

## CHAPTER 10

### APPLICATIONS: CATALYSIS BY NANOSTRUCTURED MATERIALS

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#### 10.1 VISION FOR THE NEXT DECADE

##### Changes in the Vision over the Last Ten Years

The 1999 *Nanotechnology Research Directions* report included nanoscale catalysis as one aspect of applications of nanotechnology to the energy and chemicals industries (Roco 1999). The vision centered on the recognition that “new properties intrinsic to nanostructures” could lead to breakthroughs in catalysis with high selectivity at high yield. An example cited in that report was the observation that, while bulk gold is largely unreactive, highly selective catalytic activity could be observed for gold nanoparticles smaller than about 3-5 nm in diameter (Haruta 1997). Nanoparticles and nano-structured materials have traditionally played a critical role in the effectiveness of industrial catalysts (Bell 2003), but the past decade has witnessed significant advances in the control of nanoscale materials and the characterization and *in situ* probing of catalytic processes at the atomic, active site scale.

##### Vision for the Next Ten Years

The advances in nanostructured catalytic materials in the last ten years support a new vision for nanoscience-inspired design, synthesis, and formulation of industrially important catalytic materials. The implications of further progress in “deterministic” nanocatalysis and the broad applications to energy and the environment underscore the importance of this area for future investment. As described in Section 10.2, a grand challenge and vision for catalysis at the nanoscale is providing catalytic materials that will more accurately and efficiently control reaction pathways through the precise control of the composition and structure of those catalysts, over length scales spanning 1 nanometer to 1 micron.

Such control will enable the broad development and deployment of nanostructured catalysts that can more efficiently and selectively convert lower-grade hydrocarbons into higher-value fuels and chemical products, thereby reducing dependence on oil, providing more effective pollution abatement, and efficiently harnessing solar power, and redirecting energy selectively into driving thermodynamically uphill chemical processes. Science-based protocols to build and control composite particle structures should stimulate development of improved methods for catalyst scale-up and large scale manufacturing that will be needed to broadly allow penetration of nanoengineered materials into new commercial catalyst applications.

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## 10.2 SCIENTIFIC AND TECHNOLOGICAL ADVANCES IN THE PAST TEN YEARS

A U.S. National Science Foundation (NSF) workshop, “Future Directions in Catalysis: Structures that Function at the Nanoscale,” was held in 2003 at NSF headquarters in Arlington, VA (Davis and Tilley 2003). Thirty-four distinguished participants, primarily from U.S. academic institutions, government agencies, national laboratories, and major companies assessed the state of the art in the field and provided vision statements on the future directions of catalysis research. The workshop was organized around three working groups focused on (1) synthesis, (2) characterization, and (3) theoretical modeling of catalysts. These topics formed the basic framework of a subsequent World Technology Evaluation Center (WTEC) assessment of the worldwide state of the art and research trends in catalysis by nanostructured materials; this study was conducted in 2009 by a panel of eight experts in the field (Davis et al. 2009).

Both studies (2003 and 2009) articulated the consensus view that synthesis of new nanoscopic catalysts will require fundamental understanding of molecular-scale self-assembly of complex, multicomponent, metastable systems, and that newly developed tools of nanotechnology will likely play a key role in the synthesis of new catalytic structures. Moreover, both studies reported on the extensive use of nanoscale characterization methods in catalysis and the need for new and improved *in situ* characterization methods that extend the limits of temperature, pressure, and spatial resolution to probe nanostructured catalysts in their working state. Finally, although significant advances in theoretical descriptions of complex reactions and models that span multiple time and length scales have been realized over the last decade, additional improvements are required to develop the predictive capabilities of computation, especially in liquid phase systems. A grand challenge that emerged from the 2003 workshop is “to control the composition and structure of catalytic materials over length scales from 1 nanometer to 1 micron to provide catalytic materials that accurately and efficiently control reaction pathways” (Davis and Tilley 2003). Although great strides have been made in fulfilling this challenge, significant hurdles remain.

### Synthesis of Nanostructured Catalysts

The need to control surface structure and chemical reactivity at the nanometer length scale is paramount in catalysis research and engineering. Zeolites are archetypical high-surface-area crystalline solids with nanometer-size pores and cavities that allow for highly precise manipulation of catalytic components and diffusion paths of reagents and products. For example, research in the 1980s artfully demonstrated the exquisite control of metal particle sizes in zeolite pores for hydrocarbon reactions relevant to fuels production. In particular, Pt clusters composed of only a few atoms can be readily synthesized by chemical methods in the nanometer-sized channels of zeolite L to form a catalyst that is especially active and selective for the formation of benzene and toluene from linear alkanes. However, a common problem with nanoporous catalysts is the severe diffusional resistance encountered by reactants and products that have molecular dimensions similar to those of the pores. If side products or carbonaceous deposits block the entrance to these pores, the entire interior regions of the pores can be rendered inaccessible for catalysis.

To overcome these inherent diffusional limitations, various labs around the globe have synthesized microporous zeolites (i.e., zeolites with nanometer-sized pores) with an interconnected array of mesopores (i.e., pores of much larger dimension) to improve accessibility of the internal regions of the material to reactants and products. Multiple synthetic strategies for synthesizing these hybrid micro-mesoporous zeolites have evolved recently, to include the use of:

- Novel organic structure-directing agents such as quaternary ammonium ions to template the original zeolite synthesis as well as alkyl chains to promote aggregation of the structure directors into micellar units (Choi et al. 2006)
- Elemental carbon (in the form of carbon black, fibers, nanotubes, etc.) as a template for mesopores in the zeolite synthesis gel that can be eventually removed by complete oxidation at elevated temperature (Christensen et al. 2005)
- Preformed zeolite nanoparticles as structural building blocks to form larger crystals in the presence of a surfactant (Li et al. 2005)

In the above-mentioned synthetic methods, the resulting materials contain both micropores and mesopores within a single solid particle, which greatly facilitates transport of reactants and products to the interior regions where the active sites are located. Another approach to overcome diffusional limitations is to synthesize new zeolite structures with larger-pore systems, thus avoiding the creation of very small pore dimensions altogether (Corma et al. 2006). Although this approach is appealing, there are significant challenges in the generalized synthesis of large pore materials as well as in their stability under catalytic reaction conditions.

Exciting advances have recently occurred in the synthesis of small metal and metal oxide nanoparticles with controlled size, shape, and specific surface orientations, such as Pd nanoparticles that expose the selective {100} plane for hydrogenation of dienes (Berhault et al. 2007) and CeO<sub>2</sub> nanoparticles that expose the active {100} plane for CO oxidation (Aneggi et al. 2005). These advances point toward a future in catalyst preparation that will enable practitioners to more rationally design and prepare catalysts with the specific surface structures that are required for high specificity, structure-sensitive catalytic reactions (Witham et al. 2010; Lee et al 2008).

