Recommendations for a National Catalysis Research Institute

Advanced Resources for Catalysis Science

Workshop Results

Workshop held September 21-22, 2004
Pacific Northwest National Laboratory
Richland, Washington 99352

About the Workshop

Twenty-seven experts—representing a broad spectrum—from national laboratories, industry, and universities participated in the Advanced Resources for Catalysis Science Workshop held at Pacific Northwest National Laboratory, Richland, Washington, September 21-22, 2004. The purpose of this workshop was to determine and recommend advanced resources needed to meet the grand challenges for catalysis research and development. Specific objectives included: 1) detail the specific state-of-the-art and next-generation tools needed to advance catalysis science; and 2) identify how best to ensure these tools are widely available to the catalysis research community.

The importance of catalysis to our energy, economic, and environmental security cannot be overemphasized. Catalysis is a vital part of our core industrial infrastructure, as it is integral to chemical processing and petroleum refining, and is critical to proposed advances needed to secure a sustainable energy future. Advances in catalysis could reduce our need for foreign oil by making better use of domestic carbon resources, for example, allowing cost-effective and zero-emission conversion of coal into transportation fuels. No matter what energy sources are being considered (oil, natural gas, coal, biomass, solar, or nuclear based), a clean, sustainable energy future will involve catalysis to improve energy efficiency and storage and use options, and to mitigate environmental impacts.

Recent revolutionary advances in nanotechnology and high-performance computing are enabling the breakthroughs in catalysis science and technology essential for a secure energy future. Thus, the time is right for substantially increased investments in catalysis science and technology, such as a National Catalysis Research Institute(s) that would provide, in centralized physical locations, tools dedicated to catalysis science that are too complex or too expensive for a single investigator or institution to support. This networked center(s) would facilitate high-risk, long-term, multi-investigator, multi-disciplinary research activities addressing specified challenges and needed breakthroughs.

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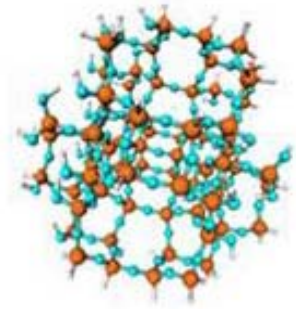
Organizers:

Douglas Ray
Charles Peden

Executive Summary

Catalysis is one of the most valuable contributors to our economy and historically an area where the United States has enjoyed, but is now losing, international leadership. While other countries are stepping up their work in this area, support for advanced catalysis research and development in the U.S. has diminished. Yet, more than ever, innovative and improved catalyst technologies are imperative for new energy production processes to ease our dependence on imported resources, for new energy-efficient and environmentally benign chemical production processes, and for new emission reduction technologies to minimize the environmental impact of an active and growing economy.



Addressing growing concerns about the future direction of U.S. catalysis science, experts from the catalysis community met at a workshop to determine and recommend advanced resources needed to address the grand challenges for catalysis research and development. The workshop's primary conclusion: To recapture our position as the leader in catalysis innovation and practice, and promote crucial breakthroughs, **the U.S. must establish one or more well-funded and well-equipped National Catalysis Research Institutes competitively selected, centered in the national laboratories and, by charter, networked to other national laboratories, universities, and industry. The Institute(s) will be the center of a national collaboratory that gives catalysis researchers access to the most advanced techniques available in the scientific enterprise**.

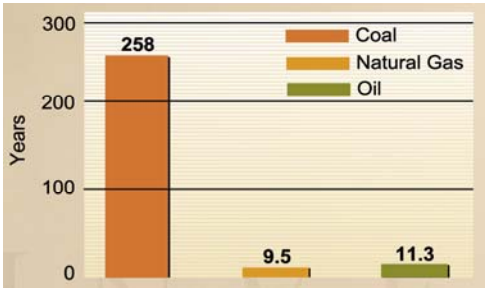
Excerpt from Opportunities for Catalysis Science in the 21st Century, May 2002:

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 to our energy, economic, and environmental security cannot be overemphasized. Catalysis is a vital part of our core industrial infrastructure, as it is integral to chemical processing and petroleum refining, and is critical to proposed advances needed to secure a sustainable energy future. Advances in catalysis could reduce our need for foreign oil by making better use of domestic carbon resources, for example, allowing cost-effective and zero-emission conversion of coal into transportation fuels. No matter what energy sources are being considered (oil, natural gas, coal, biomass, solar, or nuclear based), a clean, sustainable energy future will involve catalysis to improve energy efficiency and storage and use options, and to mitigate environmental impacts. Recent revolutionary advances in nanotechnology and high-performance computing are enabling the breakthroughs in catalysis science and technology essential for a secure energy future. Thus, the time is right for substantially increased investments in catalysis science and technology.



U.S. Fossil Fuel Reserve/Production Ratios – at current production levels, known U.S. coal reserves would last over 250 years.

***Source**: BP Statistical Review of World Energy 2004*

Advances in Catalysis Are Essential for Energy, Economic, and Environmental Security

While catalysis is considered a critical underpinning science for technologies relevant to our energy, economic, and environmental security, the United States, arguably, is no longer at the vanguard of cutting-edge work in this area. At the same time, the European Union, Japan, and other countries are pursuing catalysis as a matter of policy linked to their economic development. These policies are being promulgated through highly visible "flagship" centers devoted to catalysis science, which provide long-term, focused support for coordinated, multi-investigator, multi-disciplinary activity spanning the range of catalysis research and development. These organizational structures support a coherent integration of academic, industrial, and national research resources and efforts. There are no comparably organized and funded entities in the U.S. dedicated to catalysis research.

Although incremental improvements to catalytic processes are leading to better control of desired chemical transformations with fewer undesirable side-products, these developments alone are not enough. Instead, revolutionary breakthroughs must be achieved to fully realize the needed advancements:

- breakthroughs in photocatalysis to successfully and economically use solar energy to convert water into oxygen and hydrogen—a very clean-burning fuel.
- breakthroughs in interfacial electrocatalysis to realize, with competitive economics, the efficiency potentially attainable with fuel cells—devices that directly convert energy stored in molecules, like hydrogen, into electrical energy.
- breakthroughs in the gasification and conversion of coal into transportation fuels.
- breakthroughs in the catalytic conversion of biomass to more useful products, e.g., cellulose to glucose, to economically utilize the chemical energy stored in this renewable resource.
- breakthroughs in the development of catalysts that operate in aqueous media to fully enable the promise of "green chemistry."
- breakthroughs in the construction of nanoscale multicomponent catalysts organized in mesostructures as viable alternatives to expensive and supply-limited precious metal catalysts.

Workshops Explore Future Needs of Catalysis Science and Technology

The economic and scientific considerations that underscore the significance of catalysis science and technologies—and the opportunities for catalysis scientists and engineers to help achieve a secure energy future—have been considered in great detail in recent workshops and reports (see Sources listed below). In May 2002, the U.S. Department of Energy's Office of Science, Basic Energy Sciences Advisory Committee (BESAC) sponsored the workshop "Opportunities for Catalysis Science in the 21st Century." The grand challenge emerging from that workshop was the need "to understand how to design catalyst structures to control catalytic activity and selectivity." The resultant report, along with others, recognizes

the inherent complexity of catalytic phenomena, a complexity making interdisciplinary collaboration all the more important for expediently advancing catalysis science and technology. The prevailing theme in these reports is consistent: advances in experimentation, computation, and theory—especially those that allow the structural and chemical properties of materials to be tailored, tuned, and designed at the nanoscale—provide a unique collective opportunity for revolutionizing this field.

Building on prior observations and recommendations, the Advanced Resources for Catalysis Science Workshop convened September 21-22, 2004, at Pacific Northwest National Laboratory in Richland, Washington, to:

- define the specific state-of-the-art and next-generation tools for advancing the fields of catalysis science and engineering, and

- identify how best to ensure these tools are widely available to the catalysis research community.

