

# **Opportunities for Catalysis in The 21<sup>st</sup> Century**

**A Report from the  
Basic Energy Sciences Advisory Committee**

**BASIC ENERGY SCIENCES ADVISORY COMMITTEE  
SUBPANEL WORKSHOP REPORT**

**Opportunities for Catalysis in the 21st Century**

**May 14-16, 2002**

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## Executive Summary

Chemical catalysis affects our lives in myriad ways. Catalysis provides a means of changing the rates at which chemical bonds are formed and broken and of controlling the yields of chemical reactions to increase the amounts of desirable products from these reactions and reduce the amounts of undesirable ones. Thus, it lies at the heart of our quality of life: The reduced emissions of modern cars, the abundance of fresh food at our stores, and the new pharmaceuticals that improve our health are made possible by chemical reactions controlled by catalysts. Catalysis is also essential to a healthy economy: The petroleum, chemical, and pharmaceutical industries, contributors of \$500 billion to the gross national product of the United States, rely on catalysts to produce everything from fuels to “wonder drugs” to paints to cosmetics.

Today, our Nation faces a variety of challenges in creating alternative fuels, reducing harmful by-products in manufacturing, cleaning up the environment and preventing future pollution, dealing with the causes of global warming, protecting citizens from the release of toxic substances and infectious agents, and creating safe pharmaceuticals. Catalysts are needed to meet these challenges, but their complexity and diversity demand a revolution in the way catalysts are designed and used.

This revolution can become reality through the application of new methods for synthesizing and characterizing molecular and material systems. Opportunities to understand and predict how catalysts work at the atomic scale and the nanoscale are now appearing, made possible by breakthroughs in the last decade in computation, measurement techniques, and imaging and by new developments in catalyst design, synthesis, and evaluation.

## A Grand Challenge

In May 2002, a workshop entitled “Opportunities for Catalysis Science in the 21st Century” was conducted in Gaithersburg, Maryland. The impetus for the workshop grew out of a confluence of factors: the continuing importance of catalysis to the Nation’s productivity and security, particularly in the production and consumption of energy and the associated environmental consequences, and the emergence of new research tools and concepts associated with nanoscience that can revolutionize the design and use of catalysts in the search for optimal control of chemical transformations. While research opportunities of an extraordinary variety were identified during the workshop, a compelling, unifying, and fundamental challenge became clear. Simply stated, **the Grand Challenge for catalysis science in the 21st century is to understand how to design catalyst structures to control catalytic activity and selectivity.**

## The Present Opportunity

In his address to the 2002 meeting of the American Association for the Advancement of Science, Jack Marburger, the President’s Science Advisor, spoke of the revolution that will result from our emerging ability to achieve an atom-by-atom understanding of matter and the

subsequent unprecedented ability to design and construct new materials with properties that are not found in nature. “The revolution I am describing,” he said, “is one in which the notion that everything is made of atoms finally becomes operational.... We can actually see how the machinery of life functions, atom by atom. We can actually build atomic-scale structures that interact with biological or inorganic systems and alter their functions. We can design new tiny objects ‘from scratch’ that have unprecedented optical, mechanical, electrical, chemical, or biological properties that address needs of human society.”

Nowhere else can this revolution have such an immediate payoff as in the area of catalysis. By investing now in new methods for design, synthesis, characterization, and modeling of catalytic materials, and by employing the new tools of nanoscience, we will achieve the ability to design and build catalytic materials atom by atom, molecule by molecule, nanounit by nanounit.

## **The Importance of Catalysis Science to DOE**

For the present and foreseeable future, the major source of energy for the Nation is found in chemical bonds. Catalysis affords the means of changing the rates at which chemical bonds are formed and broken. Catalysis also allows chemistry of extreme specificity, making it possible to select a desired product over an undesired one. Materials and materials properties lie at the core of almost every major issue that the U.S. Department of Energy (DOE) faces, including energy, stockpile stewardship, and environmental remediation. Much of the synthesis of new materials is certainly going to happen through catalysis. When scientists and engineers understand how to design catalysts to control catalytic chemistry, the effects on energy production and use and on the creation of exciting new materials will be profound.

## **A Recommendation for Increased Federal Investment in Catalysis Research**

We are approaching a renaissance in catalysis science in this country. With the availability of exciting new laboratory tools for characterization, new designer approaches to synthesis, advanced computational capabilities, and new capabilities at user facilities, we have unparalleled potential for making significant advances in this vital and vibrant field. The convergence of the scientific disciplines that is a growing trend in the catalysis field is spawning new ideas that reach beyond conventional thinking.

This revolution unfortunately comes at a time when industry has largely abandoned its support of basic research in catalysis. As the only Federal agency that supports catalysis as a discipline, DOE is uniquely positioned to lead the revolution. Our economy and our quality of life depend on catalytic processes that are efficient, clean, and effective. An increased investment in catalysis science in this country is not only important, it is essential.

Successful research ventures in this area will have an impact on all levels of daily life, leading to enhanced energy efficiency for a range of fuels, reductions in harmful emissions, effective synthesis of new and improved drugs, enhanced homeland security and stockpile stewardship, and new materials with tailored properties. Federal investment is vital for building the scientific workforce needed to address the challenging issues that lie ahead in this field—a workforce that comprises our best and brightest scientists, developing creative new ideas and

approaches. This investment is also vital to ensuring that we have the best scientific tools possible for exploiting creative ideas, and that our scientists have ready access to these experimental and computational tools. These tools include both state-of-the-art instrumentation in individual investigator laboratories and unique instrumentation that is only available, because of its size and cost, at DOE's national user facilities.





# **I. Introduction**

## **A. Background, Structure, and Organization of the Workshop**

Recognition of the improved ability to measure and characterize materials and processes at the nanoscale prompted the Basic Energy Sciences Advisory Committee (BESAC) to commission a workshop to identify challenges and opportunities for catalysis in the 21st century.

BESAC was established on September 4, 1986, to provide independent advice to the U.S. Department of Energy (DOE) on the complex scientific and technical issues that arise in the planning, management, and implementation of its Basic Energy Sciences (BES) program. BESAC's responsibilities include advising on establishing priorities for research and facilities; determining proper program balance among disciplines; and identifying opportunities for interlaboratory collaboration, program integration, and industrial participation. The workshop was supported by the BES program. The workshop organization is outlined in Appendix A, and the agenda is reproduced in Appendix B.

A broad selection of experts from national laboratories, industry, and universities was invited, and about 75 of them contributed to the workshop. Participants (listed in Appendix C) were drawn from traditional subdisciplines (homogeneous catalysis, heterogeneous catalysis, biocatalysis), representing a variety of approaches to catalysis (synthesis, dynamics, analytics and spectroscopy, modeling and simulation, surface science, and materials science). Plenary presentations and breakout sessions addressed the status of catalysis science and engineering and identified opportunities for catalysis in this century, especially those emerging from improved techniques for characterization, increased capabilities for theoretical modeling using advanced computers, and recent breakthroughs in nanoscience. Each breakout session produced a substantial summary document, and this workshop report emerged from those contributions, the discussions at the workshop, and a one-day meeting of a small subset of participants and other experts held in Los Angeles on December 19, 2002.

## **B. Recent Advances in Experimental and Theoretical Methods**

The importance of catalysis to society was apparent at the outset of the workshop. Catalysts—chemical agents that bond selectively to reactant molecules to expedite rapid, stepwise scission and formation of individual chemical bonds and then uncouple (unchanged) from the products to be used over and over again—make possible the efficient control of chemical reactivity. A key advantage in catalysis is the ability of catalysts to change the reaction path, accelerating only the path with lower activation energy toward the desired products. Catalysts thereby make possible the control the chemical transformation steps leading to the desired products with minimal input of energy. The petroleum, chemical, and pharmaceutical industries, contributors of \$500 billion to the gross national product of the United States, rely on catalysts to produce everything from transportation fuels to “wonder drugs” to paints to cosmetics. The reduced emissions of modern cars, the abundance of fresh food at our stores, and the new pharmaceuticals that improve our health are made possible by the speed, efficiency, and precision of catalysts. Nature's catalysts, enzymes, show how amazingly efficient catalysts can

be—they make possible essentially all biological reactions—and, by comparison with today’s technology, they show how much opportunity there is for improvement. Control and efficiency of chemical conversion comparable to that demonstrated by Nature are in sight for countless known and unknown reactions, as we learn how catalysts work and how to engineer them for specific reactions.

The opportunities to understand and predict how catalysts work at the atomic scale have unfolded dramatically in the past 20 years with the emergence of powerful predictive methods including density functional theory (DFT); incisive instruments for imaging catalysts and reactants at the nanoscale and atomic scale, and dedicated facilities for examining catalysts as they function, even at the high temperatures and pressures used in industrial processes. Single-site catalysts are being synthesized and their mechanisms elucidated. Developments in structural biology leading to new insights into protein structure and activity are providing inspiration for the design of catalytic structures. There is an emerging ability to make uniform arrays of catalysts and to manipulate and spectroscopically probe single molecules. Advances in femtoscience will allow us to time-resolve structural changes on ultrafast time scales, thus adding new dimensions to our understanding of primary chemical reactions. Theory can now provide reliable calculations of the thermodynamics and kinetics/dynamics for model catalytic reactions. Combinatorial synthesis, rapid screening methodologies, and cheminformatics are providing new catalysts at an unprecedented rate. During the past few years, scientists have developed an emerging ability to use nanofabrication capabilities to make “manmade” or artificially structured catalyst arrays on supports that are quite different from those prepared by traditional methods. New, powerful techniques such as scanning tunneling microscopy (STM), synchrotron and neutron sources, computational methodologies implemented on terascale computers, and the impending construction of DOE’s new Nanoscale Science Research Centers all converge to place catalysis science at the threshold of new understanding and new technology.

As these opportunities have expanded explosively, so have the needs. For example, catalysts are needed

- for use in alternative energy sources and new conversion technologies such as fuel cells and devices for photolytic splitting of water to form hydrogen and oxygen,
- for the manufacture of new materials such as polymers with tailored nano-, micro-, and macroscopic properties suited for new technological applications,
- for the precise synthesis of molecules such as pure drugs without toxic stereoisomers, and
- for the production of chemicals with minimal energy input and without environmentally damaging side products.

The convergence of these recognized and increasingly urgent needs with the opportunity for dramatic advances in catalysis science makes a compelling case for increased investment in catalysis research.

### C. The Grand Challenge

Many exciting specific challenges for catalysis were identified during the workshop. Beyond them, a compelling and fundamental challenge became clear. Simply stated, **the Grand Challenge for catalysis science in the 21st century is to understand how to design catalyst**

**structure to control catalytic activity and selectivity.** Through efforts that involve both experiment and theory, we must develop a fundamental atomic-scale and nanoscale understanding of catalysis.

Meeting this challenge will make it possible to selectively activate a single bond in a multifunctional reactant to produce a desired product. It will also enable a predictive capability in catalysis science and allow the design of new catalysts and catalytic processes that approach the ultimate goal: highly active, stable catalysts that provide near-100% selectivity to a desired product with minimal use of energy. In short, success in this endeavor will result in deeper insights into catalysis and in the development of new technology that will benefit society in ways that today are almost unimaginable.

#### **D. Enabling Approaches for Progress in Catalysis**

A new investment in catalysis, to be successful, must involve an interdisciplinary approach to the science. Flexibility in our approach is required to allow the best catalytic science to flourish. This approach includes not only the sponsorship of single-investigator research, but also the sponsorship of research teams that bring together expertise from a wide range of disciplines. A unified approach to research that combines exciting advances in bioscience, molecular science, surface science, computational science, and nanoscience to address common problems in catalysis science will be able to capitalize on, for example,

- the use of modern methods of genetics and biology to optimize enzyme structures for reactions under conditions different from those of Nature;
- the precise synthesis of catalysts as components of materials that facilitate efficient applications, ranging from active, selective molecular single-site catalysts, easily separable and noncorrosive because they are mounted on surfaces and in matrices (as in enzymes), to such molecular catalysts sequenced in assembly lines (as in mitochondria); and
- design of the surfaces and matrices of these catalysts at the nanoscale to facilitate the transport of reactants, intermediates, and products for efficient applications.

