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# Progress toward Design of Solid Catalysts

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## Abstract

The 2016 Faraday Discussion on the topic “Designing new Heterogeneous Catalysts” brought together a group of scientists and engineers to address forefront topics in catalysis and the challenge of catalyst design—which is daunting because of the intrinsic nonuniformity of the surfaces of catalytic materials. “Catalyst design” has taken on a pragmatic meaning which implies the discovery of new and better catalysts on the basis of fundamental understanding of catalyst structure and performance. The presentations and discussion at the meeting illustrate rapid progress in this understanding linked with improvements in spectroscopy, microscopy, theory, and catalyst performance testing. The following essay includes a statement of recurrent themes in the discussion and examples of forefront science that evidences progress toward catalyst design.

## Catalysis and catalyst design

Catalysis is the key to control of chemical change, in processes ranging from the biological to the technological. It is used to make products including chemicals, fuels, materials, food, beverages, and personal care products, and together these have a value of roughly 5–10 trillion dollars (US) per year worldwide. Catalysis is also essential for the removal of environmental pollutants such as those generated in motor vehicles and fossil fuel-fired power plants. Thus, the science underlying catalytic technology is essential.

Catalysis science is also challenging, because almost all large-scale industrial catalysts are solids. These work at their surfaces—and these surfaces are notoriously nonuniform in both composition and structure, often being substantially different from simple terminations of the bulk material—and they undergo changes when exposed reactants.

The 2016 Faraday Discussion “Designing new Heterogeneous Catalysts” attracted a full house of researchers and practitioners, eliciting novel contributions and stimulating discussion that brought forth a diversity of ideas about what the terms “catalyst design” and “heterogeneous” mean; we address these points below.

Avelino Corma opened the Discussion, introducing the subject with a few history lessons and a linked set of case studies recounting a family of new catalysts based on insights guided by the emerging understanding of supported metal catalysts—this introductory lecture provided a basis for assessing the premise of catalyst design and the Discussants’ efforts to home in on the meaning of this term.

The history of catalyst discovery reflects the complexity of the typical catalyst surface and of the reactions that occur on it as well as the enormous array of materials that can be considered candidate catalysts. The original approach to catalyst discovery was trial and error experimentation, and it is linked to the alchemists’ search for the philosopher’s stone and their early discoveries of “contacts” which today we would call solid catalysts. The work of Fritz Haber, Carl Bosch, and Alwin Mittasch more than a hundred years ago stands as the monument to the trial-and-error approach to catalyst discovery; their work at BASF involved

the systematic testing of some 20,000 materials as catalysts for the synthesis of ammonia from  $H_2$  and  $N_2$ , with the resulting iron-containing catalyst being only little different from today's technological ammonia synthesis catalysts. These pioneers worked from the emerging principles of chemical equilibrium, chemical kinetics, and process engineering, guiding them to optimal testing. They realized the need to evaluate candidate catalysts in reactors and under conditions that mimic a potential process—thus, they used high pressures (to favor the equilibrium for ammonia formation), recycle of unconverted  $H_2$  and  $N_2$  in a continuous process for efficient use of these raw materials, and long-term testing of catalysts in operation to evaluate their lifetimes. They found a highly active and stable catalyst, a porous iron-containing mineral with a high internal surface area, and the high catalytic activity allowed operation at relatively low temperatures, favoring the equilibrium of the exothermic ammonia synthesis reaction, maximizing the conversion, minimizing the recycle of unconverted reactants, and pointing toward optimization of the process.

The trial-and-error approach is still widely practiced in technology, and it will not go away soon, because the catalyst design challenge is enormous. But catalyst testing technology has advanced markedly since the Haber-Bosch-Mittasch discoveries, and advances in catalyst testing methodology keep improving, with many highly automated rapid-throughput test systems now in operation worldwide, many of them operating on quite a small scale.