Representing a broad spectrum, 27 experts from national laboratories, industry, and universities participated. The workshop comprised five plenary presentations addressing the current state of the science and the challenges, and four breakout sessions on specific advanced resource needs for catalysis research and development:

- **Catalyst Design, Synthesis, and Characterization** – The emerging experimental and computational tools of nanoscience, when integrated and focused, will enable ground-breaking scientific advances in catalyst design, synthesis, and characterization. These new tools will allow synthesis of catalysts with atom-by-atom precision and enable unprecedented control of the specificity and selectivity of chemical transformations. Enabling these scientific advances has the potential to revolutionize our ability to address the grand challenge for 21st Century catalysis—understanding how to design catalyst structures to control catalytic activity and selectivity.

- **Reaction Dynamics and *Operando* Characterization** – Designing new catalysts requires detailed information concerning the individual steps that determine rates of reaction, in particular, information on which steps are "rate-limiting." With this information, a catalyst can be structured to facilitate these steps without a negative impact on other elementary steps. To accomplish these objectives, tools must be available that can provide nanoscale spatial and femto- to milli-second time resolution measurements during actual catalyst operation, i.e., so-called *operando* conditions.

Cutting-edge computational tools are fundamental to catalysis breakthroughs.

- **High-Throughput Methods** – A shift toward high-throughput "combinatorial" methods is changing the way catalysts are discovered, characterized, and tested. The technology is based on the use of robotics for both efficient synthesis and analytic evaluation of performance, coupled with data-intensive computing to enable the rapid discovery of promising new catalytic materials. To make a scientific impact on catalysis, combinatorial methods must also be utilized for fundamental studies.

- **Theory and Computation** – Revolutionary advances in high-performance computing hardware, theory development, and software, when benchmarked with detailed experimental results, allow realistic catalyst systems and processes to be simulated and modeled. These new tools enhance our understanding of known systems and processes by helping to interpret experimental results. They also can be used to enable the design of new catalytic materials

and processes. Furthermore, simulation allows researchers to explore temporal and spatial domains that are not accessible by current experimental methods.

Recommendations from the Advanced Resources for Catalysis Science Workshop

The overriding recommendation, endorsed by all participants in the Advanced Resources for Catalysis Science Workshop, was the need to establish one or more well-funded and well-equipped National Catalysis Research Institutes (NCRIs) competitively selected, centered in the national laboratories and, by charter, networked to other national laboratories, universities, and industry. The NCRI(s) would provide, in centralized physical locations, tools dedicated to catalysis science that are too complex or too expensive for a single investigator or institution to support. This networked center(s) would facilitate high-risk, long-term, multi-investigator, multi-disciplinary research activities addressing specified challenges and needed breakthroughs.

Additional recommendations include the following:

- Specific suites of tools dedicated solely to catalysis research are required, including suites of *operando* experimental capabilities; a suite of computational tools for structural, dynamic, and microkinetic modeling of catalytic reaction systems; a suite of high-throughput combinatorial catalytic reaction tools; and an integrated suite of experimental tools dedicated to *operando* study of catalytic systems at one or more of the nation's third-generation synchrotron light sources. A key component is the availability of a "critical-mass" of experts in these areas whose focus is collaborative catalysis research.

Catalysis will help build a clean, sustainable energy future.

- The NCRI(s) should also focus on need-based development of new experimental and computational tools for the catalysis community.

- The NCRI(s) should have evolving, well-defined, long-term research agendas selected for scientific importance and potential impact, consisting of a closely integrated group of collaborators with appropriate expertise to address the interdisciplinary research themes.

- To encourage and strengthen university, particularly student, involvement and increase the participation of industrial users from throughout the country, the NCRI(s) should include a prominent virtual component. The NCRI(s) would receive sufficient support for amplifying, integrating, and accelerating the research of individual scientists at the Institute itself and at institutions participating in the virtual collaboratory.

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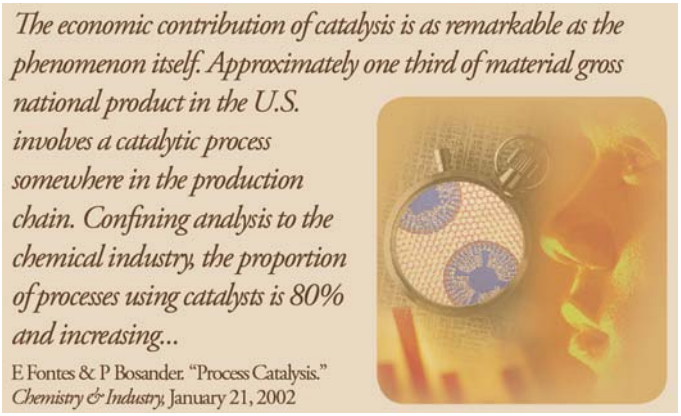
Introduction



Amid growing concerns about the future direction of catalysis science in the United States, experts from the catalysis community met to determine and recommend advanced resources needed to address the grand challenges for catalysis research and development. In this workshop, **"Advanced Resources for Catalysis Science**,**"** several recommendations were made for steps to recapture our position as the leader in catalysis innovation and practice, and promote crucial breakthroughs. The primary conclusion: **the U.S. must establish one or more well-funded and well-equipped National Catalysis Research Institutes (NCRIs) competitively selected, centered in the national laboratories and, by charter, networked to other national laboratories, universities, and industry. The Institute(s) will be the center of a national collaboratory that gives catalysis researchers access to the most advanced techniques available in the scientific enterprise.**

Catalyst materials and technologies are vital to current and future efforts to 1) reduce our need for imported energy resources by developing new energy production processes and better methods for using domestic resources; 2) develop new energy-efficient and environmentally benign chemical production processes; and 3) develop new emission reduction technologies. A grand challenge of chemistry is to understand how chemical reactions, i.e., the making and breaking of chemical bonds, occur so that reactions can be controlled to make any desired molecule at practical, meaningful rates. Numerous practical targets can serve to motivate basic research. Among them are alkane oxidation, hydrogen production from water (including photocatalytic approaches), production of fuels from biomass via chemical and biocatalytic approaches, nitrogen oxide emission control, molecular catalysts for advanced polymer materials, carbon dioxide fixation and sequestration, and viable alternatives for expensive precious metal catalysts. Breakthroughs, rather than incremental improvements, are needed in many of these complex systems areas—breakthroughs that a national center can facilitate in a basic research environment that brings together and maintains long-term support for expert, productive, and collaborative individuals.

The role of catalysis on intensifying reactions and producing desired products, while minimizing waste, cannot be underestimated.

Role of Catalysis in Energy, Economic, Environmental Security

Major energy consumers and users, such as the U.S. petroleum, chemical, biochemical, and pharmaceutical industries, are also among the world's largest producers of chemicals, ranging from "wonder" drugs to paints to cosmetics to plastics to new, more efficient, energy sources. These industries rely on their ability to produce new products by using energy-efficient, low-cost, and environmentally clean processes, with a minimum of undesirable side-products.

Catalysts are the key ingredients in 90% of chemical manufacturing processes (Bartholomew and Farrauto 2005;

Chorkendorff and Niemantsverdriet 2003). With the well-recognized increasing demand for energy and durable goods stressed by the rapidly dwindling traditional resources, and the very likely need to mitigate the impacts placed on the global climate by relying on carbon-based fuels, it is clear that catalysis will continue to be an enabling technology (National Science Foundation 2003; National Science and Technology Council Committee on Technology 2004; U.S. Department of Energy Office of Science 2002, 2003).