### **Characterization of Nanostructured Catalysts**

The rapid developments in *in situ* spectroscopic tools and atomic-resolution electron microscopy over the last decade have revolutionized the understanding of catalyst structures at the nanoscale. Modern catalysis laboratories now routinely utilize a broad suite of characterization methods such as adsorption, temperature programmed reactions, x-ray diffraction, scanning and transmission electron microscopy, and electron spectroscopies (x-ray, photoelectron, and Auger spectroscopies), as well as electron paramagnetic, and nuclear magnetic resonance, ultraviolet/visible, Raman, and infrared spectroscopies. Major progress has been made in characterizing catalysts in their working state, not simply prior to or after a catalytic reaction, with increased realization that catalysts are highly dynamic solids that often restructure under reaction conditions. Thus, new sample cells have been devised to interrogate materials by all of the photon-based spectroscopies as well as by EPR and NMR spectroscopy, while simultaneously measuring reaction kinetics and selectivities.

One recent development in characterization instrumentation involves the adaptation of electron-based methods such as x-ray photoelectron spectroscopy (XPS) and electron microscopy to conditions that more closely approach catalytic reaction conditions. For example, the high photon flux provided by a synchrotron radiation source as well as differential pumping of the reaction chamber allows acquisition of XPS data on catalytic surfaces up to millibar reaction pressures (Salmeron and Schlogl 2008; see Figure 10.1). Likewise, new sample cells for transmission electron microscopy allow for the direct observation of reactive environments on metal nanoparticles at elevated temperature and mbar reaction pressure (Hansen 2002). The use of aberration correction on high-resolution

electron microscopes has recently enabled unprecedented resolution of features on catalyst samples so that observation of single metal atoms on supports is now possible.

Synchrotron radiation methods have continued to play a major role in characterization of catalysts, since hard x-rays can be used to probe solids at high temperatures and pressures or in the liquid phase without the need for the catalyst to be crystalline. Soft x-ray synchrotron spectroscopies can provide complementary information on local surface structure and composition. Therefore, the catalysis community worldwide has quickly implemented recent improvements in energy resolution, spatial resolution, and temporal resolution of synchrotron-based characterization methods.

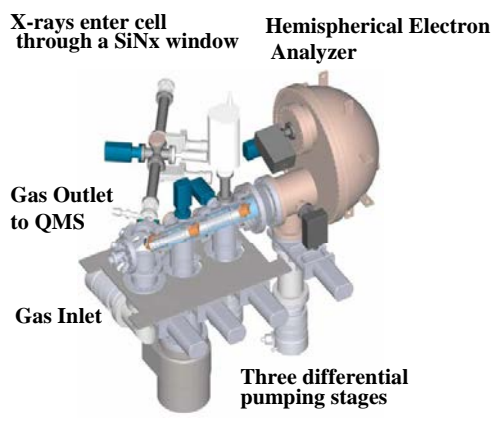


Figure 10.1. Instrument for carrying out XPS at millibar pressures and capable of being operated at high flux (courtesy of Fritz Haber Institute, Germany).

It is now possible to simultaneously acquire small-angle and wide-angle x-ray scattering from catalysts while recording the x-ray absorption spectrum, all in a time-resolved manner. Indeed, some beamlines can acquire an EXAFS (extended x-ray absorption fine-structure spectroscopy) spectrum in less than 0.1 sec, which is on the scale of a catalytic turnover event. Although commercial infrared (IR) and Raman microscopes have been available for some time and are used by some catalysis laboratories, the implementation of spatially-resolved x-ray absorption spectroscopy has taken longer to develop. Recent work in the Netherlands has achieved spatially resolved near-edge spectra on a single 600 nm iron oxide particle used for the Fischer-Tropsch synthesis reaction.

As catalyst research expands into new technology areas such as the conversion of biomass into liquid products, there will be a growing need for characterization methods that allow for interrogation of solid structures in liquid environments. Thus, the important role of national-level user facilities for electron microscopy, magnetic resonance, and synchrotron radiation studies in catalysis research will likely grow in the coming decade.

### Theory and Simulation in Catalysis

Computational catalysis has reached the stage over the last decade in which it provides a necessary complement to experimental research in the field (Figure 10.2). Advances in computer processor speeds, large scale implementation of parallel architectures, and development of more efficient theoretical and computational methods allow for complex simulations of catalytic reactions on solid surfaces that often match well to experimental results. As noted in the 2009 WTEC panel report, *An International Assessment of Research in Catalysis by Nanostructured Materials*, theory and simulation are now able to predict

structures and properties of well-defined model catalysts, simulate spectra provided by a variety of experimental tools, elucidate catalytic reaction paths and begin guiding the search for new catalytic materials and compositions.

The computational tools available today can provide structural information such as bond lengths and bond angles of surface adsorbates to within about 0.005 nm and 2 degrees, respectively, and spectroscopic features of the adsorbates within a few percent of experiment. Moreover, adsorption bond energies, activation barriers, and overall reaction energies are now routinely calculated within a couple of days at an accuracy of about 20 kJ mol<sup>-1</sup> or better. Although the energies estimated computationally are beyond chemical accuracy for predicting absolute reaction rates, computational catalysis can now be used to effectively discriminate between competing reaction paths and predict overall trends involving catalyst composition and reaction conditions.

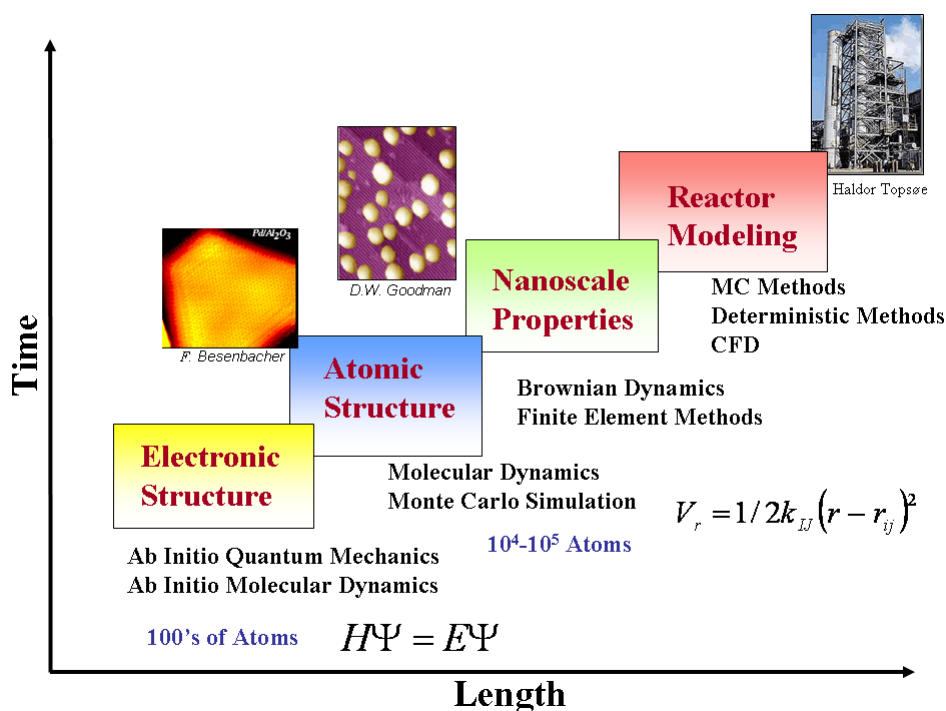


Figure 10.2. Hierarchy of time and length scales in heterogeneous catalysis, and associated modeling methods (Davis et al. 2009).