Most important for this essay, and reflecting the give and take of the Faraday Discussion, the science of surface catalysis has advanced markedly since Haber's day. An historically important example illustrating how fundamental understanding guided catalyst discovery was introduced by Corma to start the Discussion. The prototypical process is petroleum naphtha reforming, which emerged more than 50 years ago in work by Vladimir Haensel and coworkers at UOP.<sup>1</sup> Major goals were to increase the octane numbers of hydrocarbons in fuels such as petrol (gasoline). We can describe the reasoning that led to a breakthrough catalyst and a novel process as emerging from the inventors' recognition of *catalyst functions*—they realized that hydrogenation and dehydrogenation reactions are essential in the naphtha reforming process and are catalyzed by the surfaces of metals (e.g., nickel, palladium, platinum) and that reactions that lead to octane number increases result from increased branching of hydrocarbons such as olefins—which are known to be catalyzed by strong acids, which protonate the olefins to give reactive intermediates (carbocations) that readily undergo skeletal isomerization.

A practical goal was thus to increase the branching of paraffins (principal components of naphtha) to increase their octane numbers, and a route to this branching involves (1) a catalyst that dehydrogenates the paraffin on a metal surface, to give olefins, which are (2) isomerized by the acid catalyst and then (3) rehydrogenated on the metal surface. Seeing the value of having a high catalyst surface area per unit volume for high reaction rates per unit volume, Haensel and coworkers saw the value of having their metal dispersed finely as small particles (nanoparticles) to give a high metal surface area and to place these particles directly on a porous acidic support, so that the products of the initial metal-catalyzed dehydrogenation immediately migrate to the nearby acidic sites, where isomerization occurs, allowing the ensuing branched product in turn to move quickly to the metal for the final step of rehydrogenation.

Sterba and Haensel<sup>1</sup> selected transition aluminas as their catalyst supports, because these are inexpensive and can be prepared as porous materials with high internal surface areas. Knowing that the acid had to be strong and that aluminum chloride (in the presence of water)

is a strong Brønsted acid, they treated their support to convert it to a surface chloride to increase its acid strength and its catalytic activity for isomerization. The resulting catalyst consisted of metal nanoparticles on the support, and it is called a *bifunctional catalyst*, because the metal function gives the olefin from the paraffin, the acid function gives the branched olefin from the unbranched olefin, and the metal function gives the branched (high-octane-number) paraffin from the branched olefin. Because the equilibrium limitation allows the formation of only little olefin under the processing conditions, the olefin has to be transported efficiently to the metal to drain it away and speed up the overall reaction, and so the two functions have to be located close to each other on the catalyst surface and the metal particles need to be small.

The optimal metal was found to be platinum, and catalyst performance testing showed it to offer not only the expected hydrogenation/dehydrogenation activity but also high activity for dehydrocyclization reactions to give aromatic compounds such as benzene and toluene formed from *n*-hexane and *n*-heptane, respectively. These aromatic compounds have high octane numbers and were considered good fuel components (but they are minimized in applications today because they are carcinogenic).

The bifunctional catalyst was discovered substantially on the basis of early catalyst design principles—understanding of what combination of catalyst functions was needed and what kinds of materials provided them. Subsequent work in various industrial organizations, again mostly done by trial-and-error, led to better catalysts that contain not just platinum in the supported particles, but a combination of platinum with another metal, rhenium or tin.

Today, researchers seeking better catalysts have far better tools for characterization of catalysts and surface reactions than were available half a century ago. Corma illustrated the thought processes that led his research group to new, markedly improved catalysts for selective reduction of nitroaromatic compounds, as described in the following section. His methodology leads us toward an understanding of how to approach the idea of catalyst design in a realistic and nuanced way.

### **Corma's case studies of supported metal catalysts for selective reduction of nitroaromatic compounds: toward a working definition of catalyst design**

Only rather little of what was presented at the Faraday Discussion could be described as direct first-principles design of catalysts. Nonetheless, the theme of catalyst design was widely evident implicitly, and the Discussion on more than one occasion got to the point of addressing how the term “catalyst design” should be interpreted when we are far from having the capability of using first principles to determine the catalyst structure needed for a given conversion—and then to synthesize the catalyst.

The case studies that provide our foundation are the work of Serna and Corma, and a recently published perspective<sup>2</sup> by these authors provides a summary of nearly a decade's work. Our purpose here is to highlight the thought processes of these researchers, link them to the aforementioned work by Haensel, and use them as a basis for a functional interpretation of “catalyst design.”

