RSC Publishing Faraday Discussions

Perspectives on the Design of Nanoparticle Systems for Catalysis

Journal:	*Faraday Discussions*
Manuscript ID	FD-ART-06-2018-000124.R1
Article Type:	Paper
Date Submitted by the Author:	10-Jul-2018
Complete List of Authors:	Friend, Cynthia; Harvard University, Chemistry and Chemical Biology; Harvard University, Rowland Institute

Journal Name

ARTICLE

Perspectives on the Design of Nanoparticle Systems for Catalysis

Cynthia M. Friend*[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

An overview of the Faraday Discussion, “Design of Nanoparticle Systems for Catalysis”, is presented. Examples are taken from the papers presented at the meeting and from the literature to illustrate main discussion points.

Introduction

Chemical production, which relies heavily on heterogeneous catalysis, now accounts for nearly 25% of energy use worldwide. Forecasts for global energy demand and use project this number will rise to 45% by 2040 [1,2]. Current trends in energy supply and use are unsustainable -- economically, environmentally and socially. A fully integrated theoretical-computational-experimental approach to the design of selective catalysts is needed to boost energy efficiency in the industry's production processes.

Heterogeneous catalytic processes are extremely complex, requiring optimization of factors across multiple scales of length, time, pressure, and temperature; inclusive of materials synthesis, mechanistic surface chemistry and reaction kinetics. Numerous studies show that complex metal/oxide interfaces, generally present in catalysts, appear to play an important synergistic role in determining reactivity. Further, since materials are often affected by the reaction environment, pre- and on-stream activation and optimization of performance is necessary.

Historically, heterogeneous catalytic processes have been devised empirically, with broad guidelines informed by prior experience in organic and organometallic chemistry. Recent advances in theory and experiments provide tools with the potential to move beyond the traditional "trial-and-error" approach to design principles that predict and develop highly efficient heterogeneous catalysis materials systems.

There has been a revolution in the area of catalysis over the past decade enabled by synthetic control of designed nanomaterials [3-5], advances in theoretical methods and computational power [6,7], greater understanding of reaction mechanisms derived from fundamental surface chemistry [8-10], and development of novel instrumentation for probing catalytic systems under operating conditions [11,12]. This Faraday discussion revolved around the state-of-the-art in the use of these various tools to advance the design of efficient heterogeneous catalytic processes.

Four subtopics were intertwined to address the broad question: How can efficient catalytic systems based on nanoparticles be designed? The use of theory as a driving force to understand nanoparticle structure and reactivity was one major topic that also permeated all parts of the conference. Because nanomaterials can change their structure and surface composition during operation, the challenges of characterizing nanoparticulate catalysts was a second major theme. Thirdly, new approaches to catalyst synthesis were discussed. The meeting culminated in the fourth session on application of nanoparticle structures as catalysts.

Herein, I briefly summarize what I view as the general themes that emerged from the meeting that lays out challenges for future research and further advances in heterogeneous catalysis. The summary draws upon the papers presented in the conference as well as selected literature that addresses issues arising in the discussion.

The meeting clearly identified remarkable progress in the past two years and challenges that will require further advances. The meeting outlined a bright future for further advancing heterogeneous catalysts through designed nanomaterials. The meeting captured the excitement of new era in heterogeneous catalysis thanks to the leadership of Profs. Hutchings and Catlow.

Discussion

Several key points important for future advancement in catalysis emerged from the meeting. One major theme that emerged was the need for better benchmarking and standardization for both theory and experiment in order to advance discovery. Benchmarking will enable more systematic determination of the key characteristics of better catalysts. A second key point that emerged is the continued need for advanced tools for

---

[a] *Harvard University, Department of Chemistry and Chemical Biology; 12 Oxford St.; Cambridge, MA 02138 USA† Footnotes relating to the title and/or authors should appear here.*

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x characterization and understanding of catalytic function. Thirdly, the high potential for contributions of “machine learning” for catalyst discovery and synthesis were mentioned even though this was not a topic of the meeting itself.

Critical to the design of efficient (active and selective) catalytic systems is understanding of reaction mechanism and kinetics. Catalysis by its nature is controlled by kinetics; therefore, it is essential to map out the elementary steps important in a catalytic process and to determine rates constants for these steps. The combination of elementary steps and associated rate constants provides the ability to predict reaction selectivity and activity as a function of temperature and pressure.