#### **E. Consensus Observations and Recommendations**

Consensus emerged at the workshop on several key observations and recommendations:

- Catalysis will play an essential role in the solutions to major problems that our society faces: energy, environment, and more generally, the quality of life.
- The time is right for catalysis science to make unprecedented strides toward new understanding and new technology, taking advantage of recent exciting developments in rapid catalyst synthesis and screening techniques, advances in theory and computation, breakthroughs in nanoscience, and the availability of powerful analytical tools, particularly those at DOE's national user facilities.
- Catalysis scientists face a Grand Challenge: to understand and thereby control the relationship between catalyst structure and catalytic chemistry. We must develop a fundamental atomic-scale and nanoscale understanding of catalysis to design new catalysts and new catalytic technology.

- New investments in catalysis should encourage both new interdisciplinary approaches by single investigators and multidisciplinary alliances of experimentalists and theorists. National user facilities have an important role to play in these efforts.

## **F. Opportunities for an Expanded Role for the Department of Energy**

For the present and foreseeable future, the major source of energy for the Nation is found in chemical bonds. If scientists and engineers can develop the ability to understand and thereby control the relationship between catalyst structure and catalytic chemistry, the effects on energy production and use in domestic as well as industrial applications will be profound. Fabricated materials also play a key role in our society. Materials and materials properties are at the core of almost every major issue that DOE faces, including energy, stockpile stewardship, and environmental remediation. The synthesis of new materials is certainly going to happen through catalysis. The meeting of this Grand Challenge will allow the design of completely new materials, catalysts, and catalytic processes for as yet unimagined purposes and benefits.

Through its Office of Basic Energy Sciences, DOE is currently providing about 60% of the basic research funding for catalysis science and related activities in the United States. Many of the exciting recent developments that have positioned catalysis for a revolution have already been supported by the BES program. DOE is well structured to encourage and evaluate the type of interdisciplinary research programs needed in this expanded effort.

## **G. Summary of Specific Challenges and Opportunities**

A large number of challenges was identified by the participants at the workshop. The group was too small to provide even-handed representation of all areas of catalysis; nevertheless, the list below, although only a partial catalog, makes a compelling case for an increased Federal investment in catalysis. The challenges and opportunities include the following:

- To identify general trends and unifying principles that are common or specific to different classes of catalytic phenomena, (e.g., heterogeneous catalysis, homogeneous catalysis, and biocatalysis).
- To establish, using the latest in characterization diagnostics, firm relationships between catalyst structure, rates, and selectivity of elementary reaction steps.
- To build close interactions between theoretical/computational and experimental researchers to develop advanced modeling and simulation tools that are accessible to the entire catalysis community.
- To use catalysts to control the three-dimensional (3-D) structures of products, including enantiomeric selectivity.
- To efficiently prepare and screen families of prospective catalysts.
- To create bases of theoretical and experimental data and the methodologies to perform data mining with the goal of optimizing the design of new catalytic systems.
- To develop an understanding of the thermodynamics and kinetics of the nucleation, growth, and sintering of supported metal catalysts.

- To undertake *in situ* measurements of chemical, spatial, and temporal properties of working catalysts using state-of-the-art characterization methodologies, including existing and future synchrotron and neutron facilities.
- To establish an understanding of the nonuniformity of catalytic reactions.
- To predict by theory, using advanced computational resources, the essential surface species and kinetic parameters that govern catalytic steps in industrial heterogeneous catalytic processes and to provide the same type of thermodynamic and kinetic information for homogeneous catalysts.
- To use catalysis to synthesize new nanostructures.
- To prepare highly reactive, coordinatively unsaturated catalytic sites stably isolated on support surfaces, including single-crystal surfaces. Arrays of these sites will consist of multiple metal atoms and molecular catalysts sequenced in assembly lines, as in mitochondria, for tandem catalytic processes.
- To design and synthesize new, non-natural nanoporous and mesoporous supports for catalysts that control their chemical and physical properties and isolate catalysts in nanocages, controlling reactant access and product egress.
- To use the methods of nanoparticle synthesis to precisely construct clusters of metals, metal oxides, and metal sulfides on supports.

## II. Opportunities for Scientific Advances

Every researcher in the field of catalysis has a personal list of the most important chemical transformations that catalysis could tackle in the future. Many of these lists include the catalytic production of new fuels and chemicals by selective oxidation of alkanes such as methane. Current commercial “gas-to-liquid” processes involve costly, endothermic steam reforming of methane to synthesis gas ( $\text{CO} + \text{H}_2$ ), followed by conversion to methanol by CO hydrogenation or to higher hydrocarbons by Fischer-Tropsch synthesis. Direct selective oxidation to liquid fuels (methanol, gasoline, or other liquid fuels) would allow for low-capital-investment plants located at gas wells, more energy-efficient production, and lower  $\text{CO}_2$  emissions.

The development of new electrocatalysts also holds a place on most “top ten” lists for catalysis. Fuel cells represent one of the greatest opportunities for clean and efficient power generation, including electric power for transportation, but more efficient cathodes, as well as efficient anodes that use fuels other than hydrogen, are needed to allow direct oxidation of liquid fuels such as methanol. Limited petroleum resources are the source of virtually all of the feedstock for the global chemical industry; the development and use of renewable carbon sources must be a priority for the first half of this century.

This short selection of potential new technologies demonstrates that improved catalysts can have an impact on the sources of our energy, the identities of our fuels, and the efficiency with which their energy is used. To realize these improvements, we must understand how to integrate recent and forthcoming advances in catalysis and nanoscience, how to merge homogeneous and heterogeneous catalysis, how to take advantage of biocatalysis, and how to extend our capabilities in synthesis and characterization and in theory and simulation.

## A. Catalysis and Nanoscience

The electronic structure and chemical properties of compositionally identical materials are transformed when their dimensions are reduced from the macroscale through the nanoscale to the angstrom scale. A nanometer-size particle, or nanoparticle, can exhibit electronic and physical properties distinct from those of the corresponding bulk solid, and it should therefore display unique catalytic properties. Indeed, it is well known that the catalytic properties of nanoparticles of a metal differ markedly from those of larger, bulk-like particles of the same metal. Examples include the selective oxidation of propylene to propylene oxide and the oxidation of CO by gold nanoparticles, and the selective reduction of NO by iron oxide nanoparticles. Extraordinary advances in synthetic methods, in characterization techniques, and in theoretical and computational approaches offer unmistakable promise for new breakthroughs in the design of nanostructured catalytic materials.

Using recently developed methods for nanoparticle synthesis, we can control the size and composition of nanoscale catalysts. With better understanding of the connection between catalyst structure and catalytic chemistry, we will be able to tailor catalytic properties to the precise needs of a particular process.

By combining traditional molecular strategies with recently developed nanoscience methods, synthetic chemists working with materials scientists can now fabricate new catalysts using strategies such as templating, molecular precursors, self-assembly, and lithography. These advances in the synthesis of nanoscale materials provide unique opportunities to construct and design nanostructured catalysts for optimum activity and superior selectivity, the keys to maximum catalytic efficiency. At the same time, they provide confidence that the unique catalytic properties of any single nanoparticle can be replicated into many kilograms of catalyst material, all of it exhibiting the same catalytic properties, for research, pharmaceutical synthesis, or industrial processes.

Catalytic nanoparticles are typically anchored to a supporting solid, such as silica or alumina, for stability toward sintering. Because these materials are heterogeneous at the nanoscale, characterizing individual catalytic particles has been a fundamental barrier to a molecular-level understanding. Advances in nanoscale methods now allow, via microscopic and single-molecule spectroscopic techniques, characterization of the structure and electronic properties of a single catalytic nanoparticle and its unique catalytic chemistry. These new characterization methods offer unprecedented opportunities to detail the electronic and physical properties of nanostructured catalysts and to “see” these catalysts function in a realistic environment. By preparing nanometer-size islands of one oxide (such as  $\text{TiO}_2$ , to which catalytic metal clusters are relatively strongly bound), surrounded completely by domains of a second oxide (such as  $\text{SiO}_2$ , to which the clusters bind much more weakly), it should be possible to greatly reduce catalyst aggregation into larger clusters, because an activation barrier exists for diffusion of the metal from one  $\text{TiO}_2$  island to another across the  $\text{SiO}_2$  surroundings.

## Nanostructured Catalysts: Catalysis by Gold Nanoclusters

Since the discovery of the direct catalytic oxidation of ethylene to ethylene oxide, the precursor to ethylene glycol antifreeze, the chemical industry has been searching for a direct catalytic route to propylene oxide. Within the last few years, gold clusters approximately 3 nm in diameter, supported on titania as shown in Fig. 1(a), have been found to catalyze the production of propylene oxide directly from air and propylene. However, what makes these clusters special has been a mystery until recently. The catalytically active gold clusters have been shown to be approximately two atoms thick [see Fig. 1(b)] and thus resemble “rafts” on the oxide support. The electronic properties of these particles are between those of atomic gold and bulk gold and thus uniquely characteristic of the nanoscale. As long as the gold clusters maintain their unique shape and size, the partial oxidation of propylene to propylene oxide in the presence of oxygen takes place. However, gold is a highly mobile element on these surfaces, and the gold rafts rapidly coalesce into larger particles. The larger particles have the electronic properties of bulk gold and thus lose their special selectivity for making propylene oxide. Studies are under way to understand and design supports that will prevent the coalescence of the rafts.

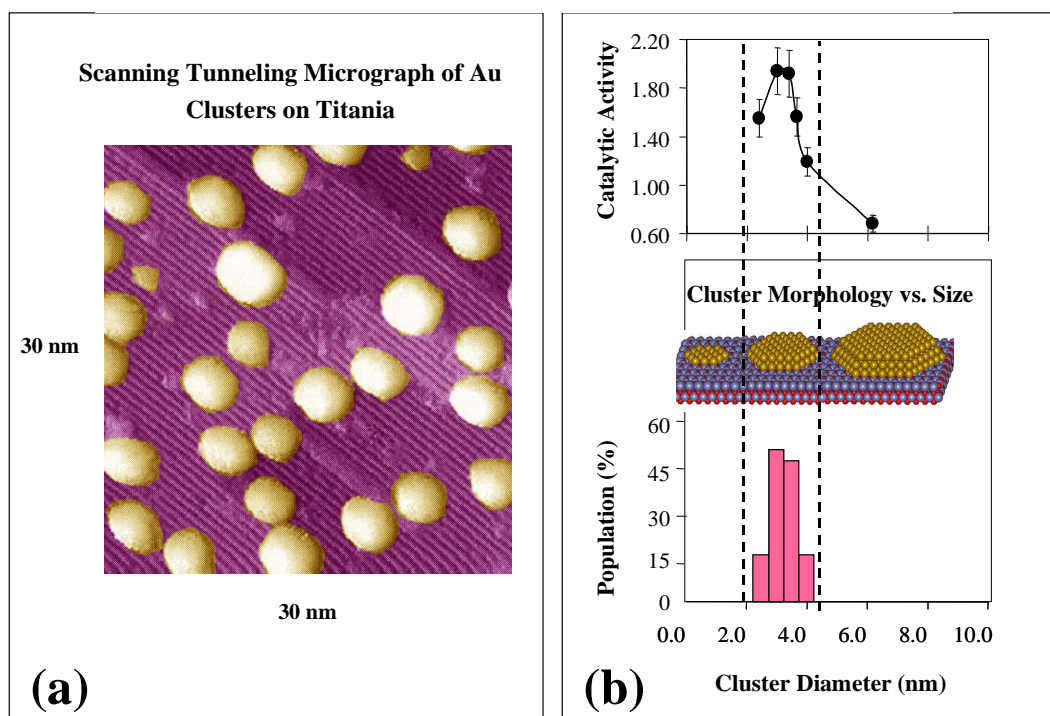


Fig. 1. Effect of cluster size and morphology on the reactivity of gold clusters supported on titania.

This particular example illustrates a more general point: as we learn the atomic details of how sintering and catalyst deactivation occur, we have the opportunity to use nanostructure itself to inhibit these processes and maintain nanoscale reactivity. The use of nanostructure in this way, to maintain and control nanostructure, bears some resemblance to the use of ligands to stabilize active catalyst centers in solution, and it begins to blur the traditional distinction between homogeneous and heterogeneous catalysis by combining some of the best attributes of both.



