

Research Activity:

Division:

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Detailee:

Team Lead:

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Catalysis Science (formerly Catalysis and Chemical Transformations)

Chemical Sciences, Geosciences, and Biosciences

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Portfolio Description:

This activity supports basic research to understand mechanisms of 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 novel or 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; chemicals and 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 chemical imaging, including ultrafast and synchrotron-based spectroscopies and neutron-based techniques, present unique opportunities for the acquisition of new knowledge in catalysis. This core 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. Multidisciplinary approaches are encouraged by means of multi-PI grants. 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 – Condensed Phase and Interfacial Molecular Science activities have complementary goals in the areas of interfacial science, surface chemistry, and quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena. The Catalysis and Solar 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 common issues and in some instances co-support synthetic research for zeolitic, membrane, 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), and the 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), have thrust areas that address catalysis research, and the Center for Nanoscale Materials (CNM) has topics and personnel in 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, homogeneous and bio catalysis, and the surface science and materials aspects of catalysis are funded by separate programs within the Math and Physical Sciences and the Engineering Directorates. 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:

Researchers supported by this CRA have achieved fundamental breakthroughs in catalysis over the last two decades. For instance, significant contributions were made to the 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 removal of NO_x , have been studied in detail over model single crystal metals and supported metals, dramatically improving 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 two decades, one of the most significant accomplishments in homogeneous catalysis was the development of practical catalysts for the metathesis of unsaturated compounds, a reaction that is ubiquitous in organic synthesis and was highlighted by a recent Nobel Prize. Other very significant accomplishments were the discovery of single-site metallocene catalysts for polymerization of alkenes, with one of its major contributors receiving a National Medal of Science, and the development of methods to study the surface science of catalysis, with its major contributor receiving another National Medal of Science. More recently, the low-temperature N_2 activation (the crucial step in ammonia synthesis) was achieved homogeneously. For their achievements, researchers in this program have been widely honored by scientific societies, as they have received most of the awards in Organometallic Chemistry given by the American Chemical Society, most of the fundamental catalysis awards given to U.S. academics by the North American Catalysis Society, two National Medal of Science awards, and the 2005 Nobel Prize in Chemistry.

Mission Relevance:

Catalytic transformations impact virtually all of the DOE energy missions. Catalysts are needed for all or many of the processes to convert crude oil, natural gas, coal and biomass 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 convert environmental pollutants, such as unwanted products of combustion or chemical manufacturing, or replace carcinogenic refrigerants such as chlorofluorocarbons.

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 long-term stability. 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. A special focus is the identification of new carbon-neutral pathways for the catalytic conversion of biologically-derived feedstocks. Those challenges can be met by coordinating fundamental research on chemical synthesis, structural characterization, mechanistic and kinetics studies, and theory-modeling and simulation.

The current challenge in inorganic synthesis is the molecular control of structure, shape, and functionality, by means of rationally designed modular ligands. For biomimetic catalyst development, priority is given to highly versatile ligands and air- or water-resistant complexes. The control of macromolecular structure is a continuing challenge. Priority is given to the design of shape-selective reaction environments.

In solid state synthesis, the current frontier is to produce catalytic materials with nanoscale control of composition, homogeneity, shape, and structure. In particular, emphasis is placed on hybrid organometallic-inorganic porous materials able to catalyze the conversion of multifunctional molecules with high selectivity. Molecular precursors may be converted into solid-state structures with designed chemical functionalities that are durable under reaction conditions. Traditional routes of surface chemistry, aqueous-solution chemistry, and high-temperature chemistry are complemented by softer routes, such as surface-functionalization of nanoparticles with coordination compounds. Organic or biological strategies may then be used to arrange the particles into preconceived patterns possessing

unique molecular recognition properties (for example, size, shape, chirality, and hydrophobicity). The interfacial interactions with anchoring ligands, supports, and solvent spheres generate fundamental challenges for exacting characterization but also ways of tuning the reactivity and stability of catalytic materials.

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 discriminated from those that are mere spectators. This is a particularly crucial need in solid-mediated catalysis and biocatalysis.

The study of reaction mechanisms is promoted by the synergistic use of theory, simulation, and experimentation. In particular, identification and structural characterization of the reaction intermediates 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 these reactions present the highest demands on catalysts. While high selectivity has been obtained with homogeneous catalysts in selected instances, heterogeneous or hybrid catalysts require substantially more study, possibly with help from biomimetics and the use of cascade or tandem reactions.

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, one of the challenges is to carry out these selective reactions under solvent-less conditions or in supercritical media or ionic liquids, while maintaining stability. For heterogeneous catalysis, the challenge is to work at extremely high temperature with high selectivity, or extremely low temperature with high activity. New challenges for all types of catalysts have arisen in activating molecules and materials derived from biorenewable resources.

Besides hydrocarbon and carbohydrate chemistry, other challenges reside in the elucidation of the catalytic mechanisms for the synthesis of macromolecular and nano materials. In one example, the catalytic synthesis of carbon or inorganic nanotubes, chirality control has remained elusive because of lack of understanding of the structure-determining steps. In another example, the nucleation and subsequent growth of silicon nanowires from silane or its derivatives on molten gold nanoparticles proceed remain little understood.

Funding Summary:

Dollars in Thousands		
<u>FY 2007</u>	<u>FY 2008</u>	<u>FY 2009 Request</u>
39,711	39,711	56,927
<u>Performer</u>	<u>Funding Percentage</u>	
DOE Laboratories	46%	
Universities	54%	

These are 3-year average 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 single-site catalysts, and thorough characterization of catalysts and reactions by means of cooperation among groups with complementary expertise in synthesis, structural characterization, intermediate and transition state characterization, dynamics simulation, and kinetics determination.

The convergence of heterogeneous, homogeneous, and biocatalysis is evolving. Ideas and approaches motivated by biological reaction systems will be used to derive new biomimetic homo- or heterogeneous analogues. Examples are the use of long-range or secondary structure and structural flexibility to affect both selectivity and also activity of inorganic catalysts. The mechanisms and pathways for charge transfer and rearrangements following non-thermal activation, such as electrochemical and photochemical activation, will also be addressed.

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 and supercritical media; (f) low-temperature heterogeneous reactions; (g) non-noble metal catalysis; (h) tandem and single-pot catalysis; (i) conversion of biologically-derived feedstocks; and (g) electrocatalytic and photocatalytic activation.