Modeling of catalytic performance is a multiscale problem, spanning substantially different length and time scales (Fig. 1). At the molecular scale [13], elementary reactive steps that occur extremely short (femtosecond) time scales define the reaction mechanism. Diffusion of reactants across the surface is substantially slower (micro-to-milli-seconds) but also depends on atomic-scale structure. Since the structure and composition of the catalyst surface determines reactivity, the initial state of the catalyst, its form during stable operation and the properties of deactivated materials all need to be understood and modeled. Evolution of these materials properties is generally significantly longer than molecular events and the materials properties all depend on the composition of the reactant phase, as described below. Finally, the specific configuration of the reactor and the macroscale properties of the catalyst bed are important because of the potential for nonuniform temperature and concentration profiles that affect rates and selectivity. The design and modeling of catalytic reactors is a well-established field that was not explicitly covered in the discussion. The other two factors: molecular-scale mechanism and evolution of catalyst materials during the course of activation, stable operation and ultimately deactivation were the topics of active discussion.

Turning first to molecular scale simulations, such as those discussed in the paper presented by Prof. van Santen [14] the power of these simulations and the remaining challenges are outlined. In the investigation of the alkylation of isobutene using ethylene catalyzed by zeolites, the kinetics of activation and deactivation were understood using a complex reaction network. Molecular-scale simulations provide insight into the nature of transitions states for key steps that control rate and selectivity which can potentially be used for designing related catalyst material that can tune the free energy of the transition state to direct selectivity. Such detailed insight requires knowledge of both reaction energetics and accurate pre-exponential factors.

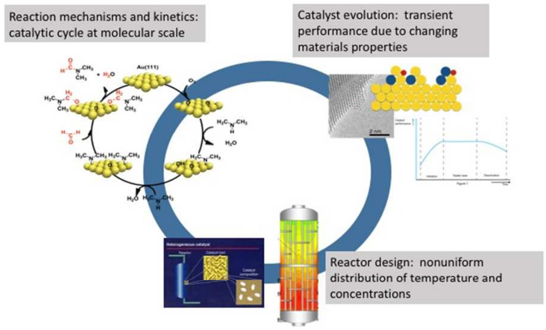

Figure 1: Schematic of multiscale nature of catalytic systems adapted from van Santen [14].

One of the major challenges to kinetic modeling at the molecular scale is accuracy—both in computing activation energies and pre-exponential factors. While electronic structure calculations, such as density functional theory (DFT) have increased in accuracy, generally they are not at the level of “chemical accuracy”. Furthermore, the calculation of pre-exponential factors is challenging, especially since anharmonicity may be important in the transition state. Recently, a “divide and conquer” strategy was developed by Sauer, etal [15]. that predicted the rate constants and pre-exponential factors to within one order of magnitude of those measured for alkylation of olefins in zeolites. Extending this approach to a wider range of systems is a promising direction of research and has potential for more accurate kinetic simulations.

Model systems

A second challenge in molecular scale modeling of complex reactions is that the network of elementary steps needs to be defined. Experimental studies on model systems are generally required. Historically, rate expressions for catalytic processes that rationalized the dependence of rate and selectivity on partial pressure were used to elementary steps via “reverse engineering”. Such expressions provided a means of interpolating reactor performance over a restricted range of temperatures and pressures. However, to obtain specific and predictive information about the molecular scale events, detailed mechanistic studies on well-defined models is necessary.

Modern surface science methods enabled detailed mechanistic studies of model systems that also serve as direct comparison to theoretical models. The elementary steps in the chemical transformations important in catalytic systems and the associated rate constants can be obtained experimentally using temperature programmed methods. Surface spectroscopy, including vibrational and X-ray photoelectron spectroscopies, provide key information about intermediates in the reaction and the state of the surface. These latter tools also provide a bridge to studies of the actual catalyst material (see below) because analogous measurements can be made on nanoparticle catalyst. Molecular scale imaging using scanning tunneling microscopy (STM) and atomic force microscopy (AFM) provide key information about local bonding and redistribution of surface species that are important in catalytic processes.