The use of catalysis to synthesize nanostructure presents still another set of opportunities. The fundamental essence of catalysis is controlling the rates at which chemical bonds are formed and broken, and this is not limited to the chemical bonds of small molecules. Materials themselves are networks of chemical bonds, and, by controlling the relative rates of bond formation, catalysis can be used to determine the composition, properties, and morphology of materials, especially metastable materials that cannot survive the rigorous conditions of uncatalyzed synthesis. Some of the best examples are nanotubular forms of carbon. In Fig. 2, straight nanotubes of carbon are grown by catalytic conversion of acetylene using iron/silica nanoparticles as catalysts. However, nanotubes of carbon sometimes grow as coils, as when iron/indium nanoparticles are used as catalysts for acetylene conversion (see Fig. 3). The atomic details of what determines the pitch and handedness of these coils—indeed, even the atomic details of why this coiling does or does not occur—are not yet known. But as we learn these details and better understand the relationships between catalyst structure and catalytic chemistry, we will have the opportunity to prepare many other forms of nanostructured matter that are presently unattainable.

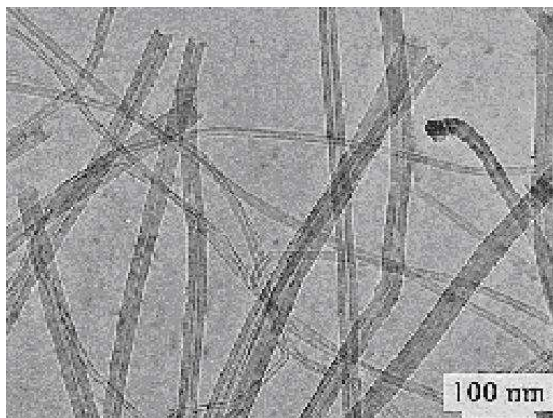


Fig. 2. Carbon nanotubes grown from acetylene using iron/silica nanoparticulate catalysts.  
Source: Z. W. Pan et al., *Chem. Phys. Lett.* **299**, 97 (1999).

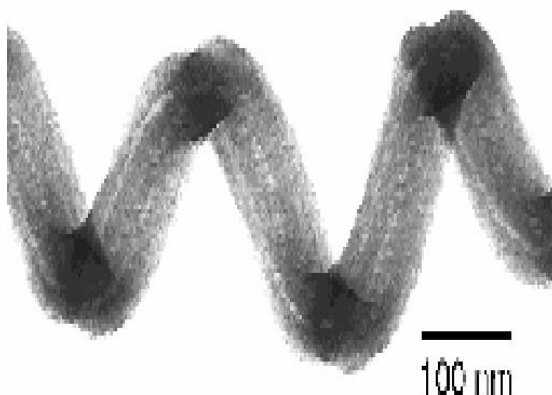


Fig. 3. Carbon nanocoils grown from acetylene using iron/indium nanoparticulate catalysts.  
Source: M. Zhang et al., *Jpn. J. Appl. Phys.* **39**, L1242 (2000).

Clearly, complete mastery of the connections between catalysis and nanostructure will be an extremely demanding challenge. Subtle changes in the composition or electronic structure of a catalyst can trigger large changes in its kinetic behavior; varied architecture of the nanoscale environment will determine the stability and activity of catalyst regions; and the nanoscale environment itself can be affected, even created, by catalytic processes. Yet all of these factors and their effects, although complex, are not indeterminate. By using the tools of nanotechnology and the guidance of theory and large-scale computations (and biology), we can learn how to control particle size and composition, how to deliberately tune these effects to achieve desirable catalytic chemistry, and how to realize the dream of combining the best attributes of heterogeneous catalysts (stability, longevity, separability) and homogeneous catalysts (tunability, predictability, controllability) in a new generation of catalytic materials.

## **B. Molecular Catalysis on Surfaces: Merging Homogeneous and Heterogeneous Catalysis**

Molecular catalysts in solution offer the advantages of uniform accessibility and uniqueness of structure that impart single catalytic cycles and selective conversions. In contrast, solid catalysts offer sites only at surfaces, which are nonuniform, with a spectrum of reactivities and low selectivities. Uniform catalytic sites on surfaces retain the advantages of those in solution, with the added benefits of ease of separation from products, lack of corrosion, and robustness for high-temperature operation.

This field is in its infancy. There is a compelling opportunity for precise design of surface catalytic sites for specific chemical conversions, such as conversion of abundant and traditionally unresponsive feedstocks, including methane and CO<sub>2</sub>. Ultimately, supported molecular catalysts will rival enzymes in their sophistication.

Most catalysts present coordinatively unsaturated metal centers that allow activation by bonding of reactants as ligands. Syntheses of supported molecular catalysts are carried out with precursor compounds that can be anchored to the support with removal of the precursor ligands. The optimum precursors include organometallic complexes with reactive ligands that are easily replaced by the support. Research in surface organometallic chemistry and catalyst synthesis has already led to impressive commercial successes, illustrated by the “single-site” metallocene catalysts for manufacture of polyolefins with tailored structures (production rates already exceed 100 billion pounds per year) and the Acetica™ catalyst (a rhodium complex anchored to a functionalized resin) for conversion of methanol to acetic acid. Whole new families of molecular surface catalysts may be envisioned, emerging from synthesis that involves integration of design of catalytic sites with nanoscale design of porous supports:

- Highly reactive, coordinatively unsaturated cations stably isolated on support surfaces. This family of catalysts provides high activity and selectivity with the catalytic sites stably isolated, accessible to reactants, and protected from reactions with each other that would cause deactivation.
- Arrays of these sites consisting of multiple metal atoms and other structures. This family represents new kinds of bifunctional or polyfunctional catalysts that can be used for sequences of reactions and facilitation of thermodynamically unfavorable steps in catalytic

cycles. Moreover, this strategy allows the sequencing of molecular catalysts in assembly lines (as in mitochondria) for tandem catalytic processes.

- Arrays of these sites mounted on regular (crystalline) surfaces. The support will contribute to the preciseness of catalyst structure as a whole for this family. Supported catalysts with chiral ligands (including the support) can be prepared for selective synthesis of biologically active molecules, such as drugs. Progress will spring from continuing integration of nanomaterials science with catalysis.
- Design of nanoporous and mesoporous supports. Development of this family of catalysts is a vigorous and expanding field; supports will be selected for both their chemical properties (as ligands for the metals) and their physical properties (controlling the steric environment of the sites as well as reactant access and product egress). Supports will range from hard (inorganic) structures to soft structures, including organic polymers, micelles, and inorganic surfaces functionalized with fuzzy organic layers to control the reaction environment. Catalytic sites can be stabilized by isolation in nanocages (e.g., in zeolites) and in nanostructured nests anchored to supports.
- Precisely constructed clusters of metals, metal oxides, and metal sulfides on supports. Nanoclusters of metals, oxides, and other materials have new, undiscovered properties, different from those of the bulk; they represent a new kind of single-site catalyst. Preparation of these nanoclusters on supports, especially when they are uniform and/or present in structured arrays, will lead to new catalytic properties, including coordinative unsaturation, defects, novel redox properties, and controlled acidity and basicity. These properties can be varied widely over wide ranges and controlled by selection of the sizes and compositions of the nanoclusters and their interactions with supports. Even extremely subtle changes in the electronic structure of a catalyst can trigger large changes in its performance, and a major challenge is to tune the catalytic properties by varying the catalyst structure on the atomic scale and the nanoscale. Catalysts with narrow size distributions are needed, both to facilitate rapid fundamental understanding and to provide high selectivities and production with minimized undesirable products. Methods for preparing these catalysts—such as patterning, imprinting, and selective surface organometallic synthesis—are developing rapidly, guided by theory and computation.

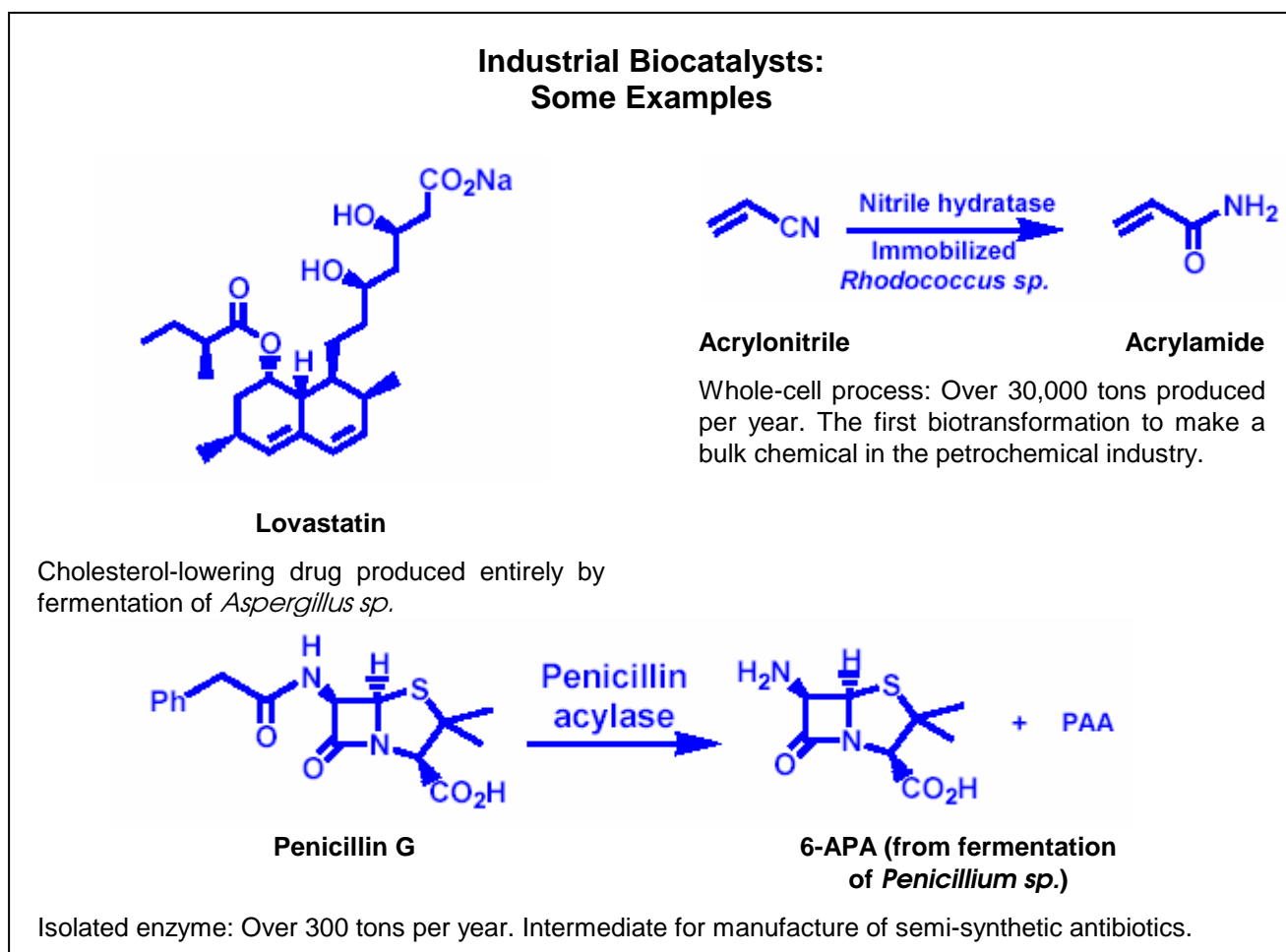
These new materials—tailored molecular catalysts on tailored supports—offer the prospects of entirely new catalytic properties, combined with two advantages:

- They can be characterized incisively, even in the working state, by methods available at modern facilities offering high-flux sources of photons and neutrons and by spatially resolved, atom-specific microscopy and spectroscopy.
- They can be modeled accurately with modern theoretical/computational methods.

Thus, the development of this class of catalysts will mark a new era of rapid advancement in catalytic science and technology as powerful theoretical and experimental methods are synergistically brought to bear. These are the catalysts that will bring researchers to a common focus and dissolve the boundaries between the traditional subdisciplines of homogeneous, heterogeneous, and biological catalysis, moving catalyst design from a tantalizing hope to commercial reality.

