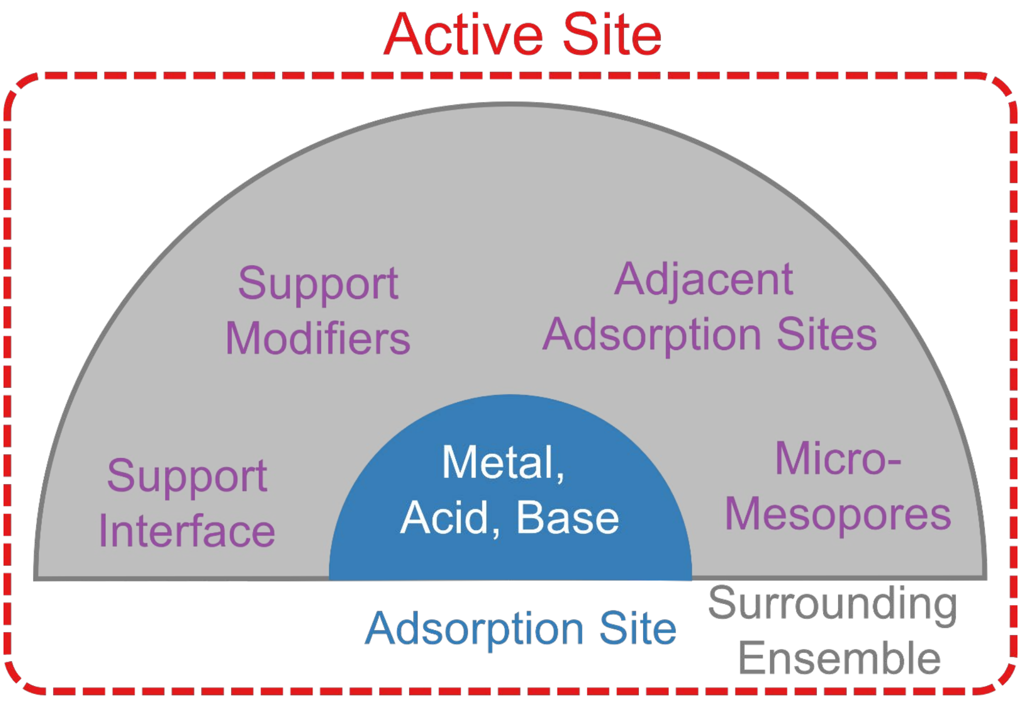

Figure 4.B.1. Schematic demonstrating a holistic view of the catalyst components that comprise the active site.

Surface characterization techniques can be used to selectively probe and quantify surface sites of different catalytic materials, as opposed to bulk techniques which average the properties of both the surface and subsurface of the catalyst. Effective active site characterization techniques are able to distinguish catalytic active sites of interest from inactive sites on the catalyst surface when correlated with catalytic reactivity. Common surface site characterization techniques leverage the specific binding between a probe molecule and accessible active sites. The number of probe molecules adsorbed by the catalyst can be quantified to determine the number of purported surface sites using an assumed adsorption stoichiometry. For example, CO chemisorption is a common surface characterization technique used to determine the number of surface metal sites present in supported metal catalysts.

In addition to quantification of probe molecule uptake, spectroscopic techniques can be applied to determine the state of the adsorbed probe molecule and provide more detailed information about the surface site. For example, adsorbed pyridine molecules probed by infrared spectroscopy can be used to differentiate between Lewis and Brønsted acidic sites on a catalyst surface. [7] Finally, several other characterization techniques can be used in conjunction with assumptions or refinements to specifically probe the catalyst surface. For example, imaging of metal nanoparticles using electron microscopy can provide a measure of the number of surface metal sites based on the particle size distribution and an assumed nanoparticle geometry.

Although the goal of most fundamental catalyst research is to understand the structure-function relationship of the catalyst active site, based on the discussion above, it is extremely difficult to identify the true active site. In most cases, the site can be inferred using a collection of characterization tools, but to date there is no single tool that will characterize the true active site with a high degree of certainty. Furthermore, catalyst surfaces are known to change under reaction conditions which may alter the nature of the active site. This section will focus on surface site characterization and will provide an overview of common characterization techniques. Each technique description will be accompanied by a brief explanation of instances where the technique is best applied, references to in-depth descriptions of the technique in the literature, and precautions to take when collecting and interpreting data using a given technique. Subsequently, a set of recommendations for reporting on surface site characterization will be provided. Finally, best practices for conducting and reporting surface site characterization to give the most rigorous and reproducible results will be discussed. In addition to references detailed below which discuss specific methods, we would refer the reader to the following references which provide detailed best practices for several of the techniques listed below. [8–10]

Common surface site characterization techniques

Fourier transform infrared spectroscopy (FTIR) of adsorbates

Common applications

- Quantifying acidic sites using the adsorption of amines or other basic probe molecules.
- Distinguishing between Brønsted and Lewis acid sites.
- Determining the distribution of acid site strength.
- Understanding metal speciation between metal nanoparticles and single atoms using CO adsorption.
- Quantifying relevant surface sites using the uptake of reactants below reaction temperature.

Precautions to take when collecting and interpreting data

- Adsorbate molecules may not be able to access all sites either due to pore confinement or steric hinderance from other adsorbed molecules. [11]
- Similar site types with different catalytic activity may not be distinguished by the probe molecule used. [12]
- Some titrants may require conditions for adsorption that are difficult to reach or maintain. For example, CO tends to be a more sensitive probe of Lewis acid sites than pyridine or deuterated acetonitrile but requires cryogenic temperatures (~ 100 K) to bind to these sites.
- Measurement of extinction coefficients requires at a minimum a volumetric uptake apparatus combined with an FTIR, and can benefit from combination with gravimetry as well. [13]
- Gas phase contributions to the spectra must be appropriately subtracted out in *operando* measurements, particularly to achieve quantitative results. [14]

- Extinction coefficients can vary widely between similar samples prepared and measured in different laboratories and may be coverage dependent. As a result, using reported values from literature should be done with caution.
- Operation at high pressures representative of some reactions requires specially designed cells.
- Diluting agents like KBr can adsorb molecules from the environment. They should be stored in clean locations such as desiccators or gloveboxes.
- Some probe molecules such as CO can cause rearrangement of catalytic materials. [15]
- IR peak locations can be dependent on the adsorbate coverage and temperature. [16]
- In commercial cells, the bulk catalyst bed temperature and the temperature of the surface of the catalyst bed under observation can differ. [17]
- Exposure of cells with evidence of corrosion to CO can result in $Ni(CO)_4$ contamination of the sample and convolute IR spectra. [18]

References for best practices

- General reference for diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments. [19]
- Identification of metal nanoparticles and single atoms. [20]
- Selection of adsorbate molecules [21] and reactors. [22,23]
- Calculating extinction coefficients. [13,24]

Uptake and temperature programmed desorption (TPD) of adsorbates

Common applications

- Determining the concentration and strength of acid sites using NH_3.
- Quantifying metal sites using CO, H_2, and N_2O adsorption and base sites using CO_2 adsorption.
- Measuring adsorbate specific binding energies, potentially at varying coverages.
- Measuring the density of acidic, basic, and redox sites in oxide catalysts using alcohol adsorbates.

Precautions to take when collecting and interpreting data

- Large probe molecules may not be able to access sites within narrow pores, leading to an undercounting of active sites. Pore size analysis should be conducted to ensure that probe molecules can access as large a fraction of the material surface as possible.
- Care must be taken that only probe molecules are measured during desorption when using thermal conductivity detector (TCD). This can be done using traps for moisture or other desorbing molecules. Mass spectrometry can also be used to identify the desorbed molecules.
- Adsorption time must be sufficient to saturate catalyst surface with adsorbate molecule.
- Pretreatment is needed to ensure catalyst is not changing over the course of the desorption sweep.
- The number of adsorption sites will depend on the temperature of the adsorption step. This information should be reported to allow for comparison between protocols.
- Probe molecules may bind at sites that are not active for catalysis. Further work is needed to demonstrate that the active site of interest is the only adsorption site.
- Temperatures for measured adsorbate desorption can depend on transport processes such as heat transfer or re-adsorption effects. Care must be taken to avoid over-interpretation of desorption peak temperatures. Multiple ramp rates can be used to ensure that data are not convoluted by heat transfer effects. [25,26]
- Adsorption may be dependent on the partial pressure of the probe molecule. The concentration used for experiments should be reported.

- Care should be taken when choosing a desorption temperature as catalysts may react with probe molecules to form new structures. For example, Cu nanoparticles can react with N_2O at high temperatures to form bulk oxides, eliminating surface sensitivity.

References for best practices

- General protocols. [27]
- Measuring zeolite acidity. [28,29]
- TPD in porous materials. [30]

In-situ titration of active sites

Common applications

- Determining the number of surface sites present under operating conditions.

Precautions to take when collecting and interpreting data

- Probe molecules must be chosen carefully. A good probe molecule can bind irreversibly to the surface site of interest for the length of the experiment and will not interact with the reactant or product molecules. Control experiments are needed to demonstrate that the probe molecule does not also bind to inactive sites.
- If multiple types of sites (with different intrinsic activity) are present, the titration curve may not be linear. For instance, the slope of the titration curve can be higher at low titrant coverage if the more active sites are preferentially titrated.
- Relationships between titrant coverage and the measured reaction rate can provide insight into the uniformity of active site catalytic activity. During transient titration measurements (where the titrant is added to a catalyst bed of finite depth) concentration gradients may result in adsorption first to sites upstream of concentration fronts rather than those that bind the titrant strongest. Conducting titration experiments under various partial pressures therefore could provide more information regarding site uniformity if different active sites bind the titrant under distinct pressure regimes.

References for best practices

- Using propionic acid to quantify the number of Lewis acid-base pairs in oxides during aldol condensation. [31]
- Using 2,6-di-tert-butylpyridine to quantify the number of acid sites in polyoxometallates [32] and zeolites [33] during isomerization.

H_2/D_2 scrambling

Common applications

- Determining supported metal dispersion, especially in catalysts with low metal loadings.

Precautions to take when collecting and interpreting data

- The reaction between H_2 and D_2 is reversible. Control experiments must be performed to determine the equilibrium conversion prior to conducting site quantification experiments. Subsequently, measurements of HD rates should be conducted at D_2 conversions below the equilibrium conversion to avoid HD consumption in the reverse reaction.
- To estimate apparent dispersion values, H_2/D_2 exchange rates must be measured at the same D_2 conversion for a control material with known dispersion to avoid overestimation of active sites.

References for best practices

- An example protocol for H_2/D_2 scrambling. [34]

Nuclear magnetic resonance (NMR) spectroscopy

Common applications

- Determining the concentration of Brønsted and Lewis acid sites using trimethylphosphine.
- Quantifying the strength of Brønsted and Lewis acid sites using trimethylphosphine oxide and trimethylphosphine respectively.
- Understanding the location of acid sites within catalysts using probe molecules of different sizes such as trimethylphosphine and trioctylphosphine.
- Determining the oxidation and bonding state of metal atoms within zeolites.

Precautions to take when collecting and interpreting data

- NMR measurements of catalyst surfaces are very sensitive to the degree of hydration and oxidation. Exposure to air will alter NMR results and may also degrade probe molecules such as trimethylphospine. Catalysts should be dried, handled in a glovebox, processed using dry solvents, and transferred in NMR tubes with air-tight seals.
- NMR measurement programs and data interpretation techniques vary between different elements and environments. Techniques that work for collecting spectra for one element or in solution will not necessarily translate to other elements or solid-state materials.
- When using probe molecules to quantify sites, care should be taken to ensure that sufficient probe molecules are provided to titrate all sites of interest. However, it is also important not to provide too much probe molecule to avoid obscuring the signal of interest with signal from unbound probe molecule. This requires first calculating an estimate for the number of sites of interest in a catalyst sample and then supplying a small excess (2 to 5x) number of probe molecules. Several different probe molecule levels should be tested to demonstrate that all sites of interest are titrated.
- When using NMR measurements to quantitatively measure surface sites, standard materials should be tested to demonstrate that all experimental parameters are set properly to allow for accurate quantification.
- Some probe molecules commonly used such as trimethylphosphine are pyrophoric and toxic and must be handled with care.

References for best practice

- General NMR information. [35]
- Acid site characterization with NMR. [36,37]
- NMR characterization of metals. [38]

Catalytic probe reactions

Common applications

- Determining the acidic, basic, and redox character of oxide materials using alcohols.
- Probing of oxidation sites using CO oxidation.
- Determining of the number of acid sites in a catalyst using alkane cracking and isomerization.

Precautions to take when collecting and interpreting data

- Ensure that reactions are run in the differential regime to minimize secondary reactions and that there are no transport limitations within the reactor. [39]

- Large probe molecules may be unable to reach sites within porous materials. Ensure that diffusional limitations do not limit the number of accessible sites. [40]
- Ensure that catalysts are not losing sites due to deactivation through processes like sintering or coking while collecting information from the probe reaction.
- Probe reactions should be known to utilize only the same sites as the reaction of interest.
- The rate of alkane cracking can be influenced by the proximity of Brønsted acid sites, [41] but in cases where their distributions are similar or are in the dilute limit, rates have been directly correlated with active site density. [42]

References for best practices

- Oxide probing with methanol.[43,44]
- CO oxidation. [45]
- Alkane cracking. [41]

In situ and operando Raman spectroscopy

Common Applications

- Determining the coverage, oxidation state, and coordination of supported oxides. [46]

Precautions to take when collecting and interpreting data

- The peak location of surface groups can be coverage, moisture, and support dependent.
- Raman lasers may cause local sample heating which can alter catalyst or adsorbate state. Care should be taken to avoid local heating by using large spot sizes, low laser intensities, moving the sample, or using a fluidized catalyst bed. Control experiments should also be conducted to demonstrate that heating effects are not an issue.
- Material impurities or defects can fluoresce in the energies of interest. Care should be taken to choose laser wavelengths that will produce Raman shifts away from fluorescent signals. Time gating detection methods can be used to increase detector selectivity for faster Raman lifetimes over longer fluorescence lifetimes.
- Signal for surface layers and species can be as much as 10^5 times weaker than bulk signal. Techniques aimed to enhance Raman responses from specific groups such as Resonance Raman are helpful to increase the signal from surface groups of interest.

References for best practices

- General information. [47]
- Supported metal oxides. [48]
- Resonance Raman, Surface Enhanced Raman, and Tip Enhanced Raman. [49,50]

Transmission electron microscopy (TEM)

Common applications

- Imaging supported metal nanoparticles, clusters, and single atoms.
- Elemental analysis and elemental mapping of selected catalyst areas when paired with energy dispersive x-ray spectroscopy (EDS).
- Analysis of the catalyst nanostructure by applying diffraction techniques and of the catalyst electronic structure using electron spectroscopy.

Precautions to take when collecting and interpreting data

- TEM images are only a small fraction of the total catalyst surface and may not be able to image small nanoparticles. Therefore, images may be biased towards the most easily imaged nanoparticles and may not be representative of the entire catalyst. Stronger claims can be made by imaging several different areas and discussing differences between them and by correlating image statistics with other bulk and surface characterization techniques when appropriate.
- The high energy electron beam may alter the catalyst during the measurement. Control experiments can be collected for *in situ* measurements to demonstrate the difference between changes caused by process condition impacts and beam effects.
- Images project 3D materials onto 2D images and may not be able to distinguish between surface and encapsulated nanoparticles. TEM can be used in combination with size dependent probe reactions or surface spectroscopy to demonstrate encapsulation. [51]

References for best practices

- Reporting nanoparticle sizes and statistics. [52]
- Applications in catalysis. [53]
- *In Situ* electron microscopy. [54]
- See report *section 3C* for more details.

Recommendations for reporting active site characterization

Surface site characterization techniques involve many parameters and assumptions that can dramatically impact their results. To ensure reproducibility, we encourage researchers to report experimental procedures and assumptions in as much detail as possible and to provide access to raw characterization data. [55,56] The availability of this information will allow for the identification of measurement steps or assumptions that could skew surface site characterization data. Detailed protocols will also be useful for the consistent characterization of catalysts reproduced in other laboratories as well as newly developed catalysts with similar surface sites.

Detailed experimental protocols are critical for future reproduction of active site characterization measurements and include aspects such as:

1. Instrument specifications, such as the detector or spectrometer used.
2. Instrument settings such as electron beam energy or laser wavelength.
3. Experimental details such as gas flow rate, temperature ramp rate, and quantities of materials used.
4. Catalyst history information such as pretreatment and storage history.
5. The purity and source of reagents used such as gas impurity levels.
6. Instrument calibration protocols such as alignment and baselining.
7. Blank or control experiments performed and their results such as signal produced by bare support.
8. The reproducibility of measurements and their uncertainty.
9. Details of data processing protocol such as baseline corrections, normalization, and curve smoothing as well as the software and equations used.

Table 4.B.1. demonstrates two sample descriptions of the same experiment to highlight the depth of information that is necessary to accurately reproduce an active site characterization experiment. These details will enable future researchers to reproduce current work as well as to identify measurement details that could influence final conclusions.

Table 4.B.1. Samples of poor and effective descriptions of a hypothetical ammonia temperature programmed desorption (TPD) experiment.