The value of experimental model systems based on well-defined samples was illustrated in the paper by Freund [16] that showed the direct link between theory and experiment. Studies of Au on thin films of ceria demonstrated the key role of O vacancies in the $CeO_2(111)$ surface in binding the Au. The combination of atomically-resolved STM images and DFT models demonstrated effect of charge transfer from Ce^{3+} to Au [17]**.** In the meeting, the preference for Au to bind to defects in ceria was further studied using DFT [18]which compared well with the prior experiments. Another example of a powerful model system is investigation of Au nanoparticles on thin-film SiO_2/Si that enabled in operando spectroscopic studies [19]. This work provided evidence for CO oxidation activity at the perimeters of Au nanoparticles, indicating a role of the oxide support.

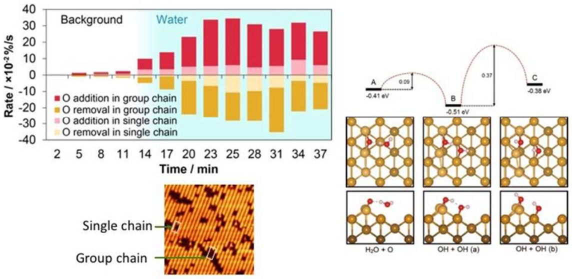

Figure 2: Investigation of mobilization of O_{ads} on Au(110) by H_2O demonstrate that water increases O_{ad} mobility affecting both in-chain and inter-chain interactions[20].

Model systems can also identify potential dynamical and cooperative effects that can play a role in heterogeneous catalysis. For example, our group has shown that one role of water in oxidative processes catalyzed by Au is mobilization and redistribution of adsorbed oxygen atoms [20]. Atomically resolved STM images of O adsorbed on Au(110) in conjunction with DFT studies reveal that formation of transient OH on the surface via reaction of H_2O with O_{ads} mobilizes the oxygen (Fig. 2). The adsorbed O is nonuniformly distributed on the surface, as observed in STM, forming groups of short chains. The O atoms at chain ends is most reactive so mobilization by water can create O active for oxidation of, for example, organic alcohols (Fig. 3) [21]. Experiments were required to identify important phenomena and theory provided insight into the underlying factors that lead to this behavior.

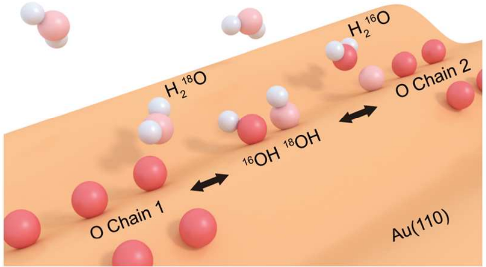

Figure 3. Schematic of oxygen exchange on ^{16}O/Au(110) under $H_2^{18}O$. The surface features are not drawn to scale, for easier visualization [20].

When model systems are used to map out complex reaction networks and associated rate constants a pathway for predicting catalytic activity over a wide range of temperatures and pressures is possible [22]. The two examples above illustrate how model systems can be used to understand bonding to the surface. In order to relate the kinetics derived from model systems to nanoparticle catalytic systems a bridge across materials complexity and reaction conditions is required. This can be achieved using well-defined nanomaterials of known composition and structure. In our studies of nanoporous $Ag_{0.03}Au_{0.97}$ catalysts, such a link was made by refining kinetic parameters measured for single-crystals using pulsed transient measurements [22-24]. Using this method, the selectivity for methanol oxidative coupling over nanporous Au was predicted for atmospheric pressure using rate constants determine on single crystals under UHV conditions.

Gates also provided several examples of model catalytic systems that have an increased degree of complexity that is more akin to supported catalysts used in industrial processes. For example, Rh pairs were synthesized on MgO using a dinuclear Rh complex [25] and used as a catalyst for ethylene hydrogenation. The dimer (Rh_2) structure was shown to persist in the catalyst material using EXAFS. These types of studies provide excellent models for catalytic processes that can also be used as a benchmark for theory.

Benchmarking theory:

The use of atomic-discuss theory to investigate catalysts and catalytic processes was a major topic of this discussion. The accuracy and level of complexity of the theory has increased dramatically recently, driven by accessible and advanced codes and by the increase in computation power available.