## C. Biocatalysis

The biological cell provides a paradigm of an integrated catalytic system from which we can learn valuable lessons. Complex networks of reactions are precisely controlled and regulated, with reactions occurring in aqueous solution and at organic-aqueous interfaces. The key components of this system are enzymes, Nature's catalysts, which can accelerate chemical reactions enormously (up to  $10^{17}$ -fold) and exhibit extremely precise chemical control, regiocontrol, and stereocontrol. The fields of biochemistry, molecular biology, and cell biology have all contributed greatly to our understanding of how enzymes perform their cellular functions. As a result, enzymes have not only provided the inspiration for the development of many ingenious chemical catalysts; they are also being used themselves to great effect in industrial applications. However, a large gap in understanding the nature of biological catalysis remains, and this must be filled before the full potential of enzymes as industrial catalysts can be harnessed.



Over the last two decades, there has been an increasing interest in exploiting enzymes as industrial catalysts for both natural and non-natural chemical processes. Indeed, there are numerous commercial examples of biological catalysis, including fermentations, whole-cell biotransformations, and the use of isolated enzymes (the sidebar on industrial biocatalysts shows

a few examples). Although these successes are significant, the challenge remains to more fully integrate biological catalysis with chemical catalysis and chemical synthesis, maximizing the potential of each. The field is poised for tremendous breakthroughs in the next decade that can have a huge impact on a number of important markets, including pharmaceuticals, fine chemicals, fuels, and commodities.

### *1. New Enzymes for Biocatalysis*

There is an urgent need to expand the toolbox of currently available biocatalysts to access new chemical conversions. Many researchers in academia, government, and industry have developed technologies for the discovery of novel biocatalysts, including screening of culture collections and, more recently, screening of libraries constructed by the direct isolation of DNA from uncultured environmental samples. These programs continue to emphasize new classes of biocatalysts with commercially useful properties, such as new selectivities, higher catalyst stability, and expanded pH and temperature tolerance. The class of enzymes most widely applied to organic synthesis today is the hydrolases. Opportunities exist, however, for the application of enzymes from all six classes (oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases), and increased biocatalysis research is needed in each class.

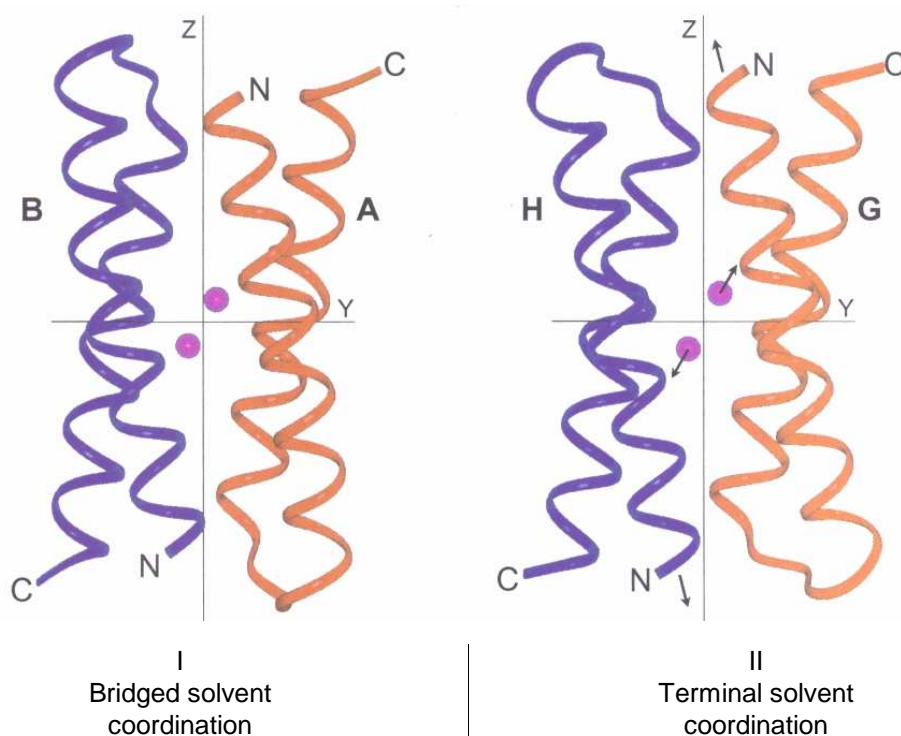
Oxidoreductases, in particular, catalyze some of the most useful chemical transformations that are often beyond the reach of synthetic organic chemistry, such as the regiospecific hydroxylation of alkanes; yet they remain underutilized in industry. This is due in part to the need for new enzymes and in part to the need for expensive co-factors such as NADH/NAD<sup>+</sup>, NADPH/NADP<sup>+</sup>, FADH/FAD<sup>+</sup>, PQQ, and ATP/ADP. A few co-factor regeneration systems have been developed, but additional research is needed, and innovative solutions are sure to arise from collaborations between biochemists, catalysis chemists, and electrochemists.

### *2. Biocatalyst Optimization by Evolution*

In a few cases, rational redesign of existing enzymes by site-directed mutagenesis has led to improvements in activities. However, such efforts have more commonly met with little success. This lack of success can be attributed to a lack of understanding of enzyme mechanisms and structure-function relationships. Rational mutagenic techniques are akin to the laborious stepwise chemical methods for improvement of nonbiological catalysts. As is the case with nonbiological catalysts, successful application of these techniques can come only from more fundamental research to shed further light on how enzymes function at the atomic scale. Exciting developments can be expected to emerge from the application of new structural and spectroscopic techniques, such as atomic force microscopy (AFM), time-resolved X-ray crystallography, and neutron scattering.

In contrast to the rational design approach, several more stochastic methods for enzyme improvement have been developed in the last decade. These methods draw upon the power of natural Darwinian evolution. Details of the techniques vary, but all of the directed evolution approaches involve an iterative process of random mutation and high-throughput screening to uncover new enzyme variants with improved properties. No prior knowledge of how the 3-D structure of the enzyme affects its properties is required.

## Artificial enzymes



The crystal structure of an artificial four-helix bundle metalloprotein shows the presence of two different dimanganese coordination environments (I and II) having bridging or terminal solvent molecules. These environments are accommodated by a novel sliding-helix mechanism (arrows in II show the directions of helix motion and ion motion) that facilitates the changes in coordination environment accompanying a catalytic transformation.

Source: R. B. Hill, D. P. Raleigh, A. Lombardi, and W. F. DeGrado, *Acc. Chem. Res.* **33**, 745–54 (2000).

Directed evolution programs can test hundreds of thousands of variants and thus sample large areas of sequence space. Results from such analyses can provide valuable information about biological solutions to a given phenotypic challenge and can be used to further understand enzyme structure-function relationships. Ultimately, the goal will be to predict enzyme structure and function from the primary amino acid sequence. In the meantime, these evolution-based technologies provide rapid access to biocatalysts tailored to meet the demands of a particular chemical process, including those occurring under extreme conditions not typically found in the cellular environment (e.g., high acidity, high temperatures, and nonaqueous solvents).

### 3. Integration of Biological and Chemical Catalysis

The pharmaceutical industry continues to demand single-enantiomer drugs, and thus the importance of enantioselective catalysts, including biocatalysts, can be expected to increase. Biocatalytic conversion of renewable feedstocks derived from cellulose, hemicellulose, starch, and plant oils into desirable products, including transportation fuels such as ethanol, hydrogen, and biodiesel, is an important economic target. This significant challenge will require long-term, interdisciplinary basic research to establish appropriate scientific foundations. In all cases, the

full economic and productivity potentials of a process built around biocatalysts can be achieved only by successfully integrating the biocatalysis step in the context of upstream and downstream chemical processing, chemical synthesis, and catalysis.

As heterogeneous catalysis, homogeneous catalysis, and biocatalysis merge into an integrated catalysis science, new developments that take advantage of the synergies can be anticipated. Combining biocatalysts and chemical catalysts can lead to exciting possibilities. A recent example is the development of dynamic kinetic resolution processes such as the stereoselective esterification of racemic alcohols using an enantioselective lipase in tandem with a ruthenium-based racemization catalyst. Future work bringing together two or more catalysts with complementary activities could lead to the ability to perform entirely novel chemical transformations. In a homogeneous system, an enzyme and a nonbiological catalyst would need to be compatible; directed evolution might be used to optimize the enzyme's compatibility. Alternatively, the catalysts could be spatially separated. For example, it may be possible to create ordered arrays of catalyst centers immobilized along nanostructures in such a way that a substrate can be processed along the complex of catalysts to give a unique product, perhaps even going through metastable intermediates. This type of substrate channeling along such a complex would be analogous in some ways to what takes place in natural modular enzyme systems, such as polyketide synthases or nonribosomal peptide synthetases.

To attain these types of integrated catalytic systems, considerable challenges must be overcome. Research should be focused on developing new and mutually compatible biocatalysts and chemocatalysts under an integrated research program.

## **D. Tools for Advancing Catalysis Science in the 21st Century**

### *1. Synthesis and Characterization*

Chemical synthesis, the production of more complex and more valuable molecules from simpler reactants, is the *raison d'être* of catalysis. Progress in catalytic synthesis will change the quality, economics, and energy consumption of our lives. New approaches to characterization of catalysts will improve the identification of species that can make this synthesis occur.

Synthesis in catalysis has a dual focus: the formation of a target molecule from a catalytic reaction and the formation of the target structure of the catalyst used for these reactions. Underlying the Grand Challenge of connecting catalyst structure with catalytic chemistry are more specific challenges in synthesis. To meet our Grand Challenge, we must understand the connections between catalyst structure and both catalytic activity and selectivity.

Using both the power of chemical synthesis and new, more powerful methods of characterization, we must strive to understand the connection between catalyst structure and the rates, order, and selectivity of the elementary reactions in a catalytic cycle. More specifically, we must understand how catalyst structure controls the relative rates and order of the individual single-step reactions, typically called elementary reactions, of a catalytic cycle.

If we can understand the connection between structure and rates of elementary reactions, we will be able to alter catalyst structures in a rational way to increase or decrease the rates of individual desired and undesired elementary reactions. This control over rate will allow us to design catalysts that are active enough to cleave strong bonds and selective enough to react at

one position of a multifunctional molecules, or catalysts that are active enough to form the desired product at high rates and selective enough to form all undesired products only at low rates. We know from Nature that such challenges can be met: for example, enzymes cleave the C-H bond of methane in the presence of many typically more reactive bonds.

New synthetic methods employing catalysts must be developed to control the 3-D structures of products. The benefits of selectivity in catalysts extend far beyond a selection of one type of bond over another. Most molecules have a 3-D structure that controls their properties, and variations in this structure have major implications for their ultimate utility. Millions of tons of linear butanol are bought each year, but branched butanol is nearly useless; billions of dollars of single-enantiomer or single-handed drugs are bought each year, but the opposite-handed isomer, or enantiomer, is useless and may even be harmful (e.g., the presence of the undesired stereoisomer in thalidomide was the cause of birth defects).

The selectivity of a catalyst can dictate the 3-D structure of reaction products, but our understanding of the connection between structure/reactivity and this type of selectivity is rudimentary. In order to design catalysts that control product architecture, this understanding must be improved. Catalysts can be used to control the relative connectivity of atoms (regiochemistry), the orientation of groups at a flat carbon-carbon double bond (*E/Z* selectivity), the geometry at one carbon atom relative to another (diastereoselectivity), and the handedness (enantioselectivity) of the entire molecule. Again, we know this challenge can be met: Nature's enzymes produce single enantiomers of amino acids and single diastereomers and enantiomers of more complex molecules such as steroids. We must become adept at generating practical catalysts for the construction of chemical building blocks (such as amino acids) and complex molecules (such as natural products).

We should undertake the efficient preparation of families of prospective catalysts. We will never reliably create a new chemical reaction or a faster version of an existing reaction by preparing just one prospective catalyst until we understand all of the details of how to design a catalyst from first principles. The road to increased activity and selectivity is paved by a myriad of structures that will teach us by experience their connections to activity and selectivity. Thus, we need to create new types of catalyst structures and new methods for catalyst preparation to provide the data and experience to show what makes a catalyst active and selective. To date, synthesis of catalysts has often consumed more time and more effort than the testing of these catalysts. Thus, we must open the bottleneck of catalyst synthesis by learning better methods to prepare families of catalysts.

