

Research Activity:**Catalysis and Chemical Transformations**

Division:

Chemical Sciences, Geosciences, and Biosciences

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Portfolio Description:

This activity supports basic molecular-level research to understand chemical catalysis and electrocatalysis, and to develop principles and predictive methods for the rational design of catalysts. It encompasses all types of catalysts for organic and inorganic synthesis and transformation reactions, including organometallic complexes, hybrid organic-inorganic compounds or porous solids, bio-inspired catalysts, interfaces of metals, semiconductors and non-metallic compounds such as oxides, carbides, and nitrides. Special emphasis is placed on nanocatalysis, to understand and use the enhanced catalytic properties that emerge at the nanoscale. Its research portfolio addresses catalytic model systems of relevance to fossil and renewable energy production, storage, and use; environmental remediation; materials synthesis; fuel cell reactions; and photocatalytic conversions. It promotes the use and the co-development of advanced synthetic, spectroscopic, and theoretical techniques that pertain to the intrinsic needs of catalysis research, such as complex but controllable compositions and structures and wide scales of time and space resolution. Nanoscale design, multiscale theory, modeling and simulation, and femtosecond and synchrotron-based spectroscopic techniques present unique opportunities for the acquisition of new knowledge in catalysis. This activity is the nation's major supporter of catalysis research as an integrated multidisciplinary activity, assembling a body of researchers from several branches of science.

Unique Aspects:

This activity funds the largest fraction of basic research in catalysis in the federal government. It seeks to cross the barriers between heterogeneous, homogeneous, and bio catalysis. The integration promotes synergism among disciplines and innovation in fundamental approaches as well as applications. In terms of instrumentation, this program has helped with the establishment of surface science and inorganic synthesis laboratories at universities and encourages the use of large-scale facilities at the Department of Energy (DOE) national laboratories. Principal investigators use synchrotron, neutron and electron sources and computational tools to significantly advance catalysis research.

Relationship to Other Programs:

This activity relates to other activities within BES. The Catalysis and the Chemical Physics activities have complementary goals in the areas of surface science, surface chemistry, and quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena. The Catalysis and Photochemistry activities also complement one another in the support of fundamental photocatalysis and photoelectrocatalysis, which are relevant to solar photoconversion and photochemical synthesis. The Catalysis and Separations activities share their concern and in some instances co-support synthetic research for zeolitic, mesoporous, hybrid, and caged materials. The Catalysis and Heavy Elements Chemistry activities also share interest in the design and synthesis of ligands and coordination compounds of lanthanides. The BES synchrotron facilities have beamlines used by Catalysis researchers, in particular the National Synchrotron Light Source (NSLS), Advanced Photon Source (APS), Intense Pulsed Neutron Source (IPNS), and Advanced Light Source (ALS). The BES Nanoscale Science Research Centers (NSRCs), in particular the Center for Functional Nanomaterials (CFN) and the Center for Nanophase Materials Sciences (CNMS), also have thrust areas that address catalysis research, and hence share some of the Catalysis activity goals.

Within DOE, the activity of Catalysis produces research outcomes of relevance to programs of the Office of Energy Efficiency and Renewable Energy and the Office of Fossil Energy. These programs have collaborated during the review of proposals in relevant initiatives, such as the Hydrogen Fuel Initiative.

The activity is coordinated with other federal agencies. At the National Science Foundation (NSF), heterogeneous and bio catalysis are funded within its Engineering Directorate while homogeneous catalysis is funded within the Math and Physical Sciences Directorate (Organometallic and Inorganic Chemistry program). Also at the NSF, the surface science and materials aspects of catalysis are spread among three divisions (Chemistry, Materials, and

Chemical and Transport Systems). The National Institutes of Health (NIH) funds the health-related applications of homogeneous, enzymatic, and bio catalysis; the Environmental Protection Agency (EPA) funds the application of catalysis to environmental remediation; and the Office of Naval Research (ONR) and Army Research Office (ARO) support the application of catalysis to military purposes.