There were several general themes that emerged in the discussion. First, modeling of reaction kinetics, as discussed above, is clearly an important and challenging problem that requires development of new methods to more accurately model the activation barriers and pre-exponential factors in key steps. As described below, rearrangement of the structure and composition of catalysts material during reaction will also need to be described and understood since such rearrangements determine what types of bonding environments are available as “active sites”.

Most of the theoretical work presented in the discussion was oriented towards modeling catalytic materials using DFT. A range of models were used, including modeling of extended solids and explicit modeling of nanoparticles—both free standing and bound to supports.

Most commonly, extended solid are used to model bonding related to catalytic processes because the application of periodic boundary conditions limits the number of atoms (and electrons) that must be explicitly modeled. The advantage of periodic models is that specific types of complexity can be introduced. For example, the potential roles of defects in metal oxides was studied for small Ni complexes on ytrrium-stablized zirconia [26]and also for Au on defective ceria [18]. These investigations both indicated the key role of vacancies on oxides in stabilizing metal centers and in charge transfer between the metal and the oxide.

Several papers explicitly modeled nanoparticles [27] and nanoparticles interacting with supports [28]. These calculations are generally very resource intensive because of the larger number of atoms explicitly modeled in comparison to periodic calculations. Often these calculations focus on nanoparticles with high symmetry, e.g. 13- and 55-atom FCC clusters, that simplifies the calculation.

The ability to now model support effects, i.e. interaction of metal nanoparticles with oxide supports, was also demonstrated during the meeting. For example, the mobility of Ni bound to yttria stabilized zirconia (YSZ) was investigated for very small clusters of

Ni (up to 4 atoms) [26]. Larger bimetallic nanoparticles of Pd-IR and Au-Rh were also modeled and the effect of a titania support was studied[28]. In these models, FCC truncated octahedra were investigated and sever specific types of structures were investigated, including Janus (2-sided) particles. Interaction of the nanoparticles with the TiO_2 support depended on the nanoparticle structure and on which metal bond to the support. For example, interaction of the TiO_2 with Ir and Rh were stronger than Pd and Au, respectively, probably reflecting stronger metal-O bonding. Generally, these studies demonstrated the complexity of metal-support interactions and the need for accurate modeling. Necessarily, these calculations had to limit the degree of relaxation of the titania slab and considered a specific subset of possible structures (Fig. 4) [28].

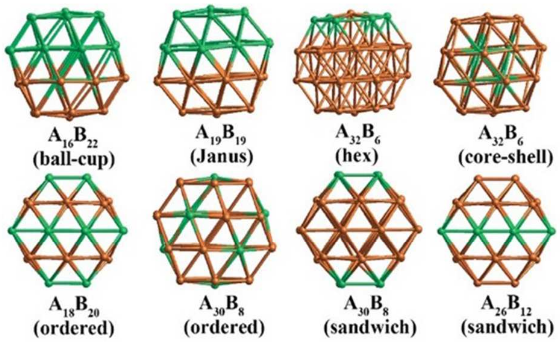

Fig.4: 38-TO nanoalloys in the "hex" configuration with the central atom of one (111) facet surrounded by a hexagon of six atoms of the other element with few possible combinations and configurations [28].

Even as DFT methods further increase in accuracy, there are several challenges remaining. First of all, there are many different flavors of DFT, as reviewed in several recent papers [29-31]. Specifically, the functionals used, the details of the calculations, including the slab thickness, unit cell size, whether dispersion corrections are included and, if so, how, the number of k points and cut-off energies used, make direct comparison of different theoretical studies challenging. These challenges are even greater for oxide materials for which accurate prediction of the band gap is not possible without introducing corrections that fit the band gap. Modeling of vacancies, as described above, is also generally challenging because the use of supercells leads to errors in the electrostatic energy [32]. Other challenges important in catalysis are selection of methods to evaluate the degree of charge transfer and the inclusion of fluxional behavior. Clearly there are a multitude of variables that determine the numerical results in DFT that generally vary in calculations on the same systems.

The potentially wide variation in DFT methods calls for more benchmarking of calculations using both experiment and comparison to other calculations. Indeed, a detailed comparison of different DFT methods has recently been reported that shows the increasing accuracy of the available methodology [33]. Even so, methodologies continue to change and evolve making one-to-one comparison challenging.