Catalysis and catalytic processes account for nearly 20% of the U.S. gross domestic product (The National Academies, Committee on Science, Engineering and Public Policy 2000). Chemical transformations in industry take a low-cost feedstock, often some type of hydrocarbon, and convert it into a higher-value product by rearranging the carbon atoms and by adding functional groups to the compound. About 5 quads (10^{15} Btu ≈ 1018 Joules = 3 x 10^{11} kW hr) per year are used in the production of the top 50 chemicals in the U.S., and catalytic routes account for the production of 30 of these chemicals, consuming 3 quads. Improved catalysts can increase efficiency, and thus reduce energy requirements, while increasing product selectivity and concomitantly decreasing wastes and emissions. *A process yield improvement of only 10% would save 0.23 quads per year* (Ruhle et al. 2001). In addition, production of the top 50 chemicals leads to almost 21 billion tons of carbon dioxide emitted to the atmosphere per year. Improved catalysts can help to reduce this burden on the atmosphere (U.S. Department of Energy Office of Industrial Technologies 2000).

Unfortunately, although catalysis is considered an important contributor to our energy, economic, and environmental security, support in the U.S. for advanced catalysis research and development has declined. At the same time, a number of other governments, the European Union and Japan, for example, are actively pursuing this area as a matter of policy linked to their economic development. These policies are being promulgated through highly visible "flagship" centers devoted to catalysis science, which provide long-term, focused support for coordinated, multi-investigator, multi-disciplinary activity spanning the range of catalysis research and development. These organizational structures support a coherent integration of academic, industrial, and national research resources and efforts. There are no comparably organized and funded entities in the U.S. dedicated to catalysis research.

Recommendations for Advancing the State of the Art

Several recent workshops have focused on identifying the scientific and technological challenges and opportunities for catalysis advancements. A notable example is the U.S. Department of Energy's Office of Science, Basic Energy Sciences Advisory Committee (BESAC) workshop "Opportunities for Catalysis Science in the 21st Century." In that workshop, a scientific "grand challenge" for catalysis was determined to be: "to understand how to design catalyst structures to control catalytic activity and selectivity." A point clearly demonstrated in this workshop, and others (e.g., National Science Foundation 2003; National Science and Technology Council Committee on Technology 2004), is that catalysis remains a vibrant and essential field of research.

The *Opportunities for Catalysis Science in the 21st Century* report notes the current scientific revolution of nanoscience, as described by Dr. Jack Marburger, the President's Science Advisor, in his address to the 2002 meeting of the American Association for the Advancement of Science. In that address, Dr. Marburger spoke of a "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." Consequently, the report presents another important conclusion:

> Nowhere else can this [nanoscale science] 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 prevailing theme among the various workshops is consistent: advances in experimentation, computation, and theory—especially those that allow the structural and chemical properties of materials to be tailored, tuned, and designed at the nanoscale—provide a unique collective opportunity in the U.S. for revolutionizing catalysis science and technology.

While the U.S. government continues to support catalysis research at roughly constant dollar levels, three very important observations are worth considering. First, inflation continues to degrade these resources, especially in terms of personnel and maintenance. Second, given their complexity, addressing many grand challenges for catalysis in the age of nanoscience requires new funding for coherently managed and focused experimental and theoretical basic research goals. Third, the challenges facing catalysis in the 21st Century include complex issues that are intrinsically interdisciplinary and require collaborative entrepreneurship among a dedicated group of investigators with a broad range of experimental and theoretical expertise. Beyond this collaboration, access to the nation's specialized computational and experimental facilities is required.

Building on the results and recommendations of the earlier workshops, the **Advanced Resources for Catalysis Science Workshop**, held at Pacific Northwest National Laboratory, Richland, Washington, September 21-22, 2004, covered two main objectives:. 1) detail the specific state-of-the-art and next-generation tools needed to advance catalysis science; and 2) identify how best to ensure these tools are widely available to the catalysis research community. Twenty-seven experts participated—representing a broad spectrum—from national laboratories, industry, and universities. The schedule comprised five plenary presentations and four breakout sessions:

- **Catalyst Design, Synthesis, and Characterization** – The emerging experimental and computational tools of nanoscience, when integrated and focused, will enable ground-breaking scientific advances in catalyst design, synthesis, and characterization. These new tools will allow synthesis of catalysts with atom-by-atom precision and enable unprecedented control of the specificity and selectivity of chemical transformations. Enabling these scientific advances has the potential to revolutionize our ability to address the grand challenge for 21st Century catalysis—understanding how to design catalyst structures to control catalytic activity and selectivity.

- **Reaction Dynamics and *Operando* Characterization** – Designing new catalysts requires detailed information concerning the individual steps that transform reactants to products, in particular, information on which individual steps control the overall rate. With this information, a catalyst can be structured to facilitate these steps without a negative impact on other elementary steps. To accomplish these objectives, tools must be available that can provide nanoscale spatial and femto- to milli-second time resolution measurements during actual catalyst operation, i.e., so-called *operando* conditions.

- **High-Throughput Methods** – A shift toward high-throughput "combinatorial" methods is changing the way catalysts are discovered, characterized, and tested. The technology is based on the use of robotics for both efficient synthesis and analytic evaluation of performance, coupled with data-intensive computing that enables the rapid discovery of promising new catalytic materials. To make a scientific impact on catalysis, combinatorial methods must also be utilized for fundamental studies.

- **Theory and Computation** – Revolutionary advancements in high-performance computing hardware, theory development and software, when benchmarked with detailed experimental results, allow realistic catalyst systems and processes to be simulated and modeled. These new tools enhance our understanding of known systems and processes by helping to interpret experimental measurements. They also can be used to guide the selection of experimental systems that are most worthy of study, or enable design of new systems. Furthermore, simulation allows researchers to explore temporal and spatial domains that are not accessible by current experimental methods.

The recommendations and conclusions resulting from the workshop are presented in this report. The overriding recommendation, endorsed by all workshop participants, was the need to establish one or more well-funded and well-equipped National Catalysis Research Institutes, which would provide, in centralized physical locations, tools dedicated to catalysis science that are too complex or too expensive for a single investigator or institution to support. These networked center(s) would facilitate high-risk, long-term, multi-investigator, multidisciplinary research activities addressing specified challenges and needed breakthroughs.

Purpose and Function of the National Catalysis Research Institute(s)

The envisioned National Catalysis Research Institute(s) will combine expertise and skills with advanced instrumentation and laboratory facilities, along with unique opportunities for networking and collaboration. To allow breakthroughs to evolve in a systematic and efficient way, a national user facility would provide the opportunities for rapidly advancing the state-of-the-art in the fundamental understanding of chemical transformations. **This collaborative, culture-changing institute(s) would focus on selected grand challenges, and would be organized and supported for the mutual amplification of the capabilities of the participating industry, national laboratories, and universities.**

The NCRI(s) will be a foundation for breakthroughs such as better methods for predicting and controlling chemical transformations and preparing complex catalysts with well-defined atomic connectivity. It will also combine the respective advantages of heterogeneous, homogeneous, and biological catalysts. This unique facility will provide an integrated suite of synthesis and characterization capabilities, tools for *in-situ* measurement of reaction kinetics and dynamics, and computation/simulation capabilities to enable understanding and unprecedented control of the relationship between catalyst structure and catalytic chemistry (both activity and selectivity). Further benefits provided by the NCRI(s) include the following:

- **Bridge the gap between materials science, physical and chemical science, catalysis, industry, and theory and simulation.** A hierarchical combination of promising young researchers and internationally recognized scientists will provide the environment to stimulate the research, as well as an essential infrastructure to catalysis leaders who, in turn, are accessible to outside users. As such, the NCRI(s) will be able to take on the big challenges not easily addressed by a single investigator or individual institution.