Recognizing the potential value of catalysts to selectively hydrogenate nitro groups in compounds with other groups that react with H<sub>2</sub>, such as olefinic groups, Serna and Corma investigated supported gold catalysts, working from the discovery that gold nanoclusters

supported on TiO<sub>2</sub> are selective catalysts for the hydrogenation of nitrobenzene to give aniline and for the hydrogenation nitrobenzenes substituted with groups such as C=C to give anilines substituted with these groups.

Part of the foundation of the work of Serna and Corma was measurement of product distributions and the inference of reaction networks in their conversions. They also used infrared spectroscopy to identify surface reaction intermediates, including nitrosobenzene, which could participate in condensation reactions and give products other than the desired substituted anilines. The authors also worked from a hypothesis advanced by several authors working with supported gold catalysts—that the gold-support interface can play an important role in the catalysis. Serna and Corma used density functional theory to show that the nitrobenzene hydrogenation reaction is favored at this gold–TiO<sub>2</sub> interface rather than on just the gold surface, and their infrared spectra showed that the interaction of nitrobenzene with the gold–TiO<sub>2</sub> interface is strong and hinders the adsorption of other molecules incorporating C=C bonds, in contrast to the situation when the support is SiO<sub>2</sub>.

These results pointed to the benefit of small gold particles on TiO<sub>2</sub>, maximizing the gold–support interface. Measurements of the kinetics of the hydrogenation reaction with such catalysts further showed that the gold particle size influenced the rate and led the authors to the further inference that the rate depended on the density of low-coordinated gold sites—which they quantified by using infrared spectroscopy of CO molecules as probes of the surface. Measuring the activities of the catalysts for HD exchange in the reaction of H<sub>2</sub> with D<sub>2</sub>, they found (consistent with their kinetics of the hydrogenation of nitrobenzene) that the activity for H<sub>2</sub> dissociation increased with the number of low-coordinated gold sites, and their kinetics of the nitrobenzene conversion pointed to H<sub>2</sub> dissociation as the rate-determining step.

Thus, Serna and Corma inferred that they could further increase the activity of their catalyst by boosting the rate of H<sub>2</sub> dissociation. Realizing that platinum is highly active for this reaction, they modified their catalyst by incorporating platinum—choosing a platinum content small enough (50–2000 ppm) to increase the rate of the desired reaction without substantially lowering the selectivity. They also observed that just platinum (without gold) supported on TiO<sub>2</sub> was not active, and so inferred that their platinum-containing gold catalyst was *bifunctional* (this reasoning connects their work to that of Haensel, mentioned above).

The authors further evaluated their improved catalyst in experiments with liquid-phase reactants under conditions (with and without solvent) that might be representative of potential applications, finding that it worked for more than about 1350 turnovers without substantial deactivation.

Further work by these authors led to yet a new generation of catalyst for the selective hydrogenation of substituted nitrobenzenes. Serna and Corma reasoned how to transform highly active but usually unselective metals exemplified by platinum into highly selective catalysts. Testing supported platinum particles as catalysts and probing their surfaces with CO and using infrared spectroscopy, they found that the selectivity for reduction of nitro groups benefited from minimizing the number of terrace sites on the platinum particles—achieved by minimizing the platinum particle size. A similar benefit was observed by adsorption of thiol ligands or partial decoration of the platinum surface by TiO<sub>x</sub> species from the support to cover these terrace sites (the coverage by fragments of the support is linked to the idea of so-

called strong metal-support interactions (SMSI)). Other species were used comparably to decorate the metal surface, and the ideas were extended to metals other than platinum.

The foregoing summary is simplified but sufficient to illustrate how a family of increasingly selective and active catalysts resulted from the following:

- elucidation of catalyst performance (reaction network elucidation; reaction kinetics determination, including elucidation of activity for H<sub>2</sub> activation with the simple test reaction H<sub>2</sub> + D<sub>2</sub> → 2HD);
- elucidation of the role of a support as not just an inert platform but rather a catalyst component that works in concert with the metal particles on it;
- extension of the idea of the support's role to recognize that support-derived species, among others, present as metal surface modifiers, work in similar ways;
- use of CO as a probe molecule to identify metal surface sites;
- use of theory in combination with experiment;
- catalyst testing under potentially applicable conditions to demonstrate satisfactory behavior in long-term operation.