At the meeting several different methods for studying binding of simple molecules on Au nanoparticles (Au_{13} and Au_{55}) and on Au(321) were compared providing a benchmark of specific methods and of extended solids (Au(321)) and nanoparticles [27] (Fig. 5). The choice of specific functional strongly influence the energy calculated for CO binding to the clusters. Calculations performed using the CCSD(T) method, which were taken as a benchmark, showed that the energetics of CO bound to the Au nanoparticles and Au(321) were essentially identical [27], whereas this is not the case at the PBE level. In related work on Pt nanoparticles (Pt_{55}, Pt_{147}, and Pt_{309}) increasing the coverage of adsorbed O increased the binding energy on a per atom basis, the effect being largest for the largest nanoparticle. This study indicates that cooperative effects, widely studied in surface chemistry experiments, including for O adsorbed on Pt [34].

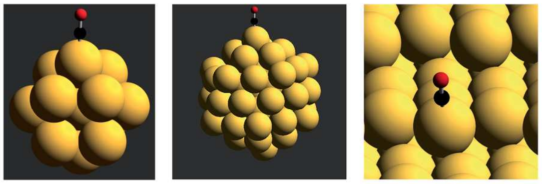

Figure 5: CO adsorbed on a Au(321) surface (right), Au55 (middle) and a Au13 (left) nanoparticle (NP). CO is coordinated to a 6-fold low coordinated Au atom on Au(321), a 6-fold low-coordinated Au atom on Au55 and a 5-fold coordinated Au atom on Au13 [27].

Comparison of theoretical to experimental results is a critical aspect of evaluating the accuracy and validity of calculations. Several useful types of information that can be obtained from experiment and compared to computed values are adsorption energies, bond distances, vibrational frequencies, geometric information (including surface restructuring), and electronic energies, including core level shifts (Table 1).

Table 1: Examples of experimental methods for measuring quantities that can be compared with experiment.

Quantity measured	Experimental available
Adsorption energies	Calorimetry; temperature programmed desorption
Bond distances	Diffraction, EXAFS, imaging methods (STM, and TEM)
Vibrational frequencies	Infrared and Raman Spectroscopy; inelastic neutron scattering
Superstructure	STM
Electronic structure	Photoelectron spectroscopy (UPS and XPS); XANES, Scanning tunneling spectroscopy

Examples of such measurements that were made for catalyst systems were integrated into many presentations. For example, IR was used to probe CO binding to Rh, RhMn and RhMnFe supported on silica [35]. X-ray absorption (XANES and EXAFS) was used to probe the Cu oxidation state and binding in catalyst for phosgene production [36]. Near ambient pressure XPS was used to quantify the Pd oxidation state and binding of CO to PdAu nanoparticles during CO oxidation [37]. These are examples of benchmarks for theory that were presented in the meeting. The opportunity for tight coupling of theory, which can provide insight into the underlying physics and chemistry of particular catalytic behavior, is illustrated by these examples and many examples in the literature.

Designer nanomaterials

The rapid advances in synthesis of designed nanomaterials with complex structure has dramatically changed the ability to produce exotic nanostructures as potential catalysts. Synthesis of various types of nanoparticulate bimetallics illustrate several different synthesis methods, including sol immobilization [38] to yield , microwave-assisted reduction of Au and Pd salts [39] to produce core-shell AuPd particles, vapor deposition onto graphite [37], and galvanic replacement using a series of coiled flow inverter reactors to create hollow bimetallic PdAg nanomaterials [40]. The support materials used also varied in these and other catalysts studied in work presented at the meeting. These examples show the wealth of synthesis methods that can be used to produce "designer" nanomaterials for catalysis.

As new synthetic methods have become available, a major challenge that emerged in the discussion is the need to directly compare the performance of different nanomaterials so as to provide insight into the key characteristics of catalyst materials for specific types of chemical transformations. As discussed for the theoretical studies, benchmarking of the performance of materials for specific types of reactions is necessary.

Benchmarking of catalyst performance is a daunting task that would require agreement on standards and a source of support for curating information made publicly available. The value of standardization has been historically demonstrated. Taking electrochemistry as an example, referencing of specific reduction potentials to a standard—the hydrogen evolution reaction under standard conditions—provides a specific metric for measurements.