Significant Accomplishments:

The science and practice of catalysis over the last several decades have led to many achievements of fundamental interest. A significant contribution has been made to the current molecular-level understanding of catalytic cracking of hydrocarbons in zeolites, reforming of hydrocarbons over supported bimetallic alloys, and desulphurization of heteroaromatics over supported metal sulfides. Reactions of importance in environmental chemistry, such as removal of NO_x, have been studied in detail over model single crystal metals and supported metals. Results of those investigations have dramatically improved the knowledge of catalyst structure-reactivity relationships. This activity has also led to fundamental advances in the catalysts required for the selective oxidation of hydrocarbons for the manufacturing of monomers, fine chemicals, and fuel additives. During the past decade, one of the most significant accomplishments in homogeneous catalysis was the development of novel single-site metallocene catalysts for polymerization of alkenes. The control of polymer tacticity resulted in property enhancement and a largely expanded use of polyalkene plastics, from extending the shelf life of food we buy to enhancing the efficiency of the cars we drive. Other very significant achievements were the catalytic synthesis of organic acids by alcohol carbonylation and the generation of important monomers by olefin metathesis. More recently, the selective oxidation of C-H bonds was achieved both homogeneously and heterogeneously. For their achievements, researchers in this program have been widely honored by scientific societies, as they have received three-quarters of the awards in Organometallic Chemistry given by the American Chemical Society, all but one of the fundamental catalysis awards given to U.S. academics by the North American Catalysis Society, And several international awards, including the Nobel Prize in Chemistry for 2006.

Mission Relevance:

Catalytic transformations impact virtually all of the DOE energy missions. Catalysts are needed for all of the processes required to convert crude petroleum and natural gas into clean burning fuels. Catalysts are crucial to energy conservation in creating new, less-energy-demanding routes for the production of basic chemical feedstocks and value-added chemicals. Catalytic science has impacted the technology used to clean up environmental pollutants, such as unwanted products from chemical production or from combustion, or by transforming toxic chemicals into benign ones, such as chlorofluorocarbons into environmentally acceptable refrigerants.

Scientific Challenges:

The grand challenge for this area of research is the *a priori* molecular-level design and synthesis of catalysts with controlled reactivity and durability. Such knowledge is of relevance for the production of catalysts that convert natural resources into energy or desired products in an energetically efficient and environmentally benign manner. That challenge can be met by coordinating fundamental research on chemical synthesis, structural characterization, mechanistic studies, and theoretical interpretation.

The current challenge in inorganic synthesis is the atomistic and molecular control of structure, shape, and functionality, all of which can be facilitated by the development of libraries of modular ligands. For the particular case of biomimetic catalyst development, synthesis and use of versatile ligands must be promoted. Likewise, air- and water-resistant complexes must receive priority. The control of macromolecular structure continues to be a challenge. Secondary structures that produce shape-selective reaction environments must be attained by the use of, for example, dendrimers, polypeptides, zeolites, and imprinted media.

In solid state synthesis, the current frontier is to produce catalytic materials with nanoscale control of composition, homogeneity, shape, and structure. A challenge is to design molecular precursors and convert them into solid-state structures with desired chemical functionalities that are durable under reaction conditions. Traditional routes of surface chemistry, aqueous-solution chemistry, and high-temperature chemistry need to be complemented by softer routes. For example, coordination chemistry may be used to build nanoparticles that are surface-functionalized with metal compounds. Organic or biological strategies may then be used to arrange the particles into preconceived patterns. These arrangements will provide molecular recognition properties (for example, size, shape, chirality, and hydrophobicity).

The characterization of synthetic catalysts demands higher spatial and time resolution under *ex situ* and *in situ* conditions. Both electronic and atomic structures must be correlated with secondary and macrostructure and their time-resolved evolution. The kinetically significant intermediates must be identified and discriminated from those species or moieties that contribute to selectivity and from those that are merely inactive. This is a particularly crucial need in solid-mediated catalysis and biocatalysis.

The study of reaction mechanisms will be promoted by the synergistic use of theory, simulation, and experimentation. In particular, identification and structural characterization of the transition states still remains a challenge for most reactions. Classical labeling, trapping and molecular probe experiments must be complemented with time-resolved *in-situ* spectroscopy in order to acquire information on bonding dynamics. The development of chemo-, regio-, and stereo-selective reactions is of primary importance to the advancement of the science of catalysis, since those reactions present the highest demands on catalysts. Conformers at equilibrium are usually separated by barriers of less than 3 kcal/mol. While high selectivity has been obtained with homogeneous catalysts in selected instances, heterogeneous catalysts require substantially more study, possibly with help from biomimetics.