The idea of catalyst functions (metal, support, second metal) enters into the reasoning and the terminology used by Serna and Corma. But an essential point for us is that their depth of reasoning and access to data providing fundamental insight into the workings of the catalysts go far beyond those illustrated by Haensel's work, reflecting marked advances in the tools for understanding catalysts that have emerged in the intervening decades.

The work of Serna and Corma set the table for this Faraday Discussion because it is exemplary in its thoroughness and integration of numerous techniques and thought processes; the inferences in their reasoning leading them to better and better catalysts (including new ones that we have not addressed here) and their assembly of the information illustrate how we should think of catalyst design today. Fundamental understanding guided these researchers to hypotheses that they tested with a battery of complementary methods and then—step by step—to the synthesis of a family of improved catalysts.

A key result—quite generally valid—is that as Serna and Corma made better catalysts, they made catalysts that were more complex in composition and structure. Oversimplifying some, we can say that the recognition of and the incorporation of more functions led to better catalysts. Again, there is a parallel with the Haensel example of naphtha reforming. And this pattern is the rule in industrial catalysis: for the most part, as catalysts are improved they become more complex in composition and structure.

Thus, it is fundamental understanding of catalysts and their functions, understanding of the roles of the various catalyst components, that provides a path toward new and better catalysts. We could call this statement a functional definition of catalyst design. A number of contributions to the Faraday Discussion illustrate the point, and we present some examples below to illustrate it, as well as some recurring themes. Keep in mind that the Discussion was based on single original research contributions and did not represent longer-term advances such as those summarized in the preceding paragraphs.

## **Recurring themes of the Discussion**

A number of themes recurred in the Discussion, including the following:

- catalyst preparation, especially of catalysts incorporating regular structures;
- multitechnique catalyst characterization, by experiment and theory;
- determination of crystalline structures in catalysts;
- characterization of catalysts by methods that have their roots in ultrahigh vacuum single-crystal surface science;
- investigation of atomic architectures of catalysts, with a focus on active sites;
- investigation of supported metal particle catalysts, with some focus on bimetallic particles with core-shell structures;
- attention to defect sites on surfaces and interactions of supported species such as metal clusters with these sites.

#### *Preparation of supported metal catalysts with beams of metal clusters*

A novel cluster beam route to the preparation of model supported metal catalysts was shown to be applicable to the production of much larger amounts (grams per hour) of catalysts than had been available by comparable methods, and even powder samples could be formed.<sup>3</sup> This new methodology opens the door to large-scale preparation of supported metal catalysts, even bimetallics, without the complications of metal salts or the expense of organometallics, and it might be expected to provide a boost to research in this important area. But the methods do not lend themselves to preparation of metals supported uniformly in porous supports.

#### *Synthesis and characterization of crystalline porous catalysts*

Catalyst preparations focused on materials with regular porous structures, including metal nodes connected by organic linkers in metal organic frameworks (MOFs)<sup>4</sup> and Keggin ions with inorganic linkers creating matrices for redox catalysis.<sup>5</sup> These frameworks consist of cationic and anionic components, and the composition of each can be tuned to incorporate various catalytic species (the materials can be catalyst supports). The inorganic materials in this class offer better prospects in terms of stability than the MOFs, but recent work has shown that some MOFs are stable at temperatures up to about 650 K, and MOFs are drawing rapidly increasing attention as catalysts with tailorable properties; there are opportunities for design of both catalyst physical properties (such as porosity) and chemical properties by choice of the node and linker components. These crystalline porous materials also offer intriguing prospects as catalysts and catalyst supports, and the literature is indicating a rapidly growing interest in them.

#### *Catalyst synthesis with guidance by theory and spectroscopy*

Many groups now use theoretical tools, and collaborations of experimentalists with theorists have become the norm. It is too early for theory to predict activation barriers of reactions (and rates of reactions) that are accurate within better than a couple of orders of magnitude, but the quantitative limitations of theory are not the essential point: theory is widely accepted for the guidance it provides in uncovering trends and in providing frameworks for researchers to think about how catalysts work and to try to make better ones. Thus, theory plays a central role in catalyst design as we understand the term and seems destined to play a greater role as the computations get faster and the theories become more accurate.