Heterogeneous catalysis is more complex because there are many possible reactions that could be used for standardization. A few classes of reactions, such as oxidation or reduction of a simple molecule, by a standardized catalyst made available to the community could be tested at a set of well-defined conditions. Accordingly, new catalysts for specific classes of reactions would be compared against this standard during testing so as to readily evaluate different performance across many different laboratories. This concept has been adopted for a standard supported Au catalyst for oxidation reactions and could be generalized further.

Further advances can potentially be made if details of catalysis synthesis procedures and characterization data were made openly available so that materials can be made and tested in different labs. Overall, the potential value of different synthetic methods for improving reactivity and selectivity and for increasing catalyst lifetime is substantial.

Catalyst evolution

One of the major challenges in heterogeneous catalysis is understanding how to create and maintain the catalyst in a state that optimizes reaction selectivity and activity. Ideally, the active catalyst state would be sustained over a long period of time or at least to be readily activated or regenerated if deactivation occurs.

Meeting this type of challenge requires an understanding of how the catalyst nanomaterials respond to treatment under different conditions after catalysts and prepared. An understanding of how specific treatments during synthesis affect catalyst materials is also required.

These challenges and opportunities were highlighted in the papers presented at the meeting. Catalysts synthesized were generally characterized by a variety of tools, including imaging of structure, spectroscopic determination of composition, and determination of particle size distribution and surface area. These pre-synthesis characterization tools provide a baseline understanding of the materials as synthesized.

The importance of investigating how catalysts evolve during operation was demonstrated by measurement of changes in the lattice constant in Pd catalysts during ethylene hydrogenation [41]using in operando EXAFS and X-ray photoelectron diffraction. The ability to correlate the rate of product formation and consumption of reactants with changes in materials properties provides valuable insight into the state of the actual catalytic material (Fig.6). Such data provide key information about structural changes and their time-scale that are valuable for detailed modeling of reaction kinetics.

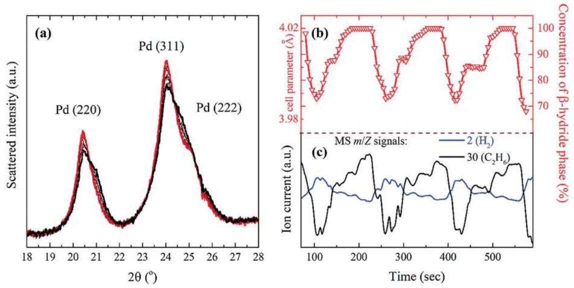

Figure 6: Time resolved, operando XRPD study during the ethylene hydrogenation reaction on a Pd/C catalyst performed under steady state feeding conditions. Panel (a) shows selection of XRPD patterns at significant times evidence of structural changes along the reaction monitored in the 2q range of the most significant Pd Bragg reflections. Panel (b) shows time evolution of the averaged Pd lattice parameter and of the fraction of the b-phase of PdHx left and right ordinate axis, respectively. Panel (c) shows time evolution of the catalyst activity monitored by using MS showing a reactant (H2, m/Z . 2) and a product (C2H6, m/Z . 30) [41].

Insight into catalyst activation and deactivation is also obtained from emerging spectroscopic and imaging methods that monitor changes in composition and structure. For example, using a combination of ambient pressure XPS and environmental transmission electron microscopy (E TEM), we demonstrated that activation of nanoporous $Ag_{0.03}Au_{0.97}$ using treatment with flowing ozone at 150 C induced segregation of the Ag to the surface, forming nanoscale patches of Ag_2O and a film of gold oxide while also removing adventitious carbon from the material [42]. Initial exposure of this oxide to a flowing mixture of methanol and O_2 at the reaction temperature of 170 C removes the oxide via combustion of the methanol, but the Ag remains localized at the surface in nanometer-scale, which is critical for the sustained selective oxidation activity.

The combination of imaging and spectroscopy is extremely powerful in understanding catalyst materials—a point made by the study of ammonia reduction on titania using both TEM and STM, capitalizing on the spectroscopic nature of TEM [43]. As both imaging and spectroscopic tools develop, there is potential for understanding the evolution of catalyst structures “on-the-fly” as measurements are being made. New methods that combine the experimental and theoretical capabilities are being developed [44]to further advance our understanding of structure-activity relationships. For example, recent EXAFS studies that use machine learning methods to interpret the data demonstrate the powerful interplay of computation and experiment [45].