A paradigm shift has begun to occur in the way catalysts are prepared. The combinatorial synthetic process that is the new *modus operandi* of the pharmaceutical industry has been tested recently as a method to prepare catalysts. Heterogeneous, biological, and synthetic homogeneous catalysts have all been prepared as groups of structures, commonly called libraries. The number of such libraries is small, and the number of members of most of these libraries is also small. However, these studies have shown the potential to mine for catalyst structures in a new way. For example, BINAP complexes are among the most famous and common catalysts for many enantioselective reactions. To date, roughly 1,000 derivatives of this ligand have been prepared, but it took 30 years to prepare them. We must find structural types that generate equally active and selective catalysts, allowing us to prepare and test 1,000 derivatives in 30 days, not 30 years.



Both biology and chemistry have shown the potential to prepare molecules in large numbers. Thousands of mutants are now commonly produced in a single experiment, and four years ago, a library of 2 million molecules was prepared to connect molecular structure with biological activity. A key need in the area of combinatorial synthesis for catalysis discovery is the development of tools for measuring and screening catalyst properties of many potential catalysts at once.

One great strength of homogeneous, molecule-based catalysts is the availability of exquisite control over the stereoelectronic environment in which substrate molecules are activated and undergo various transformations at a reactive center, and at which products are subsequently desorbed. In several areas (e.g., asymmetric catalysis and single-site olefin polymerization), the sophistication of ligand “engineering” for desired selectivity has reached impressive levels, with selectivities sometimes exceeding those of enzymatic systems.

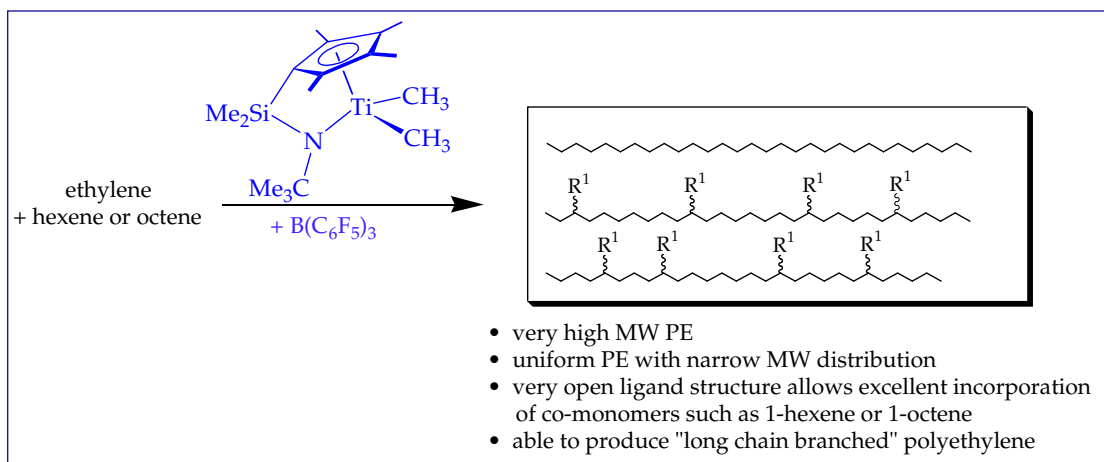
Great opportunities now exist for extending these capabilities by combining elegant molecular synthesis with other methods, including nanoscale structuring, to modify the local environments in which catalysis takes place. The consequences will be new generations of more efficient, selective, and versatile “hybrid catalysts” that combine the best of molecularly engineered homogeneous catalysts with the unique environments that only nanoscale solvent, organic structural, and solid-state environments can provide.

The various environments can be divided into covalently connected, solution-phase soft (organic) structures and hard (inorganic) structures. In the former, multinuclear catalytic centers involving cooperative interactions between suitably ligated metal ions or between ligated metal ions and other proximate functional groups effect or enhance transformations not possible with a single metal center. Recent promising results involve dimers and polymers, clusters, and dendrimers. Unique solution-phase modifications in actual catalyst environments include unusual/useful solvents such as ionic liquids, supercritical solvents, or multiphase systems (e.g., fluoruous biphasic catalytic systems). Here the attraction is in providing unusual polarities (e.g., for accelerating certain substitution reactions), and solubilities (i.e., increasing concentrations of relatively insoluble gaseous reagents), or providing means of separating the reactant, product, and catalyst.

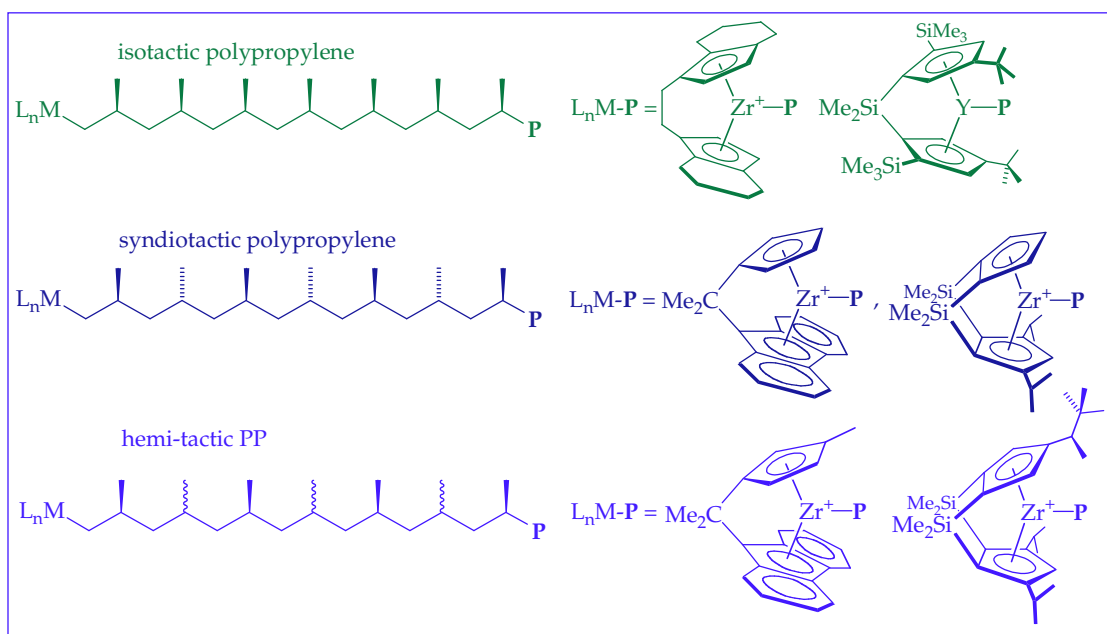
Soft environments for modifying catalytic pathways can include micellar nanoreactors, self-assembled coordination compounds, surfactants, and the internal environments of proteins. The goal is to modify the local substrate concentrations and/or the characteristics (e.g., size, shape, and polarity) of substrates that can access the active site and/or the orientation(s) in which the substrates can approach the active site and to modify the electrostatic environment at the active site.

Moreover, it is possible to create “hard” inorganic environments for molecular catalysts. The strategy here is to select, via nanoscale structural engineering, substrates that can approach the catalytic center (on the basis of shape, size, and polarity); to allow only certain portions of the substrate to attain proximity to the metal center; to protect certain parts of the catalyst ligation from aggressive reagents and/or to prevent catalytic species from undergoing deactivating dimerization reactions; or to produce products with unique anisotropy, such as oriented polyolefin chains produced in mesoporous matrices.

## New Catalysts for Improved Polyolefins



Fundamental studies supported by DOE resulted in new ligands and co-catalysts that are now used to produce superior polyethylenes on scales approaching  $10^{10}$  pounds per year. These polyolefin catalysts are so active, producing as much as 10 million pounds of polymer per pound of catalytic metal, that there is no need to separate the catalyst from the product!



New metallocene catalysts have been designed, based on fundamental studies of the mechanisms for stereocontrol, that effect exquisitely regular polypropylenes. New chiral molecules may be generated based on this new fundamental knowledge.

Hybrid and supported catalysts present particularly demanding challenges for their synthesis and characterization; a close coupling of these is essential. There are two strategies for performing truly molecular-level studies of catalytic chemistry on nanoparticle catalysts: combining single-particle characterization with single-molecule spectroscopy or macroscopic

materials, and chemical characterization applied to atomically uniform arrays of nanoparticle catalysts. A number of synthesis and characterization methods can be used with each strategy.

The single-particle approach can be implemented using nanoparticles anchored on a planar, model catalyst support. Synthetic methods include evaporation of metals, employing nucleation and growth phenomena to manipulate particle sizes; deposition of soft-landed mass-selected nanoclusters from the gas phase; self-assembly on templates or strain-relieved supports; electron-beam lithography; synthesis based on molecular precursors of nanoparticles; exchange or anchoring of molecular precursors in solution and deposition of oxidic precursors by wet chemical impregnation; spontaneous deposition on electrode surfaces; and nanomachining of metal clusters.

The approach using uniform particle arrays starts with uniformly structured support materials that achieve site isolation combined with molecular building block technologies. Many methods have been developed for fabrication of inorganic porous support materials, including sol-gel synthesis, colloidal growth, template-directed self-assembly, and supramolecular chemistry. In some cases, particularly with template-directed self-assembly, it is possible to produce highly uniform porous structures. Impregnation of these structures with molecular precursors of nanoparticles (e.g., multinuclear organometallic complexes or metal-containing dendrimers) can lead to nanoparticles with exceptional uniformity.

A large amount of experimental work has shown that we are at the cusp of meeting these challenges in synthesis. For example, we have begun to understand the mechanism by which a variety of enzymes cleave alkane C-H bonds, and we have developed synthetic, abiological catalysts that functionalize alkanes at a single position with selectivities higher than that of any enzyme. A synthetic metal complex has even been shown to react with methane in preference to its typically more reactive oxidation product methanol. Yet, the highly regioselective functionalization of alkanes is not yet practical for large-scale synthesis, and the selective reaction with methane is not yet catalytic. Several catalytic reactions with control of regiochemistry have also been discovered recently. Addition of olefins to arenes with anti-Markovnikov (linear) selectivity instead of the Markovnikov (branched) selectivity of simple acid-catalyzed reactions has been reported, and additions of amine N-H bonds to vinylarenes with control over formation of either linear or branched product has been accomplished. More work is needed to make these systems reactive enough to be practical.

Even one of the pillars of homogeneous catalysis, regioselective propene hydroformylation, is poorly understood. This reaction of hydrogen, CO, and propene occurs with regioselectivity high enough to comprise one of the largest-scale chemical reactions. However, the regioselectivity is low enough that subsequent, energy-intensive separations are still needed. Highly regioselective reactions with other alkenes, as simple as the four-carbon-containing butadiene, remain to be developed. A Nobel prize was recently awarded for the spectacular development of enantioselective catalysts that produce one hand of a product with high selectivity. However, only a few enantioselective reactions are efficient enough to be used commercially. Low turnover numbers, limited substrate scope, and the use of specialized reagents are commonplace for enantioselective reactions. We must overcome these limitations to realize the full potential of catalyst selectivity. The success of several enantioselective reactions in commercial synthesis does show that additional reactions influenced by highly active and

remarkably selective catalysts will emerge if support to meet these synthetic challenges is provided.

Catalysis represents the ultimate challenge for characterization, with reactions occurring at specific atomic sites in a complex system, on a short time scale, at high temperatures and pressures. The ideal characterization tool should provide atomic-level spatial resolution, temporal resolution, and chemical specificity under realistic reaction conditions. Although enormous advances have occurred in surface microscopies, transmission microscopies, the use of neutron and photon beams, and application of theoretical methods, many challenges remain.

