

Research Activity:

Division: Chemical Sciences, Geosciences, and Biosciences
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Portfolio Description:

The long-term goal of this activity is to develop a predictive science of chemical catalysis and reactivity. Its specific objective is to develop mechanistic understanding of chemical reactions that pertain to energy production, storage, and conservation; environmental remediation and pollution prevention; renewable and fossil resource processing; and novel materials synthesis. The research portfolio addresses catalytic reactions in solution and on gas-solid or liquid-solid interfaces (e.g., alcohol carbonylation catalyzed by organometallic complexes, and hydrocarbon reforming catalyzed by supported noble metals). This activity funds also the study of molecular processes and structure-activity relationships in chemical systems of large complexity, such as reactions that model petroleum or coal fractions processing, automobile exhaust conversion, fuel cell conversion, specialty chemical synthesis, polymer synthesis, nanomaterials synthesis, and others. As outcome of the investigation of the catalysis of chemical transformations, fundamental advances are being made in inorganic, organometallic, porous, and nano material synthesis; surface and physical chemistry; organic chemistry and chemical technology.

Unique Aspects:

This activity funds the largest fraction of basic research in catalysis in the Federal Government. In contrast with the NSF and NIH, which support the various aspects of catalysis across multiple divisions, this core research activity covers heterogeneous, homogeneous, and bio catalysis under a single umbrella. 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 National Laboratories. Principal investigators are increasingly utilizing synchrotron, neutron and computational tools to significantly advance catalysis research.

Relationship to Others:

Funding for surface science and inorganic synthesis is coordinated with the programs of Materials Chemistry and Chemical Physics in the BES division. Support for the applied aspects of catalysis of oil and coal processing and environmental remediation is provided by FE and EE. At the NSF, heterogeneous catalysis is funded within its Engineering Directorate and is heavily oriented towards reaction kinetics, while homogeneous catalysis is funded within the Math and Physical Sciences Directorate (Organometallic and Inorganic Chemistry program) and is oriented primarily towards organometallic and organic synthesis. Also at the NSF, the surface science and materials aspects of catalysis are spread among three divisions (Chemistry, Materials, and Chemical and Transport Systems). At other agencies, the NIH funds the health-related applications of enzymatic and bio catalysis, the EPA funds the application of catalysis to environmental remediation, and the ONR and 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 desulfurization of heteroaromatics over supported metal sulfides. Reactions of importance in environmental chemistry, such as NO decomposition, 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 and fine chemicals. 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 utilization 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, methane selective oxidation was achieved both homogeneously and heterogeneously. For their achievements, researchers in this program have been widely honored by scientific societies, as they have received eleven of the sixteen awards in Organometallic Chemistry given by the ACS, and eleven of the twelve fundamental catalysis awards given to US academics by the North American Catalysis Society.

Mission Relevance:

The fuel and chemical industry is a primary producer and consumer of energy. Catalysis plays an essential role in both energy production and energy conservation, as over 90% of all chemical processes are catalytic. Energy conservation and environmentally benign processing are both benefits of the high selectivity and activity achievable through catalysis. The economic impact of catalysis is outstanding, as the chemical industry is responsible for a significant fraction of the GDP (over \$900B in 2001) and is one of the few sectors that historically have had a positive balance of trade for the US (over \$20B in 2001). This program contributes the basic knowledge that relates catalytic structure to chemical functionality and to reaction mechanism. As the demand for greener processing increases, and as the use of more refractory feedstocks or the need for novel materials rises, the motivation to discover new chemical routes and hence new catalysts will also increase. Consequently, the phenomenological knowledge that must be reduced to a comprehensive set of scientific principles will continue to augment. This research funded under this activity is producing the fundamental concepts that are needed to carry out predictive catalyst design.

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 peptide ligands must be promoted. Likewise, air- and water-resistant complexes must receive priority. The control of macromolecular shape 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, hydrophobicity, etc.)

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* vibrational 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.

Besides hydrocarbon chemistry, a newer challenge is the elucidation of the catalytic mechanisms for the synthesis of molecular and nanomaterials. For example, the catalytic synthesis of carbon nanotubes is currently being optimized utilizing purely Edisonian approaches. 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 proceeds through catalytic pathways that are completely unknown. 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		
FY 2002	FY 2003 Request	FY 2004 Request
24,779	31,333	32,333
Performer	Funding Percentage	
DOE Laboratories	58.0%	
Universities	38.0%	
Other	4.0%	

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 LBNL, BNL, ORNL, NREL, ANL and Ames, 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.

April 7, 2003