- **Coordinate, expand, and develop major research programs across the U.S. to address complex scientific and technological challenges.** The NCRI(s) will attract first-class academic and industrial researchers. Along with core programs, facilities, and staff, there will be a major emphasis on dynamic and open interactions to encourage an environment that attracts the best skills in the field. The flexibility of sabbatical and short-term visits as well as joint post-doctoral candidates would allow constant flow-through or fluxion.

- **Reach a broader scientific and industrial community.** A wide range of users will be able to access state-of-the-art, specialized instruments and facilities to obtain and interpret high-quality data efficiently, expertly, and reliably.

- **Provide a gateway to other major programs facilities and infrastructures, such as the national nanoscience centers established within the DOE complex.** Capabilities and tools developed in materials synthesis, molecular-level design, and large-scale characterization and calculation will be utilized through collaboration.

- **Serve as vehicle for educating the public on the importance of catalysts.** Outreach programs will help heighten public awareness of the significance of advancements in catalyst research and development.

The energy crisis of the 1970s provided the compelling rationale for the establishment of DOE's Combustion Research Facility (CRF), a highly successful directed basic research institute. Much of the science produced in the CRF over the last 25 years has made critical contributions to revolutionary applied science advances in the efficiencies of internal combustion engines realized over this same time period. Renewed recognition of the challenges facing our future energy and environmental security now provide a compelling rationale for analogous facilities dedicated to catalysis R&D in order to realize the necessary advances in this central technology for addressing these challenges.

Thus, the NCRI(s) would provide, in centralized physical locations, comprehensive suites of tools dedicated to catalysis science. Through this networked center(s), high-risk, long-term, multi-investigator, multi-disciplinary research activities would be facilitated, addressing specified challenges and critical breakthroughs. The results of the **Advanced Resources for Catalysis Science Workshop**, discussed in this report, illustrate more fully the capabilities and tools needed to achieve these breakthroughs.

Workshop Sessions

- Catalyst Design, Synthesis, and Characterization
- Reaction Dynamics and *Operando* Characterization
- High-Throughput Methods
- Theory and Computation

Conclusions and Recommendations

Sources

Catalyst Synthesis and Characterization

A wide range of new synthesis and characterization tools are emerging that can be integrated with other capabilities in the catalysis field to more efficiently design catalysts from first principles. These tools show great potential for use in preparing new catalyst compositions, as well as in developing model systems to further study the fundamental properties of catalysts—the key to precisely designing catalysts for specific activity/selectivity.

Even with these advancements, however, the greatest challenge for both synthesis and characterization is the combination and integration of the strengths, skills, and capabilities in different fields with coordinated research activities. Often, those who master the synthesis techniques or instruments and facilities either are not part of the catalysis field or are not familiar with characterizing catalyst performance or handling catalysts properly. Those who understand the materials best often are not familiar with characterization methods and do not have the resources to develop these skills. Therefore, it still remains a major challenge to build inorganic or hybrid structures with well-controlled architecture and reactivity. Furthermore, the ideal characterization tool, capable of providing atomic level spatial resolution, temporal resolution, and chemical specificity under realistic reaction conditions, *still* does not exist. A systematic understanding of the structure-property relationships has not been demonstrated for many important catalytic reactions.

The importance of catalysis sciences to U.S. economy and national security and the great limitations of the traditional approaches to solve the daunting scientific challenges call for a national center or facility and drastically different approaches. One of the key issues associated with catalysis science is that access to and integration of a full array of state-of-the-art tools able to provide necessary fundamental information is limited for most individual researchers or research groups.

The National Catalysis Research Institute (NCRI) approach will allow materials scientists to work intimately with catalyst experts to design and synthesize materials targeted either for better activity or for gaining a better understanding of how the catalysts work, with the help of an array of state-of-art characterization tools and rapid feedback from theory and simulation. All essential instruments to meet general characterization needs will be in one location, and, even more importantly, these instruments will be highly integrated and coordinated to solve complex catalytic problems. This approach will ensure that the NCRI(s) is much more than simply a collection of instruments. The conception, construction, and operation of such a large, well-integrated characterization infrastructure go beyond what individual groups can handle. The characterization infrastructure will combine a realistic catalyst activity testing facility and the most advanced *in-situ* characterization capabilities.

In the envisioned institute, catalyst synthesis and characterization could also go hand-in-hand with theory for rapid advancement of the science. The ideal characterization would provide atomic-level sensitivity along three performance axes on well-controlled catalyst architectures: spatial resolution, temporal resolution, and chemical specificity under operating conditions appropriate for the reaction, i.e., *operando* measurements (discussed further in the next section). We would be able to distinguish atoms on the surface from those below, and locate special sites, such as facet junctions or surface vacancies, and determine their local electronic structure. With such atomic-level insights into the catalyst structure, theory could then be used to visualize the reaction itself and identify the active site and the activation barrier. With this knowledge, catalyst design can be conducted by a sound scientific approach using the tool kits developed under the synthesis area, and replace the empirical “informed trial-and-error approach.”

As noted in *Opportunities for Catalysis in the 21st Century*, methodologies developed for synthesizing catalysts should encompass multiple length scales from the molecular level up, and the macroscopic level down, into the nanoscale (over length scales from 1 nm to 1 micron) in order to build catalysts with controlled architectures and reactivities. Such integrated nanosystems that embody catalysis will have important impacts in a wide range of areas, such as environmental remediation, environmentally benign processing, sensing and diagnostics, microrobotics, fuel cells, energy conversions, and health. An institute approach will allow the exploration of the strengths and limitations of novel, impressive, and evolving synthesis tools, for example:

- molecular imprinting based on the "lock-and-key" principle, which potentially can "recognize" or selectively target specific molecules
- bottom up, self-assembly and templated synthesis on strain-relieved supports for preparing inorganic materials with extremely high surface area and well-defined, ordered pore structures
- evaporation of precursors to manipulate particle size or deposition of soft-landed, mass-selected nanoclusters from the gas phase
- exchange or anchoring of molecular precursors (including organometallic clusters or even enzymes) in solution and deposition of oxidic precursors by wet chemical impregnation
- sol-gel synthesis for preparing oxide nanoparticles and porous supports
- molecular beam epitaxy to produce a variety of nanoscale structures
- ballistic deposition to synthesize highly porous metal oxide films
- dendrimers for the synthesis of nanoscale catalysts with controlled size and aspect ratio
- inorganic supports used as ligands or confined environments for nanoclusters
- "hard" or "soft" lithography to create patterns or features on various supports
- chemical synthesis of molecular clusters with controlled sizes and functionalities
- methods for synthesizing uniform nanoparticles, quantum dots, and nanocrystals.

With advanced understanding of these evolving tools, new techniques can be identified and developed to address the critical challenges associated with the synthesis of inorganic or hybrid structures with well-controlled architecture and reactivity. First, the ability to design and synthesize uniform ("single") site architecture, i.e., monodispersed catalytic "sites" on a controlled and variable structure, is highly desirable, but very difficult, for gaining a fundamental understanding of the activity and for designing more efficient catalysts. Second, the catalytic performance most likely depends on multifunctional sites and how the active sites interact with their environments. The domain sizes, spatial distribution of, and interactions between these active sites need to be tightly controlled. Finally, the catalytic properties may also depend on the structural features on the molecular, nanometer, and micrometer scales.