Poor Description	Effective Description
Following oxidation of the catalyst, acid sites were probed through ammonia temperature programmed desorption.	After synthesis, all catalysts were stored in a solvent-free nitrogen glovebox until needed. Acid sites were characterized using an Altamira AMI-390 microflow reactor system equipped with a thermal conductivity detector (TCD). 100 mg of catalyst were loaded into a quartz U-tube (d = 0.5 in.) reactor and held between plugs of quartz wool with a thermocouple inserted into the catalyst bed. Samples were heated under 50 mL/min 10% O_2/He (certified mixture, airgas) to 723 K at 5 K/min and held at that temperature for 2 hours. The samples were then cooled to 393 K under 50 mL/min He (99.999%, Airgas) before saturating with 10% NH_3/He (certified mixture, Airgas) for 30 minutes. Excess NH_3 was removed by flowing 50 mL/min He at 393K for one hour. Temperature programmed desorption of NH_3 was performed by heating the sample from 393 to 723 K at 30 k/min and holding at 723 K for 30 minutes in 50 mL/min He. All gases were passed through a water trap (molecular sieve 5A, Thermo Scientific) prior to entering the system. The TCD was calibrated before each experiment by measuring 10 pulses of 10% NH_3/He from a 5 mL sample loop. A blank experiment was conducted for comparison with 50 mL/min He passed over the catalyst instead of 10% NH_3/He to demonstrate that all TCD signal was produced by NH_3. All results were benchmarked to the NH_3 uptake by a silica-alumina with a known acid site density. Measurements were conducted in triplicate. All reported values are the average of the three measurements with their associated standard deviation.

We also recommend that researchers report all assumptions made when interpreting surface site characterization data, such as the adsorbate to surface site stoichiometry or the shape of nanoparticles used to model electron microscopy data. For example, increasing the assumed stoichiometry of CO on metal sites from one CO molecule per surface metal atom to two CO molecules per surface metal atom would decrease the number of measured metal sites by half for a given measured CO uptake, dramatically changing calculated rates of reaction. Common assumptions made when interpreting surface site characterization data include:

- Stoichiometry of adsorbates on active sites.
- Metal nanoparticle shape when extracting the number of sites from TEM images.

- The number of different active site populations expected. For example, is it assumed that all active sites have the same activity or are there more and less active site populations being probed?

These assumptions, while often reasonable and standard, play a key role in determining the calculated surface site quantity and speciation, and therefore should be articulated to allow for reproduction and reinterpretation of the reported findings. Similarly, we recommend that authors clearly demonstrate how they have calculated TOF values from experimental results and how experimental error was propagated through those calculations to allow fair comparison of TOF values throughout the literature.

Beyond experimental details, inclusion of raw, unprocessed characterization data in the supplementary files of a published work will allow future researchers to re-process the data using different assumptions should the state of the technology change, or new interpretations of the nature of an active site arise. For example, including raw output signals from temperature programmed desorption profiles as a table of signal versus temperature readings, along with the relevant calibration information. This information could help future researchers identify similarities in desorption behavior of reproduced or newly synthesized materials. The collection of surface characterization data in a single repository may also enable future insights through the application of data science techniques across many data sets. [57,58]

Best practices in active site characterization

At its core, the examination of an active site requires correlating two experimental data sets: reactivity data, preferably under differential reaction conditions, and surface characterization data. In some cases, multiple surface sites, such as metal corner sites and meta-support interface sites, may similarly correlate with reactivity data, making unambiguous determination of “the” active site difficult. Active site interpretations are always subject to reevaluation in the context of future data; understanding and acknowledging this reality will increase the long-term importance of any given study.

While the techniques to measure heterogeneous catalyst surface sites may vary, there are several universal steps researchers can take to increase the strength of claims made based on surface site characterization measurements.

Clearly demonstrate trends in methodology

First, we encourage researchers to synthesize and characterize catalysts in which the surface concentration of potential active sites is intentionally varied, allowing for correlation of changes in activity with the change in surface site concentration. This is among the strongest evidence for inferring that a particular surface site is the catalytic active site. For example, when characterizing metal active sites using CO chemisorption, synthesizing and characterizing catalysts with a series of metal loadings enables the assessment of the relationship between the number of surface sites and the metal loading. Showing a linear correlation between the number of metal surface sites and the catalytic activity would then suggest that those metal sites, or a subset of the total metal sites, are the catalytic active site.

Several groups have demonstrated how coupling reaction kinetics with intentional variation of metal nanoparticle size and loading can enable the identification of specific active sites on the metals themselves. [59–62] For example, researchers varied the size of Pt, Pd, and Ni nanoparticles on CeO_2 to control the number of metal sites and showed that CO combustion rates scaled closely with number of metal-interface sites. This result suggested that the interfacial sites were responsible for the catalytic activity as shown in Figure 4.B.2. [59] Characterizing a series of catalysts with changing surface site concentrations, particularly when other factors such as particle size remain constant, will support claims that the intentionally varied surface site is responsible for the observed catalysis.

If the catalyst of interest is a new formulation that has not been extensively characterized in the literature, researchers are encouraged to benchmark their techniques with a similar known material. This benchmarking demonstrates that the new characterization protocol reproduces previous results. For example, when characterizing a new acidic catalyst using NH_3 TPD, researchers are encouraged to also characterize a standard material with known properties to demonstrate that the new characterization technique is appropriate for the desired materials.

In addition to comparing characterization results to benchmark materials, combining several characterization techniques improves understanding of the surface sites present in the catalyst and benefits discussions of specific catalyst active sites. Besides corroborating the quantification of catalyst surface sites, using multiple techniques may enable a more nuanced discussion of the different types of surface sites within the catalyst and aid in correlating reactivity data to subsets of surface sites. [63] Operational techniques such as modulation excitation, common in infrared spectroscopy, can be used to provide additional information about which surface sites are participating in catalysis. [64] Researchers may also consider combining their experimental characterization results with theoretical models to bolster claims of the active site identity. For example, in situ DRIFTS spectroscopy and density functional theory (DFT) modeling have been combined to suggest that the active site for CO oxidation on model Au/TiO_2 catalysts is the interface between the metal nanoparticle and the oxide support. This was achieved by observing the sites where CO is consumed and modeling a potential site and mechanism for O_2 dissociation. [65]

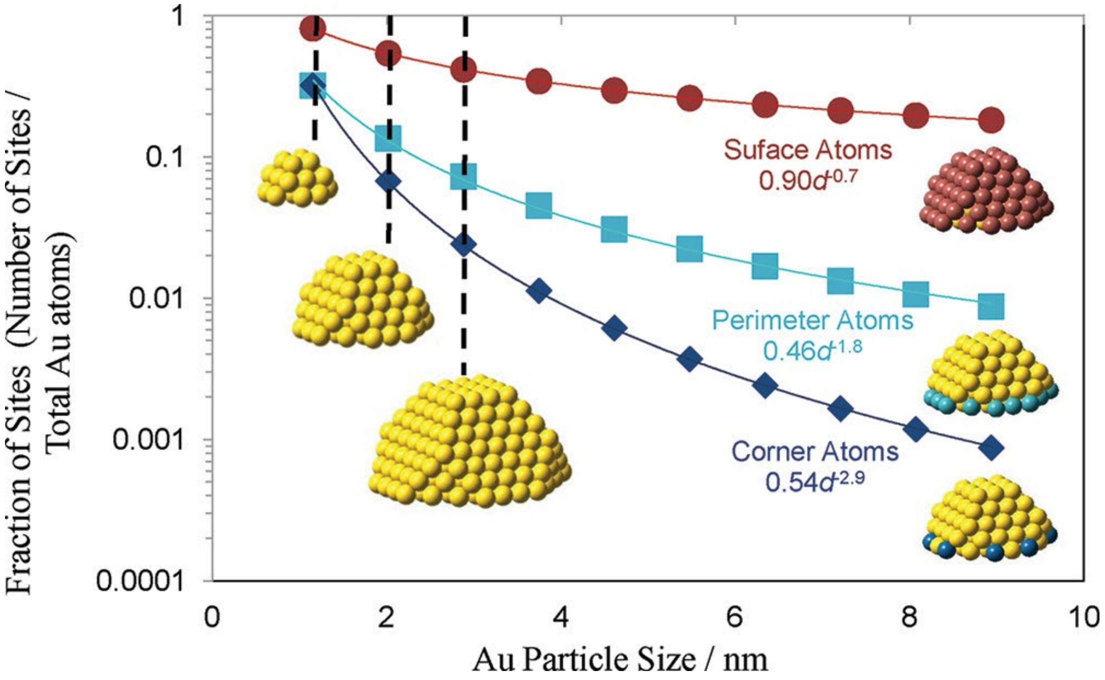

Figure 4.B.2. Variation of the fraction of surface sites (red), perimeter sites (green), and low coordinated corner sites (blue) with Au particle size in truncated cuboctahedra geometry. Reprinted with permission from [61]. Copyright 2012 American Chemical Society.

Compare characterization results to synthetic expectations and other results

Once a surface site concentration has been determined from catalyst characterization data, we encourage researchers to discuss how this number corresponds to the expected number of surface sites based on the catalyst synthesis protocol. For example, how does the uptake of CO onto a supported metal catalyst compare with the amount of metal in the catalyst system? These discussions are important for understanding the real state of the catalyst, which may be quite different from the proposed form based on the catalyst synthesis. This provides a simple check to determine the reliability of characterization results. Furthermore, differences between complementary techniques or between experiment and theoretical calculations should also be explained. We recommend that any discrepancies from synthetic expectations or other experiments be discussed to make the strongest claims about a catalyst's activity.

Consider catalyst operating conditions

We also encourage researchers to consider the catalyst operating conditions while characterizing its surface sites, as the number and nature of surface sites can change based on reaction parameters such as temperature, pressure, or atmosphere. Several techniques such as electron microscopy can be operated under conditions similar or identical to reaction conditions and can strengthen claims about the working form of a catalyst. [66] For example, past works have demonstrated the ability to observe metal sites using X-ray photoelectron spectroscopy under model reaction conditions (in situ) and to track the occlusion of those metal sites due to strong metal support interactions. [67] Others have reported the titration of acidic catalyst sites under reaction conditions while tracking product formation (*operando*). [68] In cases where in situ or operando characterization is not possible, we recommend that catalysts be characterized with the same technique before and after reaction to identify any changes that may have occurred during reaction. While this approach will not capture all changes that may have occurred during operation, it will strengthen the researcher's claims about the identity of the active site and normalized reaction rates.

Align the level of active site claims to rigor of characterization performed

Above all, we encourage researchers to align the level of their catalytic claims with the rigor of the surface site characterization and reactivity data on which those claims are based. For example, some surface site characterization techniques may not be able to distinguish between unique site geometries. In those cases, we recommend that researchers report an average site activity, acknowledging that different site types may have different individual activities. Authors are also encouraged to discuss the limits of detection of the techniques they apply to allow comparison of how experimental results relate to measurement uncertainty and to contextualize the catalytic activity of materials not thought to have any of the active site of interest. Overall, it is important that the researcher, editors, and reviewers ensure that claims are in line with the information supplied by the characterization technique to avoid misinterpretation by future readers.

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Recommendations for catalyst characterization by transmission electron microscopy (TEM)

Scanning transmission electron microscopy (STEM) and transmission electron microcopy (TEM) imaging, diffraction, electron dispersive x-ray spectroscopy (EDX), and energy loss spectroscopy (EELS) are common characterization tools for heterogeneous catalysts. [1–3] The analysis may be performed in vacuum or under in situ or operando conditions. [4,5] However, the microscopist is often not an expert in catalysis and only a few catalytic researchers have the expertise in microscopy necessary to understand all aspects of the measurements. Likewise, often times catalysis researchers that are not experts in microscopy may (mis)interpret and publish data without consulting the microscopist that acquired the data for assistance. Due to the, sometimes unappreciated, complexity of these advanced methods, there is a critical need to establish reporting standards and best practices to avoid misattributions and help advance understanding.

Common applications

TEM/STEM can be used to determine the shape and size of supported metal catalysts. Most frequently, these imaging techniques are used to determine particle size distributions (often shown in histograms connected to specific images). STEM/TEM images may also reveal bulk and surface structure for metal or oxide nanoparticles, zeolites and MOFs. Imaging may also provide information about metal distribution on the support (zoning) and the accumulation of coke on the metal particles (or support material). High spatial resolution spectroscopy such as EDX [6] and EELS [7] can provide information on local elemental composition, valence state and bonding.

EDX is particularly useful in determining particle composition for bimetallic and trimetallic systems. EELS is used to determine local oxidation state and composition of metal-support interfaces. 4D STEM (where an electron diffraction pattern is recorded at every point in the catalyst) is an emerging technique that promises to provide additional information on both structure and other properties such as charge transfer. [8,9] Electron tomography is used to obtain 3D morphology and chemistry of catalyst particles, mesoporous support for quantifying porosity and diffusion of products and reactants and/or catalyst particle distribution on the support. [10,11]

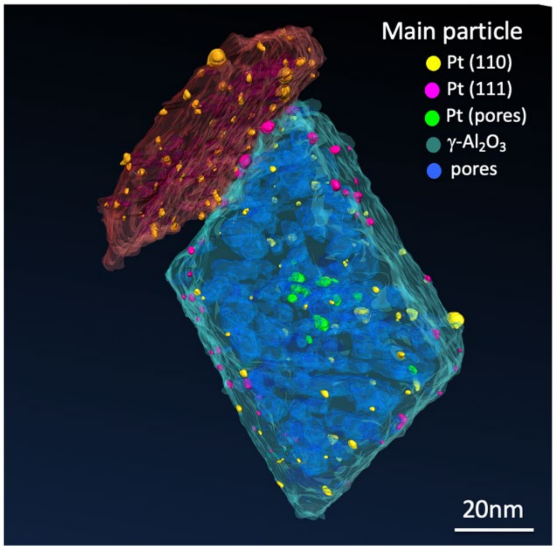

Figure 4.C.1. Tomographically reconstructed Pt/γ-Al_2O_3 catalyst. In the legend, Pt (110) refers to Pt nanoparticles deposited on the (110) teminated external surface of the Al_2O_3 nanocrystal, Pt (111) refers to Pt nanoparticles deposited on the (111) teminated external surface of the Al_2O_3 nanocrystal, and Pt (pores) refers to Pt nanoparticles deposited within the pores of the nanocrystal. Reprinted with permission from [10]. Copyright 2013 American Chemical Society.

Known limitations

- The primary limitation with any microscopy is that the technique is local, but reactivity tests capture an ensemble behavior of the entire catalyst material. Therefore, it is important that "representative" images or spectra provide a statistically authentic view of the structural and compositional heterogeneity and that researchers don't skew their results by their own biases (e.g., presenting only aesthetically pleasing images). Critically, researchers should correlate microscopy observations with the results from other techniques with complementary length scales. Quantitative assessment of highly heterogeneous samples is extremely challenging due to the limitations to sample large/statistically relevant areas, and in some cases, the fact that the analysis is possible only in thin (highly electron transparent) portions of the sample. In complex samples, analysis can often be only qualitative.
- A TEM image is a 2-D projection of a 3-D object. Crystal fringes that are observed in the image are not necessarily at the surface. In fact, the presence of lattice fringes within the bulk of the material does not guarantee a well-faceted surface. The most effective images to elucidate surface structures are profile images from the edge of a particle recorded in a zone axis orientation. This allows the surface terminations of metal nanoparticles to be determined and, under favorable conditions, allows the configuration of anions and cations to be observed at the surface of redox active oxides. [12,13]
- The resolution and sensitivity of a measurement will depend on experimental parameters and sample configurations. While experimental parameters can be controlled by varying imaging conditions or using instruments with different capabilities, the contrast limitation defined by the particle and substrate is an inescapable characteristic of the sample being analyzed and often limits the sensitivity for detecting features in catalysts.
- Most catalyst and support materials are beam sensitive. Utilizing the optimum experimental conditions that ensure a minimum of specimen damage and desirable image contrast is critical [14] The influence of the electron beam on the sample should be assessed for its impact on the measurement of interest.
- Environmental TEM/STEM setups are not generally designed to operate under plug flow conditions and are often closer to a well-mixed continuously stirred tank reactor (CSTR). [15] The window cell reactors also differ significantly from simple reactor models. [16] In order to extract intrinsic kinetics and relate observed structures to measured rates, it is necessary to develop a reactor model for the cell being employed to make operando measurements.

Recommendations for reporting data

TEM/STEM characterizations of catalysts/catalytic reactions can be performed in either vacuum, gaseous, or liquid environments. Whereas some general reporting standards should be applied in all cases, there are some differences as described below:

1. ***General***: Basic information about the conditions used to acquire the data should include a) the make and model of the electron microscope, b) the electron beam voltage, and c) associated detectors employed. For TEM applications, the electron dose should be reported and included, when possible, the total accumulated dose (not just the dose during the image exposure but also the dose associated with searching, tilting and image focusing). For STEM, in addition to the parameters described above the electron probe current and diameter, pixel acquisition time, pixel size, the convergence angle and collection angle should be reported.
2. ***Vacuum***: Column vacuum on the day of the data collection, preferably before and after the start of microscope session.
3. ***Gaseous Environments***: For in situ TEM in the presence of gases, additional information identical to that included for a laboratory microreactor must be included: background pressure around the sample before and after performing experiments, purity of gasses used, flow rate, gas pressure, heating rate, waiting period (if needed) before starting image acquisition.
4. ***Sample Preparation***: Report sample preparation techniques (grinding, sonication) and the technique used for loading the sample on the TEM grid (dry loading, wet loading). Grid material and the nature of any

support film as well as further grid preparation techniques such as plasma cleaning and/or baking should be reported as well as the identity of the sample holder material (spurious signals may result from sample holder especially during heating in the presence of gas).

5. ***Data Processing***: The method of noise reduction and image processing in the published images/diffraction patterns or spectra must be fully described following the standards established by The Microscopy Society of America i.e. "Generally, acceptable (non-reportable) imaging operations include gamma correction, histogram stretching, and brightness and contrast adjustments. All other operations (such as Unsharp-Masking, Gaussian Blur, etc.) must be directly identified by the author as part of the experimental methodology."