Current studies of catalysts employ a wide variety of techniques, such as X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), ultraviolet-visible (UV-VIS) spectroscopy, vibrational spectroscopies, solution and solid-state nuclear magnetic resonance (NMR), to describe the local and electronic catalyst structure. Surface science methodologies are superb at detailed characterization of uniform, macroscopic samples; however, for nanoscale, disordered, or amorphous catalysts or supported molecular catalysts with structures between these two boundaries, traditional techniques fail to generate sufficient structural detail for a true molecular-level understanding. As catalyst design methods blur the boundaries between homogeneous catalysis, heterogeneous catalysis, and biocatalysis, new characterization tools and techniques will be needed to address the multiple length scales present in complex catalyst systems and the multiple time scales needed to resolve the individual processes comprising the overall catalytic reaction.

Another future challenge in the characterization of complex nanostructured catalysts will be the adaptation of techniques now employed in biological and materials science. For example, NMR techniques for determining solution protein structure or solid-state dipolar decoupling techniques for determining local structure in solid-state systems could be applied to enzyme-substrate interactions in solution or to the local structure of adsorbates bound to solid-phase nanostructured catalyst systems. Breakthroughs are envisioned when the combination of these advanced techniques leads to coherent descriptions of the structure and activity of catalyst systems on length scales from 1 to 100 nm. These breakthroughs are likely to include *in situ* sample cells or reaction vessels in which multiple techniques can be used at neutron and/or X-ray scattering facilities. The combination of neutron-based structural and vibrational methods with synchrotron-based spectroscopies and *in situ* product analysis will unquestionably produce new insights into catalyst structure and function. This particular combination is exceptionally powerful because of the variation of sensitivity among light and heavy elements for X-ray and neutron-based methods. Many of these techniques will take advantage of isotopic enrichment or substitution of the catalyst or the substrate(s) to reveal information on local structure and reaction pathways.

High-resolution microscopy (both scanning probe and electron microscopy) can image individual nanoparticles at the atomic scale. *In situ* high-pressure transmission electron microscopy (TEM) can achieve atomic resolution under gas pressures up to a few torr; the first exciting results, showing morphology changes of Cu/ZnO under methanol synthesis conditions, were reported recently. For elemental mapping of compositions and determination of oxidation states, electron energy loss spectroscopy (EELS) can be used within the high-resolution TEM. Atomic force microscopy (AFM) is an attractive probe for nanostructures supported on thick

insulating oxides. Scanning tunneling microscopy (STM) can operate over wide temperature and pressure ranges.

Synchrotron-based X-ray techniques (EXAFS, XANES, standing waves) are ideal tools for *in situ* studies of local atomic structure, nearest-neighbor distances, and coordination of small clusters. Time-resolved *in situ* X-ray diffraction (XRD) of nanostructures and the monitoring of sample stability and phase transformations in reactive environments are evolving. Infrared (IR), Raman, and sum frequency generation (SFG) spectroscopies, now being used for studies of catalysts at high pressure, will provide insight into molecular characterization of nanostructure reactivity. Techniques that can be used to examine reactivity on a particle-by-particle and even on a site-by-site basis, especially under typical reaction conditions (high pressure and temperature), such as near-field optical spectroscopy and single-molecule Raman spectroscopy, are potentially powerful probes of single-particle chemistry.

Femtosecond time resolution based on pulsed free-electron sources can potentially provide, in pump-probe experiments, the time evolution of the valence electron density and illustrate just “how electrons do it.” Spin-polarized neutron experiments can be used to map out the electron distribution of paired spins in catalytic systems, providing a unique link to theory.

As outlined below, new computational techniques must be developed to analyze the data from such studies and to provide a self-consistent representation of the structural and electronic features of the operating catalyst under realistic conditions. Combined characterization and modeling methods could also generate information about the events of catalyst synthesis, such as the nucleation and growth of nanoscale, nanoporous, or self-assembled materials used as catalysts or supports. Integration of these techniques to fuse data with molecular modeling and simulation tools will facilitate analysis of data with unprecedented detail.

## 2. *Theory, Modeling and Simulation*

The role of theory and computation has changed dramatically as computers, software, and algorithms have improved. These tools can enhance the understanding of known systems, providing both qualitative and quantitative insights into experimental measurements and guiding the selection of experimental systems that are most worthy of study or enabling the design of new systems. Simulation allows researchers to explore temporal and/or spatial domains that are not accessible by present experimental methods. For example, different chemical reaction pathways not directly accessible by experiment can be explored to learn why they are not favorable or to find missing steps in a complex multistep mechanism. Accurate simulations can actually replace experimental measurements that are too costly, too difficult, or too dangerous to perform. Computational chemistry has become an enabling tool for the design of processes for controlling and enabling chemical transformations, leading to higher selectivity and lower environmental impact and energy consumption.

## Computational Chemistry

### Components of Computational Chemistry

Computational chemistry describes chemical systems at various size scales.

**Quantum scale:** Computes electron by electron, including quantization of energy. Predicts molecular structure, bonding, energy levels, and spectroscopic data.

**Atomistic or molecular scale:** Computes atom by atom using classical Newtonian mechanics and empirically determined force fields. Calculates structure and thermodynamic and transport properties.

**Mesoscale:** Between atomistic calculations and the continuum assumption of traditional materials engineering. Typically applies to systems of millions to trillions of atoms that still reflect molecular-scale phenomena.

**Bridging scales:** Theory and models to provide an interface between scales.

At the quantum scale, computations seek to solve the Schrödinger equation and describe the ground-state (and sometimes the excited-state) energies of chemical species. Other properties (e.g., molecular geometry, spectroscopic data, multipolar moments) are by-products of the quantum-level energy calculation. Quantum effects are particularly important in chemical reactions and spectroscopy, and they provide the basis for predicting interactions at the atomic and molecular scale. The atomistic or molecular scale encompasses a wide variety of computations. Properties described at this scale range from thermodynamic properties (critical points, pressures) to transport properties (mass and heat transfer) and phase equilibria. Using statistical mechanics, the results of atomistic or molecular-scale calculations can then be applied to describe behavior at the mesoscopic and macroscopic scale (e.g., process or bulk properties). Mesoscale computations describe behavior and properties of systems that reflect the molecular composition of materials, but consist of far too many atoms to compute atom by atom. Finally, bridging techniques attempt to provide continuity and interface between the various scales, allowing the results of calculations at one scale to be used as input parameters to calculations at another scale.

Further development of new theoretical methods, algorithms, and software for high-performance computers (soon with sustained performance in the hundreds of teraflops) promises to enable new understanding of the fundamental behavior of chemicals and materials at the atomic scale and the nanoscale. Effectively combining these developments with recent advances in computational molecular and materials science should make it possible to use computational chemistry and physics for the design of new and improved catalysts and to accelerate the speed of this design process by several orders of magnitude. The outcome of this process will be to turn the “art” of catalysis creation into the “science” of catalyst design.

Whereas Nature is very effective at designing catalysts (such as enzymes), humans are decidedly less so. The approach to catalyst design has generally been Edisonian: Try something. If it works, try to improve upon it by systematically changing the chemical nature of the catalyst; if it doesn't work, try something else. This approach is time- and cost-intensive, and it usually does not work well. Furthermore, catalysts developed by this approach often produce undesirable by-products, and the catalyst itself may pose an environmental hazard. For many catalytic processes, just how the catalyst works at the molecular level is still unclear.

A much more desirable approach to catalyst design is to analyze, at the molecular level, exactly how catalysts function and to use this information to discover new catalysts and to optimize the designs of others. Without this information, it is impossible to “tune” the catalyst to have the desired effect. For example, even the most sophisticated experimental techniques cannot provide many of the details of chemical reactions occurring at the surface of a catalyst or much information about how to tune a molecular catalyst to improve its performance.

Also required is the ability to predict, at the molecular level, the detailed behavior of large, complex molecules as well as solid-state materials. Although intermediate-level computations can often provide insight into how a catalyst works, the true computational design of practical catalysts for industrial and commercial applications will require accurate determination of thermodynamic and kinetic results, since a factor of 2 to 4 in catalyst efficiency can determine the economic feasibility of a process. An error of only 1.4 kcal/mol in reaction energies leads to an error of a factor of 10 in predicting an equilibrium constant, and the same error in the activation energy leads to an error of a factor of 10 in a rate constant at 298 K. This means that we must be able to predict thermodynamic and kinetic quantities to very high accuracy, on the order of tenths of a kcal/mol for thermodynamic properties and reaction rates to 25%. This represents a daunting computational task.

Other technical challenges in the computational design of catalysts include the number of different spatial and temporal scales that must be considered, the size of the active domain, the need to treat heterogeneous structures, the need to consider the effective environment in which the catalyst acts (gas phase, solid phase, solution phase, and interfaces), and the need to treat complex metal interactions, as many catalysts involve transition or lanthanide metals. Finally, it is essential to be able to predict reaction rates, because catalysis is inherently about the control of chemical transformations at the molecular level.

Further challenges arise from the fact that catalysts need to be designed for use in real environments such as chemical reactors. This means understanding reactor technology as well as materials properties at an unprecedented level. For example, the hydrocarbon oxidation catalyst vanadium pyrophosphate must be coated in order to survive in a fluidized bed reactor. The design of the coating to protect the catalyst is just as important as the design of the catalytic material.

The key advances that have occurred in making reliable predictions of catalyst behavior are developments in electronic structure theory. The two methods that have had and will have the most impact are high-level *ab initio* molecular orbital (MO) theory, such as coupled cluster (CC) methods, and density functional theory (DFT), including Car-Parinello dynamics simulations. The former can be used to provide benchmark calculations of the thermodynamics and kinetics of small to medium-size model systems against which the more approximate DFT methods can be tested and validated. Electronic structure methods, in particular DFT, are now able to treat molecular systems of sufficient size and complexity to be relevant to catalysis. Their accuracy has reached a level at which trends in interaction energies and activation energies can be described, allowing for predictions of trends in reactivity. This points directly to electronic structure theory as an important factor in the design of new catalysts, supporting the development of qualitative trends based on correlations of experimental and computational results. Even more important, the computational methods are becoming reliable enough to allow for the development of quantitative concepts—that is, concepts that can be used to direct our thinking about new processes and catalysts. For example, the development of a new alloy catalyst for ammonia synthesis was driven by modern computational methods (see Fig. 4).

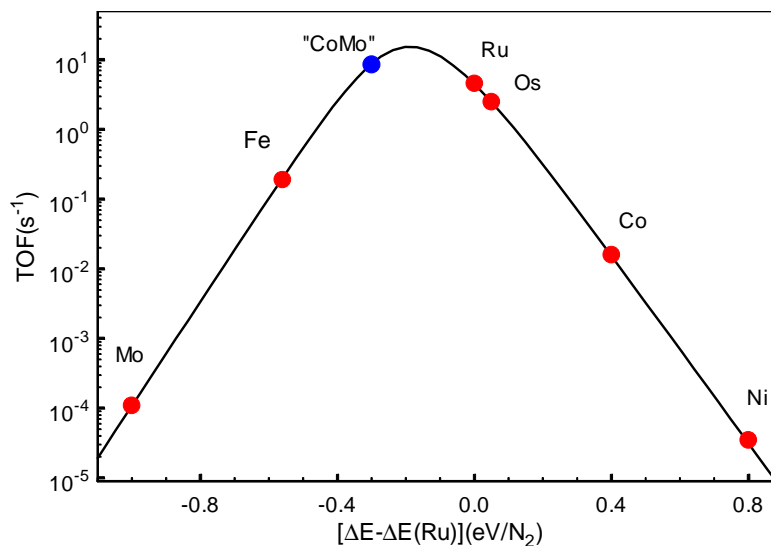


Fig. 4. Calculated trends in ammonia synthesis rates (turnover frequency, TOF) as a function of the dissociative chemisorption energy of nitrogen. The figure shows, in agreement with experimental evidence, that Ru, Os, and Fe are the best catalysts. It also indicates that a CoMo alloy catalyst with a nitrogen chemisorption energy intermediate between that of Co and that of Mo should be as good as the best elementary catalysts. The new alloy catalyst has been synthesized and tested and turns out to be the first new ammonia catalyst since Haber and Bosch that is better than Fe.

Source: C. H. J. Jacobsen et al., *J. Am. Chem. Soc.* **123**, 8404 (2001).

A second example of the use of computational approaches to catalysis was the development of a fluoride affinity scale that allowed scientists at DuPont to order the Lewis acidity of very strong Lewis acids. This led directly to the design of a mixed metal catalyst for the liquid-phase production of the refrigerant HFC-134a, the only such available liquid-phase process. The process was not commercialized because of solubility problems with the catalyst, highlighting the need to understand the fundamentals of the entire process.

