Catalytic Hydrothermal Reductions

Previous FY Cost: $ 0K
FY 1997 Cost: $161K
FY 1998 Cost: $224K
Estimated FY 1999 Cost: $ 99K

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Project Description

The ultimate success of all pressurized aqueous catalytic conversion processes depends on the ability to develop robust catalysts and supported catalysts that can withstand aggressive hydrothermal reaction conditions. During this 3-year project several research subject areas were addressed. Using powder synthesis and ceramic forming techniques unique to PNNL, ZrO_2 supports were synthesized with the required surface area, porosity, mechanical integrity, and chemical stability necessary for this application. In addition, newly emerging schemes for the formation of mesoporous structures from hybrid surfactant templates based on titania and zirconia were used to synthesize next generation supports. Stability of both noble (Ru, Pd, Pt) and base metals (Ni) were evaluated on carbon support materials. Useful candidate catalyst formulations were tested in model reactions to determine stability of the catalyst activity in the aqueous processing environment. Surface analysis techniques were used to evaluate mechanisms of catalyst degradation, as well as catalytic reduction.

Technical Accomplishments

The objective of this research is to develop a new class of aqueous catalysts and supported catalysts for use in hydrothermal conversion processes (such as Low-Temperature Catalytic Gasification and Value-Added Products from Alternative Feedstocks). The requirements for these materials are high surface area (>50 m^2/g), mesoporosity, mechanical integrity, and chemical stability. High surface area materials for catalyst supports are desirable because as surface area of the support increases, the concentration of supported active metal catalyst can increase while maintaining sufficient dispersion of the metal. Thus, a given volume of support with catalyst has increased activity. These catalytic materials will be useful in new technologies being developed for synthesis of chemicals from renewable biomass sources. The new technologies are typically water-based, avoiding the use of organic solvents, but requiring new formulations for catalysts, which can withstand degradation in water.

Based on our experience in chemical process development using catalysts in water-based systems, we have been able to survey a range of materials for compatibility with water at reaction conditions. With this information in hand and our knowledge of materials properties, we have been able to identify several areas of new materials development, which have potential for breakthroughs in this technology. During this final year of the project, we have focused our efforts in using high surface-area powders synthesized by Rapid Thermal Decomposition of Precursors in Solution (RTDS) and careful consolidation methods to synthesize and test ZrO_2 supports. These formulations were evaluated relative to use in aqueous processing.

The catalyst testing has been the evaluation of physical and chemical stabilities of the potentially promising catalysts or catalyst supports under aqueous processing conditions. Typically, catalytic materials were tested in deionized water at 200 to 350°C and 1900 psi H_2 for 70 to 400 hours. Reaction kinetics were determined as a function of time in the processing environment. Detailed chemical and physical analysis of the catalysts before and after use were undertaken to determine changes in the catalyst structure and in the active sites. With the completion of this three year effort, we have expanded our understanding of basic principles operating in aqueous processing systems. Stable catalytic materials have been identified.

Catalytic mechanisms were elucidated.

- RTDS Zirconias

PNNL's patented Rapid Thermal Decomposition of precursors in Solution (RTDS) process was used for production of zirconia powders. The task was defined as (1) prepare experimental quantities of nano-crystalline, high surface area zirconia preferably of the monoclinic phase, (2) prepare high surface area, high crush strength pellets from these powders for use as catalyst supports, (3) characterize these materials in terms of phase, crystallite diameter, and surface area, and (4) provide these materials for testing under catalytic reaction conditions.

The first year of this project (FY 1997) focused on determining which phase (cubic vs. monoclinic) of zirconia powder would be most suited for this project and determining the ideal RTDS processing conditions required for its small scale preparation. In spite of the fact that high surface area (>200 m^2/g) RTDS cubic zirconia (c-ZrO_2) powders transformed to the monoclinic form (m-ZrO_2) under catalytic reaction conditions, hence causing a decrease in the surface area, the final surface areas of the transformed c-ZrO_2 powders were still larger than those of the more stable RTDS m-ZrO_2 powders. Thus, in the second year of this project (FY 1998), work focused on optimizing the RTDS processing conditions for the large-scale synthesis of high surface area c-ZrO2 powders which were both stable under hydrothermal catalytic reaction conditions and which were capable of being processed into stable engineered forms (e.g., cylindrical pellets). During this last year of the project (FY1999), we have concentrated on bench scale production of the RTDS zirconia and the fabrication of extrudates for catalyst production. Approximately one gallon of 1/8th inch extrudates were produced. This material served as support for ruthenium catalysts, which were compared to other commercial catalyst formulations in aqueous hydrogenation reactions.

- Catalyst Comparisons with Commercial Formulations

A series of semi-batch reactor tests were undertaken as a means to evaluate the various catalyst formulations included in this program. The model reaction was the hydrogenation of xylose in aqueous solution to produce xylitol. For the tests, a 300 mL stirred autoclave was used including a high-pressure valve system for recovery of reaction products at temperature and pressure at various points during the test. With this system preliminary kinetics could be determined for the reaction in order to compare the activity of the various catalysts. Catalysts tested included commercial supported nickel metal catalysts, nickel metal catalysts with PNNL-designed promoters, and precious metal catalysts on titania and zirconia supports.

- Summary

In total, these results show good progress on several fronts for developing capabilities as well as actual new materials for aqueous phase processing catalysts. RTDS processing has produced materials, which have been formed into useful catalyst support forms and catalytic testing has been undertaken.

Publications

Elder, S. H., et al. “Zirconia Stabilized 25 Å TiO_2 Anatase Crystallites in a Mesoporous Structure” will appear in *Chem. Mater.* special addition “New Frontiers in Inorganic Solid State Chemistry” October 1998.

Darab, J.G. and D.W. Matson "Continuous hydrothermal processing of nano-crystalline particulates for chemical-mechanical planarization," *J. Electronic Materials*, Vol. 27, No. 10, 1998.

Darab, J.G. "Production of nano-crystalline zirconia-based powders using a flow through hydrothermal process," In *Nanostructured Powders and Their Industrial Application*, eds. G. Beaucage, J.E. Mark, G. Burns, and H. Duen-Wu, Materials Research Society, in press.

Darab, J.G. et al. "Production, Consolidation, Sintering, and Stability of Novel Nano-Crystalline Zirconia Catalyst Support Powders" in Advanced Catalytic Materialsó1998, eds. P.W. Lednor, D.A. Nagaki, and L.T. Thompson (Materials Research Society, Pittsburgh, PA, 1999), pp. 67-72.

Presentations

Darab, J.G., et al. "Production, Consolidation, Sintering, and Stability of Novel Nano-Crystalline Zirconia Catalyst Support Powders," Materials Research Society, Fall Mtg. – Symposium on Advanced Catalytic Materials, November 30-December 4, 1998, Boston MA.

Elliott, D.C., et al. "Development of Heterogeneous Catalysts for use in Aqueous Phase Processing," DOE National Laboratory Catalysis Research Symposium, Albequerque, February 1999.

Darab, J.G. et al. "Nano-Crystalline Particulate Catalyst and Catalyst Support Materials Generated Using a Flow-Through Hydrothermal Process," DOE National Laboratory Catalysis Research Symposium, Albequerque, February 1999.

Darab, J.G. and D.W. Matson, "Continuous Hydrothermal Production of Nanocrystalline Oxide Powders" Fine Powder Processing '99 Conference, Penn State, 1999.

Patent Application

A Method of Making Particles of Metal Oxide Having a Large Crystalline Phase by J.G. Darab