Although there has been rapid progress in computational catalysis regarding the description of catalytic reactions at the molecular level, there has been less progress on the use of theory and simulation to guide catalyst synthesis (for a recent review, see (Norskov et al. 2009) and references therein). Catalyst preparation often involves the self-assembly of metastable structures that are guided by weak interactions with molecules within the system. These structures are often further modified by dynamic rearrangements during catalytic reactions. Thus, catalyst design and predictive synthesis presents a serious challenge to the computational community, since weak forces are not well-described by current theoretical methods, and non-equilibrium structures are difficult to find computationally.

### Areas of Application and Economic Impacts

Catalyst manufacturing was one of the earliest commercial application areas for modern nanoscience methods. Important examples include sol-gel wash coat processing for the fabrication of automobile catalytic converters and use of zeolites with tailored framework structures for shape-selective chemical and fuel processing. As noted earlier, direct applications of nanotechnology in catalyst manufacturing have grown rapidly over the past decade as new synthesis and characterization methods have become available. It is estimated that synthetic methods derived from modern nanotechnology are now utilized in 30–40% or more of global catalyst products (Payn 2010; see also The Catalyst Group Resources 2010). Because these commercial methods are proprietary, relatively few application details have been disclosed in the open literature. Specific examples of recent commercial catalyst applications are given in Section 10.8. Further examples can be found in recent multiclient studies by the Catalyst Group (2002, 2010).

The global catalyst business represents an \$18–20 billion-dollar per-year enterprise with applications primarily involving petroleum refining, chemicals processing, and environmental catalysis (used with permission, The Catalyst Group Resources 2008). Most commercial catalysis innovations continue to be targeted at achieving significant improvements in product selectivity and energy efficiency for conversion and upgrading of about 80 million barrels per day of petroleum into transportation fuels and petrochemicals globally. With product values currently in the range of about \$100 US dollars or more per barrel of feedstock, global economic impacts across the full value chain for these technologies is in the range of several trillion dollars annually. For this reason, it appears likely that catalysis currently remains the most successful commercial application area for modern nanotechnologies.

The 2009 WTEC catalysis report (Davis et al. 2009) found that conversion of nonpetroleum feedstocks such as coal, natural gas, and biomass to fuels, energy, and chemicals is a high priority in nearly all of the countries visited in that study. China, in particular, has a major emphasis on non-conventional energy applications, especially those involving the conversion of coal to liquid fuels and chemicals. Significant activities in photocatalysis, hydrogen generation, and fuel cells are carried out in many locations. There is a general recognition that energy carriers and chemicals should be produced, and ultimately used, with as little impact on the environment as possible; catalytic solutions are thus being pursued in this framework of environmental sustainability. Catalytic production of ultra-low-sulfur fuels, use of renewable carbon sources and sunlight, conversion of the greenhouse gas CO<sub>2</sub> to useful products, highly selective oxidation of hydrocarbons, and catalytic after-treatment of waste streams are all being pursued vigorously around the globe. A growing area of interest is the catalytic transformation of various renewable plant sources to energy-relevant compounds such as bio-oil (a liquid feedstock that can be upgraded in combination with refinery streams), biodiesel fuel, hydrogen, alcohols, and so forth.

### Summary Statement

Catalysis by nanostructured materials is an active area of research around the globe. Its rate of growth appears to be increasing faster than that of all science, according to a detailed bibliometric analysis (Davis et al. 2009), presumably because of increasing concerns regarding future energy security and environmental sustainability. The European Union (EU) currently holds a dominant position in the world in terms of research paper output, but the rapid growth of research in Asia over the previous decade is challenging that position. Investment levels in catalysis research in the EU and Asia appear to be significantly greater

than that in the United States over the last decade. A bright spot in the analysis confirms that recent U.S. publications are the most cited in the world, which suggests that research funds in the United States are distributed effectively to the highest-quality laboratories.

### 10.3 GOALS, BARRIERS, AND SOLUTIONS FOR THE NEXT 5-10 YEARS

Over the last 30 years, the synthesis and characterization of novel nanoscale materials has advanced greatly in both academic and industrial research settings. In particular, over the last decade, programs such as the National Nanotechnology Initiative (NNI) have helped, directly and indirectly, push forward the tools and techniques required to understand and improve upon the properties of nanoscale materials. scanning transmission electron microscopy (STEM), atomic force microscopy/electric force microscopy (AFM/EFM), and focused ion beam (FIB) technique. In parallel, the development of high-throughput screening tools such as those developed by scientific equipment companies Symyx, Avantium, Hte, and others has allowed for a dramatic increase in the total amount of empirical data available. This mass of data has benefitted the experimental community directly, and it has as well provided additional pools of data for the theoretical community to develop and refine models of reaction mechanism models. The growth in national computing centers such as those at the Lawrence Livermore and, Argonne National Laboratories, LBNL, etc. has also allowed for the creation of more and more accurate mechanistic models over the last decades.

Given the great advances in synthetic methods, characterization, theory, informatics, and HTE tool development, the next challenge is to significantly broaden the practical application of this knowledge and capability. There remain many challenges in the energy and commodity chemicals industries that appear well suited to solutions based on new nanostructured catalyst systems. This work needs to take place in both academic and industrial labs, both on the fundamental research that has been enabled by nanomaterials, as well as the application of those nanomaterials towards solving the hardest problems in the field of catalysis. Some of the “Holy Grail” sought-after catalytic reactions include: selective oxidation of alkanes, oxidative dehydrogenation of alkanes to alkenes, carbon dioxide reforming, and— perhaps the most challenging case of selective oxidations— the oxidative coupling of methane to ethylene (Haggin 1993).

Many of these and other commercially valuable reactions have been pursued by industry and academic researchers for many years, but in most cases this was done prior to recent advances in nanomaterials development, and prior to the widespread use of high-throughput screening and improved modeling techniques. Two specific examples of reactions that would greatly benefit from the recent advances are described further below. If either of these is solved in the next 10 years, the country could greatly benefit greatly via better use of large projected reserves of natural gas.

#### Carbon Dioxide Reforming

Carbon dioxide reforming (CDR) of methane is a process for converting CO<sub>2</sub> in process streams or naturally occurring sources into the more valuable chemical product, syngas (a mixture of hydrogen and carbon monoxide). In CDR, a mixture of two potent greenhouse gases, methane and CO<sub>2</sub>, is converted into syngas according to the following reaction:  $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ . Syngas can then be converted into a wide range of hydrocarbon products through established commercial processes such as the Fischer-Tropsch reaction to form liquid fuels including methanol, ethanol, diesel, and gasoline. The result is a powerful technique to not only remove CO<sub>2</sub> from the atmosphere and reduce the emissions of methane (another greenhouse gas) but also to create a new alternative source for fuels that are not

derived from petroleum. Reforming with CO<sub>2</sub>, rather than the conventional steam methane reforming using H<sub>2</sub>O could be attractive in areas where water is not readily available, and it yields syngas with a 1:1 H<sub>2</sub>/CO ratio, which is a preferable feedstock for the Fischer–Tropsch synthesis of long-chain hydrocarbons.