Catalysis of bond cleavage and reformation has, for the most part, been restricted to hydrocarbons (CC, CH bonds), halogenated compounds (CX bonds), and nitrogen and sulfur containing compounds (CS, CN bonds). Moreover, past and current research has also addressed the selective addition of oxygen, hydroxyl, or nitrogen to hydrocarbon and aromatics. For homogeneous catalysis, the challenge is to carry out these selective reactions under solvent-less conditions or with green solvents such as supercritical CO₂, while maintaining stability. For heterogeneous catalysis, the challenge is to work at low temperature and pressure conditions with high activity and selectivity. For both types of catalysis, a major challenge is to obtain selective conversion for reactants such as short-chain saturated hydrocarbons and other refractory molecules. Likewise, new challenges for all types of catalysts have arisen in activating molecules and materials derived from biorenewable resources.

Besides hydrocarbon chemistry, other challenges reside in the elucidation of the catalytic mechanisms for the synthesis of molecular and nanomaterials. For example, in the catalytic synthesis of carbon nanotubes, chirality control has remained elusive because of lack of understanding of the structure-determining steps. As another example, the nucleation and subsequent growth of silicon nanowires from silane or its derivatives on molten gold nanoparticles proceed through catalytic pathways that must be understood. Finally, the synthesis of compound semiconductors and more complex nanomaterials constitute an excellent challenge for the development of catalytic science and its application to a new area.

Funding Summary:

Dollars in Thousands

<u>FY 2005</u>	<u>FY 2006</u>	<u>FY 2007 Request</u>
37,871	38,107	47,459
<u>Performer</u>	<u>Funding Percentage</u>	
DOE Laboratories	58 %	
Universities	38 %	
Other	4 %	

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

The laboratory programs are multi-investigator efforts and make use of specialized facilities at Lawrence Berkeley National Laboratory, Brookhaven National Laboratory, Oak Ridge National Laboratory, Argonne National Laboratory, and Ames Laboratory, usually involving collaborators from universities.

Projected Evolution:

The science of catalytic chemistry is still emerging. A wealth of experimental information has been accumulated relating catalytic structure, activity, selectivity, and reaction mechanisms. However, for phenomenological catalysis to evolve into predictive catalysis, the principles connecting those kinetic phenomena must be more clearly and thoroughly identified.

Better understanding of the reactivity of matter will result from more complete integration of experiment and theory, reproducible synthesis of catalysts, and thorough characterization of catalysts and reactions. An effort is needed to promote scientific cooperation among groups with complementary expertise in synthesis, structural characterization, intermediate and transition state characterization, dynamics simulation, and kinetics determination. National laboratories or university centers may serve as focal points for knowledge integration.

Following from the specific scientific challenges outlined above, it has become apparent that the convergence of heterogeneous, homogeneous, and biocatalysis must be promoted. Ideas and approaches motivated by biological reaction systems will be used to derive new biomimetic homo- or heterogeneous analogues. For example, two such particular ideas are the use of long-range or secondary structure to affect not just selectivity but also activity of inorganic catalysts, and the use of tunable structural flexibility to affect reaction pathways and hence selectivity.

New single investigator efforts are expected to be focused on the challenges mentioned. The following examples illustrate the areas where mechanistic understanding and new methodology are needed: (a) synthesis of hybrid organometallic-heterogeneous catalysts from molecular precursors such as organometallic or cluster compounds or organic-inorganic host-guest complexes; (b) synthesis of mixed metal inorganic compounds and derived high-temperature catalysts consisting of crystalline nanoporous structures with precisely positioned chemical functions; (c) selective functionalization of saturated hydrocarbons or stereoselective functionalization of complex molecules by heterogeneous catalysis; (d) characterization of kinetically relevant intermediates and catalyst dynamics with high spatial and time-resolution and *in situ* spectroscopy, microscopy and diffraction, and in particular, with synchrotron and neutron-based techniques and advanced computational techniques; (e) environmentally benign transformations using solvent-less homogeneous catalysis, low-temperature heterogeneous reactions, and tandem or programmable catalysis, i.e., precise matching of functionalities among dissimilar catalysts.