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## **INTRODUCTION**

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Heterogeneous catalytic transformations are responsible for improving the quality of our everyday life. Whether it is the ready availability of food and clothing, clean fuel for our cars, or new devices for energy conversion and storage, it is the catalytic process that makes possible the lifestyle that we all enjoy today. These capabilities are the result of more than a century of research, development, and application of heterogeneous catalytic materials and processes. Our society now faces grand challenges in energy sustainability. Heterogeneous catalysis again is at the forefront of new processes to harvest energy and convert it. Emergent areas of need and opportunity include but are not limited to conversion of nonedible biomass and natural gas to fuel molecules through thermal catalysis, the harvesting of solar energy to generate solar fuels through photocatalysis, and the conversion of chemical fuels such as hydrogen or methanol to electricity through electrocatalysis. These catalytic processes occur at solid-gas, solid-liquid, or even three-phase boundaries, as at an electrode-electrolyte-gas interface, and the efficiency of these energy harvesting and conversion processes is largely determined by catalytic performance at these interfaces. Because many of these desired energy-related conversions

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INTRODUCTION

and harvestings are new and in many cases yet to be discovered, a summary of fundamental insights and understanding of those processes is critical to progress.

A catalytic event is envisioned to occur at a catalytic "site" [1, 2]. A catalytic site consists of one or many atoms arranged into a particular configuration that provides an ideal electronic structure and geometric environment for facilitating the event. A commercial catalyst is typically heterogeneous from macroscopic to microscopic length scales. It can consist of catalytic particles of different shapes and sizes of dimensions from less than 1 to more than 100 nm, most often supported on other particles or materials that provide structural integrity and access to the active sites. In an industrial catalyst, each particle can have a different composition, and this composition can vary from the bulk to the surface. Further, these compositions can be a strong function of the reactive environment. This diversity in structure and composition makes fundamental interrogation of catalytic events on a commercial catalyst at the level of a catalytic site quite challenging. To gain fundamental understanding of catalytic reactions at this microscopic level, a practical strategy is to employ model catalysts. These models can range from materials of a composition simpler than commercial materials all the way to catalytically active single crystals with well-defined surface structures. Extensive experiments in the last four decades on model systems have revealed precious insights into the chemistry and physics of heterogeneous catalysis. However, there are some limitations of these models. For instance, a single-crystal model catalyst presents a limited interfacial surface area, which can make the detection of reaction products over such a model catalyst challenging. Nanocatalysts of well-defined size, shape, and composition provide a further step forward in terms of a closer representation of practical catalysts and better access to questions about the impact of structural and compositional factors on their catalytic performances.

The science of nanocatalysis is enabled by the ability to synthesize nanoparticles of well-controlled shape, size, and composition. To explore how structural factors impact catalytic performance, we need to decouple these interacting structural and compositional factors of an industrial catalyst through chemical synthesis [3–12]. For example, to explore potential surface-structure-dependent catalytic activity or selectivity we could keep the size and composition of nanoparticles of a catalyst the same but vary shape of a catalyst. The surface structure of a catalyst with a different shape can be varied through chemical synthesis [13–17]. Chapter 2 reviews the control of nanocatalyst structural parameters through chemical synthesis by which shape, composition, and nanostructure can be controlled. In this chapter, the fundamental mechanisms of growth of metal nanoparticles are introduced. Controlled syntheses of intermetallic nanocatalysts, nanostructured catalyst particles, and coreshell nanoparticles are reviewed.

Colloidal synthesis offers an elegant approach to manipulate the structure of a crystallographic surface, size, and composition of nanocatalysts. The surface of a  $2 \times 2$  nm nanoparticle or larger likely presents multiple combinations of catalyst atoms packed with different distances and relative orientations. The occurrence of nonhomogeneous catalytic sites on larger surfaces may decrease catalytic selectivity by opening undesired reaction pathways. An alternative strategy is to synthesize a

catalyst anchoring singly dispersed metal atoms on a given substrate [18–21]. Charge transfer between singly dispersed metal atoms and their nonmetallic substrates can tune the adsorption energy of reactant molecules [21] and thus potentially vary the activation barrier of a catalytic reaction. For example, the formation of a singly dispersed Pt atom bonded to oxygen atoms of FeO<sub>x</sub> substrate (Pt<sub>1</sub>-O<sub>n</sub>-Fe<sub>m</sub>, n is the number of Pt-O bonds) has been shown to exhibit high CO oxidation activity [18]. However, achieving singly dispersed catalytic sites on a substrate through chemical synthesis is quite challenging. Alternatively, subnanometer metal clusters with a specific number of atoms [22, 23] can be prepared through physical methods including thermal vaporization, laser ablation, and magnetron and arc cluster ion deposition techniques. These physical methods can produce clusters with a specific number of atoms on a given substrate. The ability to vary the number of atoms of a cluster offers the opportunity to study site-specific catalyses. Chapter 3 summarizes these physical approaches to the preparation of size-specific catalysts (M<sub>n</sub>, n = 1-20), including a discussion of methods and cluster sources.