Unfortunately, no established industrial technology for CDR exists today in spite of its tremendous potential value. A primary problem is due to side reactions from catalyst deactivation (i.e., coking) induced by carbon deposition via the Boudouard reaction ( $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ ) and/or methane cracking ( $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ ) resulting from the high-temperature reaction conditions (Kroll, Swaan, and Mirodatos 1996). The coking effect is intimately related to the complex reaction mechanism, and the associated reaction kinetics of the catalysts employed in the reaction.

Improving the selectivity of the reaction towards the desired syngas product while simultaneously reducing the coking on the surface of the catalyst will require novel approaches to catalyst surface design and fabrication, most likely enabled by the advances in nanomaterials synthesis and characterization.

### **Oxidative Coupling of Methane to Ethylene**

Ethylene is the largest chemical intermediate produced in the world and is utilized in a wide range of important industrial products, including plastics, surfactants, and pharmaceuticals. It has a worldwide annual production in excess of 140 million metric tons, of which over 25% is produced in the United States. Global demand growth for ethylene remains robust at about 4% per year (Ren and Patel 2009). Ethylene is primarily manufactured via high-temperature steam cracking of naphtha, with a smaller amount being made from ethane. The endothermic cracking reaction requires high temperatures (>900°C) and high energy input for both the reaction and product-separation processes. This results in steam cracking being one of the largest consumers of fuel as well as the largest CO<sub>2</sub> emitter of any commodity chemical product (Ruth et al. 2002).

A potentially promising reaction for direct natural gas activation is the oxidative coupling of methane (OCM) to ethylene:  $2\text{CH}_4 + \text{O}_2 = \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$ . The reaction is exothermic ( $\Delta H = -67$  kcal/mole) and to date has only been shown to occur at very high temperatures (>700°C). In the reaction, methane (CH<sub>4</sub>) is activated on the catalyst surface, forming methyl radicals which then couple to ethane (C<sub>2</sub>H<sub>6</sub>), followed by dehydrogenation to ethylene (C<sub>2</sub>H<sub>4</sub>). Since the OCM reaction was first reported over 30 years ago, it has been the target of intense research interest, but conventional catalyst preparations have not yet afforded commercially attractive yields and selectivities. Numerous publications from industrial and academic labs have consistently demonstrated characteristic performance of high selectivity at low conversion of methane, or low selectivity at high conversion (Labinger 1988). To break this cycle, a catalyst with a specific activity for CH<sub>4</sub> bond activation at lower temperatures (<700°C) must be developed. It has been over 15 years since the last large-scale efforts in industry and academia were focused on this reaction. During that time, the advent of bottom-up nanomaterials synthesis, high-throughput screening, advanced characterization, and improved modeling have all made great advances. If these advances are now applied to this problem, it appears that significant strides could be made in pushing the selectivity higher at lower temperatures, thereby resulting in a commercially viable process which could simultaneously reduce our dependence on oil, and reduce our CO<sub>2</sub> footprint.

Breakthroughs in difficult, yet high-reward, reactions like OCM will likely require focused effort and broader partnerships between academia, the national labs, innovative small businesses, and the multinational chemical companies.

#### 10.4 SCIENTIFIC AND TECHNOLOGICAL INFRASTRUCTURE

In recent years, substantial progress has been made in the synthesis of new, nanoscopic catalysts. A critical contributor to that progress lies with advances in instrumentation that makes possible monitoring of catalysts in their working state. This allows researchers to close the loop between catalyst structure and function. Further progress requires a better fundamental understanding of the molecular-scale self-assembly of complex, multicomponent, metastable systems. This in turn will depend on critical advances in theory and simulation, as well as the development and accessibility of new *in situ* characterization methods that will provide the requisite spatial, energy, and time resolution, allowing the study of catalysts in their working state.

In particular, instrumentation must be developed that will allow probing of nanostructured catalysts under the appropriate conditions of pressure and temperature, while maintaining the highest spatial resolution possible. High-resolution microscopy in which dynamic reshaping of metal nanocrystals can be studied *in situ* would provide important insights into the mechanisms of catalytic action in nanostructures. Complementary, integrated means of carrying out high-throughput synthesis and screening of nanostructured catalysts would allow faster convergence to optimal structures and compositions.

As stated in Section 10.2, synchrotrons have played a major role in catalyst characterization, since the hard x-rays they generate can probe solids at high temperatures and pressures (catalytic “working conditions”), or in the liquid phase, without the requirement that the catalyst be crystalline. It is important that large-scale, complex, and expensive facilities such as synchrotrons, high resolution electron microscopes, and high field magnetic resonance equipment be made broadly available to the community of researchers in nanocatalysis.

While *computational techniques* related to theory and simulation of catalytic reactions have recently shown major progress, further improvements are needed to enhance the *accuracy* of computational methods, particularly for reacting systems, and to develop *predictive* capabilities. The accuracy of the methods is still an issue for reacting systems, and there needs to be a better connection between the simulation of adsorbates on surfaces and their rate of transformation to products. Thus, more work is needed to link *ab initio* methods used to describe the structure and energetics associated with adsorbed species to the atomistic simulations needed to describe their diffusion and reaction on the surface. More capability is also needed in the use of theory and simulation to guide *catalyst synthesis* at both the atomic scale and at larger length scales representative of catalyst support structures. Theoretical methods also do not handle very well the description of photoexcitation events that would occur during photocatalysis, an area that is likely to become more important in the next decade as researchers search for better ways to utilize solar energy.

#### 10.5 R&D INVESTMENT AND IMPLEMENTATION STRATEGIES

The 2009 WTEC catalysis report (Davis et al. 2009) noted that “the overall level of investment in catalysis research in Europe appears to be higher than that in the United States.” The report also noted that cooperation between universities and companies in this field is more common in Europe and Asia (related to the intellectual property environment), and also that “European and Asian countries have done an excellent job combining academic research with

national laboratory activities.” All of these observations provide some valuable benchmarks for future U.S. investments in this area. Major developments in computation and synthesis are required, and perhaps most importantly, the appropriate instrumentation must be developed and made available to the community of researchers. The ability to monitor catalysts with the appropriate resolution (spatial, temporal) in their working state is critical to understanding and thus control of nanostructured catalysts. Investments should be made to make more widely accessible both large-scale national facilities and specialized state-of-the-art instrumentation, and funding should also support the development of next-generation instrumentation. Nanostructured catalysis has the potential to profoundly affect our quality of life, and this should be reflected through investments in research and development in this area, commensurate with societal impacts in the areas of fuels, chemicals, and energy efficiency.