New computational and experimental approaches are enabling scientists to gain detailed insights into the steps involved in chemical bond formation and means of controlling the energetics of transforming the chemical bonds from a set of reactants to a set of products. For example, in order to control the oxidation of small organic molecules, researchers must understand the potential energy surfaces governing the oxidation of the organic molecules leading to the most stable product,  $\text{CO}_2$ , which is usually undesirable (unless the goal is to destroy a compound such as a pollutant), in order to control the reactions so that this path is not followed. Besides the obvious impact on the chemical industry, the controlled oxidation of alkanes is a critical component to the use of renewable resources for fuels and feedstocks, as well as to the production of liquid fuels.

This discussion points out the need for the development of a systematic informatics for catalysis. Systematic thermochemical and kinetics data for well-characterized systems are essentially absent, making it difficult to develop reliable structure–reactivity correlations. Computational approaches will be the most efficient way of generating systematic databases, especially given the loss of U.S. expertise and capability in the measurement area for these



important properties. Computation will play a larger role as the methods provide more accurate and reliable results and as computers become faster, enabling the study of more and larger systems. One example of such an approach is the prediction, cited above, of Lewis acidities. Another is the revision of the heat of formation of the key reactive intermediate OH by 0.5 kcal/mol from a 50-year-old value with an uncertainty of  $\pm 0.05$  kcal/mol, on the basis of a combination of very high level computation and experiment. Quantities such as the free energy of solvation of ions, even those as simple as the proton, cannot be easily obtained from experiment, but new theoretical approaches now allow the calculation of such quantities with some reliability.

Powerful theoretical tools are emerging as key ingredients of modern catalysis research. Semi-empirical and first-principles quantum mechanical (QM) descriptions of the electronic structure of molecular and solid-state systems can be used to interpret experimentally determined spectroscopic properties [obtained via, e.g., IR, Raman, EELS, XPS, EXAFS, SFG, or ultraviolet photoelectron spectroscopy (UPS) techniques]. Although DFT can often predict relative barrier heights and reaction energetics, it has difficulties with the prediction of absolute values with currently available functionals. Thus, DFT must be calibrated on the basis of experimentally determined barrier heights and/or very high level and computationally expensive *ab initio* MO methods.

At the heart of catalysis is the control of chemical transformations, and the ability to predict reaction rates is key to gaining a fundamental understanding of catalytic processes. Thus, computational studies need to put structure and dynamics on an equal footing. The ability to reliably predict reaction rates is lagging the ability to predict thermodynamics. This is still the case for simple gas-phase processes and is certainly true for complex reactions in solution, in the large inorganic molecules relevant to homogeneous catalysis, and on surfaces for which even the dynamics of molecules moving on the surface are difficult to predict reliably. Characterization of the long-time and rare-event dynamics typical of catalyzed reactions is seriously limited for computational approaches and presents a challenge. In some cases (e.g., photocatalysis and charge transfer catalysis), quantum effects in dynamics are important, and methods are just now becoming available to treat such processes.

An overall goal of theory is to seamlessly link various approaches, from quantum mechanics at different levels of approximation, to improved tight-binding models for very large systems (100,000 atoms), to model potentials for molecular dynamics simulations, to kinetic models, to catalysis design optimization methods. Computational chemistry involves calculations at the quantum scale, the atomistic or molecular scale, and mesoscales, as well as methods that form “bridges” between scales. New and promising computational approaches are emerging, including linear scaling QM methods, embedding techniques, improved Car-Parinello methods for coupling molecular dynamics with electronic structure theory, new kinetic approaches for predicting rates of reactions in solution, path-searching methods (both configurational and dynamic), kinetic Monte Carlo sampling schemes, and evolutionary algorithms.

The direct coupling of theory and experiment is an extremely strong combination and is needed to advance catalytic science and our understanding of how to control chemical transformations. No experiment reveals every detail and no calculation is perfect, but the combination provides the most profound and detailed insights into how chemical reactions proceed and how

we can control their finest details. Among the most demanding computational challenges are accurately solving QM equations for systems large enough to be of value to real catalyst systems; extracting unifying concepts that help to identify the critical parameters determining catalytic activity and selectivity; and using calculations in developing systematic databases for searching out correlations between catalytic activity/selectivity and other materials properties.

In summary, theoretical contributions to the design of catalysts from first principles come at many levels:

- Modeling and understanding catalytic processes at the electronic/atomistic level; that is, proposing atomic structures, suggesting reaction pathways, computing reaction energetics, modeling reaction dynamics, and identifying key parameters controlling a catalytic process.
- Developing methods for bridging the large gaps in temporal and spatial scales that separate elementary molecular processes from the statistical behavior that governs chemical kinetics at the macroscale.
- Identifying general trends and unifying principles common or specific to various classes of catalytic phenomena: heterogeneous, homogeneous, and biological. At the level of electronic structure theory, there is no distinction between solid, molecular, and biological catalysts. Theory will therefore be an important component in the integration of the different subfields of catalysis. The development of a common language in heterogeneous, homogeneous, and enzyme catalysis will have to be based on the fundamental properties of a catalyst that determine its ability to activate a bond.
- Creating databases of both theoretical and experimental results and developing methodologies to perform data mining and optimization approaches to guide design of new catalytic systems.

Given the advances that are occurring in computer systems, we can lay out the following goals for computational catalysis.

- Computing power of 50 teraflops: accurate calculations for realistic, isolated homogeneous catalyst model systems (<1.0 kcal/mol thermodynamics, <50% error in reaction rates).
- Computing power of 250 teraflops: accurate calculations for realistic homogeneous catalyst model systems in solution and heterogeneous catalysts in vacuum (<1.0 kcal/mol thermodynamics, <50% error in reaction rates).
- Computing power of 1000 teraflops: accurate calculations for realistic homogeneous catalyst model systems in solution and heterogeneous catalysts in the presence of gases and liquids (<1.0 kcal/mol thermodynamics, <50% error in reaction rates).

### 3. *Dynamics and Kinetics*

Catalysts increase the rates of reactions that proceed via sequences of steps such as diffusion, bonding of reactants to catalysts, transformation of species bonded to catalysts, and uncoupling of products from catalysts. The temporal behavior of these steps, along with transport phenomena, determines the overall rate of the reaction. Designing new catalysts requires detailed information concerning these individual steps and, in particular, information on which steps are “rate-limiting” so that a catalyst can be structured to facilitate these steps without a negative impact on other elementary steps.

The dynamic processes of catalysis involve motion and energy transfer on length scales ranging from that associated with the atoms and electrons of the substrate-catalyst combination to that of large-scale reactors. The processes span huge ranges of time scales, from femtoseconds at the quantum level to years in catalyst deactivation. Integration of these dynamic processes provides a rigorous foundation for prediction of kinetics of catalytic processes.

Capabilities for understanding and integrating these dynamic phenomena have increased dramatically, facilitated by new experimental and computational tools, particularly those centered in national laboratories. Recent progress is indicated by measurements of detailed conformational dynamics of single biomolecules. Furthermore, it is now possible to achieve femtosecond temporal resolution and nanometer spatial resolution for charge transfer events.

Measurements characterizing dynamical events with exquisite space, time, and energy resolution— even in single nanostructures— are now within reach, and these coincide with the emerging opportunities for synthesis of single-site catalysts, including individual nanoclusters mounted on support surfaces that can be imaged and characterized spectroscopically. The motions and rearrangements of the substrate and catalyst atoms can be accounted for; inputs from single-event dynamics of these elementary components would allow assessment of the assumptions underlying normal averaging methods. Furthermore, advances in computational approaches may allow us to simulate the processes directly and thereby eliminate the need for such averaging.

Much remains to be done to consolidate the opportunities and integrate dynamics and kinetics into catalysis by fostering collaborations between theorists and experimentalists and setting a foundation for integration of biological catalysis, homogeneous catalysis, and surface catalysis, which are unified by the character of the dynamic processes.

### **III. A Strategy for Success: Integration**

As noted above, a key goal for catalysis research is the integration of skills across a wide range of areas, including catalyst synthesis, catalyst characterization, determination of reaction pathways and the dynamics of elementary processes, and theoretical methods for predicting the structure of active centers and their catalytic properties. The direct coupling of theory and experiment is an extremely strong combination and is needed to advance catalytic science and our understanding of how to control chemical transformations. No single experiment reveals every detail and no calculation is perfect, but the combination provides the most profound and detailed insights into how chemical reactions proceed and how we can control their finest details. At the level of the atom and the chemical bond, there is no distinction between solid, molecular, and biological catalysts. The development of a common language in heterogeneous, homogeneous, and enzyme catalysis will have to be based on the fundamental properties of a catalyst that determine its ability to activate a bond. We need to integrate these different subfields of catalysis through novel experimental and computational/theoretical approaches. This will truly enable us to use all of the advances in the various subdisciplines to achieve an integrated understanding of how to control chemical transformations.

DOE currently funds user facilities for X-ray and neutron scattering, electron microscopy, nanoscale technology, integrated surface science, and computation at its national laboratories.

These facilities provide strong intellectual, financial, and national incentives for promoting catalysis science in the United States, allowing the design and execution of complex experiments and integration with theoretical efforts. Facilitating and linking the work of industry, academia, and national laboratories will drive the new developments and discoveries in catalysis that will enable the United States to regain its superiority and maintain its lead in this pivotal economic engine.

What remains to be established is a mechanism for exploiting these tools for the evolution of catalysis science. Examining the landscape of successful science promoted at national user facilities reveals models for success that can be used for better coordination of catalysis research. A common theme of these programs is the development of collaborative teams who use the user facilities to do their own research as well as to integrate research in a field.

## **A. Linking Basic Discoveries with Applied Technologies**

As is the case for other areas of science and engineering with immediate technological applications, there is an inevitable evolution of the field of catalysis. As basic concepts in catalysis have been recognized and articulated and as new catalysts have been discovered, catalysis has found many new application areas. Each of these in turn has spawned its own set of new concepts fundamental to that area and evolved into yet more finely differentiated application areas. Developments in fundamental science laboratories can often be translated into industrial processes, and the information gained by industry in producing a working process helps to provide further direction to the scientist pursuing fundamentals, in terms of important areas of research where new concepts are needed. For example, the discovery of homogeneous Ziegler-Natta polymerization catalysis led to (1) the development of supported catalysts of remarkable uniformity, (2) homogeneous catalysts that make highly linear polymer with exquisite control of tacticity, and (3) other homogeneous catalysts that make highly-branched polymer with essentially random stereochemistry. Research in each of these differentiated areas is very active, with new applications being developed for each of the different kinds of polymers and new understanding obtained as to how the functioning of the different catalytic sites can be altered and improved. This inevitable evolutionary process is unplanned and largely uncontrolled, but it has been extremely beneficial—indeed, it is the major reason why catalysis is so broadly used in so many different areas with such specific advantage in each area.

In parallel with this evolution, there has been an evolution in how catalysis research is conducted in industry. Beginning in the 1940s, many energy and chemical companies developed in-house research programs to build upon basic findings reported in the open literature, with the primary goal of enabling and significantly improving large-scale processes. However, the past 15 years these industrial basic research programs have largely disappeared. Furthermore, the support of fundamental basic research in chemistry and materials by the energy and chemical industries has declined overall. Industry remains well suited to applying new basic discoveries leading to new catalysts and catalytic processes with economic and social benefits. These ideas often arise from research undertaken with a longer range and more fundamental outlook

In view of these trends, how can we ensure that research and development in catalysis will support society in meet the critical challenges that it faces? Federal funding agencies, DOE in

particular, can positively influence the evolution of the field of catalysis. By articulating the importance of catalysis, sponsoring workshops, maintaining national facilities, continuing and bolstering funding for fundamental research in catalysis, and emphasizing interdisciplinary Grand Challenge research, DOE can minimize the risks that broad, potentially very significant areas of catalysis research will be left untouched, either because no one has recognized an immediate application or commercial incentive to drive work into these areas or because there has been a gap in the pace of new discoveries.