Catalyst characterization is the primary window through which to obtain insights into structure and mechanism. Characterization of a catalytic site demands methods with fidelity at the nanoscale or smaller. It is particularly challenging to achieve this level of detail in the presence of a real reaction mixture at actual catalytic temperatures, and thus the first tier of analysis is often carried out *ex situ*, or outside of this environment. Spectroscopic and microscopic analysis carried out *ex situ* under ultrahigh vacuum (UHV) allows surface structures and processes to be studied in exquisite detail and are the foundations of much of our understanding of surface catalytic processes. The reaction environment can and often does have a significant modifying influence on surface properties and reactivity, and thus increasingly analytical methods have been developed to be applied *in situ*, or "in place" [9, 24–31]. There is some debate in the catalysis and surface science communities regarding the precise meanings of *in situ* and the related term *operando*. We draw no particular line between them here, recognizing instead that analysis under any set of conditions can provide useful insights into catalytic behavior.

Both surface and bulk properties are relevant to catalytic reactivity. Although heterogeneous reactions by definition occur at the interface between a catalyst and reactant/product phase, the process of catalysis actually includes activation of an assynthesized catalyst, catalytic reaction, and adverse processes leading to the deactivation of a working catalyst. Activation may involve chemical transformations of both the catalyst surface and bulk. For example, the iron oxide  $Fe_2O_3$  is chemically transformed into the active iron carbide during activation for the Fischer-Tropsch synthesis (FTS) from CO and H<sub>2</sub> [32, 33]. There are numerous other examples of reduction of a metal oxide to an active metal or oxidation of a metal to an active oxide, carbide, sulfide, or similar. Characterization of chemistry and structure of the surface and bulk of a catalyst nanoparticle using representative techniques are presented in Chapter 4.

The surface energy of a material is sensitive to the environment it is exposed to, including the type, temperature, and pressure of any reactants. As a result, a catalyst may "adapt" to its environment by exposing different surface structures [34, 35]. To

capture this relationship between environment, structure, and activity, it is necessary to characterize a catalyst as it undergoes reaction, *in situ* [9, 24–31, 33, 34]. *In situ* X-ray absorption spectroscopy, ambient pressure X-ray photoelectron spectroscopy, environmental electron microcopy, and high-pressure scanning tunneling microscopy have enabled direct probing of the catalytic surface and its activity under reaction conditions. Chapter 5 provides a brief review of X-ray absorption spectroscopy, one of the more widely used *in situ* characterization techniques. It reviews the design of *in situ* reaction chambers for X-ray absorption spectroscopy and their application to catalytic energy conversion processes.

The recent rapid advances in heterogeneous catalysis science owes as much to the development of theoretical tools able to reliably model reactions at heterogeneous surfaces ab initio (or from "first principles") as it does to the revolutions in synthesis and characterization described earlier. In fact, it is somewhat ironic that fast and cheap computing power made possible by the shrinking of microelectronics to the nanoscale has enabled computational models of catalytic reactivity at the same scale! Semiempirical bond-order conservation methods were the first to be widely applied to heterogeneous catalysis [36], but today density functional theory (DFT) models [37, 38] dominate the field. Fundamentally, DFT provides a mapping from the geometric arrangement of a set of atoms to the distribution of electrons about those atoms and the total internal energy of the system. The DFT models of today emerged from cross-fertilization of methods developed in the condensed matter physics community to describe solids and in the chemistry community to model molecular systems. These DFT tools can be applied consistently to systems of any dimensionality and can access length scales on the order of one to several nanometers, fortuitously just the length scales of interest in heterogeneous nanocatalysis.

The first challenge in applying DFT to heterogeneous catalysis is to craft models that faithfully capture the important structural and compositional properties of the system of interest. Chapter 6 describes the essentials of constructing and validating a DFT model of a heterogeneous metal interface. It presents the key underlying model approximations and the types of information accessible from the models, information that includes the structure, stability, and spectroscopy of surface species, reaction pathways, and activation energies. Chapter 6 touches on the added complications of surface coverage effects, of solid–liquid interfaces, and of electrochemical surface reactions, all in the context of nitrate reduction catalysis on Pd.

While DFT can be a powerful tool for developing mechanistic insight, one of its most exciting applications is to the predictive discovery of new catalytic materials. Chapter 7 reviews the history and state-of-the-art in heterogeneous catalyst screening. At the heart, this screening relies on the identification of descriptors of catalytic activity—quantities that can be calculated relatively quickly for many materials and that can be shown to correlate with catalytic activity. Ultimately, the success of these descriptor models can be traced to the reliability of the bond-order conservation approximations that launched the field. Greeley demonstrates the approach in the context of electrocatalytic chemistry and touches on the importance of predicting both activity and stability in making practically useful predictions.