Recommendations for best practices

Imaging, spectroscopy, and diffraction techniques available in transmission electron microscopes represent a powerful suite of characterization tools that can provide micro-, nano- and atomic-scale information about heterogeneous catalysts. However, extracting reliable and reproducible information about a sample is not necessarily intuitive and often depends on the operator's judgement, assessment, and knowledge of the system of interest. Such dependence on the operator's technical skills and knowledge, and the need for complex input from the operator during the data acquisition process hinders the ability to fully automate TEM analysis of high-surface-area materials which often have wide variations in particle size, shape, aggregation state, phases and crystal structure. In cases where the operator is not the catalysis researcher themselves, it is imperative that there is good communication between the catalysis research and the microscopist on the details of data collection and the interpretation of the resulting images. The following list of best practices is expected to enhance the reliability and reproducibility of electron microscopy analyses of heterogeneous catalysts.

Instrument calibration

Although effort is taken by most instrument scientists to keep calibrations up to date, those calibrations should be validated by the instrument user. For catalyst samples with crystalline supports, calibrations can be checked by measuring lattice spacings of the support material, provided XRD shows no significant strain or lattice expansion. Nanoparticles should not be used for this calibration since their lattice parameters can vary quite significantly from the bulk material. [17] In the case of non-crystalline supports, a suitable internal standard can be used. For a more complete discussion of calibration, see Williams and Carter. [1]

Radiation damage

Imaging and spectroscopy should ideally not significantly alter the structure or composition of the catalyst. However, many samples show behavior which is far from ideal, and the critical dose or dose rate at which changes occur should be reported along with the method used to determine them. [18] While theories exist regarding beam irradiation mechanisms and potential strategies to minimize damage, most catalyst systems are complex and involve multiple damage mechanisms. Thus, determining optimal conditions based solely on theory can be challenging. For beam-sensitive specimens, empirical evaluations by varying experimental conditions, including dose, dose rate, electron voltage, and specimen temperature, should be performed to obtain representative images and spectra. Ideally at the beginning of an experiment, it is helpful to record images, diffraction patterns and spectra as a function of dose and dose rate to quantify the radiation damage response. One simple way to establish this is to first record images at low magnification, when the beam is spread out. After high magnification images, you should return to low magnification imaging and compare the images before and after. Changes in the catalyst microstructure are readily visible and can be identified, indicating that the beam is influencing the images obtained.

Unfortunately, these evaluation studies can be challenging to publish in journals with reasonable visibility. However, I believe that such studies are essential for advancing the field, and we should encourage their publication to benefit the entire community.

Statistically representative sampling

In a typical catalytic reactor, billions or trillions of particles are associated with the macroscopically obtained activity and selectivity. As a first rule, it is important to image multiple areas of the sample selected randomly and without operator bias, at low magnification. If multiple regions of the sample look similar in terms of morphology and composition, then it is worth proceeding to higher magnifications to perform more detailed analysis. If randomly selected regions show very different structures and compositions, the sample is heterogeneous and then it is best to prepare a new catalyst. It is best to quantify this process to give validity of the homogeneity of the sample. This may involve quantitative descriptions of particle size distribution, number of samples/areas investigated, number of spectra recorded, and so on. Statistics for particle size distributions should be reported including, but not limited to number of particles counted, standard deviation and/or variance of the distribution, average particle size, and how that average was computed (e.g., arithmetic mean, Sauter mean, volume mean, etc.). Critically, the lower end size limits for the imaging approach must be established. This depends not only on the atomic number difference between the particle and support but also on the thickness and roughness of the support as well as the imaging mode. Chemical mapping (EDX) can aid in determination of sample uniformity when particles are not “visible”. In this context, EDS analysis of various regions can be presented, so the reader can judge if the presented image is indeed a representative region of the sample. Often, the presented images in published work do not have similar loading of the various components as the bulk analysis. By reporting the EDS analysis of the field of view, the authors provide confirmation that the images are truly representative of the sample as a whole. However, users should be aware that mapping is also fraught with potential complication as some elements may be mobile under the beam and therefore difficult to quantify accurately. [19] Attention should also be paid to collection conditions (e.g., electron dose rate, dead time, total number of counts, etc.) to ensure spectra are similar and not skewed toward the area being investigated.

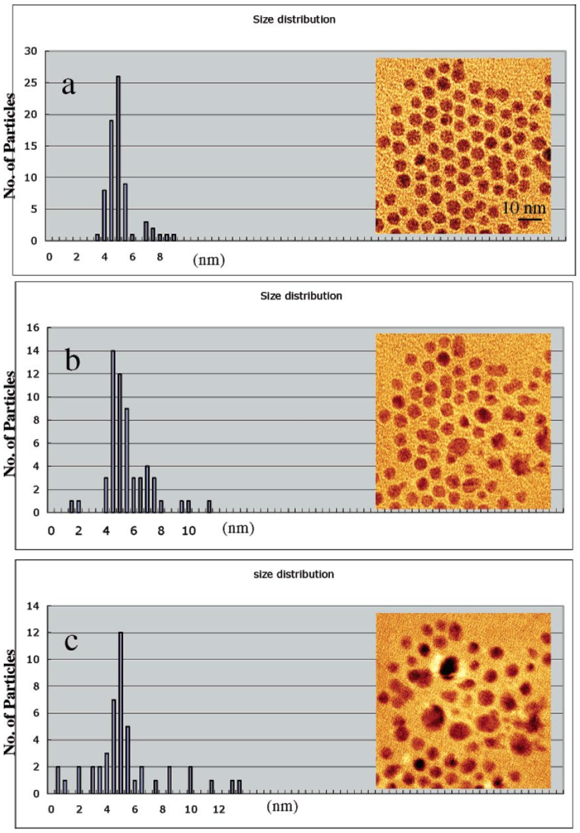

Figure 4.C.2. Study of the sintering of Au nanoparticles due to exposure to an electron beam. Size (diameter) distributions and electron micrographs of passivated gold nanoparticles (a) before and after electron exposure with a dose of (b) 4 and (c) 12 mC/μm^2. The histograms display the number of particles as a function of their diameters. Reprinted with permission from [20]. Copyright 2006 American Chemical Society.

Operando experiments

There is a need to clarify operando versus in situ measurements. In order for a measurement to be described as operando, reviewers must insist on a measure of conversion that is clearly demonstrated to be made in a kinetically-controlled regime. [21] Otherwise, the experiment is in situ. This is consistent with the use of the term by early research in Raman spectroscopy. [22] An operando is characterization of a catalytic material during reaction with the simultaneous measurement of catalytic activity/selectivity (preferably under differential conversion). The methods of determining the activity and selectivity must be defined. Ideally, an operando experiment would provide a quantitative measure of chemical kinetics. [23–25]

For thermal catalysis, this would typically involve a quantitative estimate of the reaction rate normalized to the active component of the catalysts (the surface area, active sites, etc.). Temperature calibration of the sample holder is critical to the reporting of the environmental condition. Comparison of in situ measurements with other techniques can help identify any discrepancies.

Bimetallic nanoparticles

Beyond particle size, a major question in bi- or multi-metallic samples is the location and local ratio between each component. This includes particle stoichiometries as well as any possible structure-composition correlations such as core-shell or Janus structures. Because catalysis is a local phenomenon, heterogeneity in particle structures and compositions can lead to a tiny fraction of particles performing most of the catalysis. Therefore, determining stoichiometry as locally as possible is of utmost importance in bimetallic systems, making STEM-EDX [26,27] and EELS [28] powerful tools in the hands of catalysis researchers to complement bulk techniques such as XAS or ICP-OES. STEM EELS can also be employed to provide not only spatially resolved elemental information, but additional information on bonding. The information is atom-specific, similar to X-ray absorption spectroscopy, providing information on the oxidation state, and in favorable situations also nearest neighbors and bonding to the support (using the technique EXELFS which akin to EXAFS).

The possible presence of compositional heterogeneity makes it all the more critical in bimetallic samples that adequate statistics on particle stoichiometries are collected, and any structural heterogeneities are described qualitatively. Variations in the number and composition of nanoparticles can be a function of the variable metal distribution in the as-prepared sample. Larger field of view analysis, as afforded by scanning electron microscopy (SEM), is beneficial to perform for identifying such inhomogeneities prior to performing S/TEM. In some cases, the composition may shift dramatically as a function of the particle size, [26] and care should be taken to note correlations between the two.

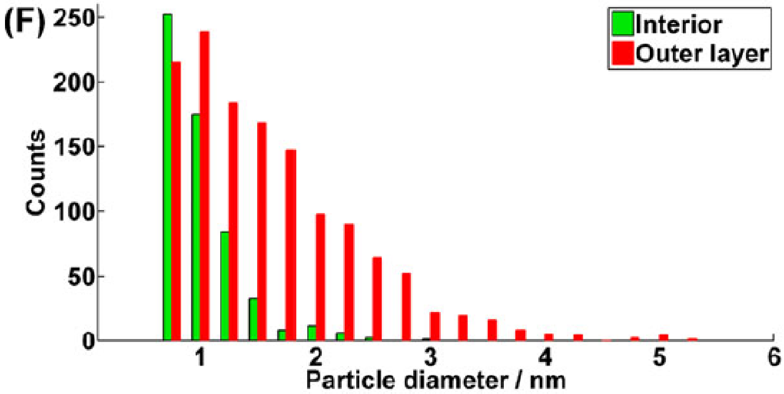

Figure 4.C.3. Particle size distribution of Pt-Pd nanoparticles supported on a γ-Al_2O_3 support. The catalyst microscope samples were prepared by a "lift out" method, involving the encapsulation of the catalyst particles in a resin epoxy and extracting cross sectional, TEM ready samples from the bulk using a FIB/SEM instrument. Using this technique Pingel et al. find that the Pt-Pd nanoparticles near the external surface region of the γ-Al_2O_3 are much larger than those found further inside the γ-Al_2O_3 samples. All Pt-Pd nanoparticles were found within pores of the γ-Al_2O_3 support. Reprinted with permission from [29] by John Wiley and Sons.

The signal-to-noise ratio (SNR) of EDX spectra of nanoparticles is a function of their size, beam current, accelerating voltage and collection angle of the energy dispersive detector. There can be considerable variation on the quality of an EDX spectrum from a 1 nm particle from differently configured STEMs. Short collection times are preferred to limit radiation damage during spectroscopy but also limit SNR, further increasing the challenge in quantifying the composition of small clusters. In some favorable cases, especially for lighter elements, EELS may provide improved SNR due to inherent higher collection efficiency of the technique. Likewise, EDX may provide improved SNR for heavier elements.

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Recommendations for catalyst characterization by x-ray absorption spectroscopy

The limited supply of beamlines for synchrotron radiation techniques combined with the need for peer review of beamtime proposals results in limited access to the facilities compared to the demand. This often results in significant time pressure for the researcher during their allotted experiment times. Additionally, this can lead to low prioritization of repeat experiments and testing experimental controls. In the face of this challenge, there is a need for researchers to establish standards for reporting and best practices for both data acquisition and analysis to ensure the community can fully contextualize their results and analysis. For users outside of catalysis groups with expertise in X-ray absorption spectroscopy (XAS), scientific collaboration is critical to the success of beamline experiments. Detailed knowledge of the chemistry provided by the catalysis scientists and technique expertise provided by the beamline scientists are both required to achieve success.

Common applications

XAS can provide important electronic and structural information about a catalyst sample. [1] X-ray absorption near edge structure (XANES) can provide information regarding the oxidation state and local coordination geometry of the atom of interest. The extended X-ray absorption fine structure (EXAFS) provides information regarding the local bonding environment surrounding the element of interest. [2] This can include the number and identity of the neighboring atoms, their corresponding bond distances, and the structural disorder present in the bonding distances of the absorber to the neighboring atoms. Analysis of the average local bonding environment can inform broader catalyst properties. For example, this information can be used to determine the average nanoparticle size and shape. Moreover, this information can be determined under in-situ and operando conditions. [3] In addition, the edge step under a given experimental condition is proportional to the concentration of the atom of interest. [4] New users are referred to *XAFS for Everyone* as a valuable introductory text for the technique. [5]

Recommendations for best practices

- EXAFS signal is sensitive to the uniformity of the sample. Proper sample preparation can save hours of data collection time and analysis time. For many samples a fine powder (ground with mortar and pestle) can be adhered to tape for ex situ measurements. Particulate size should be related to the absorption length. This only works when the larger particles are removed, and several tape layers are stacked together to form a uniform sample. One of the best sample preparation methods for solids is to grind a sample well, mix it with a low atomic number inert diluent such as BN or cellulose and press the sample into a pellet. Examples of well-prepared and poorly prepared samples are shown in Figures 4.D.1 and 4.D.2. If the sample is well ground this method has a high probability of giving excellent quality spectra, free of effects due to pin holes. As mentioned above the total absorption of the sample and everything else between I_0 and I_t should be known to be less than 3 absorption lengths and the edge step of the element of interest should be around 1 absorption length. Perform these calculations ahead to save time at the beamline. [5–9]

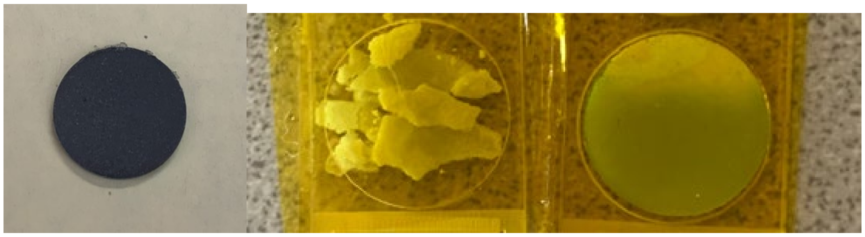

Figure 4.D.1. Example of good and poor pellet preparation practices. *left:* Uniformly cored pellet, *middle:* Pellet that disintegrated in transit. *right*: pellet showing the gradient of concentration, as a result in insufficient mixing of the target material and the matrix.

Figure 4.D.2. Example of good and poor sample-on-tape preparation practices. *left:* uniform sample on tape. *right*: non uniform sample

- Measuring the XAS of a metal foil of appropriate thickness from the element of interest can help for both energy calibration/spectral alignment and determining the EXAFS amplitude reduction factor S_0^2. If a metal foil is not available then the use of metal oxides, sulfides etc. of a known high purity standard (both in regard to metal purity and oxidation state purity, i.e., avoid references with low, potentially mixed oxidation states) with a known crystal structure can provide a substitute for metal foils.
- For XANES studies, it is best practice to measure a reference compound simultaneously with the unknown sample. The energy point density through the absorption edge should be related to the absorption edge energy as higher energies are broader and have longer core hole lifetimes. Make sure that incremental energy step is small enough so that the features are well resolved. Scans can be collected at different point densities to determine if they are the same. If so, then the lower density is sufficient. X-ray monochromators typically used in XAS measurements use two Si (111) crystals. The Si (111) intrinsic energy resolution can be approximated as 1.4 e-4. resulting in 0.6 eV resolution at Ti K edge and ~1.5 eV at Pt L_3 edge. It is a useful rule of thumb to set points spacing in the XANES region at the value corresponding to 0.2 x resolution, which corresponds to 0.1 eV step at Ti K edge and 0.3 eV at Pt L_3 edge. In these studies, be sure to collect sufficient pre-edge region data so that the data can be properly normalized. At least 50 eV below the edge should be collected (up to 200-300 eV can be useful for establishing linearization).
- For high quality EXAFS spectra about one million counts are required at each data point for a statistical error of 0.1%. The statistical error can be measured in the $\chi(k)k^2$ spectra at 10 Å^{-1} (since at that point the data is multiplied by 100%). The RMS error should be about 0.1 for high quality data in that region. It is important to remember that the counting statistics should be related to the square-root of the number of counts. To decrease the noise level by a factor of two, one needs to count 4 times longer (assuming statistical noise). [10]
- XAS is contaminated with so-called glitches resulting from diffraction on specific orientations of monochromator crystals. If the crystals are not physically changed or rotated, the energy position of the

glitches remain the same (as opposed to the diffraction from the sample crystallites which manifest themselves in a similar manner – however the latter's energy positions change with sample orientation with respect to the incoming beam direction.) If the sample is homogeneous and devoid of pinholes and the time constants of the detectors are the same, then the effect of the glitches on the XAS spectrum is minimal. Care should be taken when de-glitching to avoid removing meaningful points from the spectra. Automated deglitching on series of spectra should be carried out with extreme caution.

- Fits that include scattering paths beyond the nearest neighbor scattering should be attempted. As scattering paths become longer, they become more susceptible to destructive interference caused by disorder in the sample. It should be noted that anticipated structures can be examined for destructive interference prior to the beginning of the experiment. However, in order for reviewers/other researchers to judge claims for the coordination environment, the best fits of longer scattering paths should be clearly indicated. Care should be taken to fit to an appropriate range. It is recommended to look at data out to R =10 Å as the amplitude at high R is related to S/N. Therefore, data at high R can reveal the quality of the data. Looking at the amplitude at high R then allows one to determine the contribution of noise to the measured signal at the R of interest. [11] The number of adjustable parameters must be matched to the fitting range according to the Nyquist theorem. [1,5]
- It has become popular to use multiple k-weightings and wavelet transforms in the comparisons of data and fitting of the theory to the measured spectrum. There are two common approaches: the first is to use discrete k-weightings of 1, 2, and/or 3. The other is to use a wavelet transform. The wavelet transform preferentially emphasizes one section of the chi(k) data in the Fourier transform. Because different atom types have different k-dependent effective scattering amplitudes using a variety of k-weightings can help show these differences in the data. One simple example is for a metal oxide. The first shell is oxygen. Oxygen has a larger scattering amplitude at low k, while the second shell metal has larger scattering amplitude at high k. Using a k-weight of 1, the first shell oxygen will have more signal strength in the FT compared to the metal signal (first peak will be strong and the second peak will be relatively weaker). Using a k-weight of 3 will reverse this trend emphasizing the second shell signal in the FT (first peak will be weaker and the second peak will be strong). When using wavelet transform the three-dimensional plots should be scaled to the same values or the color scale should be explicitly stated as shown in Figure 4.D.3. When comparing the Fourier transform of different data sets be sure to use the same parameters and/or explicitly state what is the same and what has been changed and why.