## B. National Facilities and Capabilities

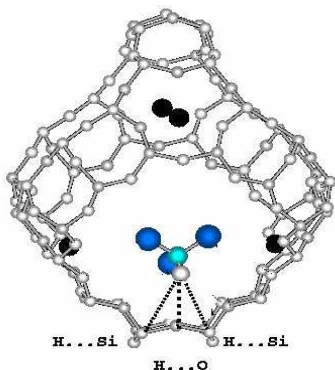
DOE, through BES, uniquely provides the support for the large national user facilities such as synchrotron light sources, neutron scattering facilities, and the new nanoscience facilities that enable scientists to perform experiments with equipment that is too expensive for individual investigators or even universities to own or is too complicated for a single research group to manage. For reference, Table I outlines some of the techniques that use synchrotron radiation and neutron beams along with their particular applications to catalysis research.

**Table I. Catalysis research techniques that use synchrotron radiation and neutron beams**

Key Issues of Catalysis Characterization	Synchrotron Radiation and Neutron Scattering Capabilities
Global structure: crystallographic phases, composition, morphology, disordered and defects structure, aggregate, clusters and colloids in powders and solutions	X-ray and neutron diffraction: <i>in situ</i> measurements of samples embedded in electrolytes or biological solutions, inside heated or pressurized cells, and under oxidizing or reducing atmospheres
Local environment: elemental and oxidation-state resolution	EXAFS, XANES, and neutron diffraction and spectroscopy using isotopic substitution
Determination of adsorbate–substrate interactions, intermediate species, products	Vibrational fingerprints via IR and neutron vibrational spectroscopy; core level shift via XPS and NEXAFS
Electronic structure and electron transfer in chemical reactions	UPS: valance band; XES: atom-specific density of states; electron yield spectroscopy: laser-induced femtosecond dynamics
Global kinetics	Nondestructive, noninvasive, and quantitative measurements; high-flux sources: real-time studies of global kinetics of catalytic processes
Trace-element analysis	Neutron activation analysis, X-ray emission fluorescence spectroscopy
Surface chemistry: molecular diffusion	Neutron quasi-elastic scattering
Chemistry: nanostructure relation	Highly focused X-ray beams: real-space imaging and reciprocal-space scattering of nanostructured materials; probe a single nanoparticle; scanning sub-nanoparticle
Structure: chemical functions relation	Neutrons provide keen resolving power to differentiate heavy and light elements and neighboring elements in the periodic table within a composite. Anomalous scattering of X rays near an absorption edge provides element-specific information. Substituting hydrogen with deuterium in neutron scattering samples enables labeling of specific functional groups by isotopic substitution in polymers and biological systems.
Multidimensional imaging	Concurrent, <i>in situ</i> measurements of spatial, chemical, temporal properties on one beam line

Because a table cannot fully convey the power of these techniques or the value of the information that they provide about catalytic sites and processes, the sidebar on neutron scattering provides a better illustration of how these techniques enable atomic-detail pictures of actual binding and catalytic site environments in complex solid systems.

### Neutron Scattering: A Powerful Tool for *In Situ* Probing of Catalytic Processes

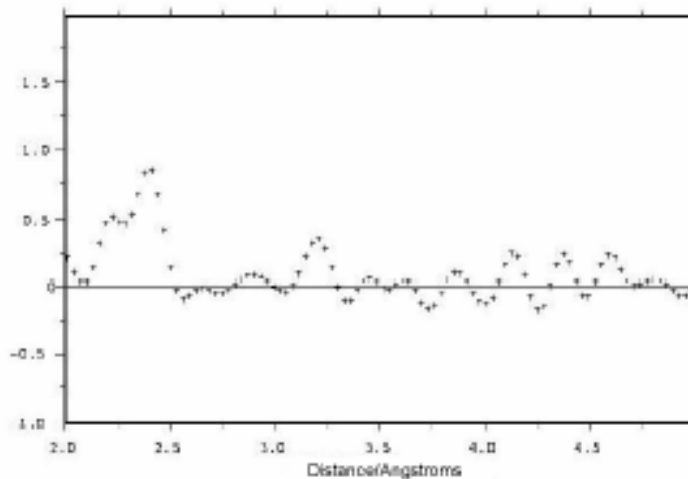


Neutron scattering techniques can probe molecular binding and reactions at active sites while the catalytic reaction occurs. The Spallation Neutron Source (SNS) has the intensity to revolutionize such studies by addressing the need for high intensities that are presently unavailable. In such scattering, the isotope dependence of neutron scattering cross sections can be utilized to obtain structural information by way of differential pair distribution function (PDF) analysis of diffraction data, and is relatively unique access to hydrogen, a central player in many catalytic processes. This “real-space” approach to structure also does not require perfectly ordered crystalline systems.

In a recent example, a so-called “H-EXAFS” neutron scattering experiment provided direct evidence that the binding of chloroform,

$\text{CH}_3\text{Cl}$ , in the supercage of a zeolite, NaY, is governed by the formation of a hydrogen bond with a framework O atom (figure above). Analysis of the neutron diffraction data provides the pair distribution function (PDF). Peaks at 2.25 and 3.25 Å (right) correspond to (C)H...O and (C)H...Si distances as shown (above). The peak at 2.4 Å corresponds to the intramolecular H-Cl distance.

Source: J. Eckert, C. Mellot-Draznieks, and A. K. Cheetham, *J. Am. Chem. Soc.* **124**, 170 (2002).



A number of mechanisms could be employed to assist catalysis research at the national user facilities and to encourage outside users to use the facilities for characterization. These include developing mechanisms to give researchers rapid and continued access to beam lines for exploratory studies, increasing the number of dedicated neutron and synchrotron beam lines to support catalysis research, developing end stations for capabilities unique to catalysis studies, and providing access to simpler instrumentation, such as mass analysis and gas chromatography, to allow complementary characterization to be conducted on site.

It is also important to make the user facilities more “user friendly.” For example, the facilities could provide outreach programs to educate the catalysis community about facilities, procedures, and new developments, and to encourage suggestions from the catalysis community for facility improvements. They could also provide and publicize sabbatical and visiting-scholar

programs to enable extended stays at the facilities and provide housing for minimum living costs for visitors. They should also explore means of providing remote access to data and remote control of experiments, where possible, to minimize user travel.

Finally, users need access to the high-end computational resources, nanofabrication facilities, and characterization instrumentation at the national user facilities. These resources are often too expensive or labor-intensive for universities or industrial laboratory facilities to maintain. Examples include photoemission electron microscopy (PEEM) with femtosecond lasers, transition electron microscopy tomography systems, high-performance computers, and NMR/electron spin resonance (ESR) tomography systems to provide the temporal and spatial resolution needed to make real advances. Having capable scientific staff that can support and run complex apparatus on a wide range of problems is something that a national user facility often does well. Nanofabrication is beginning to be used in catalysis research, and having facilities available for such nanofabrication will be important at these facilities.

### C. A National Agenda for the Future

That catalysis science is a critical component of the Nation's economic and energy security future has been amply demonstrated by numerous studies, such as *Opportunities in Chemistry* (the Pimentel report, 1987),<sup>1</sup> *Frontiers in Chemical Engineering* (the Amundsen report, 1988),<sup>2</sup> and *Catalysis Looks to the Future* (the Bell report, 1992),<sup>3</sup> and by a number of workshop reports, such as *Carbon Management: Implications for R&D in the Chemical Sciences*,<sup>4</sup> and the report of the October 2002 BESAC workshop on "Basic Research Needs to Assure a Secure Energy Future."<sup>5</sup> It is an underpinning science for many present and future technology needs, as highlighted in Ref. 5. The Nation's need for the knowledge that catalysis research can provide is real and urgent, but it is not currently being met by either the Federal sector or the private sector.

In setting its research agenda for the 21st century, the Federal sector must identify and support areas of research that will provide the foundations for the evolution of our current scientific infrastructure into a form that will meet the emerging needs of this new century. That is, the challenges represented on the Federal research agenda for this new century must be sufficiently grand to drive our infrastructure in directions that will meet the uncertainties of the future. One such grand challenge is the development of an understanding, at the molecular level, that will allow us to manipulate, to predict, and ultimately to control chemical reactivity. Catalysis is one of the sciences at the heart of this challenge.

<sup>1</sup>George C. Pimentel and Janice A. Coonrod, *Opportunities in Chemistry: Today and Tomorrow*, National Academies Press, Washington, D.C., 1987.

<sup>2</sup>Commission on Physical Sciences, Mathematics, and Applications, *Frontiers in Chemical Engineering: Research Needs and Opportunities*, National Academies Press, Washington, D.C., 1988.

<sup>3</sup>Commission on Physical Sciences, Mathematics, and Applications, *Catalysis Looks to the Future*, National Academies Press, Washington, D.C., 1992.

<sup>4</sup>Commission on Physical Sciences, Mathematics, and Applications, *Carbon Management: Implications for R&D in the Chemical Science (A Workshop Report to the Chemical Sciences Roundtable)*, National Academies Press, Washington, D.C., 2001.

<sup>5</sup>*Basic Research Needs to Assure a Secure Energy Future: A Report from the Basic Energy Sciences Advisory Committee*, February 2003 (available at <http://www.sc.doe.gov/bes/BESAC/reports.html>).

# Appendix A

## WORKSHOP ORGANIZATION

**Organizer:** J. M. White, University of Texas–Austin

**Plenary Lecturers:**

John Frost, Michigan State University  
Wayne Goodman, Texas A&M University  
Jens Norskov, Technical University of Denmark  
Tobin Marks, Northwestern University

**Breakout Sessions and Chairs:**

*Catalysis design driven by fundamental research*

Mark Barteau, University of Delaware

*Linking basic research to applications through collaborations*

Alexis Bell, University of California–Berkeley

Simon Bare, UOP LLC

*Biocatalysis*

John Frost, Michigan State University

*Homogeneous catalysis*

John Bercaw, California Institute of Technology

*National facilities—photons, neutrons, and end stations*

Chun Loong, Argonne National Laboratory

*Spatially resolved and atom-specific microscopy and spectroscopy*

Steve Pennycook, Oak Ridge National Laboratory

*Tuning reactivity by tailoring nanostructures*

Wayne Goodman, Texas A&M University

*Theory, modeling and simulation*

Roberto Car, Princeton University

*Dynamics and kinetics*

Bruce Kay, Pacific Northwest National Laboratory

J. M. White, University of Texas–Austin

*Synthesis of nanostructured materials for catalytic applications*

Peter Stair, Northwestern University



## **Appendix B**

### **WORKSHOP AGENDA**

#### **Tuesday, May 14, 2002**

- 8:00 AM Charge to participants—Bill Millman and Mike White  
8:30 AM Plenary Talk—John Frost (Michigan State University)  
8:45 AM Plenary Talk –Wayne Goodman (Texas A&M University)  
10:15 AM Break  
10:30 AM to end of day:

##### **Breakout sessions**

- T1. Catalyst design driven by fundamental research—Mark Barteau
- T2. Biocatalysis—John Frost
- T3. National facilities: photons, neutrons, end stations—Chun Loong
- T4. Tuning reactivity by tailoring nanostructures—Wayne Goodman
- T5. Dynamics—Bruce Kay and Mike White

6:30 PM Dinner

#### **Wednesday, May 15, 2002**

- 8:30 AM Plenary Talk—Jens Norskov (Michigan State University)  
8:45 AM Plenary Talk—Tobin Marks (Northwestern University)  
10:15 AM Break  
10:30 AM to end of day

##### **Breakout sessions:**

- W1. Linking basic research to applications—Simon Bare and Alex Bell
- W2. Homogeneous systems—John Bercaw
- W3. Spatially resolved and atom specific microscopy and spectroscopy—  
Steve Pennycook.
- W4. Theory—Roberto Car
- W5. Synthesis of nanostructured materials for catalytic applications—Peter Stair

#### **Thursday, May 16, 2002**

- 8:00 AM Reports from breakout sessions (10), 20 minutes each.  
(Participants other than breakout chairs and whoever they choose to work with  
them are free to depart at noon.)  
1:00 PM Breakout session chairs meet to discuss report writing

#### **Friday, May 17, 2002**

- 8:00 AM Report writing

## Appendix C

### WORKSHOP PARTICIPANTS

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