

## Catalysis Science

### Portfolio Description

This activity develops the fundamental scientific principles enabling rational catalyst design and chemical transformation control. Research includes the identification of the elementary steps of catalytic reaction mechanisms and their kinetics; construction of catalytic sites at the atomic level; synthesis of ligands, metal clusters, and bio-inspired reaction centers designed to tune molecular-level catalytic activity and selectivity; the study of structure-reactivity relationships of inorganic, organic, or hybrid catalytic materials in solution or supported on solids; the dynamics of catalyst structure relevant to catalyst stability; the experimental determination of potential energy landscapes for catalytic reactions; the development of novel spectroscopic techniques and structural probes for *in situ* characterization of catalytic processes; and the development of theory, modeling, and simulation of catalytic pathways. Capital equipment funding is provided for items such as ultrahigh vacuum equipment with various probes of interfacial structure, spectroscopic analytical instrumentation, and specialized cells for *in situ* synchrotron-based experiments, and computational resources.

### 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. This program encourages the use of large-scale facilities at DOE national laboratories to significantly advance catalysis research.

### Relationship to Other Programs

This activity is closely coordinated with several programs within BES. The Condensed Phase and Interfacial Molecular Science program, a part of the Chemical Physics activity, supports fundamental aspects of interfacial science, surface chemistry, and quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena. The Solar Photochemistry activity supports complementary aspects of photocatalysis and photoelectrocatalysis, while the Physical Biosciences activity supports aspects of enzymatic catalysis. The Separations and Analysis activity supports the synthesis of organic and inorganic materials relevant also to catalysis. The Heavy Elements Chemistry activity supports the design and synthesis of ligands and coordination compounds of lanthanides. The Materials Synthesis activity covers among others, materials of interest for catalysis. The BES synchrotron facilities have beamlines used by catalysis science researchers, in particular the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), and the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). In addition two BES Nanoscale Science Research Centers (NSRCs) have thrust areas that provide unique capabilities for the synthesis and characterization of nanoscale catalysts.

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 catalysis portfolios of other federal agencies are typically restricted to particular applications or dispersed across the agency. The National Science Foundation (NSF) funds heterogeneous catalysis mainly within their engineering directorate; and it funds homogeneous and bio catalysis mainly within their Mathematical and Physical Sciences directorate. The National Institutes of Health (NIH) funds the health-related applications of homogeneous, enzymatic, and bio catalysis; the Environmental Protection Agency (EPA) funds environmental remediation catalysis; and the Defense agencies support catalysis for military applications.

### **Mission Relevance**

Catalytic transformations impact an enormous range of DOE mission areas. Particular emphasis is placed on catalysis relevant to the conversion and use of fossil and renewable energy resources and the creation of advanced chemicals. Catalysts are vital in the conversion of crude petroleum and biomass into clean burning fuels and materials. They control the electrocatalytic conversion of fuels into energy in fuel cells and batteries and play important roles in the photocatalytic conversion of energy into chemicals and materials. Catalysts are crucial to creating new, energy-efficient routes for the production of basic chemical feedstocks and value-added chemicals. Environmental applications of catalytic science include minimizing unwanted products and transforming toxic chemicals into benign ones, such as the transformation of chlorofluorocarbons into environmentally acceptable refrigerants.

### **Significant Accomplishments**

Major breakthroughs over the past three decades have resulted as a consequence of basic catalysis research funded by this core research activity. In particular, the molecular-level understanding of catalytic processing of hydrocarbons led to many new concepts explaining the functioning of metallic and non-metallic catalysts. Consequently, such understanding led to novel catalyst designs, accelerating the development of practical catalysts, some of which are in industrial use today. Examples are new families of synthetic zeolites and noble metal alloys for petroleum reforming catalysis; mixed sulfides and phosphide for hydroprocessing; mixed metal oxides and supported metal nanoparticles for the processing of combustion exhaust pollutants; etc. 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. 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. The discovery of single-site metallocene catalysis in the polymerization of alkenes led to new processes for the widespread fabrication of polymers, and recognition of its major author with a National Medal of Science. The development of new methods to study the surface science of catalysis also led to a National Medal of Science for its major author. The low-temperature  $N_2$  activation (the crucial step in ammonia synthesis) with organometallic complexes was attained. 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, and most of the fundamental catalysis awards given to U.S. academics by the North American Catalysis Society.

## 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.

In inorganic synthesis, the molecular control of structure, shape, and functionality, must be pursued by means of rationally designed modular ligands. In solid state synthesis, emphasis is placed on catalytic materials with nanoscale control of composition, homogeneity, shape, and structure, and in particular, hybrid organometallic-inorganic porous materials able to catalyze the conversion of multifunctional molecules with high selectivity and durability 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 catalysis have arisen in activating molecules and materials derived from biorenewable resources.

### **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.

In the immediate future, research will focus on the chemistry of inorganic, organic, and hybrid porous materials, the nanoscale self-assembly of these systems, and the integration of functional catalytic properties into nanomaterials. New strategies for design of selective catalysts for fuel production from both fossil and renewable biomass feedstocks will be explored. Increased emphasis will be placed on the use of spectroscopy and microscopy to probe both model systems in vacuum and realistic catalytic sites. Research on catalytic cycles involved in electrochemical energy storage and solar photocatalytic fuel formation will receive increased emphasis.