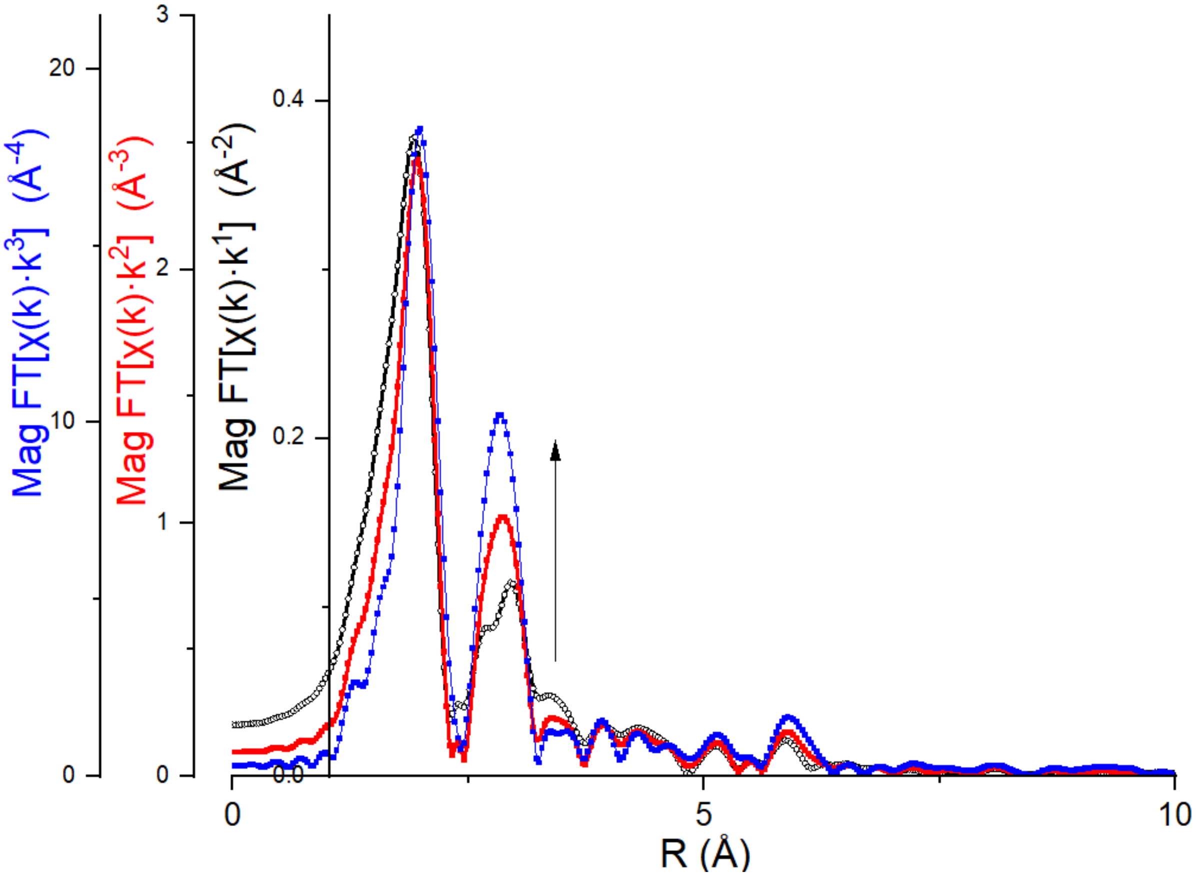

Figure 4.D.3. Magnitude of Fourier transform of χ(k)·k^{kw} for MoS_2 with kw=1 (black), kw=2 (red), and kw=3 (blue). The first shell Mo-S signal is bigger proportion compared to the second Mo-Mo signal for kw=1 with ratio of roughly 0.4/0.1, compared to kw=2 with ratio of 2.5/1, compared to kw=3 with ratio of 20/10. The higher Z element has more contribution at high k, hence higher k-weighting in the FT emphasizes the second shell relative to the first shell. This simple tool can be used to prove the second neighbor of a similar or not similar atomic number compared to the first neighbor.

- Since EXAFS is not sensitive to the presence of minority species, claims of the structure should match the rigor of the data analysis. Best fits should be contrasted with negative fits to justify claims. For example, in analysis of "single atom" catalysts, it is insufficient to show only M-X fits (where X is the ligand atom from the support, e.g., O, C). It must be demonstrated that while adding an M-M scattering path might improve the statistical measure of fit quality, it does so by including non-physical parameters, such as negative coordination numbers or σ^2 values. When comparing different fits to the data, report the reduced-chi-square factor. When this measure changes by a factor of two, there is statistical evidence that one model is better than the other model. Even then, one must use caution, as it has recently been shown that samples with mixed populations of "single atom" site and cluster sites can lack M-M scattering features in EXAFS. [12] XANES may be more sensitive to the presence of minority species and should always be analyzed in parallel to EXAFS data.
- For bimetallic samples, it is best practice to measure and model both edges if possible. Fits should be consistent, for example, the distance and the mean square disorder terms for A-B and B-A bonds must be the same, and the number of A-A and B-B as well as A-B and B-A bonds should match the sample composition. [13]
- The potential for beam damage to the sample should be recognized and checked, and if found present avoided. Even at medium flux beamlines, changes in oxidation state and agglomeration of metal particles under the beam have been observed. [14]

- There is a need to clarify operando versus in situ measurements. In order for a measurement to be described as operando, we must insist on a measure of conversion that is clearly demonstrated to be in a kinetically controlled regime. Otherwise, the experiment is in situ.
- Reactors at the beamline are sometimes designed with XAS considerations in mind. Consequently, there are many barriers to claiming operando conditions. Issues with pressure drops across beds, mass and thermal transport limitations, tension between requirements on the sample for both reactivity and XAS measurements (e.g., catalyst particle size) can all limit an experiment to in situ rather than operando status. In the absence of kinetic parameters measured at the beamline that match those measured in laboratory microreactors, more basic measurements such as TPR data should match between both systems before any claims of operando status are made. Simple space velocity matching is not adequate, as Reynolds number and flow regime can vary greatly even at the same space velocity in different reactor and cell setups. Diffusive flux cells can be problematic in that the gas might not reach the entire sample uniformly.

Known limitations

- XAS, using its traditional method of data collection, is a bulk average technique which provides structural information that is the average for the element under investigation. As temperature increases, the usable k-range of the data may be shortened due to decreased signal to noise ratio because of increased thermal disorder (represented by the σ^2 factor increasing), resulting in increased uncertainty in the fit. Other factors that may influence the usable k-range, and thus the uncertainty of the fit, include the presence of monochromator glitches and/or additional absorption edges within ~1 keV from the absorption edge of interest. Monochromator glitches are inherent to the optics used in the beamline and may be mitigated by switching monochromator crystal sets. Interfering adsorption edges occur in 4f elements where the proximity of L_3 and L_2 edges limits the available k-range for L_3 -edge XAS measurements (e.g., La), or with impurities of 5d elements in samples of nearby elements (e.g. Re impurities in a W containing sample).
- There are two different common collection modes for XAS data. High concentration samples (ca. >1 wt% element) are most often measured in transmission mode. In this case the absorption by the sample is obtained from the natural log ratio of the incident x-ray intensity (I_0) divided by the transmitted x-ray intensity (I_t). The total x-ray absorption from all the absorbers in the X-ray beam between I_0 and I_t should be less than three absorption lengths (preferably two). The change in the absorption at the absorption edge of the element of interest should be around 1 absorption length. [5] It is a best practice to report the absorption edge step for transmission measurements. Typical edge steps in transmission mode measurements should be greater than 0.1 in order to extract quality EXAFS data. For dilute samples, the absorption due to the element of interest is not enough to obtain a strong signal. In this case, the absorption by the sample can be more robustly determined from the X-ray fluorescence (I_{FY}) from the sample divided by the incident X-ray intensity. When measuring fluorescence XAS, it is best practice to measure both the transmission and fluorescence signals from a sample together simultaneously. When both the normalized transmission signal and the normalized fluorescence are compared, they should be identical. Self-absorption manifests itself in the attenuation of the fluorescence signal which causes the absorption edge to be broadened, intensity of the white line dampened and the EXAFS oscillations to be attenuated. [5]
- It is not straightforward to determine the concentration limit of the XAS-active species in the catalyst where publication quality data can be recorded on the relevant time scale of the catalytic process. This depends on several factors including but not limited to: beamline flux (number of x-ray photons on the sample per second), detector type (solid state detectors such as silicon drift or germanium detectors are generally more sensitive than integrating fluorescence detectors but the noise in detectors data may become a problem); the support (high Z element containing support typically interferes with measurement of light element active phase; when support and active phase contains neighboring elements, fluorescence from the lighter element makes the

measurement of the other more difficult). With that, at modern synchrotron facilities, in the ideal case of high Z element on light matrix (e.g., Rh on SiO_2) the concentration limit for insertion device beamline is ~0.05 wt. % and for bending magnet beamline is ~0.2 wt. %.

- Linear combination fitting, principal component analysis or multi-variate curve resolution alternating least squares fits of the XANES region can be made to estimate the speciation of the catalyst. [5] Using known spectra to model the unknown sample is highly accurate when the individual species within the composite are known and can be measured independently. In cases when the individual species are not known, there can be uncertainty in assuming a specific set of references. In addition, the molecular symmetry will impact the observed intensity. For example, compounds of tetrahedral symmetry will typically have larger pre-edge features as compared to octahedral compounds and mixtures of such compounds complicate quantitative analysis. Additionally, as the basis set of component spectra increases, so does the danger of over-fitting the data, leading to fits which are statistically successful but are not scientifically meaningful.
- *In situ* concentrations of the element of interest can be determined from edge jumps. However, in transmission mode the sample thickness must be held constant. In fluorescence the data must be taken with constant detector gains and the distance between the sample and detector must be held constant. This can be particularly useful for in-situ electrocatalytic measurements of leaching of the element of interest. During an in-situ measurement, the edge jump should remain constant if the element of interest is not moving into or out of the X-ray beam due to the experimental measurement conditions. This is a very good check for in-situ and/or operando measurements.

Recommendations for reporting data

Publications should include:

1. An example of the data in all the spaces: E, k, and R.
    a. Show the non-normalized XANES (mu(E)·x) or normalized XANES with additional edge jump. The units on XANES data are unitless and are not arbitrary.
    b. The background removed EXAFS data (chi(k)·kw). The units are in inverse angstroms with exponent of kw (i.e., chi(k)·k^2 has units of Å $^{-2}$).
    c. The Fourier Transform (FT) magnitude and either the real or imaginary parts. The real and imaginary parts show more information than the magnitude and are more robust in demonstrating differences between data sets. Be sure to use the same Fourier transform parameters when comparing the FT of different data sets. List the k-range and k-weight parameters in the caption or text. The units of the FT are one more inverse angstrom power than the EXAFS data. i.e., Mag FT[$\chi(k)\cdot k^2$] has units of Å $^{-3}$.
2. Details of the sample including loading of all elements in the sample and how it was prepared for and what form it took during XAS analysis.
3. Details on the XAS measurement should include detection channel, harmonics rejection, type of monochromator and crystal cut, beam size, gasses in ion chambers, type of detector, estimate of the photon flux, and the reference foil. Furthermore, information regarding how energy was calibrated and how spectra were aligned should also be reported.
4. Details on catalysis should include reactor used, gas and fluid flow rates, how the gases are mixed, purity, additional purifiers/traps, temperature, pressure, and if possible, conversion and product selectivity.
5. Details on the analysis should include all the paths considered with their CNs, R, ΔR and σ^2 factors, and the scattering path E_0 values. The k range and R range (number of independent points) and total number of fitting parameters should be given. Any variables that were fixed or constrained in the fitting must be clearly identified. The number of independent points and the number of variables for the degrees of freedom should be given. Any CIF files used should be provided. Paths used in the fit should be indicated. It is best practice to

show the real or imaginary parts of the FT data with the fit and offset below the contribution from each path to the fit.

6. Uncertainties in the extracted parameters, with a reference and/or details of how they are derived, should be reported. All conclusions/summaries should reference extracted parameters with +/- following the value and appropriate significant figures.

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Recommendations for catalyst testing

Introduction and summary

At its core, catalysis science combines examinations of chemical bond breaking and formation events at catalytic sites and measurements or predictions for rates at which these events happen. The catalyst and the reactive species undergo complementary changes during each catalytic cycle and the structure of the catalytic material may simultaneously evolve at separate timescales. The defining characteristic of an ideal catalytic sequence, however, is its inherent circularity that restores the catalyst to its nascent state at the completion of a closed reaction sequence that transforms reactants to products. Consequently, evaluation of these reaction events, their selectivities, and their rates of occurrence endures as a quintessential component of catalysis science and reaction engineering. Methods to measure these processes and to accurately identify the contributions of reaction events intrinsic to the catalytic cycle, transport of mass or energy, and evolution of the catalytic structure fall within the purview of catalyst testing.

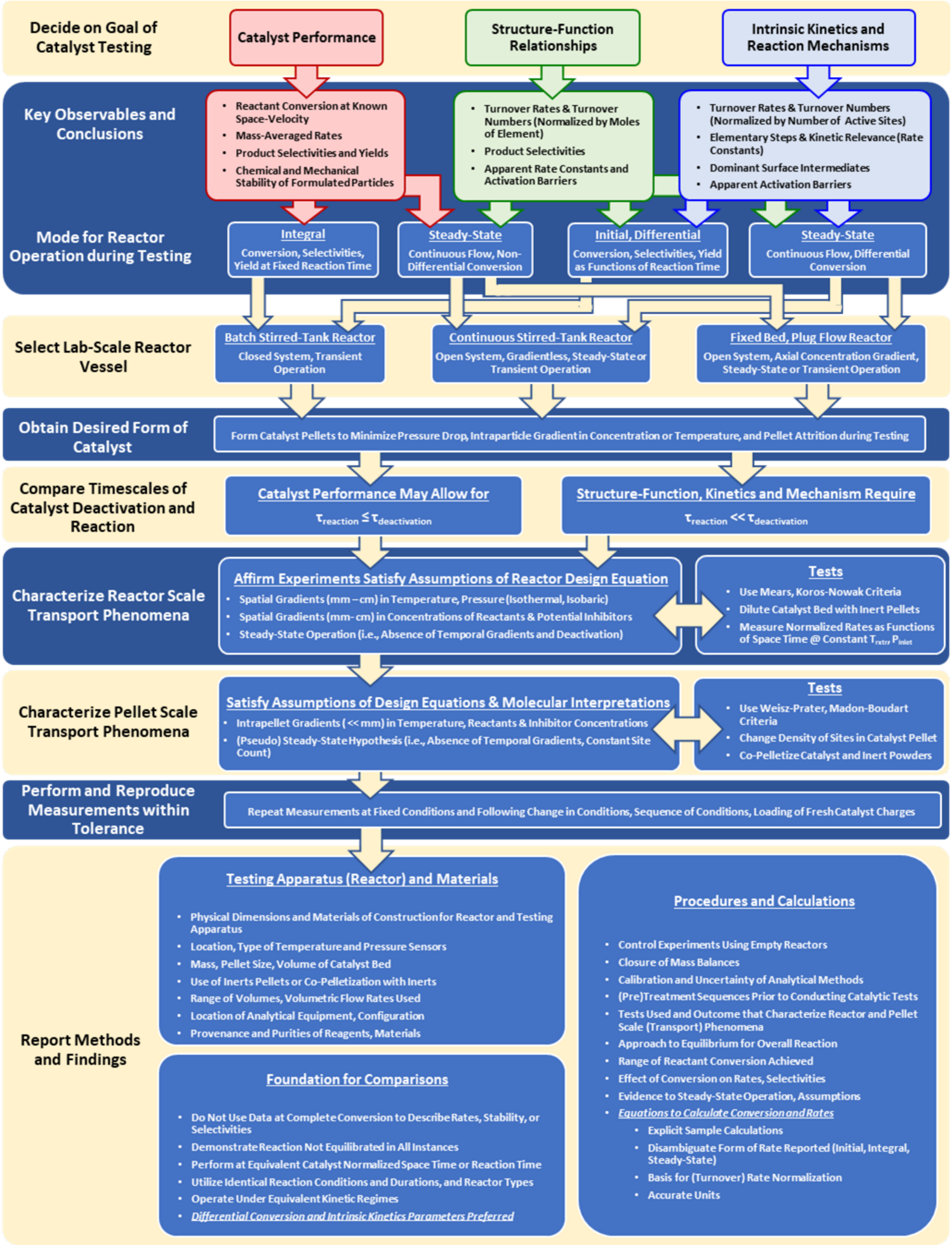
Catalyst testing typically serves to achieve multiple objectives, which include:

- *Catalyst Performance*. Stability of the material, time-on-stream characteristics of rates, selectivities and yield, regenerability of the initial state or structure of the material.
- *Structure-Function Relationships*. Quantitative comparisons between material descriptors (e.g., elemental composition, textural or morphological properties, or atomic coordination of elements) and observed catalytic rates and selectivity.
- *Determination of Mechanisms and Intrinsic Kinetics*. Identification of the reactive intermediates and intervening elementary steps responsible for consuming reagents and forming products.