From a practical application standpoint, two of the more promising, but difficult, frontier areas for nanotechnology in catalysis are predictive design and fabrication of bulk catalyst particles with nanoengineered porosity over multiple length scales. This will require development of better, cost-effective structure-directing methods to further control the size, shape, and atomic surface structure of highly dispersed materials, as well as of methods to better produce well defined micro- and mesoporous support structures. Better synthetic methods to build and control composite particle architecture over multiple length scales should spur development of improved tools for catalyst scale-up and large-scale manufacturing that will be needed to broadly allow the penetration of nanoengineered materials into commercial applications.

There is also a strong need for improved reaction modeling capabilities that better couple catalyzed reaction pathways with molecular transport in micro- and mesoporous materials over multiple length scales, e.g., multiscale modeling integrating transport in multicomponent powders or pellets with fundamental surface reaction kinetics. Advances in this area should strongly facilitate more efficient design, development, and optimization of next generation commercial catalyst structures.

## 10.6 CONCLUSIONS AND PRIORITIES

Catalysis by nanostructured materials offers tremendous potential for more efficient, low-cost, and environmentally sustainable production of energy carriers and chemicals in manners consistent with environmental sustainability. Although tremendous progress has been made in this area, substantial challenges remain. Research priorities should build on the substantial recent progress in this field to be able to dramatically affect some of the ‘Holy Grail’ reactions described in Section 9.3. In particular:

- There have been recent successes in beginning to characterize some catalytic processes “in the working state”, under “real” conditions of elevated temperature, pressure and reactant flux. In addition monitoring of “single turnover” events, that is, single catalytic events, has been realized. The ultimate objective is a complete snapshot of a multi-step catalytic process under “working state” conditions.
- There has been steady progress in the ability to control the size, structure and crystalline composition of nano-sized catalysts. To fully exploit these structures, it is critical that progress be made in ensuring the robustness and stability of those nano-sized catalysts through the catalytic process itself.

- Ultimately, research priorities for nanostructured catalysts have the overall goal of realizing precise control over the composition and structure of catalysts over length scales spanning 1 nm to 1 micrometer, allowing the efficient control of reaction pathways.

In order to realize those researcher priorities, better understanding and control is required in the synthesis of molecular-scale, multicomponent, metastable systems and the assembly of these systems into larger, bulk composite particle structures. Advances in nanoscale characterization techniques are needed, especially those that will allow *in situ* monitoring under the conditions of temperature and pressure that characterize the “working state” of the catalysts. Finally, significant advances are required in theoretical descriptions of complex catalytic reactions that will provide predictive capabilities.

Given the critical importance of the highest-quality characterization tools, a priority should be in the investment of resources to develop instrumentation to facilitate *in situ* nanoscale characterization. Another priority should be to provide the means of making such instrumentation, including national resources such as synchrotron beamlines, more widely accessible to the research community. Given the importance of this area to meeting environmental, energy, and sustainability challenges, strong industry-academic collaborations should be encouraged and facilitated.

In addition to methods of studying catalytic reactions, significant effort should be dedicated to solving the most challenging and beneficial reactions discovered but not conquered over the last 50 years. In particular, developing catalysts that enable the successful use of natural gas feedstocks for commodity chemicals, ranging from the ubiquitous olefins (ethylene and propylene), to aromatics and gasoline, instead of the current predominant use as a heat source. If dedicated effort were given to one or two of these reactions, significant progress from R&D to commercial demonstration-scale plants could likely be achieved in the next 10 years.

### **10.7 BROADER IMPLICATIONS FOR SOCIETY**

More efficient and selective catalysts could have a profound impact on energy generation and efficiency, pollution abatement, the production of commodity and specialty chemicals and pharmaceuticals, and global economic health and development. Thus, R&D in the area of nanostructured catalysts will have a profound effect on society and its standard of living. Indeed, the WTEC catalysis report (Davis et al. 2009) noted that the key applications stimulating most catalysis research worldwide are related to energy and the environment. Not only will developments in catalysis directly impact society through new, improved, and cheaper, products, but larger-scale impacts similar to those of the Haber-Bosch process of the early 1900s are possible. For example, enabling the use of natural gas as a source of commodity chemicals, instead of burning it will have many positive impacts simultaneously: e.g. decrease U.S. dependence on oil, increase the value of natural gas in North America, decrease CO<sub>2</sub> and total greenhouse gas emissions, and decrease global demand on petroleum.

## 10.8 EXAMPLES OF ACHIEVEMENTS AND PARADIGM SHIFTS

### 10.8.1 Direct Observation of Single Catalytic Events

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The tools of nanotechnology developed over the last decade enabled researchers to observe and analyze for the first time individual catalytic events on solid surfaces under realistic operating conditions. Whereas spectroscopic methods have been used for many years to probe the reactivity of catalytic surfaces and microscopic methods were able to reveal the atomic structures of the catalysts themselves and sometimes the organization of adsorbate overlayers on the catalytic surfaces, single-molecule resolution of catalytic turnover events has proven to be elusive. In 2006, M. Roeffaers and colleagues published a landmark paper in *Nature* in which they demonstrated how wide field microscopy can be used to map the spatial distribution of catalytic activity on a crystal surface by counting single turnover events (Roeffaers et al. 2006). While individual elementary reactions may occur on the subpicosecond time scale and therefore cannot be followed by this methodology, it is quite evident that the overall turnover of a catalytic cycle can be monitored with typical turnover periods in range of  $10^{-2}$  to  $10^2$  seconds.

The principle of the Roeffaers experiment is illustrated schematically in Figure 10.3. The catalyst was a Li-Al layered double hydroxide (LDH) in the form of stacked sheets that assemble into prismatic crystals with large basal {0001} planes. The presence of both  $\text{Li}^+$  and  $\text{Al}^{3+}$  in the gibbsite-type sheets results in a net positive charge that is balanced by anions located between the sheets. When those charge-balancing species are  $\text{OH}^-$  anions, the solid LDH functions quite effectively as a Bronsted base and can therefore catalyze reactions such as hydrolysis, esterification and transesterification. Roeffaers et al. mounted a single crystal of the LDH catalyst onto a microscope slide with the basal {0001} plane parallel to the cover glass. The researchers then proceeded to use a non-fluorescent ester of fluorescein, 5-carboxyfluorescein diacetate (C-FDA) as a probe of the catalytically active base sites of the LDH because the reaction products from either hydrolysis of the C-FDA ester in water or transesterification of the ester with butanol are fluorescent. As shown in Figure 10.3, irradiation of the hexagonally-shaped crystal of LDH with an appropriate wavelength allows for direct observation of the hydrolysis or transesterification of C-FDA in condensed media.

The bright spots in Figure 10.4 correspond to the catalytic formation of single fluorescent product molecules formed by either transesterification with butanol (Figures 10.4a--d) or hydrolysis of C-FDA (Figures 10.4e--h). The authors were able to record the time evolution of the spot pattern (corresponding to catalytic turnover of individual active sites) and the movement of spots across the surface from diffusion of reaction products. The distributions of reaction rates as summarized in Figures 10.4c and 10.4g enable direct correlation of individual site activities with spatial positions on the catalyst surface.