But when catalysts are as complex structurally as the typical industrial solid catalysts, experiment still provides more useful guidance than theory. For example, manganese tungstate catalysts for selective oxidation of short-chain alkanes prepared by Li et al.<sup>6</sup> were intended to have a balance of acid-base and redox sites. Preparation of these catalysts was guided by Raman spectra recorded during the synthesis, as well as high-resolution transmission electron microscopy and field emission scanning electron microscopy images, X-ray diffraction data, X-ray photoelectron spectra, and porosity data characterizing the resulting materials. The data allowed some rationalization of the synthesis chemistry and some hypotheses about the nature of the catalytic sites, but the complexity of the materials and the presence of defect sites, notwithstanding the presence of some pure phases, limited the understanding of the surface species to hypotheses that are no doubt simplified. This work demonstrates the magnitude of the challenge of catalyst design even when powerful arrays of techniques are available to characterize the syntheses and the properties of the resulting materials.

### *Catalyst characterization by X-ray diffraction, spectroscopy, and imaging*

The presentations included many characterization results determined by X-ray diffraction crystallography, pointing to the fact that many of the reported catalysts incorporated (portions of) crystalline material. Commonly reported surface characterization methods were X-ray photoelectron spectroscopy and the workhorse infrared spectroscopy, continuing long-established trends. Raman spectroscopy was also much in evidence, suggesting that this technique is on the upswing in catalysis research.

Imaging methods, some of them quite novel in catalysis research,<sup>7,8</sup> were also used widely in the work reported at the Faraday Discussion, and these included characterization of zeolite-containing cracking catalysts investigated on the scale of microns. Important components of industrial catalysts for hydrocarbon cracking in the manufacture of petrol incorporate binders and amorphous components in addition to zeolite crystallites, and results presented at the Faraday Discussion demonstrate their high degrees heterogeneity—on the scale of microns—perhaps a surprising result in view of the enormous scale of application of cracking catalysts.

High-resolution electron microscopy was also widely applied in the work reported at the Discussion. This has become a workhorse technique and is evidently widely accessible. It was frequently used to provide evidence of bulk phases present in catalysts, but rarely to provide evidence of individual atoms in catalysts, although the recent literature indicates that numerous groups now have the capability of imaging individual heavy metal atoms on supports consisting of light atoms—because the contrast is maximized when the atomic numbers of the supported atoms and those of the support are far different from each other. This capability has triggered a surge of research in single-site supported metal catalysts, commented on further below.

### *Catalyst characterization by techniques with a foundation in ultrahigh vacuum single-crystal surface science*

Another theme in the Discussion was the application of experimental methods that have emerged from the foundation of classic ultrahigh vacuum surface science. It was evident from the Discussion how much this science has evolved since its beginnings in investigations of single crystals of metal more than half a century ago; researchers now routinely investigate structurally complex materials such as metal particles on thin oxide films mounted on single

metal crystals, which are good electrical conductors and facilitate experimentation with UHV spectroscopies. Experiments done with such samples are providing insight into how the underlying support (substrate) can influence the electronic properties of the metal particle and thus its reactivity and catalytic character.

Thus, O'Brien et al.<sup>9</sup> prepared thin films of MgO(111) on Ag(100) crystals and formed nanoparticles of gold on the MgO surface, investigating the samples under UHV conditions with low-energy electron diffraction, X-ray photoelectron spectroscopy, infrared spectroscopy, and scanning tunneling microscopy. They found that charge transfer through the MgO film markedly affected the chemistry of the gold and species adsorbed on it. When the gold was present as small, essentially two-dimensional clusters, CO<sub>2</sub> adsorbed at the gold edges (the metal–support interface—see the summary above of the Serna-Corma work), reacting to form oxalate species. But when the temperature of the sample was raised to 500 K, the gold morphology changed markedly, resulting in three-dimensional particles, which were not reactive with CO<sub>2</sub>. Electron transfer from the underlying silver was inferred to have facilitated the morphological change and thus the marked change in reactivity of the gold. These results indicate a strong influence of the support that is important in catalysis broadly, and well-defined model catalysts were needed to elucidate the phenomena.

