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Heterogeneous Oxidative and Polymerization Processes

William Tumas*, Kevin C. Ott, and R. Thomas Baker

Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). We performed experiments directed at understanding novel catalysts and the use of supercritical carbon dioxide as a reaction medium for catalytic reactions. We participated in program development activities with individual companies and with trade organizations to develop research and funding strategies for catalysis on a national level. This work has helped to identify scientific and technological opportunities for catalysis research in industry and for large national initiatives such as global climate change. Our work has poised the Laboratory to participate in a spectrum of activities where catalysis science and technology will play a role.

Background and Objectives

The goal of this project was to enhance the Laboratory's capabilities in catalysis research and develop future programmatic opportunities through collaboration with key industrial partners and other national laboratories, and by working with industrial groups such as the Council on Chemical Research (CCR) to develop national agendas for prioritization of catalysis research and funding. Our work with these groups was directed at exploring the current and future needs in catalysis science and identifying Laboratory capabilities (either currently existing or that could be developed), which would result in future funding to the Laboratory.

Catalysis plays a fundamental role in the economy, environment, and public health of the nation by providing low-energy pathways for conversion of chemical feedstocks to the building blocks of commerce such as fuels, polymers, plastics, pharmaceuticals, and agrochemicals, and by removing pollutants from combustion and petrochemical processes. Catalysts, materials that accelerate chemical transformations without being consumed in the process, are used in the production of chemicals and materials that account for > 20 % of the Gross Domestic Product. Catalysis will also play a key role in future DOE and national objectives in Global Climate Change, Clean Chemistry, and other energy-related issues that face the United States in the next century.

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The objective of our work was to develop both our technical acumen and position the Laboratory to compete for future large initiatives that will include catalysis science and technology.

Importance to LANL's Science and Technology Base and National R&D Needs

The research and program development activities we performed relate to the Laboratory's complex experimentation and measurement, and high performance computing and modeling competencies. The study of catalysis requires a multidisciplinary team approach to enable the breakthroughs required for future clean energy and chemicals production. The skills required for catalysis research are the same skills as required for many Laboratory mission-oriented problems, and through this project we sought to develop catalysis science capabilities at the Laboratory that would also provide a mechanism for maintaining Laboratory skills in such areas as interfacial science, spectroscopy, physical chemistry, reaction dynamics, and theory and modeling.

Approach and Accomplishments

This project was comprised of an experimental part directed at catalysis for alternative feedstock and carbon dioxide utilization, and a program development portion devoted to focusing Laboratory capabilities toward future programmatic opportunities. Through our program development efforts, we sought to attract additional funding on the national level for catalysis that the Laboratory would then subsequently compete for from a position of strength. As a part of this effort we participated in a number of national forums and industrial/academic workshops and visits to industrial companies to identify the scientific challenges and technological needs of catalysis research in the decades to come. From these roadmapping exercises, we have developed a vision and a plan for catalysis research at the Laboratory, and have developed strategies for obtaining funding from a number of DOE and other federal customers.

Experimental

We began our experimental investigations by studying the synthesis and reactivity of novel oxidation catalysts consisting of microporous zeolites having a small fraction of tetrahedral sites replaced with redox-active transition metal ions, titanium and vanadium in particular. These catalysts have demonstrated remarkable activity in the reaction of alkanes with peroxide under very mild conditions, and we began to explore their structure by developing magnetic resonance spectroscopy approaches. This research was later integrated with other similar research being performed under University of California Directed Research and Development (UCDRD) funding.

Subsequently, we focused on examining catalytic processes in supercritical carbon dioxide to provide innovative, environmentally benign chemical processes, and to utilize carbon dioxide as a reagent for chemical synthesis. This work focused on two classes of reactions that are industrially significant and could lead to waste minimization/solvent replacement. They were 1) palladium-catalyzed reductive carbon-carbon bond-forming reactions (Heck reaction) to produce pharmaceutical intermediates, and 2) cobalt-catalyzed air oxidations of cyclic hydrocarbons to produce polymer intermediates. Our work on the Heck reaction revealed supercritical carbon dioxide can be used as an alternative solvent for the Heck reaction. We examined a number of catalysts for the reaction of iodobenzene with styrene in the presence of triethylamine. Perfluorinated phosphine catalysts dramatically increased conversions to 99% after 12 hours at 90 degrees Centigrade and 5000 psi. We have found carbon dioxide to be an effective cosolvent for the direct cobalt-catalyzed air oxidation of cyclohexane and cyclohexanone to adipic acid, a precursor to nylon. Oxidation of cyclohexane at 95 degrees Centigrade produced adipic acid with selectivities higher than those of conventional solvents (>80%) at low conversions (up to 4%). Direct air oxidation of cyclohexanone in supercritical carbon dioxide proceeded at higher rates.

Program Development

During the period of this project, we have worked closely with a number of individual chemical and energy companies to identify their current and future scientific and technological needs. This was done in order to obtain a complete picture across the industry of where the focus of our efforts should lie, and to lay the groundwork to provide compelling arguments to augment federal funding for research in catalysis science and in the allied disciplines. With program offices at the Laboratory, we also worked closely with potential DOE and EPA customers to assess their needs in programs where catalysis either does or could play a role.

On the national level, we became involved in the US chemical industry's 'Vision 2020' process to roadmap the path forward for the chemical industry. This process is being driven by the Council on Chemical Research (CCR), an organization sponsored by US chemical manufacturers with the American Chemical Society and other trade and professional organizations. Our involvement centered around putting together a workshop on catalysis as it relates to identifying and prioritizing the critical needs of the chemical industry in the area of chemical synthesis. For CCR, we partnered with Sandia National Laboratory to organize and run this workshop. We called together approximately 50 of the nation's top minds in catalysis from a cross section of academia, industry, and government in addition to select representatives of federal agencies. The goal was to prioritize the chemical industry's critical needs in catalysis research directed towards chemical synthesis. The product of the workshop was a catalysis roadmap listing detailed technical research investments associated with the most important

critical needs as applied to a list of "big impact" research areas. The intent was for this roadmap to become a planning document useful to funding agencies.

The major finding of the roadmapping exercise was the prioritization of research needs in catalysis research. Eight major research areas were identified. Workshop participants ranked these areas and the top four critical needs are:

- enabling catalyst design through mechanistic, experimental, and computational chemistry,
- in situ techniques for catalyst characterization,
- high throughput catalyst synthesis and testing, and
- synthesis of catalysts with specific site architecture.

This roadmap is a living document, and will be updated on a regular basis through the Vision 2020 process.

These program development activities have resulted in four funds-in agreements from companies, the development of two substantial proposals to DOE/OIT with industrial collaborators, and the development of an EPA Green Chemistry Center at Los Alamos. The technical and the program development activities have positioned the Laboratory well for participation in major DOE global climate change initiatives that have been proposed for FY 1999.