The exciting observation of catalytic turnover at a single-site level was soon followed by another study in which a redox catalytic reaction was monitored at the molecular level as it occurred on individual metal nanoparticles (Figure 10.5). Xu et al. (2008) discovered that spherical gold nanoparticles catalyze the reduction of non-fluorescent resazurin to fluorescent resorufin by  $\text{NH}_2\text{OH}$ , which provided the basis for single molecule observation, as depicted in Figure 10.5a. (Xu 2008). The evolving catalytic reactions on a single 6 nm Au particle were recorded by monitoring the bursts of light at a fixed location (marked by the arrow in Figure 10.5b) and plotting the light intensity with time, as shown in Figure 10.5c.

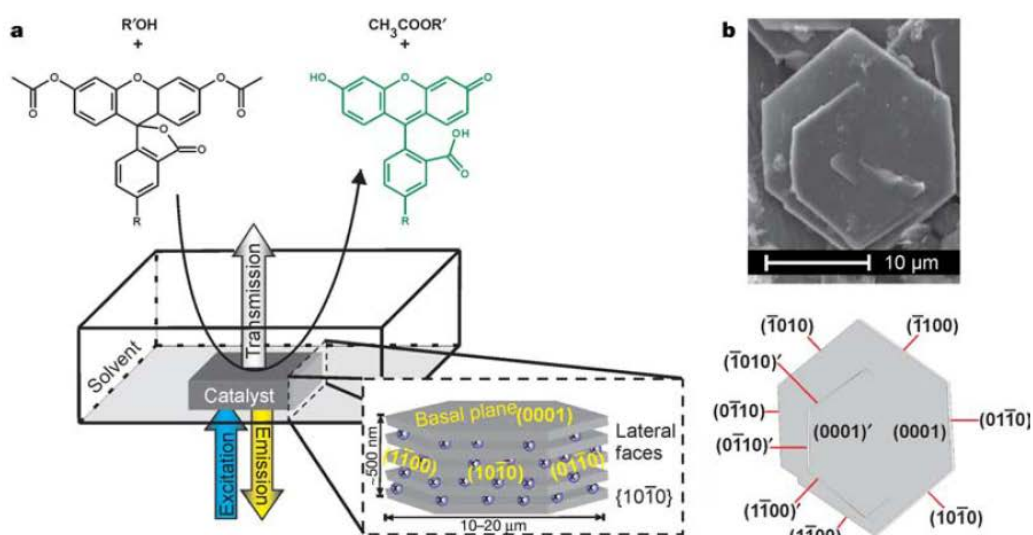


Figure 10.3. Experimental set-up. (a) Schematic drawing of the experimental set-up: the LDH particle is exposed to fluorescein ester ( $R = -\text{COOH}$  for C-FDA;  $R = -\text{H}$  for FDA) in  $R'\text{OH}$  solution ( $R' = -\text{H}$  for hydrolysis;  $R' = -n\text{C}_4\text{H}_9$  for transesterification). A wide field microscope with 488 nm excitation light was used. The inset shows the different crystallographic faces of a hexagonal LDH crystallite with indication of the Miller indices. (b) Scanning electron micrograph of a typical LDH crystal with assignment of the different crystal faces for the intergrown crystal (from Roeffaers et al. 2006).

The intensity of the fluorescence bursts was generally the same value, which indicates the turnover of one reactant resazurin molecule to one product resorufin prior to desorption from the gold particle. (In about 1% of the trajectories, the intensity of a spot was double the normal value, which suggested that two product molecules were co-adsorbed on the gold nanoparticle, as illustrated in Figure 10.5d.) The time period in the center of Figure 10.5c labeled as  $\tau_{\text{off}}$ , in which there was no fluorescence from the Au particle, corresponds to the time in which the Au particle was either bare or had non-fluorescent species adsorbed on its surface. The time period labeled as  $\tau_{\text{on}}$  corresponds to the time that product was adsorbed on the Au surface, prior to desorption into the liquid phase. From the intensity profile, a statistical measure of the overall catalytic turnover frequency of the reaction on *a single gold nanoparticle* was calculated.

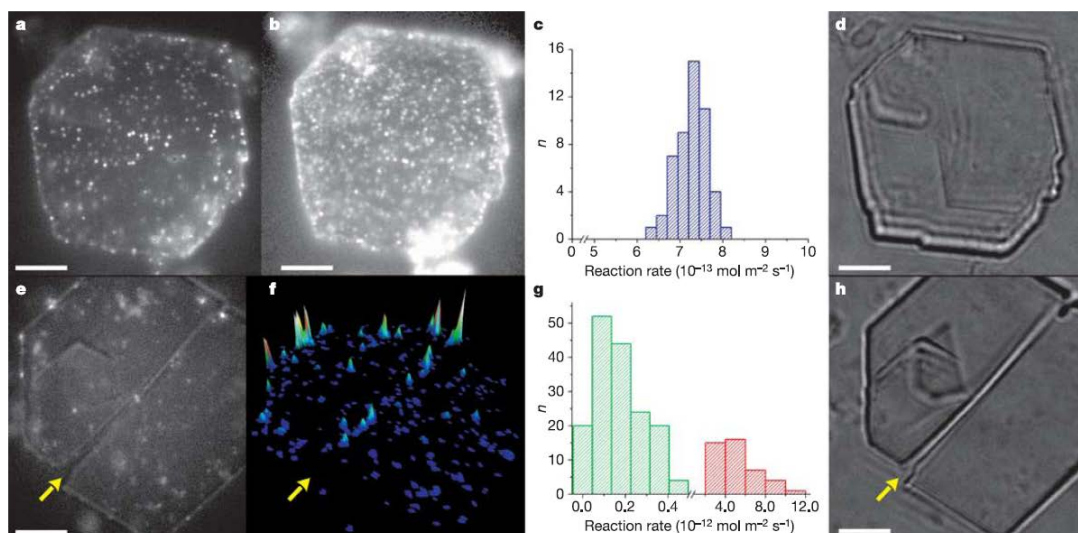


Figure 10.4. Wide field images of catalytic reactions on individual LDH particles. Transesterification of C-FDA with 1-butanol at 40 nM (a) and 700 nM (b) ester concentration on the same LDH crystal. (c) Distribution of initial reaction rates for  $1 \mu\text{m}^2$  domains on the crystal faces ( $n = 50$ ). (d) Transmission image of the crystal. (e-h) Hydrolysis of 600 nM C-FDA on LDH crystal. (e) Fluorescence image, showing formation of single product molecules mainly at crystal edges (96 ms per image). (f) Accumulated spot intensity on the same crystal over 256 consecutive images. (g) Distribution of initial reaction rates for  $1 \mu\text{m}^2$  domains on the faces of the LDH crystal ( $n = 207$ ). The distribution clearly shows two statistically different subpopulations. The fast population corresponds to active domains located on the  $\{1010\}$  faces (right graph), whereas the  $\{0001\}$  faces host the slow population (left graph). (h) Transmission image. Scale bars,  $5 \mu\text{m}$ . Arrows in e, f, h indicate the same viewing direction on the same crystal (Roeflaers et al. 2006).