A link between UHV surface science measurements and those made with high-area porous catalysts was also illustrated by the work of Wang et al.<sup>10</sup> These investigators carried out kinetics experiments with a TAP (temporal analysis of products) reactor to infer that atomic oxygen is an intermediate in the catalytic oxidation of methanol to formaldehyde (but not the oxidation of CO) taking place on porous catalysts consisting of silver and gold. The same research group had earlier found evidence of such intermediates on single-crystal gold by using classic UHV surface science methodology.<sup>11</sup> The link between the flow reactor experiments with a porous catalyst and results of UHV experiments with single crystals is noteworthy—and uncommon—such connections are not general because the reactive surface species that are important in catalysis are often not stable enough to survive under UHV conditions.

Both the O'Brien and Wang examples illustrate how single-crystal surface science has evolved since its inception and how the methods of that science continue to provide fundamental insights into the workings of more complex (heterogeneous) catalysts.

#### *Catalytic sites and their characterization by theory*

A number of contributions were also directed to the dominant class of crystalline porous catalysts, zeolites. With their regular structures, these materials attracted the attention of theorists, extending a tradition of investigations of zeolite deprotonation energies, with evidence of how the deprotonation energy varies from a two- to a three-dimensional material<sup>12</sup> and how framework topology and Brønsted site location affect key steps initiating processes such as the industrially important conversion of methanol to olefins.<sup>13</sup>

Some work involved calculations based on theory to elucidate the role of individual catalytic sites on surfaces, which were, however, represented in a simplified way as periodic slabs without account taken of the electrolyte present during catalysis.<sup>14</sup> The catalyst sites incorporated reactive oxo groups with various degrees of coordination by cobalt cations corresponding to three different terminations of Co<sub>3</sub>O<sub>4</sub>. These were investigated for catalysis of the oxygen evolution reaction whereby two molecules of water are oxidized to give O<sub>2</sub>

with generation of electrons for the photocatalytic or electrocatalytic production of transportation fuels by the reduction of water or carbon dioxide. The calculated results led Plaisance et al.<sup>14</sup> to a statement of design principles for the optimal catalyst for the oxygen evolution reaction at a given overpotential (this was shown to be the rate determining step). This was a timely topic for the Faraday Discussion because it deals with specific, realistically represented catalytic sites, an important reaction, and an application of theory that leads to a clearly articulated statement of a design principle for the reaction investigated.

### **Confronting structures of highly heterogeneous catalysts**

Except for the relatively regular crystalline catalysts exemplified by zeolites, MOFs, and linked Keggin ions, almost all of the catalysts reported in the Discussion were heterogeneous to a substantial degree, and some were highly heterogeneous. Attempts to resolve the heterogeneity involved laborious characterization by multiple complementary techniques. The approach is illustrated by the work of Maganas et al.,<sup>15</sup> whose supported catalysts (represented in a simplified way as VO<sub>x</sub>/SBA-15) were characterized by Raman and X-ray absorption spectroscopies and theory, and by comparisons with molecular catalysts. The results led to hypotheses about the key surface species; the work illustrates the magnitude of the challenge of structural elucidation of complex solid catalysts.

### **Themes seldom stated in the Faraday Discussion**

#### *Amorphous catalysts*

Many of the catalysts prepared in the work described at this Discussion are rather complex materials, but, remarkably, most of them are to a degree crystalline, notwithstanding the importance of amorphous materials in practical catalysis—exemplified by the transition aluminas, such as those investigated by Haensel. But understanding of the details of structure of amorphous solids still severely lags the understanding of details of the structures of crystalline materials. Thus, the emphasis on crystalline materials in the work presented at the Faraday Discussion reflects a tendency of researchers to go where the established techniques allow progress, rather than to attack the most challenging catalysts and reactions.

#### *Industrial catalysts and catalysis*

Except for work with technological catalysts for hydrocarbon cracking, there was scant mention of industrial catalysts, consistent with the reality that design of such catalysts is for the most part not quite realistic. The work on the cracking catalysts made clear that they are highly heterogeneous and raised questions about whether preparations to decrease the degree of heterogeneity—likely requiring greater expense—might bring practical benefits. There is a lack of information to address this question.