Testing of heterogeneous catalysts involves contacting these solid materials with a fluid within reactor vessels, which requires that reactor hydrodynamics and mixing be considered when evaluating catalyst performance. Diffusive transport of reactants and products also influences rates, selectivities, and catalyst lifetimes, particularly for porous materials. The effects of these transport processes (i.e., fluid flow, mass and heat transfer, and mixing) depend strongly on reactor and catalyst geometry and length scales, and hence, catalyst performance does not scale directly among all forms of lab-scale reactors (characteristic dimensions commonly below 0.1 m). Moreover, performance in lab-scale reactors cannot directly predict performance within industrial-scale reactor vessels (characteristic dimensions often much greater than 1 m). However, reactor performance can be predicted at many length scales and reactor configurations when catalyst testing yields intrinsic rates and selectivities of catalytic events.

As a result, intrinsic measurements of catalytic kinetics possess the greatest value for the science and application of catalysis. Such measurements require that lab-scale reactors are selected and operated in a manner appropriate to either (1) eliminate or suppress the effects of transport and catalyst evolution during measurements, or (2) characterize and account for the influence of mass and energy transfer and hydrodynamics during testing and data analysis. In both cases, investigators should report sufficient details concerning catalyst testing apparatus, reactor vessel, and tests or validation performed to justify conclusions related to case (1) or case (2). With an emphasis on establishing reporting standards for catalyst testing, a few key questions emerged as focal points for the panel discussion. First, what particulars of catalyst testing should be reported or demonstrated to ensure that catalyst performance characteristics and measurements are reproducible (e.g., fluid flow configurations, pressure, pressure drop, and temperature or temperature gradients), catalyst bed loading, method for forming catalyst pellets and placing them within reactor vessels, sub-complete conversion, effects of residence time on rates and selectivity, etc.)? Second, are there metrics or benchmark materials that should be required in catalyst testing (e.g., specific rates, selectivity comparisons at iso-conversion, turnover number, benchmark solid acid or metal cluster formulations, etc.)?

A synopsis of the discussion on standardizing measurements and reports of catalyst testing follows. Scheme 5.1 depicts a corresponding workflow with guidelines and recommendations that may prove useful for researchers. Success in achieving the goals of these studies (e.g., structure-function relationships, determination of reaction mechanisms) include observations from catalyst testing but also rely on precision synthesis of catalytically active materials; appropriate characterization of the catalyst formulation by in situ or operando characterization and spectroscopy; development of predictive reaction models and use of complementary kinetic methods (e.g., kinetic isotope effects); and integration of computational tools (e.g., *ab initio* calculations, molecular dynamics, and multiscale modeling). Best practices for several of these requisite methods are discussed in previous sections of this report. Here, we address the best practices of catalyst testing.



Scheme 5.1. Workflow for planning, executing, and reporting the results from catalyst testing.

Technical recommendations to improve rigor and reproducibility

Laboratory reactor selection and design

Previous literature has already highlighted the key role of laboratory reactor design and selection in reliable measurements of catalyst testing. [1–3] These foundational concepts bear repeating because lack of adherence to these principles remains a significant impediment to reproducibility of catalytic performance characteristics among research laboratories. Catalyst testing in reactor vessels frequently involves conditions different from the ideal requirements used in the definition of reaction rates (e.g., gradients in concentration and temperature, transient operation, back-mixing, etc.). We first outline the limiting conditions for reactor operation to help clarify reasoning used to develop recommendations for data acquisition and reporting and to illustrate how transport and catalyst evolution impact observed performance. [4]

Table 5.1. Questions and responses that span limiting cases of transport, hydrodynamics, and time dependent aspects of catalytic systems.

Question	**Response**	
	No	Yes
Is there exchange of mass?	Batch	Flow
Is there exchange of heat?	Non-isothermal/Adiabatic	Isothermal
Is operation at constant pressure?	Non-isobaric	Isobaric
Is residence time in a flow vessel unique?	Back-mixing/Stirred Tank Reactor	Plug-Flow Reactor
Are rates time-dependent in a flow vessel?	Steady-State Operation	Deactivation/Induction Periods
Are time dependent characteristics in a batch reactor only due to reaction?	Deactivation	No Deactivation

It is evident that many reactor configurations and modes of operation are employed in catalyst testing – commonly packed bed reactors, recycle reactors which depending on the mixing efficiency and superficial velocity can operate as stirred tank reactors or batch reactors if no outlet is provided, or conventional batch reactors. We do not discuss specific reactor configurations except to note that data from catalyst testing are most readily interpreted when researchers select and operate their lab-scale reactors to achieve nearly isobaric, isochoric, and isothermal operation in hydrodynamically ideal reactors (e.g., plug flow reactor, continuous stirred tank reactor, or batch reactor). As such, reports should employ experimental protocols, functional tests (Madon-Boudart [5]), or established empirical relationships (e.g., Koros-Nowak, [6] Mears [7]) to affirm that reactor bed configurations appropriate for catalyst testing were achieved. It is unlikely that results would be reproduced accurately in other reactors when such methods are not used. ***Many of these recommendations can be summarized by the simple principle: eliminate gradients of temperature, pressure, concentrations, and rate with respect to position and time.***

We highlight a few key issues and criteria:

Isothermal and isobaric operation:

Temperature and concentration (i.e., activity or chemical potential) are driving forces for catalytic reactions. These variables affect rates of reactions but also the thermodynamic end point for a reaction (i.e., equilibrium). Consequently, it is imperative that isothermal and isobaric operation be achieved in lab-scale reactors. Attempts to account for spatial gradients in temperature or concentration reduce the likelihood of reproducing a measurement and introduce greater uncertainty in the interpretation. To achieve isothermal and isobaric operation, researchers must report methods and instrumentation used to acquire temperature and pressure conditions relevant for catalyst testing (e.g., make, model, and accuracy of apparatus) and the location of these devices. For example, the temperature of a catalyst bed frequently differs from the temperature at the outer wall of a reactor or the inner surface of a furnace. Thus, thermocouples located within a catalyst bed frequently show temperatures that differ by significant values with the former being more appropriate for obtaining reproducible measurements. Yet, measurement of temperature and pressure at a single location does not ensure isothermal or isobaric operation. Care must be taken to select materials of construction and to demonstrate that the thermocouple does not catalyze reaction and affect the interpretation of data. Best practices in ensuring isothermal operation require assessment of intraphase and interphase temperature gradients following criteria developed by Mears, [7,8] Anderson, [9] and Balakotaiah et al. [10] In many cases, isothermal operation can be achieved by diluting catalyst pellets with inert pellets of comparable size within beds and by pelletizing catalyst powder with inert powders. However, excessive dilution can result in reactor bypass in certain limiting cases. [11,12] Along the same lines, isobaric operation may be achieved by increasing catalyst pellet diameters, decreasing packing fraction, decreasing catalyst bed length or volumetric flow rates or by increasing reactor diameter as described by the Ergun equation among others. If isobaric operation is not feasible in lab-scale reactors, then pressure drop must be reported, and suitable corrections included in reporting catalytic data. [13]

Concentration gradients in reactors:

Rates of reactions and catalyst deactivation most commonly depend on the concentrations (i.e., thermodynamic activity) of species introduced or formed during the reactions including the reactants, intermediates, and product molecules. Therefore, spatial gradients in the concentrations of these species can give rise to similar or greater differences in rates throughout reactors. These gradients are difficult to characterize directly but can be minimized by operating at sufficiently high ratios of the feed flow rates to mass of the catalyst bed. The presence and significance of concentration gradients in a flow reactor should be assessed directly by measuring rates at multiple volumetric flow rates of the entering fluid with a single charge of catalyst. Gradients may be considered insignificant when apparent rates do not vary when fluid flow rates increase and decrease by a factor of two. As a heuristic, low reactant conversions (<5-10%) often lead to negligible reactant concentration gradients. Reaction rates frequently depend on concentrations of intermediate and product species formed during catalysis. Significantly, the concentrations of these species at the inlet of a flow reactor or at the start of a reaction in a closed vessel are equal to zero, and therefore, any non-zero concentration represents a relatively large rise in concentration. The resulting spatial gradients in reaction rates caused by product inhibition may be minimized by intentionally feeding small concentrations of the product (Figure 5.1.) or a molecule with similar chemical function (e.g., substituting one aromatic hydrocarbon for another). [14] ***Rates measured without assessment of concentration gradients or with immeasurable concentration gradients (e.g., at complete conversion of reactants) lead to irreproducible and uninterpretable results.***

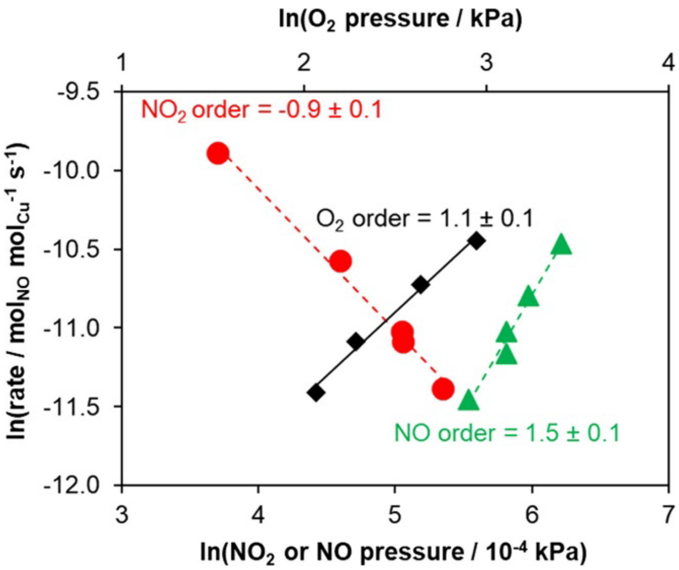


Figure 5.1. Natural log of the NO oxidation rate at 543 K as a function of NO_2 pressure (●), O_2 pressure (♦), and NO pressure (▲). All kinetic data points included in this plot were obtained with NO_2 co-feeding. NO_2 pressures between 0.004 and 0.022 kPa were used for NO_2 orders. NO pressure between 0.02 and 0.05 kPa were used for NO orders, O_2 pressures between 8 and 20 kPa were used for O_2 orders. Space velocities were maintained at ~1300 s^{-1}. Reprinted from [14] with permission from Elsevier.

Contacting pattern in flow reactors:

Although laboratory scale reactors frequently do achieve the criteria for ideal plug flow in packed bed flow reactors, criteria have been reported to affirm that no significant deviation from plug flow configurations results. [2] These criteria are equally important for gas-solid and gas-liquid-solid reactors and become more challenging to satisfy for systems that exhibit non-turbulent flow (i.e., low Reynolds numbers) and when using short catalytic beds. [15] Correlations to determine particle fluid mass and heat transfer [16] as well as illustrative case studies highlighting the key role of these parameters in determining catalyst performance, highlight the role of bed scale mixing and gas solubility. [17]

Steady state operation:

Meaningful comparisons of catalytic data between reactors and across laboratories require that identical or very similar conditions are employed for catalyst testing. Most investigators report measurements of temperature, pressure, flow, and catalyst loading for flow reactors. In addition, an equally important aspect to document and report is the dependence of rates as a function of time-on-stream to demonstrate whether data were acquired under condition of steady state operation or not. The best practice for researchers is to report rates measured as a function of time in flow reactors to directly show the approach and achievement of steady state or to document clearly how corrections for catalyst deactivation are incorporated in calculations of catalyst performance. When transient operation is observed prior to attaining steady state operation, researchers should report the occurrence of such transients in published results and present representative measurements within supporting information. Similarly, batch reactor data should include data taken as a function of time and the method for analyzing the data be described explicitly (e.g., differential, integral, or initial rate analysis). These measurements are necessary to show how reported rates depend on concentrations of species and to demonstrate rates do not conflate reaction progress and catalyst deactivation.

Reproducibility and controls:

Best practices in ensuring reproducibility in catalyst testing include several forms of experimentation that provide greater evidence that the measured rates reflect the contributions of the catalytic material introduced to the reactor. Randomizing the sequence of process parameters in catalyst testing allows for the deconvolution of catalyst deactivation from intrinsic kinetics and the use of reference or benchmark conditions repeated in independent experiments provides opportunities to assess deactivation rates. Measurements of rates with empty (or blank) reactors or reactors filled with inert solids demonstrate the presence or absence of surface reactions on the reactor walls or fluid transfer lines or homogeneous reactions within the fluid. Mass balances and the closure of mass balances must be reported. In addition, the methods to calibrate analytical instruments and the accuracy of the analytical methods should be described.

Schemes that communicate the reactor flow configuration together with the form and location of devices used to measure temperature, pressure, and flow rates and the methods to control these parameters should be described. Flow rates of fluids (volumetric, molar, and superficial) must be known and controlled (e.g., mass flow controllers, pumps) to accurately establish flow patterns and regimes within reactors and to accurately control the composition of mixtures formed by combining multiple fluids within the apparatus. These needs indicate that practitioners individually calibrate devices used for these purposes with an independent flow measurement device (e.g., bubble flowmeter for gases, gravimetric measurement of displaced liquid) and frequently confirm that the calibrations remain accurate by measuring flowrates of mixtures upon the reactor.

It is also a best practice to report protocols for materials of construction for the reactor, source and chemical purity of all chemical reagents, chemical traps and adsorbents used to purify reagents, etc. All these data can readily be included in supporting information that accompanies most published manuscripts. These descriptions should be reviewed and updated for each and every publication to capture changes to equipment used for catalyst testing.

Pellet scale phenomena relevant for catalyst testing

Reproducible laboratory scale catalyst testing requires not only that a researcher be cognizant of the bed scale gradients, described above, but also of interphase gradients (e.g., transport of heat and mass across boundary layers between fluids and solids or between gas and liquid interfaces) and intraparticle gradients (e.g., diffusion of heat and mass within porous solids). These gradients impact rates but are not directly sensible by measurement devices or analytical methods available in most laboratories. ***Therefore, the presence or absence of these gradients should be either estimated using reported non-dimensional parameters or experimentally probed by varying diameters of pellets, the number of reactive sites per pellet, the volumetric flow rates of fluid through a fixed bed, the agitation rate of a batch stirred tank reactor, etc.*** Many prior reports document these methods and discuss the calculation of appropriate non-dimensional parameters [18] (Figure 5.2) based on the observed or estimated reaction rate over a catalyst particle of known physical properties and some estimate of the kinetics of the underlying reaction. Noteworthy among these are the Weisz-Prater criterion, [19] Koros-Nowak criterion, [6] the Mears criterion, [7] and the Madon-Boudart criterion. [5]

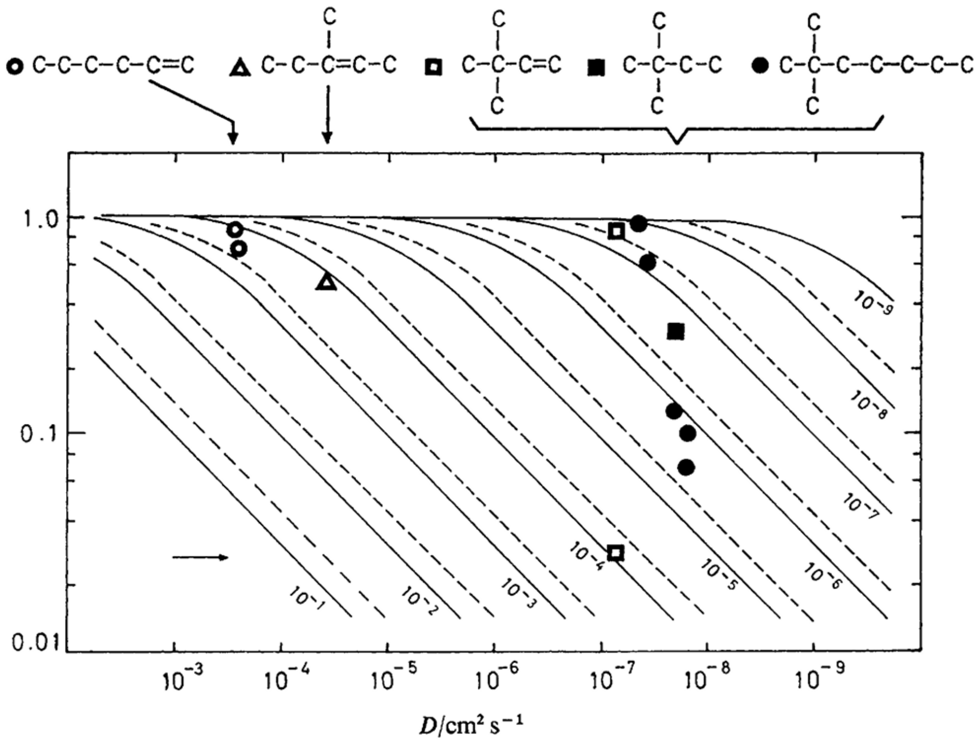


Figure 5.2. Effectiveness factor *h* dependence on diffusivity for different R^2k values. Reproduced from Ref [18] with permission from the Royal Society of Chemistry.

Thorough discussion and instruction on the application of these criteria can be found in many textbooks and publications, [1,2,20] which we recommend to readers. In addition, we highlight an online web-based tool in the public domain (GradientCheck, www.GradientCheck.com), [2] that allows researchers to input various parameters for their system in an effort to estimate the likelihood that a reactor contains consequential gradients of temperature, pressure, or concentrations throughout the catalyst bed or within individual pellets. Use of these criteria will greatly reduce the sources of error in acquiring reliable and reproducible data in catalytic tests.

We take this opportunity to present a set of best practices in data acquisition and reporting relevant for pellet scale phenomena in catalyst testing:

Ideal flow patterns, steady state conditions, isothermal and isobaric operation: Many of the criteria for assessing interphase and intraparticle gradients require that ideal flow patterns, steady state conditions, isobaric and isothermal operation are achieved in the reactor bed (see prior section). Subsequently, the presence or absence of more localized gradients can be assessed. While it is not always feasible to do so, the best practice is to report conditions, methods, and criteria examined to assess the role of heat and mass transfer gradients at the pellet scale. In addition, the best practice involves appropriate choice of limiting conditions (e.g., higher temperatures, lower volumetric flow rates, etc.) for this assessment, because heat and mass transfer gradients at the pellet scale may appear for certain conditions used in a sequence of tests but not at others.