Conclusions and Looking ahead

This Faraday discussion on nanoparticle materials for heterogeneous catalysis underscored the major advances in experiment and theory that have increased understanding of catalytic systems. The discussion also highlighted the need for continued development of methods that will further elucidate major factors in determining catalytic function at the vast, relevant scales of length and time. Looking forward, challenges in developing a unified and standardized approach to evaluating catalysts and computational methods will be critical to future progress. In the future, better integration of theory, computation and experiment have the potential to drive such advances.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

I acknowledge the support received through the Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Award Number DE-SC0012573. I also thank and acknowledge Dr. Challa SSR Kumar for technical and editorial support in preparing this paper.

Notes and references

1 *httpcdn.exxonmobil.commediaglobalfilesoutlook-for-energy-outlook-for-energy.pdf*.
2 E. Worrell, D. Phylipsen, D. Einstein and N. Martin, *Energy use and energy intensity of the U.S. chemical industry*, 2000.
3 L. M. Gilbertson, J. B. Zimmerman, D. L. Plata, J. E. Hutchison and P. T. Anastas, *Chem Soc Rev*, 2015, **44**, 5758–5777.
4 Z. Fan and H. Zhang, *Chem Soc Rev*, 2016, **45**, 63–82.
5 J. De Yoreo, D. Mandrus and L. Soderholm, *Basic Research Needs for Synthesis Science*, 2017.
6 S. Hammes-Schiffer, *Acc. Chem. Res.*, 2017, **50**, 561–566.
7 G. Crabtree, S. Glotzer, B. McCurdy and J. Roberto, *Computational Materials Science and Chemistry: Accelerating Discovery and Innovation through Simulation-Based Engineering and Science*, 2010.
8 M. L. Personick, R. J. Madix and C. M. Friend, *ACS Catal.*, 2016, **7**, 965–985.
9 C. M. Friend and B. Xu, *Acc. Chem. Res.*, 2017, **50**, 517–521.
10 B. Xu, L. Zhou, R. J. Madix and C. M. Friend, *Angewandte Chemie International Edition*, 2010, **49**, 394–398.
11 F. F. Tao and P. A. Crozier, *Chem. Rev.*, 2016, **116**, 3487–3539.
12 J. Dou, Z. Sun, A. A. Opalade, N. Wang, W. Fu and F. F. Tao, *Chem Soc Rev*, 2017, **46**, 2001–2027.
13 B. Xu, R. J. Madix and C. M. Friend, *Chem. Eur. J.*, 2012, **18**, 2313–2318.
14 R. A. van Santen, A. Sengar and E. Steur, *Faraday Discussions*, 2018, **68**, 2337.
15 G. Piccini, M. Alessio and J. Sauer, *Angewandte Chemie International Edition*, 2016, **55**, 5235–5237.
16 Q. Pan, L. Li, S. Shaikhutdinov, Y. Fujimori, M. Hollerer, M. Sterrer and H.-J. Freund, *Faraday Discussions*, 2018, **12**, 79.
17 Y. Pan, N. Nilius, H.-J. Freund, J. Paier, C. Penschke and J. Sauer, *Phys. Rev. Lett.*, 2013, **111**, 206101.
18 A. Chutia, D. J. Willock and C. R. A. Catlow, *Faraday Discussions*, 2018, **16**, 405.
19 Y. Odarchenko, D. J. Martin, T. Arnold and A. M. Beale, *Faraday Discussions*, 2018, **355**, 1399.
20 F. Xu, I. Fampiou, C. O'Connor, S. Karakalos, F. Hiebel, E. Kaxiras, R. J. Madix and C. Friend, *Phys Chem Chem Phys*, 2018, **20**, 2196–2204.
21 F. Hiebel, S. Karakalos, Y. Xu, C. M. Friend and R. J. Madix, *Topics in Catalysis*, 2017, **363**, 706–9.
22 C. Reece, C. M. Friend and R. J. Madix.
23 R. Fushimi and J. Gleaves, *Current Opinion in Chemical Engineering*, 2018, **21**, 10–21.
24 K. Morgan, N. Maguire, R. Fushimi, J. T. Gleaves, A. Goguet, M. P. Harold, E. V. Kondratenko, U. Menon, Y. Schuurman and G. S. Yablonsky, *Catalysis Science & Technology*, 2017, **7**, 2416–2439.
25 D. Yang, P. Xu, E. Guan, N. D. Browning and B. C. Gates, *Journal of Catalysis*, 2016, **338**, 12–20.
26 A. Cadi-Essadek, A. Roldan and N. H. de Leeuw, *Faraday Discussions*, 2018, **23**, 43.
27 W. Dononelli and T. Klüner, *Faraday Discussions*, 2018, **50**, 10064.
28 I. Demiroglu, T. Fan, Z. Li, J. Yuan, T. Liu, L. Piccolo and R. L. Johnston, *eprints.whiterose.ac.uk*.
29 J. Hermann, R. A. DiStasio Jr and A. Tkatchenko, *Chem. Rev.*, 2017, **117**, 4714–4758.
30 A. Jain, Y. Shin and K. A. Persson, *Nature Reviews Materials 2016 1:1*, 2016, **1**, 15004.