In conjunction with synthesis, characterization is essential for establishing 1) a fundamental understanding of synthesis pathways and the relationships between the assembly methods and the structures obtained from these assembly pathways, and 2) a fundamental understanding of the structures of the catalysts and their functions—i.e., the ability to catalyze chemical reactions. Recent rapid advances

have led to significant tools and concepts critical for tackling this "grand challenge," albeit with often complex and costly instrumentation. In addition, the hallmark of state-of-the-art catalyst characterization in recent times has been the use of multiple tools that can provide complementary information on the geometric and electronic structure of catalytic materials and on chemical bonding and transformations of reactants, intermediates, and products on catalyst surfaces. The NCRI approach will provide unparalleled access to and integration of numerous new tools and concepts specifically tailored for catalyst characterization:

- Rapid advances in high-resolution electron microscopy techniques, including *in-situ* high-pressure transmission electron microscopy (TEM) with electron energy loss spectroscopy (EELS), can achieve atomic resolution under gas pressures up to a few Torr while performing elemental mapping of compositions and determining oxidation states. Also, the combination of high-resolution energy filtered imaging, Z-contrast or annular dark field imaging, and aberration-free microscopy enables sub-nanometer analysis of the active elements.

- Recent developments in atomic force microscopy (AFM) make it an attractive probe for nanostructures supported on thick insulating oxides.

- Scanning tunneling microscopy (STM), capable of atomic-scale measurements, yet able to operate over wide temperature and pressure ranges, is particularly useful for *in-situ* study of particle morphological changes on a catalyst in various environments.

- Synchrotron-based X-ray techniques (EXAFS and XANES) are ideal tools for *in-situ* studies of local atomic structure, nearest neighbor distances, and coordination of small clusters.

- High-pressure (10 Torr) photoelectron spectrometers for studying *in-situ* surface reactions opens up the possibility of observing transient intermediates on catalyst surfaces.

- Spatially resolved photoelectron spectroscopies (LEEM, PEEM) permit examination of composition and electronic structures on the nanoscale.

- Infrared and sum frequency generation spectroscopies, now being used for studies of catalysts at elevated pressures, will provide insight into molecular characterization of nanostructure reactivity.

In addition, an institute approach, with its cohort of practitioners, local and across the nation, will be able to identify and address, with a coherent voice, the needs for enhancing and expanding the "toolbox" to unambiguously characterize these structures. This is particularly important as new synthesis methods for nano-sized catalyst materials begin to be fully realized. Catalysts provide one of the ultimate challenges in characterization, with reactions occurring at one or more specific atomic sites in a highly complex, often disordered, and dynamic system. Highly chemically specific information over several orders of magnitude of time and length scales and relatively high temperature and pressure, i.e., *operando* conditions, must be obtained. With these approaches, the ideal characterization tools, capable of providing atomic-level spatial resolution, temporal resolution, and chemical specificity under realistic reaction conditions, can be established.

Reaction Dynamics and *Operando* Characterization

In the preceding section, the complexity of catalysis is underscored and the necessity of using multiple complementary characterization probes noted. To further underscore the complexity and to emphasize a critical characterization goal of catalysis science, this section focuses on the temporal behavior of catalytic systems. While essential, it is insufficient to characterize catalytic systems by static structural methods; rather, the "bond breaking-bond making" steps taken and the time, space, and energy dependence of these steps along the path from reactants to products must be characterized. To move catalysis science forward and to relate fundamental and applied catalysis science, it is essential to gain knowledge regarding reaction mechanisms that are resolved into elementary steps under conditions applicable to technologies.

A useful analogy can be made between catalysis and a typical manufacturing process, as illustrated below. In the latter, raw materials enter the factory and are transformed via a series of coordinated steps, the manufacturing process, into finished products. If the manufacturing steps cannot be assessed directly, the process can be described only through inferences from observations made on the raw materials and the finished products.

Analogy Between Typical Manufacturing Process and Catalysis

In a catalytic process, the steps also often must be inferred, because experimental capabilities for directly probing these processes historically have not been available., In short, traditional characterization has relied on analysis of what entered (reactants + catalyst) and what exited (products + catalyst). Thus, only inferences could be drawn from analysis of reactants, products, and macroscopic parameters such as temperature and pressure. While these studies served a clearly useful purpose in the past, realizing potential future technological advances requires measurements of elementary steps under real-time working conditions. In addition to *in-situ* reactant and product measurements, surface and bulk properties must be assessed simultaneously, or at the very least, multiple probes should be brought to bear on the problem.

Characterizing the kinetics of the elementary steps of a catalytic process is not only desirable, but required, to advance the science. Microkinetic models that accurately describe known catalytic processes provide the basic understanding for developing improved processes and improved catalysts for these reactions, and for considering how reaction conditions affect the activity and selectivity. In some cases, such studies can reveal alternative approaches to the process with distinct advantages over traditional conditions. For example, several catalytic processes (e.g., high-space-velocity, low-contact-time, high

temperature, ultra-short reactor beds) have been developed by predicting which way conditions should be changed to gain selectivity without loss of activity. In some instances, dramatic gains in activity have been obtained as well (Deluga et al. 2004; Deutschmann and Schmidt 1998; Goralski et al. 2000; Wheeler et al. 2004). Furthermore, only with such a microkinetic understanding of well-defined model catalysts (e.g., the pure metals or large metal particles supported on an inert oxide) does a fundamental understanding emerge on the effects of catalyst modifications that lead to improvements, such as the addition of reactive supports (e.g., ceria) or size effects for particles below 6 nm in diameter (particularly for the less reactive metals like gold). Thus, microkinetic models are required to address the basic scientific issues underlying particle size and support effects, among many other structure/function issues for catalyst materials.

Enabled by revolutionary advances in measurement and synthesis capabilities, and in our ever-expanding knowledge of surface chemical reactions on transition metals, there is now an unparalleled opportunity: catalysis science and engineering practitioners can access these elementary steps and remove the "dark cloud" describing them. It can be reasonably argued that determining and characterizing these elementary steps, i.e., the mechanistic details and microkinetics, of a catalytic reaction is the most crucial fundamental information required to improve current catalysts and to invent new catalytic materials and processes.

Like the grand challenges for catalyst characterization described in the Catalyst Synthesis and Characterization section, experimentally measuring the kinetics and dynamics of elementary steps, and then understanding the measurements is, by nature, an extremely complex enterprise for a catalyzed reaction. Atomic motion, electron flow, and energy flow in the whole system must be taken into account; i.e., the reactants, catalyst, intermediates, and products must all be considered while functioning. Indeed, while the catalyst, by definition, is "unchanged" at the end of a catalytic cycle, it is actively engaged in the process and transiently changes its characteristics along the reaction path. Underscoring the importance of measurements made while functioning, these changes are critical to realize the goals of catalysis, i.e., high activity and exquisite selectivity for the desired chemical product.

Using the manufacturing analogy, we want to build a better "manufacturing plant" that, beginning with certain raw materials, produces a desired product with higher quality at lower cost. In the language of chemical catalysis, we want to build a better catalytic process that accomplishes the same ends—desired product with higher selectivity (higher quality) and do so faster at a given temperature (lower cost). Thus, while individual catalytic reaction event dynamics and overall process dynamics are equally critical research areas, a central goal for 21st Century catalysis science and engineering is development and deployment of tools designed to study catalysts under real-time working conditions. Known as *operando* measurements, these tools measure catalyst structure, kinetics, and dynamics while the process is operating.

Operando structural characterization is needed to define structure/function relationships. This characterization must be interfaced to rate and dynamics measurements of the elementary steps at the same conditions, both globally and locally at the nanoscale, with better distance and time resolution. To illustrate, consider, for example, two reactions being intensively researched: CO oxidation over Ru and ethylene epoxidation over Ag. There is now strong evidence showing that the working catalyst in both cases comprises several layers of bulk-like metal oxide that wets the metal, rather than the metallic surface itself as thought until a few years ago. Surely, our understanding of catalysis and its advancement potential would increase dramatically if we could routinely answer, with direct evidence, even these most basic structural questions about the nature of the working catalysis surface. In many cases, the situation is even more complex, underscoring even more strongly the need for *operando* measurements.