Controls and reporting practices: Unfortunately, these criteria can rarely be applied in *ex post facto* comparisons of catalyst tests conducted between reactors and between laboratories, because many parameters used to assess the role of interphase and intraparticle gradients depend upon material and process parameters (e.g., particle diameter and morphology, reactor wall temperature) that are not routinely reported. Therefore, the best practice is to pursue these calculations and report in every case study. Best practice also includes reporting both the methods and the results of these calculations, which can be achieved in simple tabular format either in the publication or in the supporting information that accompanies the manuscript.

Courses of action when gradients are intrinsic to reactions: We anticipate scenarios where heat and mass transfer gradients are difficult to eliminate or unavoidable due to the intrinsic reaction network (e.g., in cases of cascade reactions, bifunctional systems with gaseous intermediates), when strongly exothermic or endothermic reactions are involved, or when using non-standard reactors (e.g., membrane reactors). In these scenarios, researchers should describe both the reactor and the catalyst properties in sufficient detail for other groups to reproduce a close approximation of the combined system. In addition, they should explicitly mention what the plausible impact of these gradients are on the evaluation of catalyst performance and the reported conclusions. If feasible, researchers should also discuss any parametric studies that allow them to determine the magnitude of these gradients under the conditions of operation.

Recommendations for reporting results of catalyst testing

An impediment to comparisons of catalyst testing data among laboratories, and thus reproducibility in catalysis, is the use of metrics in reporting that render comparisons either infeasible or inaccurate. The prevalence of this shortcoming among publications in catalysis research, we describe both recommended practices and common pitfalls encountered when reviewing reports of performance during catalyst testing.

Report normalized rates of reaction and not conversion or temperature required to attain a specific conversion: The fractional conversion of a specific reactant in a catalytic process is an extensive quantity that depends sensitively on reactor dimensions and hydrodynamics (e.g., plug flow or back-mixing), process parameters (e.g., mass of catalyst bed and fluid flow rate) in addition to intensive catalyst properties (e.g., mass normalized rate at a specific combination of temperature and concentrations). Consequently, reactant conversions can be manipulated (inadvertently or intentionally) to achieve any value ranging from nearly zero conversion to complete (or equilibrium) conversion by simply varying space velocity in flow reactors (the ratio of fluid flow rate to catalyst quantity; or time in batch reactors), temperature, heat and mass transport, or hydrodynamics. While the choice of a common set of reaction conditions within a study does allow comparison among the samples at that condition of choice, the use of conversion as a metric of catalyst performance renders difficult comparison to reports from the literature. Similarly, the temperature required to attain a specific chemical conversion (e.g., 50% of the limiting reagent) can be biased by changing fluid flow rates and catalyst bed loading, while fixing all other experimental parameters.

Finally, data reported at complete or equilibrium conversion has little to no scientific or technical value, except as part of a sequence of data that show the approach to these high conversions from much lower values. [21] The ability to achieve complete conversion does not represent a unique property of the catalyst or provide a quantitatively significant measurement, because these values may be controlled by fluid flow rates (or reaction time in a batch reactor), temperature, etc. Furthermore, the space time, reaction time, or temperature required to first achieve complete (equilibrium) conversion frequently is less than the time or temperature reported.

Therefore, researchers should report normalized (or specific) rates of reactions in addition to the full units used for these calculations, and particularly those obtained at steady-state or a pseudo steady-state operation. A hierarchy of preferences exists for the basis for normalizing reaction rates. The rates of these chemical events ((moles of events) $(s)^{-1}$) are typically determined by the rate of appearance of depletion of a specific molecule (e.g., (moles of product) $(s)^{-1}$), which succeeds most frequently for reaction systems that involve few individual steps and involve reactants and products unique to each step. Most preferably, these rates are normalized by an estimate for the number of purported active centers in the catalyst bed. These values may be described as site-time yields (STY) and possess units consistent with (moles of products) $(\text{moles of active sites} \cdot s)^{-1}$. In these cases, the number of active sites in the catalyst bed will be assessed by in situ reactive titration techniques or spectroscopic methods, and the experimental procedures, assumptions, and calculations should be reported. If such information is unavailable, then rates should be normalized by the number of exposed atoms of the catalytically active element as assessed by ex situ methods (e.g., chemisorption of carbon monoxide, hydrogen, oxygen), which should be reported in units consistent with (moles of product) (moles of exposed element ·s)$^{-1}$. Less preferably, the rate can be normalized by total quantity of the active element present within the sample and should be indicated with units similar to (moles of product) (moles of element ·s)$^{-1}$. Least preferably, rates would be normalized by total mass of catalyst (mole product) (gram catalyst ·s) $^{-1}$. The order of preference corresponds to the increasingly unique and informative nature of these normalized rates with turnover rates signifying a specific characteristic of the intensive catalytic properties of the material and mass averaged rates representing a value which does not readily allow comparison among catalysts formulated with different compositions or by different methods. Yet, all are preferable to reports of fractional conversion. Still, even these metrics have potential to provide imprecise comparisons of catalyst testing data if process conditions are not identical. However, normalized rates best represent the intrinsic characteristics of a catalyst formulation, and thus, represent the best practice in reporting results of catalyst testing.

We anticipate scenarios where an abundance of reaction pathways and species and/or network connectivity prevents accurate assessment of rates of individual steps. In such cases, specific rates of reactant consumption and rates of product formation be reported, however, practitioners must consider that multiple reactions contribute to these measurements. Along similar lines, steady-state operation may not be obtained in catalytic chemistries where catalyst deactivation or spatiotemporal variation in rates are endemic. Here, the best practice is to report turnover numbers (i.e., the integral of normalized rate from initiation of catalysis to complete deactivation).

Procedures and calculations in reporting of catalyst testing: Researchers should explicitly report equations and definitions used as metrics of performance for catalyst testing (e.g., selectivity, normalized rate, conversion, etc.). A detailed description of procedures used in assessing results and/or sample calculations for a data set should be included in the manuscript or supporting information. These reporting practices would eliminate common pitfalls such as considering that a low single pass conversion of the reactant (e.g., below 10% chemical conversion) demonstrates true differential conversion. As stated earlier, the regime of differential conversion is defined by a range of conversion throughout which the change in concentration of all species that affect rates (i.e., reactants, intermediates, and products) remains negligible. The definition of what may be considered negligible changes in rates and selectivities may differ with the use of the data, and therefore, researchers must determine what this means for their purposes and report that criterion. In cases where products inhibit the rate, there is virtually no conversion low enough to give differential behavior without cofeeding product or chemical surrogates for the reaction products. [14] Here, particular care is needed to properly report results of catalyst testing. The effects of these processes on measured rates should be directly assessed by measuring rates of formation of products and consumption of reactants as functions of fluid flow rate through the catalyst bed to functionally ascertain the range of fractional reactant conversion that can be demonstrated to be truly differential conversion at the conditions employed.

A corollary of this point is the necessity for researchers to report all material and process parameters at which the catalyst testing studies are undertaken. These should be exhaustively enumerated in the text and in captions that accompany any tables and figures where results of catalyst testing are presented. We make it a point to note that catalytic materials invariably undergo thermal or reactive pretreatments prior to the assessment of catalytic performance. It is incumbent upon researchers to detail these procedures for pretreatment explicitly in their report. These should include not only final temperatures of thermal treatment but rates at which temperatures were ramped or durations for which they were held constant, fluid flow rates, catalyst bed loading, pre-mixing or pre-heating of fluids, etc. Additionally, if a claim is made comparing with industrial catalysts, whenever possible, exact reaction conditions should be followed, including pretreatment, activation, regeneration etc. If possible, a commercial catalyst procured from an industry should be used for comparison. Differences between the performance of lab synthesized materials and commercial catalysts (i.e., formulated materials with many additional components used to modify catalytic, chemical, and mechanical properties) can stem from multiple sources due to differences in composition (and trace contamination), support pore structure, and the presence of additional components to reduce particle attrition (i.e., binders). Therefore, measurements of commercial catalysts can serve as benchmarks accessible to other research groups, despite the reasons for differences in performance being more difficult to ascertain.

For tests performed in continuous flow reactors, the time sequence of conditions used during catalyst testing should be described, and researchers should return to a common set of conditions (i.e., fluid flow rate, inlet fluid composition, reactor temperature). Testing often involves a series of different steps including variation in flow rates, inlet composition, and reactor temperature. Although a catalyst may achieve an apparent steady state at each set of condition, those results may depend on the order of conditions selected due to changes in the structure of the catalyst that are irreversible on the timescale of the catalyst testing procedure. Examples of these types of changes include nanoparticle sintering or agglomeration, deactivation due to the accumulation or loss of material (e.g., organic residues or coke, contamination by metal or sulfur in the feed, dissolution or sublimation of the catalyst). The presence of such processes can be identified by confirming that reaction rates and selectivities remain constant at a common set of conditions and are not affected by the duration or sequence of the stages used to test the catalyst. The protocol used for confirming the absence of changes should be reported. When catalysts do evolve irreversibly, the nature of these changes must be reported, and the sequence of steps used during testing must be described in detail. Otherwise, the outcome of these tests cannot be reliably reproduced by other researchers even if all other details of the catalytic materials and apparatus are identical.

For reactions that are known to be limited by chemical equilibria, practitioners should discuss how thermodynamic constraints may or may not influence the reported rates and conversions. When appropriate, the approach-to-equilibrium values, which equal the reaction quotient divided by the equilibrium constant, should be provided.

Finally, selected catalyst testing measurements should be replicated a minimum of three times to demonstrate the reproducibility of the complete workflow and to allow for the calculation of uncertainties that account for all steps in the process of loading, pretreating, and testing a catalyst within a reactor. Sources of uncertainty detected by this approach include error in the mass of material loaded into the reactor, non-idealities in hydrodynamics caused by the position of the solid with the catalyst (e.g., channeling), uncertainty in the temperature of the catalyst due to differences in the position of thermocouples and other factors. These forms of uncertainty cannot be captured by simple propagation of error from individual measurements (e.g., flow rate and thermocouple calibrations performed in absence of a catalyst).

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Recommendations for collective, community actions to improve rigor and reproducibility

In the previous three sections, we have presented recommendations for best practices of common methodologies and what data is important to report in the literature. For specific materials classes, we have also made recommendations for specific characteristics that should be considered and/or reported, and proposed materials that individuals and individual labs could use as benchmark materials. These recommendations rely on individual actions. However, during the workshop, many community wide issues were identified as potential barriers and challenges to efforts to improve R&R in catalysis research. During workshop discussions and via a post-workshop electronic survey, participants provided their input on issues that should be considered in possible future efforts or actions that may potentially be pursued to improve R&R. These discussions are summarized below.

Suggestions for community wide efforts

Even if suggestions in the previous section are followed rigorously by a researcher reporting results, and even if a researcher attempting to reproduce reported results is equally rigorous, there are still extenuating circumstances that may render specific measurements irreproducible. Some of these are discussed earlier in the report, but bear repeating here.

Differences in raw material sources (i.e., impurities)

The presence of impurities is one of the leading causes of irreproducible measurements and synthesis. [1–4] Specifically, changes in impurities due to different lot numbers of suppliers or global differences in raw material sources for specific reagents can impact the reproducibility of previously reported chemistry. [5] By nature of the impurity being an unknown, irreproducibility due to this factor can be particularly difficult to identify.

Instrument differences or errors

There are anecdotal examples wherein nominally the same measurements that are performed following the same procedures, but made on different instrumentation, have resulted in different data. These differences can arise from various factors that may include differences in hardware or configuration (e.g., the use of different furnaces that may not have well characterized heating zones, specific components with different measurement precisions, the presence of impurities from different gases sources or residue left from previous analyses, etc.), or software and data reduction techniques. Without explicit comparison of similar instrumentation and results, these issues can be difficult to identify.

Details in protocols assumed unimportant and left unreported

Even with homogeneous and uniform samples of a material, detailed procedures for sample storage, treatment and analysis, and minimization of instrument error, additional impediments to R&R can be introduced by user error. Different researchers that follow the same procedure may execute certain steps differently in practice. It is well-understood within the community that the exact details of sample history and steps used in catalyst (pre)-treatment can play a strong role in determining material structure and behavior. Additionally, the exact details of the analysis and testing protocols used to evaluate a certain material property or behavior can influence the final outcome, including factors that seem trivial at the time. Again, without rigorously comparing procedural steps between different measurements, these factors can be difficult to identify.

Sample Storage

Finally, we will emphasize a recurring theme in every section of this report that is often not discussed at all in the literature or in publications. Researchers should provide more details about how samples are stored after preparation and prior to testing. Many catalysts that are studied are meta-stable materials. In addition to specific pretreatments, the material storage environment could impact both the materials catalytic performance and characterization data. Important details such as the duration of storage (e.g., the time between initial synthesis and testing), location (e.g., out on a benchtop vs. in a glovebox), and specific details about the environment (e.g., specific solvents that may be also stored in a glovebox) could be contributing factors to an apparent lack of reproducibility between laboratories.

Suggested future action #1: Catalysis focused interlaboratory studies

As described earlier in this report, a common strategy to establish standard properties of benchmark materials is through an interlaboratory study (ILS) that encompasses a broad range of instrumentation (e.g., commercial, home-built) across the participating labs. An ILS performed in this way would help researchers recognize the source of instrumentation error, and eventually troubleshoot the origins of the differences and uncertainties. Once an ILS has established a standardized procedure for a measurement, future studies performed in individual labs that rely on this established procedure to perform benchmarking measurements may then identify new cases of instrumentation error that may arise as new versions and configurations are provided by the same (or new) manufacturer. This is also valuable for specific labs to perform troubleshooting on their instruments later. Further, if the ILS encompasses similar materials from different sources, it can also be useful to help identify sample impurities and sample storage conditions that negatively impact measurements. Finally, seemingly inconsequential details of sample measurement methodology could be identified.

The community would benefit greatly from more sponsored studies, specifically focused on measuring the variance of reaction rate measurements between labs, of which there is little precedent, even from the well-known EURO-PT activities. As described earlier in section 1 of the report, we expect that the acceptable variance of different chemistries catalyzed by different material classes may differ significantly. **Our immediate recommendation is for the community to organize several parallel ILS focused on different material classes and chemistries.** These efforts should encompass a wide range of materials and be funded by critical stakeholders of the community, mainly federal funding agencies and industrial companies.

If conducted, these studies could naturally lead to the adoption of certain benchmark materials and standardized methodologies. An important consideration in the development of standardized protocols is to not use them in a “gatekeeping” manner to stifle innovation or research discovery. Protocols should not be developed to use as a tool of enforcement, but rather as a way to more accurately compare the structure or behavior of a new catalyst material to a benchmark material, or to compare the accuracy of a new modality of measurement to a conventional modality of measuring the same material property.

Suggested future action #2: Consider mechanisms to provide benchmark materials broadly

If suitable benchmark materials can be developed, the next challenge will be to sustainably produce these materials. Indeed, although the Euro-Pt project demonstrated that valuable information could be gained from the study of benchmark materials, the ultimate failing of the project is that the material stock was extinguished. [6] In regard to continuously producing benchmark materials, an important technical challenge is the structural and compositional heterogeneity that will exist from sample-to-sample, even within a given batch of material, let alone among differently prepared batches of nominally the same material. Therefore, a procedure for reproducibly obtaining sufficiently large quantities of a representative sample is needed to successfully perform benchmarking measurements across researchers in the community.

During the workshop, many possibilities were discussed. In some cases, it may be possible to obtain previous generation catalysts by request from industrial chemical producers for use as benchmark materials. One caveat to this approach is that most industrial catalysts behave differently in different ways that depend strongly on their handling and activation procedures. Participants described that highly formulated industrial catalysts generally have complex and proprietary multi-step activation protocols, so catalyst testing in a research lab would not provide results truly comparable to commercial catalyst implementation. Similarly, the precise synthesis method and composition for the commercial material are not likely to be disclosed. However, the acquisition of samples of industrial catalyst samples still provides a consistent unactivated pre-catalyst starting material that may then be handled and activated with well documented procedures to provide greater consistency among or within given laboratories and practitioners. However, we note that the quantity and availability of such materials may be limited and could also change over time.

Another route that can be beneficial, but perhaps less robust, is to compare a newly synthesized material to a simpler one that is available for purchase from a commercial supplier, even if the purchased material is not fully characterized or if the material displays variability between batches. The assumption is that this approach will introduce less variability between samples than if each individual laboratory attempts to perform the complete synthesis and activation of a material independently. For example, commercially available metal catalysts synthesized without ligands (e.g., Pt on γ-Al_2O_3) can be used to validate that a measured property originates from the metal rather than being an artifact of synthesis, such as due to differences introduced by trace elemental residues from the metal precursor (e.g., chlorine) or adsorbed ligands. This comparison to the ostensibly bare metal is especially important for syntheses of more complex materials. A single batch of a commercially available material can also be used to compare results obtained by different researchers using a given characterization method or test of catalytic reactivity and is especially useful for training new researchers in a lab to ensure reproducibility or for training individuals on experimental techniques in a classroom setting.

