

## Catalysis Science

### Portfolio Description

This activity develops the fundamental principles behind the rational design of catalysts and the deliberate control of chemical transformations. The chemistry of most interest pertains to the conversion of energy resources. Medicinal and human chemistry are outside the scope of this activity. Research includes the elucidation of catalytic reaction mechanisms and kinetics; the synthesis of catalytic sites, molecular ligands, metal clusters, and reaction environments designed to tune 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 specific to catalytic pathways.

### Unique Aspects

This activity funds a large fraction of the basic research in catalysis science in the Federal government. In particular, it supports novel research into energy-specific catalytic chemistry, and into plant-derived chemistry and hybrid solid-state/organic chemistry. The newer advances require complex expertise in different areas of science and engineering, seldom possessed by single individuals, hence this activity has funded small teams dedicated to interdisciplinary research. An important element of this activity is the emphasis on maximizing the atom and energy efficiency of the transformation of natural or man-made chemical resources. Such optimization usually demands the discovery of new chemical pathways not present in nature; hence bio-inspiration is important but insufficient for progress. Control of catalytic pathways requires not only new catalysts, but also finely tuned processes that must be developed specifically for the intended chemical applications. While advanced materials synthesis, enhanced by molecular-level theory and new in-situ instrumentation, is key to designing new catalysts, they are not sufficient for the discovery of more efficient and long-lived chemical transformations. To specifically pursue efficiency, researchers in this program synergistically combine approaches used in heterogeneous, homogeneous, or bio catalysis, and reaction engineering, usually pushing the individual frontiers. For operando and in-situ characterization of working reactions, catalysis researchers must increasingly resort to techniques with high spatial and time resolution and molecular-level sensitivity, and they also participate in the advancement of such techniques. Most instruments are lab-based but DOE facilities are utilized as needed.

### Relationship to Other Programs

- The Condensed Phase and Interfacial Molecular Science program and the Computational and Theoretical Chemistry program support some aspects of interfacial science, surface and solution chemistry, quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena.
- The Solar Photochemistry activity supports some aspects of photocatalysis and photoelectrocatalysis, while the Physical Biosciences activity does so for enzymatic catalysis.
- The Separations and Analysis activity and the Materials Discovery, Design and Synthesis Team support the synthesis of organic and inorganic materials relevant also to catalysis.
- The BES synchrotron facilities have beamlines customized for catalysis science researchers.

- Two BES Nanoscale Science Research Centers (NSRCs) have thrust areas that provide unique capabilities for the synthesis and characterization of nanoscale catalysts.
- Several EFRCs and the Joint Center for Artificial Photosynthesis Hub support investigators and topics relevant to catalysis.
- The Catalysis Science activity produces research outcomes of relevance to programs of the Office of Energy Efficiency and Renewable Energy, and the Office of Fossil Energy. Other federal agencies also support catalysis research, but not comprehensively: National Science Foundation (NSF), National Institutes of Health (NIH), Environmental Protection Agency (EPA), and the Defense Department agencies.

### **Significant Accomplishments**

Researchers funded by this activity have received numerous awards from national and international scientific societies. They have innovated on the molecular-level understanding of catalytic processing of hydrocarbons and carbohydrates, for example:

- Selective oil reforming and hydroprocessing pathways with new families of synthetic zeolites and noble metal alloys, mixed sulfides and phosphides;
- Selective oxidation of hydrocarbons for the manufacturing of synthetic fuels, commodity and specialty chemicals, with novel mixed metal oxides and supported metal nanoparticles;
- High-yield metathesis of unsaturated compounds with new organometallic transition metal complexes, a ubiquitous reaction that brought a Nobel Prize to two PIs;
- Polymerization of alkanes and alkenes with novel single-site metallocene catalysis, responsible for a large fraction of all oil-derived and biomass-derived industrial polymers, which led to a National Medal of Science to a program PI;
- Selective and high-yield rearrangement of C-C, C-O, and C-H bonds in organic molecules, thanks to atomic-level control of nanoparticle composition, support interface, and reconstruction, which evolved from classical surface science and merited a National Medal of Science to a program PI;
- Low-temperature nitrogen splitting and CO activation with novel organometallic complexes and heterogeneous catalysts, a highly sought breakthrough. Nitrogen splitting is the essential step in the synthesis of ammonia and fertilizers; and water-gas shift via CO oxidation with water is responsible for the synthesis of most industrial hydrogen. Ammonia and hydrogen production account for over 5% of the world's energy use.

### **Mission Relevance**

Catalytic transformations impact a large range of DOE mission areas. Particular emphasis is placed on catalysis relevant to the conversion and use of fossil and renewable energy resources, such as the conversion of crude petroleum and biomass into clean burning fuels and materials. Catalysts are used in fuel cells and batteries as well as photocells. Catalysts are essential for energy-efficient routes for the production of basic chemical feedstocks and value-added chemicals, as well as for minimizing the production of unwanted products.

### **Scientific Challenges**

The unique challenge for Catalysis Science is to predict and control catalytic reaction mechanisms and rates in order to design new and more efficient ways to convert natural or man-made products. A special focus is the identification of carbon-neutral pathways for the catalytic conversion of biomass-derived feedstocks, which are characterized by multiple chemical

functionalities. New hybrid organometallic-inorganic porous catalysts are able to match in their structure the multifunctionality required by the feed. To synthesize such catalysts, traditional 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 achieve unique molecular recognition properties (for example, size, shape, chirality, and hydrophobicity). The interfacial interactions provoked by ligands, supports, and solvent spheres generate ways of tuning the reactivity and stability of catalytic materials.

The characterization of synthetic catalysts demands 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. In particular, characterization of the reaction intermediates and pathways typically resorts to labeling, trapping, and molecular probe experiments 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 challenging, particularly with heterogeneous or hybrid catalysts, sometimes demanding the use of cascade or tandem reactions. For homogeneous catalysis, one of the long-term 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.

### **Projected Evolution**

The science of catalytic chemistry is still emerging. Much experimental information has been accumulated relating catalytic structure, activity, selectivity, and reaction mechanisms. Phenomenological catalysis is however evolving into predictive catalysis by means of integration of experiment and theory, reproducible synthesis of single-site catalysts, and thorough characterization of catalysts and reaction mechanisms. The convergence of heterogeneous, homogeneous, and biocatalysis is progressing. Examples are the use of long-range or secondary structure and structural flexibility to affect both selectivity and also activity of inorganic catalysts, or the use of non-thermal activation, such as electrochemical and photochemical activation. At present, research is leading to the substitution of noble and rare elements by non-precious and abundant elements or compounds. New chemical functions are being achieved by utilizing mesoscale or collective properties of materials. Natural products of fossil and renewable origins are being converted into common intermediates that serve as platforms for the energy-carrier and chemical industries of the future. Catalytic cycles for electro- or photo- activation of abundant chemicals are also receiving special attention.