As outlined above using the manufacturing analogy, the relationships among atomic-level structural details of a working catalyst, the elementary-step dynamics, and the overall activity and selectivity of a process demand better knowledge of molecular-level kinetic parameters of elusive rate-controlling elementary steps and the structural factors that influence them. At present, the kinetic parameters for the rate-determining elementary steps on surfaces in almost all catalytic reactions of industrial importance may have been inferred but have *not* been independently determined. Because these critical steps are relatively slow, and therefore very challenging to measure, their rate constants have been inferred from fitting the net catalytic reaction rate data to various models, wherein these rate constants were treated as fitting parameters, i.e., empirical constants with limited fundamental content. It is essential to pursue directly measuring the rates of these key elementary steps and relate their changes to changes in the catalyst surface structure. A central component must, of necessity, be *operando* measurements.

This kind of measured *operando* detail will not only provide fundamental insight, especially regarding the catalyst-intermediate interactions for rate-determining steps, it will also be invaluable for benchmarking microkinetic computational modeling studies, rendering them useful as predictive tools. In short, *operando* measurements, by themselves, should not be the sole goal. Rather, close coupling of instrument development and computational/theoretical development is necessary. While it requires long-term coordinated team effort, successfully pursuing the following elusive goal is now plausible. **Goal**: seamless connections from theoretical modeling, to *operando* structural characterization, to *operando* rate measurements, to microkinetic modeling, to structural modification with feedback to optimize catalyst structure and operating conditions. Approaching this goal requires a richly instrumented, well-staffed facility that does not now exist.

Examples of specific *operando* catalysis tools for realizing the objectives discussed here would include:

1. High-resolution TEM equipped with reaction cell and incorporating surface and fluid phase optical spectroscopy, and reaction product analysis facilities that could include mass spectrometry, gas and/or liquid chromatography. A suite of transient and steady-state kinetics facilities with excellent reactant and product determination and *in-situ* transient surface or material characterization. *In-situ* methods would include FTIR, NMR, Raman, SFG, X-ray or neutron spectroscopy or scattering/diffraction, high-pressure XPS and scanning probe microscopies (Requejo et al. 2004; Rider et al. 2002; Weckhuysen 2002).

2. At least one of the proposed X-ray facilities and the proposed neutron-based facility would reside at a national facility dedicated to providing synchrotron X-rays or neutrons to the research community. For *operando* catalysis, X-rays or neutrons alone are not satisfactory; the facility should be dedicated to catalysis research and include at least two ancillary/complementary measurements for verifying relationships made in other facilities on the basis of the same measurements.

3. Tools for spatio-temporal resolution of dynamics with molecular time and length scales that are coupled with “averaging” measurement and characterization techniques. In this way, a direct connection can be made between results obtained across the relevant time and length scales of catalytic processes.

As has been concluded in numerous workshops on catalysis science and engineering, the cost and complexity of such characterization tools, alongside the critical need for multiple measurements on identical operating systems, points toward an integrated suite of tools located in an NCRI collaborative facility.

The time is also right for high scientific productivity from these types of experiments. Ultrahigh vacuum (UHV) surface chemistry experiments over the past two decades have demonstrated several ways to

cleanly prepare many adsorbed species that are thought to be the key intermediates in many catalytic reactions of great importance to efficient and clean fuel utilization and/or environmentally friendly chemical production or pollution cleanup. However, these intermediates react too slowly to convert them to products while observing them in UHV. A new level of insight into the role played by these catalytic intermediates and the kinetics of their key conversion steps would be forthcoming from a truly **combined** approach in catalysis. In this combined approach, these intermediates first are produced as in UHV but then converted with high-pressure reactants into products while monitoring the temporal evolution of surface species and their concentrations using *in-situ* and *operando* instrumentation. Equally essential is the key role that powerful full computational methods (like DFT) can play in helping to guide and interpret such experiments and ascertain the energetics that control the reaction steps involved.

High-Throughput Methods

There has been a revolution in the science and technology of molecular synthesis and analysis, especially for molecules of biological and pharmaceutical importance. This development, based on a methodology generally referred to as combinatorial, or *combi*, employs "libraries" of synthetic building blocks, rapid screening methodologies, and data management (informatics). This revolution has provided a dramatic increase in the productivity of the individual researcher; has led to materials and chemicals that would otherwise have remained undiscovered, through exploring new parameter space; and in general has changed the way the researcher thinks about approaching a challenge involving materials discovery.

In light of the promise provided by these new, high-throughput, techniques, combinatorial methods for the rapid synthesis and screening of catalyst materials have also been developed and described. While these new methods constitute a step forward for research, they mainly provide a more elegant Edisonian framework for identifying candidate catalytic materials. A more visionary approach, however, perceives an optimal combinatorial method that joins the elements of a rapid-screening synthesis and testing with additional techniques aimed at developing a fundamental understanding of catalyst behavior. This fundamental understanding might be assisted by various rapid pre- and post-characterization methods, sophisticated microscopy, and computational chemistry. To reach this optimal approach, new methodologies are needed to provide rapid analysis in all these areas. Establishing this capability and putting it into practice would be a breakthrough distinguishing an NCRI combinatorial center from other combi facilities.

Overview of Combinatorial Center

Combining state-of-the-art testing with state-of-the-art analysis would increase the efficiency and productivity of catalysis research, as the research community would have ready access to the most sophisticated instrumentation and diverse expertise available. Positioned within an NCRI, such a combinatorial center would allow researchers to investigate targeted problems, and to interact with a large group of talented staff to gain a more fundamental and predictive understanding of the catalyst system they are investigating. The experience and expertise of the participants will ultimately help shape the nature of the center itself.

Thus, there is an expectation that the topics to be investigated using combinatorial methods would span a wide range, from fundamental mechanistic studies to practical development of next-generation catalysts for chemical, petrochemical, and energy applications. Within an NCRI combinatorial center, new and novel capabilities would continue to define the "state-of-the-art" and augment capabilities of other national and private laboratories. The combinatorial center proposed here would be a focal point for new research methodologies to advance catalysis science and technology, and would provide a means to increase the interaction between industry, academia, and the national laboratories. Not only would establishing this collaborative, essential capability be of interest to DOE's Office of Science, but participation by other DOE offices as well as industry would be critical. An example of existing industry involvement in this field can be seen in the NIST Combinatorial Methods Center directed at polymeric materials.

The overall role of such a combinatorial center is viewed as a means for greatly increasing the current fundamental understanding of catalysis and surface science, with a strong emphasis on structure-property relationships. Broadly, the important goals include:

- Combine theory with modeling, including both microkinetic and reactor-scale modeling capability.

- Develop methodology for rational catalyst design.
- Develop new and unique tools, especially characterization tools.
- Develop methods for rapid, parallel analytical techniques.
- Provide the opportunity to study "every variable in every direction."
- Extrapolate beyond the existing data through the use of computational methods such as molecular mechanics and density functional theory.

To make the most efficient use of personnel and funds, the center would have a focus that reflects its national importance, and, while not exclusive, it should help define priorities. A significant focus, for example, would involve developing renewable energy aimed toward sustainability.

The components or "modules" that would be integrated to comprise an NCRI combinatorial center are summarized below:

Module for Characterization of the Active Site

In order to maximize output and productivity, techniques are needed that allow sample analysis in parallel rather than sequentially. This type of characterization/analysis is currently available for techniques such as X-ray diffraction and infrared/Raman, but new advances would be necessary to enable somewhat more exotic techniques such as EXAFS and XANES to be applied in this manner. The development of a "benchtop synchrotron" is a potentially exciting method to facilitate EXAFS and XANES studies. To the extent that analysis tools are required beyond those available at the center, it is the expectation that extensive expertise and facilities in other national laboratories will also be made available so that all the characterization tools can be brought to bear on the problem. In this case, the additional analysis would be for a specific sample or samples and would not be investigated in a combinatorial manner.