Production of standardized benchmark materials by a single source—research lab or commercial supplier—was viewed as being prohibitively challenging to sustain at the current time and alternatives were proposed. One alternative is for individual laboratories to produce materials that are internally consistent and prepared according to best practices for minimizing uncertainty and adventitious impurities. This route would greatly benefit from the ability of laboratories to share their synthesis, characterization, and reaction results in a (crowd-sourced) database that could be referred to from publications. The growing combination of results from such materials could expose similarities and differences across laboratories that help refine synthesis, characterization, and reactivity methods between laboratories. Such an effort would not result in the need to reveal proprietary work on new materials and would provide a means to improve reproducibility across growing skill levels (i.e., new researchers) and at academic and industrial laboratories. As the number of crowd sourced entries increase, it is expected that similar (or perhaps clustered) results could emerge that would increase understanding as to the nature of the influence of various synthetic practices, or characterization/reaction methodologies, that are currently lurking variables that result in variability or irreproducibility.

Finally, an interesting alternative is to rely on university core facilities to provide materials and benchmarking services to the community. An example of one such facility is the Reactor Engineering and Catalyst Testing (REACT) core facility at Northwestern University. [7] A laboratory such as this could use standardized protocols to continuously synthesize and test benchmark materials, then sell the materials to individual researchers within the community at cost. However, more of these types of facilities need to be established in order to serve the entire community. Additionally, an important question is how to provide sufficient funding for such an initiative, in a manner that does not pass the cost onto the user, as this will lead to the exclusion of researchers and laboratories with insufficient funds from using these services. Various funding models for self-sustaining operations of independent laboratory and testing facilities, whose mission is to provide such benchmarking services to support the research community, were discussed. One option may be to acquire independent sources of funding for a community-wide benchmarking facility at a much larger level (e.g., center-level), that would cover the costs associated with researchers in the community using their services.

There would be value in having groups with similar expertise (e.g., multiple catalyst benchmarking facilities, certain advanced characterization techniques (e.g., TEM/STEM), etc.) form a network. This could provide a forum for ongoing discussion of reporting standards and best practices. Data and samples could be shared to facilitate benchmarking for data acquisition and analysis. Of course, resources are limited for such activities, but such a network may be able to provide efficient approaches for improving best practices in at least some areas. Some limited form of data sharing may be the least inexpensive to implement and could provide excellent resources for new researchers entering the field by allowing them to compare their analysis with that of others. Round-robin sample analysis may be of interest to subsets of people working in related areas (e.g., zeolites, oxides, support metals). These specialists may be motivated to provide resources for such a limited interlaboratory study if it will directly impact their ongoing research. Structure will need to be developed to establish and sustain such a network for it to have a significant impact in the field.

Suggested future action #3: Producing training videos and learning modules

To increase the adoption within the community, the working group also proposed possibilities for short courses and workshops around benchmark materials synthesis and characterization and reactivity evaluation methods. These educational tools are needed to help the broader catalysis community implement benchmark materials into studies and to enable accurate comparisons and interpretation of catalyst performance.

To help the broader catalysis community adopt best practices in benchmarking of materials, we propose the creation of a series of training resources. These resources include: (1) publications highlighting guidelines for best practices in benchmark catalyst synthesis and testing; (2) corresponding training videos on techniques and specific best practices; and (3) workshops and short courses. The first two distribution methods represent readily accessible, on-demand resources with broad reach, while the latter provides opportunities for more in-depth, hands-on training and interactions with expert trainers.

The primary target audience for these training resources would be new PIs and trainees, and the goal would be to facilitate transfer of the types of fundamental knowledge that are commonly handed down from generation to generation in well-established lineages of catalysis laboratories and researchers. Making access to training on these key fundamentals more readily accessible has the potential to increase the diversity of perspectives in the field of catalysis by enabling new researchers from a range of backgrounds to establish research efforts more easily in this area. Concurrently, the overall quality of published results would be expected to increase as both established and new researchers become more familiar with how to ensure rigor and reproducibility in the collection and interpretation of their data.

The proposed publication would take the form of a written beginners' guide that outlines common pitfalls in the synthesis of reproducible and well-defined catalyst materials. These guidelines would cover challenges with certain classes of precursors, considerations for the use of different support materials (variations among commercial materials, complexity introduced by reducibility), and key parameters to consider for steps such as thermal treatment and drying. The publication would also direct readers to existing detailed resources on topics in the synthesis of specific classes of catalysts, including review articles, perspectives, and book chapters. This existing information is currently challenging to find—particularly for new researchers—because there is no centralized record of well-written texts. The publication would also include a decision tree to help researchers choose the best synthesis approach to minimize undesired complexity and uncertainty while still providing an appropriate and sufficient benchmark for their synthesis, characterization, or catalytic process.

Videos and workshops would be focused on specific techniques, such as the synthesis of supported metal nanoparticles via strong electrostatic adsorption, calcination and activation of catalyst materials, and measurement of catalyst dispersion. The emphasis here would be on the critical "tips and tricks" that enable successful and reproducible materials synthesis. Videos could be used by new researchers to learn synthetic methods while minimizing time spent on trial-and-error optimization of literature protocols. Successful completion of a particular synthesis or technique could also serve as a means of validating the training progress of new student researchers. There is precedent for disciplines to establish crowd-sourced, educational sites, such as LearnChemE.com. [8] Administrators of these site would be valuable resources for participants in this effort to help establish similar resources for catalysis specifically.

Workshops provide a venue for interaction with an expert, who would be able to provide real-time feedback and answer questions in a way that is not possible with a static video. Such workshops could take place independently as part of a multi-day summer school or in tandem with a conference. The ready availability of virtual platforms for hybrid workshop formats also allows the reach of these efforts to be expanded beyond individuals who are able to attend in person, thereby increasing accessibility.

Finally, training modules and workshops for all measurements used commonly in catalysis research can help minimize user error for newcomers into the field. This sort of training can be made broadly accessible to the research community and be updated frequently in summer schools or workshops held at national society meetings or online in web meetings. Much of this can also be done in virtual and asynchronous format, through videos and tutorials. Best practices can be adopted from the education field to reach younger generations of learners and more diverse groups of learners, which learn by a variety of learning styles and more visual and video-based training modules. It was also noted that such training materials are common in certain specialty measurements (e.g., synchrotron XAS) wherein performing measurements also involves access to and communication with technical experts, as opposed to more routine and widely available measurements (e.g., surface area).

Broader questions regarding community adoption and incentivization

Data storage, formatting and accessibility

An important aspect of the community generating and using benchmark data is the development and curation of a database, and a funding mechanism to support and maintain this database. Currently, there is a lack of funding mechanisms for the construction and curation of community-wide databases; for certain methods (e.g., XAS), each beamline or facility has their own database, but efforts to try to compile and share these together across the community have not been successful. More discussion on who would own and maintain such a database is required, but the solar testing facility (NREL) could provide a model for such an effort.

Clear and precise guidelines would need to be developed to determine data and metadata information and formats for entries into a centralized database, for the variety of data sets that are used and generated by researchers in the community. It is also important to report the properties in an archivable way that can easily be read in future years by artificial intelligence, in order to increase the adoption of machine learning tools in the catalysis field. Ideally, the field could move towards a data sharing environment where meta-data is attached to the raw data and other groups can analyze the raw data themselves, and effort should be made to embed meta-data the image and/or spectral data so that each image or spectra carries with it a report of all the information suggested as relevant in this document (it is noted that although manufacturers each prefer their own proprietary file formats, users can pressure them into making their image analysis software freely available or providing alternative open-source file formats). This would allow different researchers to analyze the same raw data set using different approaches, especially as information about data analysis methodologies advances. For example, wavelet analysis of spectra has become an important method for the field, however, care must be taken for interpretation of these plots as often the intensity scales are not provided, and the reference compound data range must be matched to experimental sample data. Further, repeat measurements on a representative sample from the same group would establish the quality of the measurement at the beginning of each study, such as XANES/EXAFS spectra of a given reference material and condition at the start of each beamline run, and these data could be entered into a benchmarking database.

One option to develop a useful database could be the creation of a crowd-sourced database where researchers could self-report information that can be searched. This could be housed as a funded part of a national lab or hosted at a professional society (perhaps NAM or ACS). Although it would be difficult to ensure that all the data that enters such a database would be reliable, this can be improved by requiring certain reporting details alongside the raw data, and crowdsourcing may allow community convergence on an acceptable set of standards in data reporting. This effort becomes more powerful if there are a handful of benchmarking materials for which data that can be reported and compared against among researchers. This may also allow identifying discrepancies (e.g., impurities in new batch or lot numbers of a standard material) while also meeting goals associated with training exercises. The crowd-sourcing approach also circumvents the problem of synthesizing and maintaining one large batch of standard material. Consistent reporting of various types of standard materials, as new lots or batches become available, or as new materials are explored, can then allow the community to make progress through this database. Additionally, ASTM standards that already exist for reporting can be used for this database and be improved upon in a crowd-sourcing effort if modifications are needed for more specialized contexts.

Journal publications

An important question is how to incentivize the community to use benchmark methods and materials, but without strict enforcement or “gatekeeping” of their research that would prevent publication of the work in a journal, but rather intended to improve the quality and the R&R of the work.

Generally, detailed descriptions of methods and procedures can be documented, and reproduced without concerns of plagiarism or copyright infringement, by inclusion in the supporting information documents with appropriate referencing to earlier work. This would also ensure consistent application of methods and procedures across studies and including this information in the supporting information would not compromise the length or readability of the main text. Another helpful activity for the research community that has been well-received is for journals to occasionally publish perspectives and editorials to describe issues related to R&R in their field generally, or on specific technical issues that commonly recur during the review process of papers in their journal. These editorials and perspectives can discuss best practices, without providing explicit prescriptions or “gatekeeping” procedures, that can adapt with progress in the field and help improve R&R in research being performed by newcomers into the field. They can also provide guidance on what type (or rigor) of evidence is needed to support what conclusions or claims are stated in a manuscript; extraordinary claims require extraordinary evidence.

Various journals may decide, depending on their mission and goals, to adopt different levels of requirements, guidelines, or details as related to the R&R of results in the manuscript under consideration. Some specific journals may decide to adopt checklists of details and data that need to be provided for a given measurement or study, which are also provided to reviewers to help improve the quality of the peer-review process. These checklists may be presented in the form of guidelines or best practices for submission, so that an author can provide their own reasoning to explain why they may have chosen to use an alternate approach, which would allow flexibility and room for innovation and new discovery of materials and methods. One issue that would need to be addressed is how to ensure uniform and consistent application of such detailed rubrics or guidelines across all of the editors who oversee the manuscript review process at a given journal. One potential solution is to solicit a review who’s main (or sole) focus is on the R&R aspects related to the specific measurements being performed in the study. Considerations of how procedures can or should comply with principles of FAIR (findability, accessibility, interoperability, and reusability) data access is also a worthy point of discussion.

Other journals may decide on mechanisms to store raw data files that can be accessed and verified by reviewers and other researchers in the community. Furthermore, it could be useful if data from experiments are provided with the minimal extent of post-processing; this creates transparency in data interpretation, helps to avoid bias in interpretation of raw data, and allows other members of the community to interpret raw data. This last point is beneficial as it helps to both identify errors in data workup and offer differing interpretations of the data.

Research proposals

Another important question is how to incentivize the adoption of mechanisms and actions to improve the quality and the R&R of the research being proposed or done, but without strict enforcement or "gatekeeping" of research ideas within the community, especially new and innovative ones that could have transformative impacts.

General guidelines and best practices can help improve the quality of research proposal ideas when being conceived by the researcher, and how these are evaluated and assessed by a reviewer or funding agency. As part of the research aims and tasks, explanations can be provided as to how data might be benchmarked and validated, especially for the development of new methods, materials, catalysts, and reactions.

More stringent or prescriptive requirements would require changes in incentivization and funding support by the sponsoring agency. For example, additional funding would need to be provided in the budget to perform benchmarking experiments that would be included in reports, publications and presentations, and a separate appendix (such as a "Rigor & Reproducibility Plan", similar to a "Data Management Plan") may need to be provided so that it can be evaluated by a reviewer.

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Appendix A: Workshop structure and agenda

Workshop structure and organization

The workshop is organized in three phases. The proposed timeline for the three phases is depicted in Figure A.1. This format differs significantly from the typical workshop format that might involve only an in-person session. There were several reasons that motivated this multi-phase and hybrid workshop: 1) taken together, there was more content than could be discussed within a two-day in-person workshop, 2) in-person discussions would benefit from participants having time beforehand to think about the various issues and topics, specifically learning from efforts undertaken in other scientific fields and considering them within the context of the catalysis field, and 3) participants may have varying degrees of interest in the long-term goals of this effort that will take place in phase 3.

Figure A.A.1. Timeline of the workshop depicting the three-phase approach.

Phase I: overview

Phase 1 was a set of virtual activities to help define the scope of the problem in our field and prepare workshop participants for meaningful discussions. It consisted of two stages. In the first stage, we solicited anonymous feedback from the catalysis community on the workshop topic, primarily through an online survey that was disseminated by various electronic and virtual means, including via regional clubs of the North American Catalysis Society (NACS). The aggregated feedback from this survey is summarized in Appendix C.

The second stage consisted of a half-day virtual "seminar" held on April 4, 2022, that was open to the public. The purpose is to contextualize the "reproducibility crisis", both in science reporting in general and specifically in the field of heterogeneous catalysis, while obtaining insights from scientists in other fields. Most of us have anecdotes concerning failures to reproduce data internally within our group or observed an apparent lack of rigor in reports in literature, but how far spread is the problem? What are possible systemic, institutional, or individual causes? How do researchers think about these problems in other fields? Can this problem be "solved," and what would even be considered progress? What does it mean for data to be reproducible? The proceedings of the phase I workshop were recorded and is available for viewing at our website **–** www.catalysisRR.org**.**

Phase I: agenda

Time (CST)	Speaker
9:30 AM	***Welcome and Introduction*** Neil Schweitzer, Northwestern University
10:10 AM	***The Ongoing Battle for More Credible Science: Identifying Interdisciplinary Lessons*** Jennifer Tackett, Northwestern University Editor-in-Chief, Clinical Psychological Science
10:50 AM	***Lessons Learned from Systematic Studies of Experimental Replication in Adsorption Science*** David Sholl, Georgia Institute of Technology and Oak Ridge National Lab
11:30 AM	***The Importance of Standard Operation Procedures for Catalysis Research Accelerated by Artificial Intelligence*** Annette Trunschke, Fritz Haber Institute
12:10 PM	***The Data Sea Scrolls*** John Kitchin, Carnegie Mellon University
12:50 PM	***A Unique Journal for the Publication of Reproducible Methods for the Synthesis of Organic Compounds*** Rick Danheiser, Massachusetts Institute of Technology Editor-in-Chief, Organic Syntheses
1:30 PM	***Panel Discussion*** Moderator: Bruce Gates (UC Davis) Panel: Susannah Scott (ACS Catalysis) Junwang Tang (Chinese Journal of Catalysis) Davide Esposito (Nature Catalysis) Johannes Lercher (Journal of Catalysis)
2:30 PM	*Adjourn*

Phase II: overview

Phase 2 was an in-person, two-day session that was held on July 21-22, 2022 at the Big Ten Conference Center in Rosemont, Illinois, and included various mechanisms to incorporate input and discussion from virtual attendees. The main purpose was to discuss two overarching topics: 1) Standardized reporting in technical manuscripts and proposals, and 2) Developing benchmarking standards. The agenda included keynote speakers to elaborate on specific examples within these two broad topics, who discussed in detail their experience establishing standard methodologies and materials for research measurements and data analysis. Additionally, we hosted a series of breakout sessions and full group discussions. Each day, six breakout groups will discuss the sub-topics listed in the table below. Day one has two breakout group sessions; attendees will participate in two different groups this day.

Day 1 - Standardized Method Reporting	Day 2 - Guidelines for Benchmark Materials
Bulk Catalyst Synthesis	Supported Metal Nanoparticles
Deposition Synthesis	Single Atom Metals
Bulk Characterization	Metal Oxides
Site Characterization	Zeolites
Catalyst Testing	Metal Organic Frameworks
Advanced Characterization – XAS, TEM	Bifunctional Materials

The outcome of the breakout group discussions were summarized in the previous sections of this report. These sections contain some standard definitions for important concepts in the field, recommendations for standardized measurements, known uses and limitations of different measurement types, and recommendations for researchers and reviewers for strong proposals and publications. Some critical questions we asked participants to consider included:

- What minimum information about specific measurements or procedures should be required for publications?
- What best practices should be required to be reported by journals?
- What materials would serve as reasonable, general benchmark materials? Are commercially available materials suitable benchmarks?
- Which measurements need to be benchmarked in publications?
- If groups provide or synthesize their own benchmark materials, what minimum information should be included in publications? How much information should be required in subsequent publications?
- How do we incentivize the community to use benchmarking? How can proposed benchmarking protocols be enforced fairly across institution types?

Speakers and full group discussions were broadcast via Zoom to virtual participants and were advertised broadly to the community via social media/email. Breakout group sessions were not broadcast to uninvited participants, only to the few invited participants that could not participate in person. During the breakout groups discussions, general, virtual participants had the opportunity to engage in discussion and leave feedback using an online forum: www.padlet.com.

The workshop had about 70 total participants (including the chair, co-chair, and workshop committee, See Forward at the beginning of the report).

We had 42 invited, general professional participants. Professional participants were selected through an internal nomination process. Workshop Committee members were asked to submit 20 names of individuals they would recommend as participants. Based on the submitted names, the chair and co-chairs, selected specific individuals with the goal of constructing a well-rounded, diverse group. In selecting invited participants, we considered researcher expertise, researcher institution type (R1 academic, R2 academic, MS/BS granting academic, national lab, and industry), researcher experience (years since PhD was granted), and personal demographics. We also invited 12 student participants – exemplary senior graduate and post-doc students that plan to pursue an academic career. Students were nominated by workshop participants. Nominated students were then required to submit a one page essay detailing their experience, their future plans, and why they want to attend. Final invitations were selected by a workshop subcommittee. Finally, we invited 6 speakers to the workshop. The speaker topics can be viewed in the workshop agenda. Abstracts are available in Appendix B.