There was correspondingly a lack of input into the meeting regarding catalyst deactivation; often catalyst stability is crucial to economic application, and it is not surprising that this topic was largely missing. The whole notion of designing catalysts for increased stability is largely untouched.

#### *Catalysts for new and emerging processes*

There was little said at the Discussion regarding processes for conversion of natural gas, although these have grown markedly in importance recently with the advent of low-cost natural gas in some parts of the world, especially North America. This inexpensive gas has abruptly changed the emphases in catalytic practice and catalysis research in ways that point to opportunities for future Faraday Discussions.

Catalytic biomass conversion was also largely missing from this Discussion. Growth of this field has slowed after a massive surge, as the field is faced with challenging economics and an uncertain future in terms of the commitment of public subsidies to make processes realistic. It is another highly active area of catalysis research and worthy of attention in future Discussions, and the question looms about whether we may envision a sustainable future fuels industry without massive applications of biofuels.

#### *Characterization of catalysts in the working state and novel applications of catalytic reactors*

Characterization of catalysts while they are functioning provides the best opportunities to distinguish the surface species that are engaged in catalysis rather than being bystanders, although the heterogeneity of surfaces and the possible minority status of the catalytically relevant species mean that even this depth of characterization is often insufficient. The catalysis research community has made great strides in adapting spectroscopic and other measurement techniques to catalysts in reactive atmospheres and in operation, often in flow reactors. Examples of the spectroscopies used for working catalysts are infrared, Raman, ultraviolet-visible, electron paramagnetic resonance, X-ray absorption, and Mössbauer.

#### *Catalysts to which the term “design” might most accurately apply*

The complexity and heterogeneity of most solid catalysts make the challenge of true design daunting, but there are catalysts that are simple enough in structure that the idea of design takes on significant meaning. Catalysts in this class that are being intensely investigated today are so-called supported “single-site” catalysts.<sup>16,17</sup> These typically consist of isolated metal cations on the surfaces of oxide, zeolite, and MOF supports, and the recent advent of atomic-resolution scanning transmission electron microscopy has led to reports from numerous groups showing these cations, especially when the metals have high atomic numbers and the supports consist of atoms with low atomic numbers, so that the contrast between the supported metals and the support is maximized. An example of catalysts in this class are the cobalt oxide catalysts described in the Discussion by Plaisance et al.,<sup>14</sup> but the cobalt was too low in atomic number to facilitate atomic-resolution imaging.

One can formulate a list of design variables for single-metal-atom complexes on supports that are crystalline (e.g., zeolites and MOFs). These include the metal, the metal nuclearity (number of metal atoms in the catalytic sites), support, and other ligands on the metal.<sup>17</sup> Such catalysts can be synthesized by reactions of organometallic precursors with support surfaces, and when the chemistry is precise, the result is essentially molecular species bonded to the support by metal–oxygen bonds. Such catalysts when synthesized precisely are much less heterogeneous than the typical solid catalyst and provide quite some legitimacy to the notion of catalyst design.

## **Conclusions**

“Heterogeneous” is a term that describes essentially all solid catalysts, and the degrees of nonuniformity are often pronounced and provide daunting challenges to detailed structure characterization, let alone design from first principles. Consequently, the term “catalyst design” has taken on a pragmatic meaning which implies the discovery of new and better catalysts on the basis of fundamental understanding of catalyst structure and performance, often including a recognition of specific catalyst components and structural features that perform specific functions, such as bonding to one reactant molecule strongly to the exclusion of other potential reactant molecules, bonding of reactant molecules to more than one feature of a surface, and recognition of which surface compositions (e.g., of one metal vs. another) provide optimal activity of selectivity for a given reaction. Fundamental understanding of catalysis has advanced rapidly as catalyst characterization methods have improved, and especially significant are experiments with complementary spectroscopy, microscopy, and catalyst testing linked with theory; particular benefits are associated with spectroscopic investigations of catalyst surfaces in the functioning state and with density functional theory representing surface catalytic sites that are identified spectroscopically and have a relatively high degree of uniformity. It is these scientific advances that have gradually made the notion of catalyst design more and more a reality.

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