Module for Structural Aspects

The work in this module would examine length scales greater than the active site. A primary component would be various microscopy tools used to characterize morphology, composition, and phase relationships through various imaging capabilities. Thermal imaging in conjunction with microscopy shows promise as an important emerging capability.

Module for Mechanistic and Kinetic Studies

Components would include the capability to measure heats of adsorption; methods to characterize parameters related to diffusion within the solid; and methods to determine kinetically rate-limiting steps, for example, through transient experiments or isotopic labeling studies.

To complement high-throughput experimental tools, computational methods, ranging from molecular mechanics and density functional theory calculations to tools for designing experiments, are an essential part of the overall capabilities. There exists the possibility to use the computational tools to carry out high-throughput virtual experiments and to compare with experimental results. The ultimate goal of these efforts will be to achieve true rational design of catalysts by combining these computational efforts with the large amounts of analytical data available from the high-throughput analytical methods.

Additional Capabilities of the Center

While the discussion here has focused on the development of high-throughput capabilities related to heterogeneous catalysis, analogous "modules," such as liquid phase NMR and HPLC, could be available in high-throughput form for homogeneous catalyst studies.

Interaction of the Center with Industry

To be of relevance to industrial operations, interested companies would need to participate in the development of combi tools and would expect this center to include capabilities for reactor design and scaleup. The industrial teams would provide hands-on input and be involved in all aspects of the development work. The center would need resident expertise from chemists, materials scientists, and chemical engineers capable of process modeling. The capability to synthesize and analyze a wide array of different catalytic systems, from mixed metal oxides to zeolites, would be important for broad-based applicability of the center tools. As such, the scope in terms of hardware for such an effort would incorporate multiple high-throughput reactors and synthesis unit operations, and characterization tools.

In general, the work carried out at the combinatorial center should be publishable, and some sharing of the costs would need to be borne by the participating organization. To the extent that issues may arise regarding intellectual property development or investigation of proprietary materials, the model developed elsewhere by synchrotron facilities, such as the Advanced Photon Source (APS), might be appropriate for the combi catalysis center.

Summary

The successful implementation of the combinatorial approach to research will not only allow for more rapid and efficient catalyst development, but will also allow potentially important regions of parameter space to be explored that otherwise will remain uncharted using only conventional approaches.

Theory and Computation

Over the last few decades, computational methods have become the "third prong" of research, along with formal theories and experiment. With the advent of powerful computers and development of efficient algorithms, modeling of complex systems becomes more and more attractive as a partner with experimental work. Rather than each pursuing separate agendas, coupling in a truly synergistic fashion is now not only plausible but necessary for the types of advancements needed in catalysis.

In catalysis, the challenge for theory is to develop a fundamental and predictive understanding of the controlling factors of catalytic reaction mechanisms from quantum chemical, kinetic, atomistic, and continuum models. Provided scientists doing experiments and computation are in constant dialog, computations of controlling factors can help find and design catalysts with higher activity, specificity, and stability. Catalytic processes span many length and time scales. The challenges for theory and computations in catalysis research span the range of these scales. Close coupling between experimental observations and theory, modeling, and simulations will provide unprecedented capabilities to design more effective, selective, and robust catalysts.

It is widely agreed among scientists and engineers that modern theory, computation, and informatics are critical to advancing the understanding of catalytic processes at the *molecular level*. For meaningful advances to be realized, there must be, at key points and many levels of description, critical contact with experimental work; e.g., what is predicted with theory and computation must also be measured experimentally. Otherwise, necessary benchmarking of both aspects will leave unresolved ambiguities at troublesome levels. The best way to accomplish this is to organize a catalysis research institute that includes both experiment and computation, and rewards productive interactions.

Computational Methods: Validation and Benchmarking

While the importance for coupling theory, computation, and experiment cannot be overemphasized, each must continue to develop tools independently. Thus, for theory and experiment to become full partners in synergistic research, gaps in theoretical models need attention. Then validation and benchmarking could become common practice in catalytic research. To press forward the frontiers of theory and modeling for catalysis science, the following items need attention:

1. Theory must be able to create atomistic models that capture more details of real catalyst systems.

2. There is a need for a hierarchy of models with systematically improved accuracy.

3. While a primary goal of theory will continue to be to determine thermodynamics and kinetics of catalytic processes, it should not be limited to this area. In particular, we also need convenient ways to calculate experimental observables, like vibrational spectra, optical spectra, X-ray spectra, NMR spectra, etc.

4. A statistical mechanics description of catalytic systems is required. We need robust tools such as microkinetic models, kinetic Monte Carlo, continuum models, which cover different length and time scales and reflect the nonhomogeneity of real systems.

5. Models are needed that take into account the structure of a catalyst evolving with pressure, temperature, and progress of chemical reactions.

Verifiable, high-quality experimental data characterizing the structure, dynamics, and kinetics of catalysis and catalysts are critical for validating/benchmarking computational methods. How and at what points do experiment and computation actually overlap is a complex question that requires careful consideration by experts in both computational and experimental catalysis. These validations are needed for homogeneous catalysis (molecular level), biocatalysis (supramolecular level), and heterogeneous catalysis (solid state/interface level).

An example of this difficulty can be seen when considering the transition state. In computational catalysis at the atomic-molecular level, this is a common structural, dynamic, and kinetic component, but experimental access to the structural and kinetic details of this putative entity is difficult. However, *operando* microscopy, spectroscopy, and spectrometry measurements, often with nanoscale spatial and sub-picosecond time resolution, are now plausible experimentally. Thus, for selected systems, it is feasible to span a wide range of length and time scales, with verifiable structural, dynamic, and kinetic data.

Databases

Reliable experimental and computational databases, and the accompanying computational tools to access and mine them, are not well-developed for catalysis science. DOE only recently began supporting work in this area, at Purdue University. Successful development and, especially, utilization will require the catalysis community's participation in gathering and submitting specific data in a common format. Different users and uses make defining the data to be included/excluded a subjective process, but even some data would be much better than no data at all. Thus, here again it was recognized that one or more well-funded catalysis research institutes would play a special role in enabling significant progress to be made in this developing area of catalysis science.

In entering into database development, it might be helpful to begin with a small number of test cases of great interest to the community, e.g., partial oxidation of some small molecule like methanol, some aspect of Fischer-Tropsch synthesis, and/or Ziegler-Natta catalysis. It would be useful to select examples where there is plausible overlap of homo-, hetero-, and biocatalysis.

With the emergence of high-throughput methods, including combinatorial methods, there is an opportunity for direct linkages to one or more experimental databases with parallel development, testing, and execution of many informatics and data management/mining tools.

Software and Theory Needs

Density functional theory (DFT) has played a key role in advancing computational catalysis, because this approach can provide a good description of the geometries and frequencies for a wide range of transition metal complexes as well as solids at the local and non-local levels. An issue with DFT is the absence of, at the present stage of development, exchange-correlation functionals that are accurate or reliable enough to be used for predictions of catalytic behavior, both activity and selectivity. The ability to predict reaction activation energies accurate to a fraction of a kcal mol^{-1} is necessary if errors by factors of 10 or more are to be avoided in assessing/predicting absolute activities, i.e., the turnover numbers that are central to catalysis.

A critical issue, therefore, is how to go beyond DFT in directions that have potential for improving absolute accuracy for predicting/assessing experimental turnover numbers and selectivities. In addition,

improvements of the computational scaling and efficiency of accurate molecular orbital methods, such as coupled cluster, CCSD(T), and multi-reference methods, MRCI, are needed.