The ability to observe single-molecule catalytic events on surfaces allows the field of heterogeneous catalysis to explore the influence of metal particle size on a variety of reaction kinetic parameters such as activity, selectivity, and deactivation, as well as to explore the effects of dynamic restructuring of catalytic particles on surface reactivity. A major challenge with translating this technique into general catalysis practice involves the present requirement for a change in the fluorescent nature of a molecule upon reaction. This constraint prevents the study of the vast majority of commercially -relevant chemical transformations by this technique. Nevertheless, the fundamental concepts derived from these works and continued developments in microscopic methods will surely lead to a new era of nanotechnology used in the study of catalytic reactions on solid surfaces.

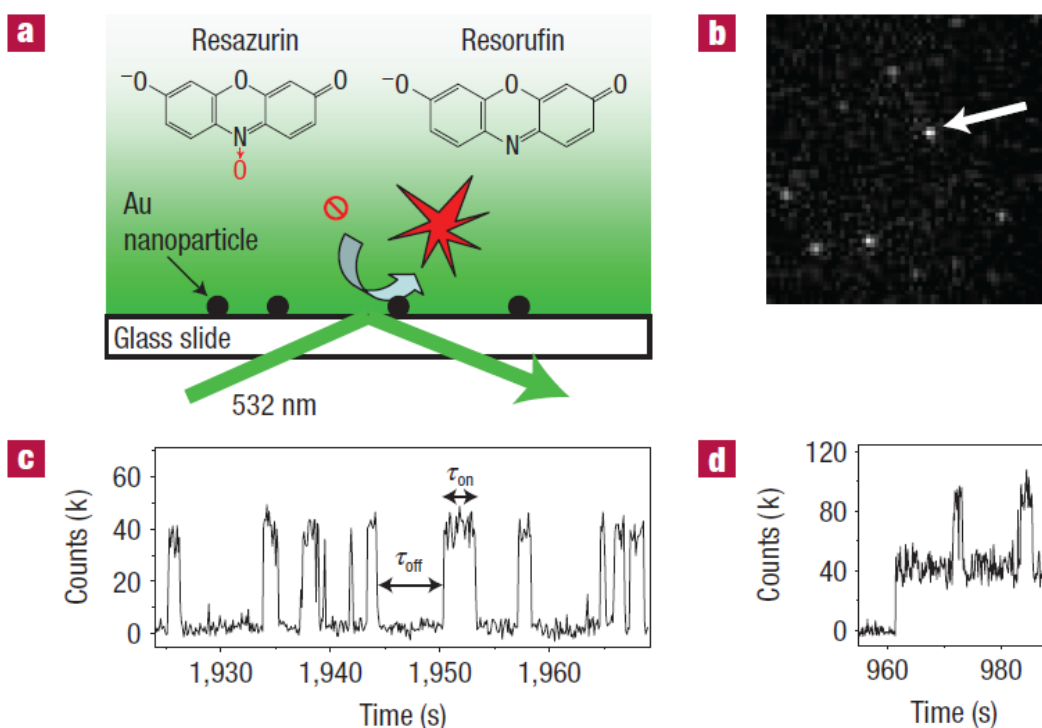


Figure 10.5. Single-turnover detection of single-Au-nanoparticle catalysis. (a) Experimental design using total internal reflection fluorescence microscopy. (b) A typical image ( $\sim 18 \times 18 \mu\text{m}^2$ ) of fluorescent products during catalysis taken at 100 ms per frame. The pixel size is  $\sim 270 \text{ nm}$ , which results in the pixilated fluorescence spots. (c) A segment of the fluorescence trajectory from the fluorescence spot marked by the arrow in *b* at  $0.05 \mu\text{M}$  resazurin and  $1 \text{ mM}$   $\text{NH}_2\text{OH}$ . (d) A segment of another fluorescence trajectory showing two on-levels at the same conditions (from Xu et al. 2008).

## 10.8.2 Representative Commercial Catalyst Applications

### Contact person: S. Mark Davis, ExxonMobil Chemical

Two recent example applications for nanoengineered microporous materials into shape-selective ExxonMobil catalytic processes are (1) selective hydroisomerization catalysts for producing high-quality lube basestocks from paraffinic gas oils (process also known as MSDW<sup>TM</sup>), and (2) catalysts for producing ethylbenzene from ethylene and benzene more selectively (also known as EBMax<sup>TM</sup>) (Santiesteban, Degnan, and Daage 2008). Normal paraffin hydroisomerization takes place inside the channels of a proprietary, medium-pore-size zeolite. By carefully tailoring the pore size and crystal morphology, it is possible to create large differences in molecular diffusion rates, so that normal paraffins are able to enter and preferentially react to produce methyl-branched isoparaffins, but larger or highly branched molecules are excluded from accessing the active sites.

A different strategy in the ethylbenzene case uses a medium-pore-size zeolite containing a mixture of 10-ring and 12-ring windows. In this case, it appears that most catalysis takes place on the external surface or in the near-surface region of the zeolite. Specifically, 12-ring surface pockets appear effective for single alkylation reactions that produce the desired ethylbenzene product, whereas molecules that diffuse inside into the zeolite cages have restricted mobility and are more prone to multiple alkylation reactions. Alternative catalyst systems for paraffin hydroisomerization and aromatics alkylation catalysts have been recently

developed using similar principles in other industrial laboratories including those of Chevron, Axens, Sinopec, and UOP.

Haldor Topsoe Laboratories has recently developed several new catalyst families where the dispersed phase structure is strongly influenced by modern nanosynthesis methods. One innovation is the BRIM™ catalyst family for hydrodesulfurization (or HDS) of diesel and other distillate petroleum streams (Haldor Topsoe Corporate Website 2010). In these systems, special catalyst synthesis methods are used to produce highly dispersed, promoted molybdenum sulfide particles that are more active and are sulfided more efficiently during catalyst pretreatment. Recent, detailed characterization studies using high-resolution electron microscopy and complementary methods showed that the edges of the small metal sulfide particles show semi-metallic electronic states that contribute to high catalytic activity (Laurisen et al. 2007). Haldor Topsoe has also recently commercialized new Fence™ catalysts for syngas conversion to methanol. In this case, small alumina particles with controlled size distribution are intimately formulated together with copper on zinc oxide, which is the active catalyst phase. The alumina acts as a structural promoter, which efficiently inhibits copper sintering and thereby improves long-term catalyst activity maintenance (Svennerber 2009).