Heterogeneous catalysis is ultimately concerned with chemical kinetics. Complementary to longitudinal screening for catalyst discovery is the development of robust, reliable models of catalytic rates and their dependence not only on materials properties but also on reaction conditions. Observed catalytic activity is a convolution of the contributions of many microscopic reaction steps, one or many of which may directly control the overall observed rate. Chapter 9 describes the mechanics both of constructing a microkinetic, elementary step mechanism from DFT calculations, to translating the results of these DFT calculations into thermodynamic and kinetic parameters suitable for a kinetic model, to then integrating and interrogating that model. This work involves a careful weaving together of concepts from statistical mechanics, reaction rate theory, and macroscopic reactor kinetics. Chapter 8 demonstrates the reliability of this complete approach to water–gas shift catalysis on a Pt surface.

DFT-based models have had a profound impact on heterogeneous catalysis, derived not only from its direct predictive power but also from the conceptual microscopic framework in provides for understanding catalysis. The field continues to progress rapidly, in part through the development of more quantitatively reliable DFT methods. Many opportunities exist in exploring new types of materials and more complicated structures, such as the interface between a nanoscale catalyst particles and supports, to capturing the interplay and dynamics of a catalyst surface in a reactive and transient environment, to relating these microscopic details to observable measures of activity, and to capturing transformations over the life cycle of a heterogeneous catalyst.

Thermal catalysis is the heart of conversion of biomass to fuels [1, 2]. As compared to catalysts for chemical transformation in chemical industries, those used for biomass conversion and purification of fuels need to address the issue of the sustainability of the catalyst materials. Catalytic selectivity in energy conversion is also a critical factor as the sustainability of environments is aligned to the suitability of our energy landscape. Thus, a high selectivity of catalysts in energy conversion is necessary for maintaining a sustainable green environment. Chapter 9 reviews the recent progress in catalytically upgrading lignocellulosic materials to transportation fuels. This chapter highlights the design of robust, efficient, economic catalyst, and mechanistic understanding of catalytic processes in converting the renewable energy source, nonedible biomass to fuel molecules.

Another application of thermal catalysis in energy science is the purification of fuels, for example, removal of CO from  $H_2$  stream. Hydrogen is the key reactant in low-temperature proton exchange membrane fuel cells. Until a breakthrough in water-splitting driven by visible light can be achieved, most of the hydrogen fuel will be produced by thermal catalysis or electrolysis. CO is a by-product during steam reforming of hydrocarbons to hydrogen. However, the tolerance of electrodes (Pt or Pt-based alloy) of fuel cells and batteries for CO in  $H_2$  is quite low (<30 ppm). Unfortunately, the CO concentration downstream of a low-temperature industrial water–gas-shift (WGS) process can be as high as 3–5%. Improved WGS processes and preferential oxidation of CO in the presence of  $H_2$  (PROX) are necessary for purification of  $H_2$ .

Chapter 10 presents strategies for the catalytic removal of CO in  $H_2$  through WGS and PROX on nanocatalysts.

Photocatalysis offers the promise of harvesting solar energy to induce chemical transformation and generate solar fuels. The advantage of this approach is the sustainability of energy sources. Photoinduced generation of electrons and holes at the photocatalyst surface facilitate redox processes (e.g., water-splitting to generate hydrogen and oxygen). Deposition of cocatalysts such as Pt and  $IrO_2$  is an important factor in promoting these redox processes. Details of the photocatalytic process of water-splitting and challenges facing optimization of the process and promotion of photoconversion efficiency are presented in Chapter 11. Another solar-fuel-related catalytic process is conversion of  $CO_2$  to  $C_1$ -based molecules using semiconductor photocatalysts. Chapter 12 reviews the photocatalytic conversion of  $CO_2$  along with mechanistic details.

Electrocatalysis processes play a major role in the design and development of fuel cell technology and rechargeable battery technology. Significant efforts have been made toward the development of catalysts from earth-abundant elements. Significant strides that have been made in the synthesis of metal nanoparticles have led to the development of electrocatalysts for improving electrode kinetics. The challenges remain to overcome the limitation imposed by oxygen reduction reaction at catalyst surface during the electrocatalysts, discusses their electrocatalytic behavior, and deliberates the challenges these electrochemical technologies face.

We have made a concerted effort to present state-of-the-art developments in the area of nanocatalysis. The variety of topics from synthesis, characterization, and modeling to applications to a range of energy conversion processes provides an overview of modern catalysis and current trends in nanocatalysis research. We would like to thank all the contributors for providing a scientifically stimulating discussion in their respective chapters.

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