For broad and effective utilization, software should be user-friendly as, for example, in NWChem. Standard software is needed that takes output from electronic structure codes such as Gaussian or Molpro and enables rate constant and model kinetic calculations.

To move catalysis science forward, access to integrated hardware and software systems is essential. This access could be accomplished, in part, through a Virtual Catalysis Center. In addition, the computational catalysis community can move the overall catalysis agenda forward by developing a Grand Challenge Computational Problem; i.e., garner a large resource allocation at the Nation's major computational centers, and use the resource to solve a significant problem in catalysis science. This action would raise awareness of the importance of computing in catalysis and the role of large machines in addressing national scientific and technical needs such as catalysis.

Given the advances in methods and software described above, the fundamental science goals that could be accomplished on next- and future-generation computer architectures in computational catalysis are, in order of increasing capability:

- 50 TFlops: accurate calculations for realistic, isolated (single molecule or a single cluster) homogeneous catalyst model systems (errors <1.0 kcal/mol in thermodynamics, <50% error in reaction rates).

- 250 TFlops: accurate calculations for realistic homogeneous catalyst model systems in solution and heterogeneous catalysts in vacuum (errors <1.0 kcal/mol thermodynamics, <50% error in reaction rates).

- 1000 Tflops: accurate calculations for realistic homogeneous catalyst model systems in solution and heterogeneous catalysts in solution (errors <1.0 kcal/mol thermodynamics, <50% error in reaction rates).

Delivering capabilities to the computational catalysis community for addressing these complex, demanding problems could best be accomplished by a combination of user-based facilities and integrated software with strong infrastructure support.

Summary

To summarize and reiterate a point made several times earlier: While theory and modeling, like experimental work, must continue to advance its own tools and methods, for the most meaningful advances in catalysis science to be realized, there must be, at key points and many levels of description, critical contact with experimental work. The best way to accomplish this is to organize catalysis research institutes that include experiment, theory, and modeling as partners and to reward productive interactions among them.

Conclusions and Recommendations

As with many recent workshops on catalysis science, the **Advanced Resources for Catalysis Research Workshop** again recognized the central importance of catalysis to our energy, economic, and environmental security. Catalysis is a vital part of our core industrial infrastructure, as it is integral to chemical processing and petroleum refining, and is critical to proposed advances needed to secure a sustainable energy future. Advances in catalysis could reduce our need for foreign oil by making better use of domestic carbon resources, for example, allowing cost-effective and zero-emission conversion of coal into transportation fuels. No matter what energy sources are being considered (oil, natural gas, coal, biomass, solar, or nuclear based), a clean, sustainable energy future will involve catalysis to improve energy efficiency and storage and use options, and to mitigate environmental impacts.

Although current incremental improvements to catalytic processes are leading to better control of desired chemical transformations with fewer undesirable side-products, these developments alone are not enough. With recent revolutionary progress in nanotechnology and high-performance computing enabling breakthroughs in catalysis science and technology, the time is right for substantially increased investments to fully achieve advancements in:

- photocatalysis to successfully and economically use solar energy to convert water into oxygen and hydrogen—a very clean-burning fuel.

- interfacial electrocatalysis to realize, with competitive economics, the efficiency potentially attainable with fuel cells—devices that directly convert energy stored in molecules, like hydrogen, into electrical energy.

- gasification and conversion of coal into transportation fuels.

- catalytic conversion of biomass to more useful products, e.g., cellulose to glucose, to economically utilize the chemical energy stored in this renewable resource.

- development of catalysts that operate in aqueous media to fully enable the promise of "green chemistry."

- construction of nanoscale multicomponent catalysts organized in mesostructures as viable alternatives to expensive and supply-limited precious metal catalysts.

The workshop's primary focus was to: 1) detail the specific state-of-the-art and next-generation tools needed to advance catalysis science; and 2) identify how best to ensure these tools are widely available to the catalysis research community.

The overall recommendation emerging from the workshop, and endorsed by all participants, was the need to establish one or more well-funded and well-equipped National Catalysis Research Institutes (NCRIs) competitively selected, centered in the national laboratories and, by charter, networked to other national laboratories, universities, and industry. The NCRI(s) would provide, in centralized physical locations, tools dedicated to catalysis science that are too complex or too expensive for a single investigator or institution to support. This networked center(s) would facilitate high-risk, long-term, multi-investigator, multi-disciplinary research activities addressing specified challenges and needed breakthroughs.

Further recommendations from the breakout sessions include the following:

- Specific suites of tools dedicated solely to catalysis research are required, including suites of *operando* experimental capabilities; a suite of computational tools for structural, dynamic, and microkinetic modeling of catalytic reaction systems; a suite of high-throughput combinatorial catalytic reaction tools; and an integrated suite of experimental tools dedicated to *operando* study of catalytic systems at one or more of the nation's third-generation synchrotron light sources. A key component is the availability of a "critical-mass" of experts in these areas whose focus is collaborative catalysis research.

- The NCRI(s) should also focus on need-based development of new experimental and computational tools for the catalysis community.

- The NCRI(s) should have evolving, well-defined, long-term research agendas selected for scientific importance and potential impact, consisting of a closely integrated group of collaborators with appropriate expertise to address the interdisciplinary research themes.

- To encourage and strengthen university, particularly student, involvement and increase the participation of industrial users from throughout the country, the NCRI(s) should include a prominent virtual component. The NCRI(s) would receive sufficient support for amplifying, integrating, and accelerating the research of individual scientists at the Institute itself and at institutions participating in the virtual collaboratory.

Sources

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Appendices

A – Workshop Agenda

B – Participants

C – Abbreviations

Appendix A – Workshop Agenda

Tuesday – September 21, 2004

8:00 am	Welcome and Introductions – Doug Ray, Pacific Northwest National Laboratory
8:15	Background and Workshop Goals – Doug Ray and Chuck Peden, Pacific Northwest National Laboratory
9:00	The Science Case – past workshop reports – Mike White, University of Texas at Austin

Recommendations for facilities needs from past workshop reports

9:45	Synthesis and Materials Characterization – Bruce Gates, University of California at Davis
10:15	Reaction Dynamics and *Operando* Characterization – Charlie Campbell, University of Washington
10:45	High-Throughput Methods – Chris Snively, University of Delaware
11:15	Theory and Computation – Dave Dixon, University of Alabama
11:45	Working Lunch – Discussion of Morning Presentations and Charge to Breakout Sessions
1:00 pm	**Breakout sessions** Synthesis and Materials Characterization Reaction Dynamics and *Operando* Characterization High-Throughput Methods Theory and Computation
4:00	Breakout Session Reports
5:30	Reception
6:00	Dinner

Wednesday – September 22, 2004

7:30 am	Breakout Sessions Reconvene
8:30	Breakout Session Final Reports
9:30	General Discussion
11:30	Closing Remarks
12:00 pm	Adjourn

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Appendix C – Abbreviations

AFM	atomic force microscopy
APS	Advanced Photon Source (Argonne National Laboratory)
BESAC	Basic Energy Sciences Advisory Committee (U.S. Department of Energy)
CCSD(T)	coupled-cluster with single and double and perturbative triple excitations
DFT	density functional theory
DOE	U.S Department of Energy
EELS	electron energy loss spectroscopy
EXAFS	extended X-ray absorption fine structure
FTIR	Fourier transform infrared spectroscopy
HPLC	high performance liquid chromatography
LEEM	low-energy electron microscopy
MRCI	multi reference configuration interaction
NCRI	National Catalysis Research Institute
NERSC	National Energy Research Scientific Computing Center (Lawrence Berkeley National Laboratory)
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
PEEM	photo emission electron microscopy
SFG	sum frequency generation
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
UHV	ultrahigh vacuum
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy