

Catalysis Science

Portfolio Description

This activity develops the fundamental principles behind the rational design of catalysts, and the deliberate and informed control of chemical transformations. Emphasis is on the understanding of the reaction mechanisms, enabling precise identification and control of catalytic active sites. The chemistry of most interest is the sustainable conversion of energy resources and the mitigation of environmental impacts of energy production and use; other areas outside DOE's missions are not considered. Research includes the elucidation of catalytic reaction kinetics and mechanisms. As part of such mechanistic studies, the program supports 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, organometallic, or hybrid catalytic materials in solution or supported on solids; the dynamics of catalyst structure relevant to catalyst activity and stability; the experimental determination of potential energy landscapes for catalytic reactions; the development of novel spectroscopic techniques and structural probes for *in situ* or *in operando* characterization of catalytic processes; and the development of theory, modeling, and simulation specific to catalytic pathways.

Scientific Challenges

The unique challenge for Catalysis Science outlined in a BES workshop on *Basic Research Needs: Catalysis for Energy*¹ is to understand mechanisms and dynamics of catalyzed reactions in order to design new and more efficient pathways for the conversion of natural or artificial resources to fuels and chemicals. A special focus is the identification of catalytic carbon-neutral routes to long-term energy sustainability. For that purpose, new catalytic systems are needed that might involve novel hybrid organometallic-inorganic porous catalysts with multifunctional active sites required for new challenging reaction environments. 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 induced by ligands, supports, and solvent spheres generate ways of tuning the reactivity and stability of catalytic materials. Indeed, one of the grand challenge identified by a recent report from the Basic Energy Sciences Advisory Committee on the *Challenges at the Frontiers of Matter and Energy*² focused on the design of revolutionary new forms of matter with tailored properties.

The characterization of synthetic catalysts demands spatial and temporal 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

¹ https://science.energy.gov/~media/bes/pdf/reports/files/cat_rpt.pdf

² https://science.energy.gov/~media/bes/besac/pdf/Reports/Challenges_at_the_Frontiers_of_Matter_and_Energy_rpt.pdf

reactions is challenging, particularly with heterogeneous or hybrid catalysts, sometimes requiring the use of cascade or tandem reactions. For this, appropriately accounting for weaker forces (including van der Waals interactions) on catalytic chemistry has become recognized as an essential element of the science. 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 catalyst 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 via integration of experiment and theory, reproducible synthesis of single-site catalysts, and thorough and precise characterization of catalysts and reaction mechanisms. The convergence of heterogeneous, homogeneous, electro-, photo-, and bio-catalysis is progressing. Examples are the use of long-range or secondary structure and structural flexibility to affect both activity and selectivity of inorganic catalysts, or the use of non-thermal activation, such as electrochemical and photochemical activation. At present, research is leading to identification of catalytic carbon-neutral routes to long-term energy sustainability, such as thermocatalytic production of H₂, NH₃ (outlined recently by a panel of experts in a report, *Sustainable Ammonia Synthesis*³), and other chemicals without secondary greenhouse gas emissions; selective and low-temperature activation of lower or higher alkanes or multifunctional molecules using non-precious or non-metallic catalysts; catalytic reaction mechanisms influenced by weak forces in confined or open catalytic environments; electrochemical and photo-electrochemical conversion of natural compounds or secondary products into chemicals and fuels; reactions in water, ionic liquids, and under extreme conditions; and quantitative and reproducible determination of kinetics and mechanisms, open source computational approaches, and shared databases leading to benchmarks for catalytic properties.

The Catalysis Science program does not fund research on: (1) synthesis of pharmaceuticals or, more generally, fine chemicals unrelated to energy applications; (2) cellular or organismal catalyzed reactions; (3) non-catalytic reactions; and (4) process or reactor design and optimization.

Significant Accomplishments

Over the last 20 years, the Catalysis Science program has advanced the molecular-level understanding of catalytic processes that underpin energy resource conversion and utilization. Significant accomplishments in this program include the design and controlled synthesis of catalyst active-site environments, characterization tools to unravel catalyst-structure relationships, and computational methods integrated with experimental design to predict system behavior. Examples are given below:

³<https://science.energy.gov/~media/bes/pdf/reports/2016/SustainableAmmoniaReport.pdf>

- In the theory of heterogeneous catalysis, scientists identified the most important parameters determining the catalytic properties of transition metal surface catalyzed processes leading to a set of catalyst design rules.
- Advanced tools and methods for operando-structural characterization have significantly improved the ability to investigate structure-function relationships in catalysis with sufficient detail and precision to enable catalyst improvement.
- In the field of advanced synthesis, researchers developed new methods for molecular control of single-site and multi-functional catalysts enabling new chemical pathways and tandem catalysis.
- Comprehensive studies were completed on selective oil reforming and hydroprocessing pathways utilizing new families of synthetic zeolites, noble metal alloys, and mixed sulfides and phosphides.
- New pathways were developed for selective oxidation of hydrocarbons leading to synthetic fuels and commodity and specialty chemicals, utilizing novel mixed metal oxides and supported metal nanoparticles.
- High-yield metathesis of unsaturated compounds with new organometallic transition metal complexes has led to novel routes to specialty and commodity chemicals.
- Polymerization of alkanes and alkenes with novel single-site metallocene catalysis is responsible for a large fraction of all oil-derived and biomass-derived industrial polymers.
- Selective and high-yield rearrangement of C-C, C-O, and C-H bonds in organic molecules was made possible by atomic-level control of nanoparticle composition, support interface, and reconstruction, areas that evolved from classical surface science.
- Low-temperature dinitrogen reduction and CO activation with novel organometallic complexes and heterogeneous catalysts has been advanced. Dinitrogen reduction 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.

Unique Aspects

This activity is the largest single source of Federal funding for basic research in catalysis science that is focused on novel energy-relevant chemical transformations. An important element of this activity is the emphasis on maximizing atom and energy efficiency, which usually demands the discovery of new chemical pathways. Directing reactions along those pathways requires new catalytic processes developed specifically for the type of feedstock, energy source, and desired product. While advanced materials synthesis, molecular-level theory and new *in situ* instrumentation are key to designing new catalysts, they are not sufficient for the discovery of more efficient and sustainable chemical transformations. To specifically pursue efficiency, researchers in this program synergistically combine approaches used in heterogeneous, homogeneous, bio-, electro-, and photo-catalysis, as well as reaction engineering and computational chemistry. For *in operando* and *in situ* characterization of working reactions and for simulation of reaction pathways, catalysis researchers must increasingly resort to techniques with high spatial and temporal resolution and molecular-level sensitivity, as well as methods of theoretical and computational chemistry, many times contributing to the advancement of such methods. They extensively use laboratory scale instrumentation as well as DOE scientific user facilities.

Mission Relevance

Advances in the science of catalytic transformations impact a wide 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, chemicals, and materials. Catalysts are used in fuel cells and batteries as well as photocells for the production, storage, and utilization of chemical energy. Catalysts are essential for energy-efficient and sustainable routes for the production of basic chemical feedstocks and value-added chemicals, as well as for minimizing the production of unwanted byproducts.

Relationship to Other DOE Programs

- BES synchrotron facilities have customized and dedicated beamlines for catalysis science researchers. The Synchrotron Catalysis Consortium (SCC) funded by this program has been the first of its kind in the United States with a mission to promote the utilization of synchrotron techniques for cutting-edge catalysis research under *in situ* conditions.
- Within BES, other programs support research that is synergistic with the Catalysis Science program efforts, which is coordinated when appropriate:
 - Condensed Phase and Interfacial Molecular Science program and the Computational and Theoretical Chemistry program cover interfacial science, surface and solution chemistry, quantum mechanical theory, molecular modeling, and simulation of catalytic-related phenomena.
 - The Solar Photochemistry activity supports photocatalysis and photoelectrocatalysis, while the Physical Biosciences and Photosynthetic Systems programs do so for enzymatic catalysis providing foundational knowledge for the design of biomimetic catalysts.
 - The Separations and Analysis activity and the BES Materials Discovery, Design and Synthesis team in the Materials Sciences and Engineering Division support the synthesis of organic, inorganic and hybrid materials that are often relevant for catalysis.
 - BES Nanoscale Science Research Centers (NSRCs) have thrust areas that provide unique capabilities for the synthesis and characterization of nanoscale catalysts.
 - The Joint Center for Advanced Photosynthesis (JCAP) is an energy innovation hub whose scope encompasses the discovery and development of photocatalyst materials and processes for water splitting and CO₂ reduction.
 - Several Energy Frontier Research Centers (EFRCs) study and utilize catalysts and catalytic approaches while pursuing their specific research goals.
- 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: National Science Foundation (NSF), National Institutes of Health (NIH), Environmental Protection Agency (EPA), and the Defense Department agencies.