Headwaters NanoKinetix, Inc., has also reported application of nano-based synthetic methods into the formulation of new commercial catalyst systems. One example is the NxCat™ system for direct hydrogen peroxide synthesis from hydrogen and oxygen (Headwaters NanoKinetixTechnology Innovation Corporate Nanokinetix n.d.; see also (Zhou 2006; Rueter 2006). Proprietary techniques are used to produce uniform supported 4 nm platinum-palladium alloy particles with mostly (110) surface orientation that is needed for high selectivity. This new catalyst system received an EPA Green Chemistry Award from the U.S. Environmental Protection Agency (EPA) in 2007 and is now being commercialized through a joint venture between Headwaters and Evonik. Another Headwaters innovation includes the NxCat™ system for more selective reforming of naphtha to produce high-octane gasoline. Earlier surface science and catalysis studies by Somorjai and colleagues (Davis, Zaera, and Somorjai 1984) showed that (111) platinum surface orientation is needed to more selectively catalyze paraffin dehydrocyclization to high-octane aromatics. (S. Davis 1984). Scientists at Headwaters identified new, structure-directing synthetic methods for producing high-area supported catalysts that appear to exhibit a higher degree of this platinum surface orientation (Headwaters NanoKinetixTechnology Innovation Corporate Nanokinetix n.d.; see also Zhou and Rueter 2004; Trevino, et al. 2009; Zhou et al. 2009; Zhou, Trevino, et al. 2009; Zhou, Trevino and Wu 2010). Headwaters has also reported application of nanoengineering in development of new hydroprocessing catalyst systems.

Modern nanotechnology has also had significant influence on the tools utilized to carry out industrial catalyst research and development. High-throughput, combinatorial methods for rapid robotic synthesis, characterization, and parallel screening at the laboratory scale have fundamentally changed the catalyst discovery process. Enabling technologies for these tools span several areas, including microsensors, micromachines, microelectronics, fast analytics, and data visualization and modeling. While much work remains to more directly extend these types of tools into catalyst development and commercial manufacture, there appears to be exciting potential for these types of developments over the next several years.

### 10.8.3 Fuel Cell Electrocatalyst R&D

**Contact person: Alex Harris, Brookhaven National Laboratory<sup>35</sup>**

Barriers to commercialization of fuel cells have been substantially reduced by research on electrocatalyst materials. Studies undertaken at BNL since 2002 led to the realization that the electrochemical activity of metals could be tuned by putting a single atomic layer of one metal over another, and more specifically by synthesis of tailored core-shell nanoparticles, with one or two layers of atoms of one active metal decorating a core particle comprised of a second metal. These core-shell nanocatalysts were further developed under funding by the fuel cell program in EERE in the period 2003--2010. The research has resulted in electrocatalysts for fuel cells that demonstrate a 4- to 20-fold reduction in the amount of expensive platinum necessary for good performance and show important improvements in long-term stability.

Based on these promising results and starting in 2005, BNL entered into cooperative research and development agreements (CRADAs) funded by industrial partners such as (GM, Toyota, UTC Fuel Cells, and Battelle to further progress in scale-up and to assess commercial potential. The commercial partners now believe that these core-shell nanocatalysts are currently the most promising electrocatalyst path for commercialization of low-temperature fuel cells for automotive and stationary applications.

This R&D program has generated numerous patents and patent applications, and the intellectual property portfolio has been an important factor in attracting CRADA and commercialization partners, enabling opportunities for a competitive market position. BNL's Laboratory's Technology Maturation Program (TMP) provides funding to advance the technological readiness for laboratory inventions, including scale-up or life-cycle demonstrations/testing, in order to improve commercial potential. In this case, the BNL TMP funding supported the scale-up of the synthesis from test quantities (milligrams or less) to 10-gram batches and the development of an in-house membrane electrolyte assembly (MEA) fabrication and fuel cell test station for testing larger-scale assembled fuel cells. This scale-up effort has been critical to moving the technology from the laboratory to deployment.

### 10.9 INTERNATIONAL PERSPECTIVES FROM SITE VISITS ABROAD

With the exception of the Chicago Workshop on the Long-Term Impacts and Future Opportunities for Nanoscale Science and Engineering held in Chicago, March 9–10, 2010, catalysis was not discussed within its own breakout session in the Hamburg, Tokyo/Tsukuba, or Singapore international workshops associated with this study, although the theme of catalysis did come up in sessions such as photonics and plasmonics and energy. Within these sessions there was a general recognition of the importance of more efficient and specific catalysts in a variety of energy-efficient processes. For example, nanophotonic devices might locally and specifically couple in light to photocatalysts, driving the catalytic process.

At the U.S.-Japan-Korea-Taiwan workshop held in Tsukuba, Professor Kazunari Domen of the University of Tokyo presented some work specifically focused on catalysis, including work being carried out by Professor M. Haruta of Tokyo Metropolitan University, and a long-time leader in this field. Figure 10.6 represents Haruta's work, shown at the workshop, and illustrates the differences in nanostructure of poorly active and highly active Au-based catalysts. Otherwise, no significant considerations were given to specific visions,

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<sup>35</sup> Supported by the Department of Energy (DOE) Offices of Basic Energy Sciences (BES) and of Energy Efficiency and Renewable Energy (EERE)

opportunities, and challenges for nanoscale catalysis. It should be noted, however, that the 2009 WTEC study included a broad review of international activities, and the reader should refer to that report for a recent global perspective in nanotechnology research trends applied to catalysis (Davis et al. 2009).

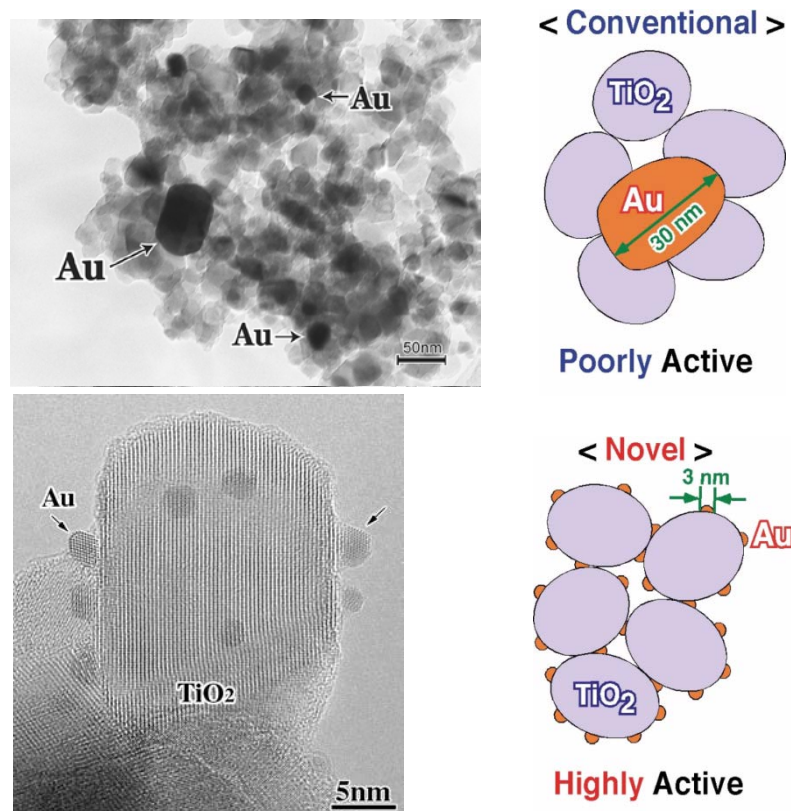


Figure 10.6. Comparison of the nanostructure of poorly active and highly active Au-based catalysts (courtesy of M. Haruta).

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