31 B. Himmetoglu, A. Floris, S. de Gironcoli and M. Cococcioni, *International Journal of Quantum Chemistry*, 2013, **114**, 14–49.
32 D. Vinichenko, M. G. Sensoy, C. M. Friend and E. Kaxiras, *Phys. Rev. B*, 2017, **95**, 235310.
33 L. G. Verga, J. Aarons, M. Sarwar, D. Thompsett, A. E. Russell and C. K. Skylaris, *Faraday Discussions*, 2018, **116**, 3594.
34 M. Berdau, G. G. Yelenin, A. Karpowicz, M. Ehsasi, K. Christmann and J. H. Block, *J Chem Phys*, 1999, **110**, 11551–11573.
35 M. Dimitrakopoulou, X. Huang, J. Kröhnert, D. Teschner, S. Praetz, C. Schlesiger, W. Malzer, C. Janke, E. Schwab, F. Rosowski, H. Kaiser, S. Schunk, R. Schlögl and A. Trunschke, *Faraday Discussions*, 2018, **46**, 1358.
36 S. Guan, P. R. Davies, E. K. Gibson, D. Lennon, G. E. Rossi, J. M. Winfield, J. Callison, P. P. Wells and D. J. Willock, *Faraday Discussions*, 2018, **12**, 3824.
37 A. V. Bukhtiyarov, I. P. Prosvirin, A. A. Saraev, A. Y. Klyushin, A. Knop-Gericke and V. I. Bukhtiyarov, *Faraday Discussions*, 2018, **109**, 18535.
38 L. Prati, A. Villa, A. Jouve, A. Beck, C. Evangelisti and A. Savara, *Faraday Discussions*, 2018, **96**, 292.
39 A. G. R. Howe, P. J. Miedziak, D. J. Morgan, Q. He, P. Strasser and J. K. Edwards, *Faraday Discussions*, 2018, **244**, 113.
40 L. Torrente Murciano, K. Wu and Y. Gao, 2018.
41 A. L. Bugaev, O. A. Usoltsev, A. Lazzarini, K. A. Lomachenko, A. A. Guda, R. Pellegrini, M. Carosso, J. G. Vitillo, E. Groppo, J. A. van Bokhoven, A. V. Soldatov and C. Lamberti, *Faraday Discussions*, 2018, **173**, 185.
42 B. Zugic, L. Wang, C. Heine, D. N. Zakharov, B. A. J. Lechner, E. A. Stach, J. Biener, M. Salmeron, R. J. Madix and C. M. Friend, *Nature Materials*, 2017, **16**, 558–564.
43 M. Ek, I. Beinik, A. Bruix, S. Wendt, J. V. Lauritsen and S. Helveg, *Faraday Discussions*, 2018, **116**, 3487.
44 A. Belkacem, C. M. Friend and Y. Zhu, *Basic Research Needs for Innovation and Discovery of Transformative Experimental Tools*, 2017.
45 J. Timoshenko, D. Lu, Y. Lin and A. I. Frenkel, *J. Phys. Chem. Lett.*, 2017, **8**, 5091–5098.