Phase II: workshop agenda

Start Time (CST)	**Thursday, July 21, 2022** **Topic: Best practices for reporting data in manuscripts and proposals**
7:00 am	Breakfast
7:45 am	Introductory Remarks
8:00 am	***Development of Standard Methods of Analysis of Catalysts by ASTM D32*** Steven A Bradley, Bradley Consulting Services
8:30 am	***Tools to help enable measurement comparability*** Pamela Chu, National Institute of Standards and Technology
9:00 am	***Standardization in X-ray Absorption Spectroscopy - Possible or a Dream?*** Simon R Bare, SSRL, SLAC National Accelerator Laboratory
9:30 am	Coffee Break
10:00 am	Morning Breakout Group Discussion
12:00 pm	Lunch
1:00 pm	Full Group Discussion – Recap of Breakout Group Discussions
2:30 pm	Coffee Break
3:00 pm	Afternoon Breakout Group Discussion
5:00 pm	Adjourned for Dinner
	Friday, July 22, 2022 **Topic: Recommendations for the use of benchmark materials**
7:00 am	Breakfast
7:45 am	Introductory Remarks
8:00 am	***Harmonizing, benchmarking and validating measurements: experiences from solar cell testing*** Nikos Kopidakis, Solar Energy Research Facility, NREL
8:30 am	***Calibration and Testing: An OEM Perspective*** Jeffrey Kenvin, Micromeritics Instrument Corporation
9:00 am	***A summary of the activities and results from EuroCat: EuroPt-1*** Robert Weber, Pacific Northwest National Laboratory
9:30 am	Coffee Break
10:00 am	Breakout Group Discussion
12:00 pm	Lunch
1:00 pm	Full Group Discussion – Recap of Breakout Group Discussions
2:30 pm	Workshop Adjourned

Phase III activities

Phase 3 will be a series of initiatives that can lead to actionable plans and outcomes moving forward. During the phase 2 workshop, and by a virtual survey of participants afterward, feedback was obtained regarding various considerations that should be taken into account, to help ensure the creation of inclusive and accessible infrastructure for the entire research community and to identify potential funding sources for essential capital and personnel effort. These recommendations and guidelines are summarized in Section 5 of this report. Some of the phase 3 activities that were discussed include:

- **Producing training media and workshops:** The methodologies described herein for various types of measurements would further benefit the community if training material were available for new practitioners within the field. Thus, strategies are needed to develop, produce and disseminate training media. Critical questions to be answered include: Who will produce the media? How will media be distributed to the community? How can these efforts be funded? This session may also explore ideas related to specific training opportunities for students, such as research experiences for undergraduate (REU) programs and visiting student opportunities.
- **Establishing a database of experimental data:** Databases of standardized data are critical in chemistry and related fields for ensuring the reproducibility of methods between distinct labs. The standard testing methodologies for specific measurements and recommendations for benchmarking materials resulting from Phase 2 raises the opportunity to establish an experimental database of standardized measurements. Critical questions to be answered include: Who maintains and houses the database? What data should be accepted to the database (e.g., only new data, historical data, only reactor data, single crystal data)? Given standard procedures/methods, how should data be scrutinized? Is funding available to establish a database? How is the database sustained beyond initial funding?
- **Forming a network of testing labs:** An ambitious plan is to establish a national network of testing facilities that will support the training activities and database described above. These labs would be run by expert scientists and equipped with state-of-the-art instrumentation. Additionally, they would be able to provide the research community with benchmarked materials, synthesized in-house, with verified testing performances. Critical questions to be answered include: Where should labs be housed, and what areas of catalysis should they specialize in? Should benchmarking material be synthesized by labs or commercially available? How do we ensure equal access of resources across the academic institution spectrum? Should labs provide training to external institutions, how should this work logistically? What funding mechanisms are available to establish the network? How will the labs be funded in the long term?

Appendix B: Workshop keynote talk abstracts

Development of Standard Methods of Analysis of Catalysts by ASTM D32 - Steven Bradley

ASTM D32 Committee on Catalysts is charged with the development of test methods and practices pertaining to catalysts, zeolites and related materials. Such standardized test methods are widely used by industry for evaluating material specifications and assist organizations to compare results by using the exact same procedures. The primary focus of D32 has been on heterogeneous catalysts including both raw materials and finished catalysts as used in the refining industry. The Committee has published 49 methods, practices and guides and the rigorous procedure used by the Committee to develop these standards will be discussed. Recently issued standards on pore volume of powdered catalysts by water adsorption (D8393) and jet cup attrition index of catalysts (D8414) as well as using optically imaging to determine particle size and shape of catalyst materials, which is to be balloted shortly, will be used as examples of the process. A consensus is required before issuance of any standard and this includes thorough discussions of all comments and negatives during the balloting process. An interlaboratory study where repeatability and reproducibility data for the method is obtained is a critical part of the development of a test method. All test methods include a precision and bias statement and the data from this study is published as a research report that is available from ASTM. How such a study is designed and conducted will be discussed. Input for future methods, guides or practices will be requested.

Tools To Help Enable Measurement Comparability - Pamela Chu

To promote U.S. innovation and industrial competitiveness and assure the quality and comparability of measurement results, NIST conducts measurement science activities ranging from fundamental and applied research to the development and dissemination of analytical methods, reference materials, reference data, and documentary standards. NIST also provides guidance in best practices and resources which optimize the discoverability, usability, and interoperability of large information-rich data sets. To help identify stakeholders' needs, NIST actively engages the measurement communities through voluntary consensus standards development organizations, consortia, interlaboratory studies, and workshops. An overview of these approaches with an emphasis on specific areas most likely to address the catalysis research community needs will be presented.

Standardization in X-Ray Absorption Spectroscopy - Possible or a Dream? - Simon Bare

The concept of standardization in X-ray absorption spectroscopy (XAS) has been a topic in the XAS community since the early 1990's but it is still a concept rather than a reality. Why is this? How many participants in this workshop or journal editors are aware of these efforts? In this presentation I will provide a history of the attempts to introduce standardization and some of the difficulties that have made this problematic.

The initiative of standardization started by the Standards and Criteria Committee of the International XAFS Society (IXAS) who issued a report in 2000. These meetings faded but were revised as Q2XAFS - a series of meetings working towards standardization with both IXAS and the IUCr XAFS commission. There were meetings in 2011, 2015, and 2017, and the next one is planned in 2023. However, only the most recent one resulted in a series of peer-reviewed papers. But as stated in the summary paper "the XAFS community is moving towards implementation of internationally approved standards and protocols". Will there ever be accepted standardization? What topics should be addressed in the upcoming 2023 meeting?

Harmonizing, benchmarking and validating measurements: experiences from solar cell testing - Nikos Kopidakis

I will show the pathway that the solar cell (or photovoltaic, PV) testing laboratories have taken to harmonize and benchmark measurement protocols aiming to provide reliable and repeatable results to the PV community at all levels (academic and industrial R&D). I will show how these efforts, that begun ~30 years ago, eventually led to the formal international standards for PV device testing that are in widespread use today. The lessons learned and the practices applied can help any field address rigor and reproducibility in their measurement.

Calibration and Testing: An OEM Perspective - Jeffrey Kenvin

Rigor and Reproducibility are 'routine' demands for instrument calibration. The practice of calibrating a device and the tools required to perform the calibration have evolved and improved dramatically over the last decade. The Rigor and Reproducibility extends beyond calibration of devices to service, laboratory testing, accessories such as reference materials, and the ongoing use of devices. This presentation includes a brief review of the legacy practices and a case study examining the current strategy and practice of calibrating a gas adsorption instrument. Additionally. a second case study will be used that features the testing and certification of material textural properties that are required by users to monitor and validate the ongoing performance of their device.

A Summary of the Activities and Results from EuroCat - Robert Weber

EuroCat was part of a program designed to "link individuals and laboratories to share information on surface reactivity and catalytic properties of highly [exposed] metals and alloys". There were four standard EuroCat materials: 6% Pt/SiO_2, 20% Ni/SiO_2, 2% Pt/C and 2% Pt/Al_2O_3. Here I have reviewed the literature on just the first, so-called EuroPt1. It was prepared by Johnson-Matthey and then distributed in 200 g aliquots to 8 different laboratories who subjected it to tests of its composition, physical characteristics and catalytic activity:

- Chemical and physical analysis (concentrations of metals and impurities)
- Other physical techniques (electron microscopy, electron spectroscopies, magnetic measurements, EXAFS)
- Adsorption (physisorption, chemisorption, titration, porosity)
- Catalytic activity and selectivity (hydrogenation) and "exchange" (between olefins and paraffins)

There was excellent concordance for many of the measurements and the results were summarized in a series of publications in Applied Catalysis that come close to exemplifying how to reproduce results in catalysis. The presentation will conclude with an analysis of the detailed measurements of the metal domains that uses an approach like Fokker-Planck evolution of the domains instead of the more usual approach devised by Wynblatt and Gjostein.

Appendix C: Community feedback on issues related to rigor and reproducibility

Prior to phase I, a survey was broadly disseminated to the heterogeneous catalysis research community, including via e-mails to local chapters of the North American Catalysis Society (NACS) and other electronic and social media platforms. This survey contained several questions and prompts to solicit open-ended feedback from the community on topics relevant to phases II and III. The aggregated feedback to these survey questions is provided below.

Q1: What measurements do you think should be standardized (or not) when reviewing manuscripts or proposals?

1. Catalytic rates, turnover frequencies (TOF), and conversion
    1. Clear evaluation/calculation and reporting for mass transport effects. Some means demonstrating that catalytic or kinetic rates is deconvoluted from these effects.
    2. Differential conversion for presentation of kinetic data, product inhibition measurements.
    3. Determination of initial rates, accurate catalytic rates, pseudo steady state conditions.
    4. The requirement for the reporting of a TOF necessitates an attempt to characterize the number of active sites using appropriate techniques (e.g., titration, chemisorption).
    5. More thorough descriptions of experimental conditions, reactor setups, catalyst formulations (e.g., particle morphology) and details to help improve reproducibility.
2. Characterization techniques (e.g., BET, TPO/TPD, XPS, XRD, microscopy)
3. Selectivity
    1. Assessment of closure of mass balance, as this directly affects the conversion and selectivity meaning.
    2. Reporting selectivity at a constant conversion, defining the limiting reactant, awareness of adsorbed material on the catalyst surface.
4. Catalyst stability and deactivation
    1. Deactivation and recyclability must be assessed at significantly less than 100% conversion and away from equilibrium
5. Reproducibility of data
    1. More accurate use of error bars and estimated uncertainties (how to report them)
    2. Much more emphasis on the definition and reporting of experimental methods including all data reduction methods (e.g., software used, curve-fitting procedures).
    3. Experimental description must be complete enough that skilled scientists can attempt to replicate.
    4. When possible, measurement and presentation of data on benchmark catalysts.

Q2: What terms or concepts in catalysis do you find ambiguous, or could benefit from better definition or standardization? Describe up to 5 in the space below.

1) Terms: Conversion, turnover frequency (TOF), active sites, selectivity, characterization, reduction/oxidation relationship to activity, acidity, strong metal-support interaction (SMSI), surface area, bifunctional catalysis.

2) Concepts: Drawing conclusions from little evidence (EXAFS, detection limits); details of catalyst preparation, estimation of uncertainties/errors, definitions of activity in homogeneous and heterogeneous catalysis, accurate costs of economics, H_2 spillover.

Q3: Are there other topics we should consider organizing a breakout session on at the workshop? Describe up to 5 in the space below.

- Minimum acceptable levels of burden of proof in characterization, best practices, standardization.
- Catalyst synthesis and benchmarks.
- Active site quantification, activity benchmarking.
- Benchmarks for classes of reactions.
- Definition of ambiguous catalytic terms.
- Role of combining theory and experiments to improve R&R.
- Benchmarking computations.
- Benchmarking and normalizing electrochemical measurements, electro- and photocatalysis as emerging areas to set direction. What issues are similar and different to thermal catalysis?
- What is the value of improvement in R&R and what is success?
- Preventing benchmarks from being a gatekeeper or stifling innovation.
- How to manage reference materials and their use?
- How to format and store raw data amenable to machine learning?
- How to improve rigors and consistency of the peer review process at journals?
- How can R&R accelerate the path to commercialization for catalytic materials?
- How to incentivize responsible public reporting (e.g., not overselling results to publications)
- Best practices or standardization of data visualization (e.g., plots)
- Increasing the acceptability of reporting negative results.

Q4: What barriers may prevent you from adopting and using standards (e.g., control materials, measurements) in your research?

1. Nonexistent or high costs of standard or benchmark materials.
2. High degree of difficulty or lack of infrastructure to perform measurements.
3. Accessibility to and gatekeeping of shared facilities or instruments.
4. Lack of sufficient collaborators with the right expertise or instrumentation.
5. Amount of material needed for characterization may be prohibitory.
6. Lack of financial resources to carry out extra measurements to improve R&R.
7. Overly cumbersome methods or measurements, given the intended purpose of the study.
8. If standards are not held up by journal or funding sources, or hiring/promotion and recognition opportunities, to provide incentivization.

Q5: What challenges would you anticipate encountering in your research if certain data sets and formats were required to be uploaded to a centralized database?

1. Extra time and effort spend formatting and vetting data and uploading to a database.
2. Issues related to disclosure of information that may be proprietary or have IP value.
3. Inadequate access to software for data analysis, data reduction, or data visualization.
4. Variety of computational codes and formats for data.
5. Complexity of the information and how that to design an efficient database.
6. How to enforce quality control before entering data in a database?

7. Forced to collect irrelevant data for purpose of databases.
8. Biased or centralized control of research by database owners.

Q6: If rigor and reproducibility standards were to be adopted as a requirement by some (but not all) journals or funding agencies, how would that influence your decision to submit your manuscripts or proposals to those venues?

1. Would encourage submission (majority response).
2. Depends on what would be needed (minority response).
3. Would not influence decision (minority response).
4. Would discourage submission (minority response).

A few representative comments:

- “It depends how intrusive the requirements are. The need to reproduce measurements 3-5 times on different samples, for example, may be trivial in some situations but take months of work for others.”
- “Not at all. Already there are so many hurdles to publish and inconsistencies in the process.”
- “I would prefer to submit to these journals or funding agencies.”
- “I would support those venues, but only if I fully agreed with the standards”
- “Probably the same - but it would increase my readership of those journals.”
- “I think this sets a bar for submission, which I support.”
- “It could make it more difficult to write proposals and get them submitted by the deadline, acting as a barrier from submitting to certain funding agencies that would further separate the well-funded researchers and/or researchers upper tier universities from those at lower tier universities.
- “Similarly, while well-intentioned, it could become a barrier to publishing rigorous, but simple/short publications at those journals, and slow the rate of publication (could have positive and negative consequences.”
- “Don’t make it a funding mandate”

Q7: General feedback, thoughts or comments.

- What resources/tools/databases already exist today that could help with improving the rigor and reproducibility in heterogeneous catalysis research?
- Concerned that any guidance and/or recommendations from the workshop could come with unintended consequences that benefit some researchers at the expense of others. Mechanisms to ensure all researchers have access to any required/recommended benchmarking tools (e.g., through low-cost/free communal characterization facilities spread across the country) and standard samples (e.g., through making these extremely affordable and/or free through federal grant support) both seem important.
- Concerned that changes to R&R could disproportionately affect pre-tenured faculty, as the requirement to collect data on standard samples and with a wider range of characterization tools to publish/submit a proposal would inevitably delay the timelines for both, which could put added pressure on pre-tenured faculty under pressure to publish and attract external funding.
- Explaining the necessity of collecting rigorous benchmarking data to fit these changed field-wide norms in tenure dossiers might be difficult as these would not be shared across other areas of Chemistry/Chemical Engineering. New expectations for publication and proposal writing in catalysis may disproportionately affect those at the start of their careers and at smaller institutions.
- It's great that this is occurring. I do think it's important that the metadata be considered very carefully.
- It would be helpful to harmonize these concepts across both homo and heterogeneous catalysis

- It may exclude researchers that do not have enough resources in terms of both money and time.
- I think putting a cap on publications indexed to funding would really go a long way towards your desired outcomes. There is an incentive to publish that has led to just that, publications. If there is a cap, publication quality would increase substantially.
- Higher participation of undergraduate students in Co-Op and Summer internships in well-established labs.
- Although we cannot change the past, we can take current steps to ensure that we do not continue to propagate some of the inadequate practices that have been prevalent in the heterogeneous catalysis literature. I believe that this workshop is necessary and very relevant as we are increasingly moving into a stage where advanced computational and statistical tools are being developed using openly accessible experimental data sets. Standardization of experimental protocol and benchmarks would help ensure that low fidelity data sets do not hinder development of predictive models that further catalysis science. Furthermore, the fruitful results of this workshop may help reduce the time spent trying to reproduce key literature results that are relevant to a researchers work.
- I think our field of experimental catalysis desperately needs higher standards for rigor and reproducibility. Unfortunately, the challenge is that it is not just a minority, but perhaps even a majority, of catalysis papers that have flaws with respect to either methods or interpretations. Any standards for rigor and reproducibility would have to be developed with great care to apply to all scenarios and would likely step on many researchers' toes (for better or for worse).
- As stated above, I feel that the problem is not so much in poor data, but in the rush to publish "big" claims.
- Individual labs cannot necessarily be trusted en masse and would really only support results reported by third party (independent) measurers of performance.
- Forget one-size-fits-all solutions. Heterogeneous catalysis is a very heterogeneous field of research. Not recognizing that is neglecting the reality.
- Best to present catalyst performance in general format that allows reader to convert to their favorite measure of activity/ selectivity.
- Many studies are very hard to reproduce. Much more descriptive experimental sections and repeatability of catalyst synthesis is needed.