

**TITLE: CATALYSTS FOR HIGH CETANE ETHERS AS DIESEL FUELS**

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## **ABSTRACT**

### **OBJECTIVE**

This project aims at the development of catalysts and processes for high cetane ethers from precursor alcohol mixtures synthesized from H<sub>2</sub>/CO synthesis gas. The following three specific tasks have been defined:

- Preparation and testing of solid acid catalysts for ether synthesis. This task involves preparation of strongly acidic tungstena/zirconia catalysts and optimization of the surface concentration of the catalytic acid groups. Further catalyst development entails anchored sulfonic acid and sulfate catalysts. Reaction studies involve conversion of alcohols to unsymmetrical high cetane ethers using continuous flow gas-phase reactor systems.
- Reaction mechanisms and kinetics. This task involves determination of reaction rates as a function of operating variables, primarily reaction pressure, temperature, and molar ratio of reactants. Computational studies provide insight into the energetics of reaction pathways and transition states from reactants to products.
- Characterization for insight into catalyst optimization. The solid acid centers involved in the catalytic reaction are subject to quantitative analysis of their concentrations and strengths through a combination of surface area measurements, X-ray powder diffraction, optical spectroscopy, and high resolution X-ray photoelectron spectroscopy.

## ACCOMPLISHMENTS TO DATE

A tungstena-zirconia catalyst, based on Mobil Technology Co. patents on catalysts for paraffin isomerization, was prepared and studied for alcohol dehydrocondensation and dehydration reactions. The mixture of isobutanol and methanol converts over this solid acid catalyst to the unsymmetrical ether methylisobutylether (MIBE), dimethylether (DME), and at higher temperatures to isobutene (IB) and smaller amounts of isooctene. It was shown that the ether-forming reactions obey kinetic laws consistent with a two-site catalysis whereby the precursor alcohols are adsorbed on proximal acid sites. Quantitative XPS analyses of the W dispersion (W/Zr ratio demonstrated a complete dispersion of  $\text{WO}_3$  on the zirconia surface) and Brønsted acidity and strength (adsorption of amines revealed *ca* 10-12% strong Brønsted acid surface functionalities) were carried out. While the activation energies for partial processes to form MIBE, DME, and IB over the doped zirconia catalysts were similar to those over earlier studied Nafion-H, the latter catalyst produced superior rates particularly for MIBE formation. This work was presented and published last summer at the International Congress on Catalysis at Granada, Spain.

A novel disodium 1,2-ethanediol bis(hydrogen sulfate) salt precursor-based solid acid catalyst was prepared and demonstrated to have significantly enhanced activity and high selectivity in producing MIBE or isobutene from methanol/isobutanol mixtures. The sodium salt of the glycoldiester of sulfuric acid was synthesized for us at Dow Chemical Co. We then replaced the sodium by ammonium ion using an ion exchange column and anchored the complex to the surface of zirconia. XPS, NMR, and optical spectroscopy analyses were used to verify the successful synthesis of this catalyst precursor and the stability of the catalyst after calcination and removal of the bridging ethyl spacer. This catalyst was tested at 175 °C and 101.3 kPa, and it was shown that this catalyst had 78% higher activity for coupling methanol/isobutanol = 1/1 to MIBE than a conventional synthesized  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalyst. Progressively increasing the reaction pressure increased the space time yield and selectivity of MIBE, while decreasing the formation of isobutene.

A theoretical study of this class of Brønsted acid catalysts localized the transition state of the reactants *via* a dual-site  $\text{S}_{\text{N}}2$  mechanism on the catalysts studied here. A remarkable feature of this mechanism is a concerted transfer of the methyl group from adsorbed methanol to the oxygen of adsorbed isobutanol, and of three protons between the alcohols, surface acid sites, and leaving water molecule. Computations indicate that the sulfated zirconia is a slightly stronger acid than  $\text{CF}_3\text{SO}_3\text{H}$  (a model for Nafion-H) by 1.3-1.4 kcal/mol. However, the superior activity of Nafion-H is attributed to the flexibility of the structure and a relatively high concentration of its sulfonic acid groups.

## SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Oxygenated diesel fuels are of importance to both environmental compliance and efficiency of diesel engines. Unsymmetrical ethers with one light alkyl originating from abundant sources such as methanol or ethanol and one heavy alkyl such as isobutyl, obtainable from isobutanol produced from natural gas- or coal-derived  $\text{H}_2/\text{CO}$  synthesis gas or isobutene derived from petroleum, have ideal cetane and vapor properties for immediate use in diesel-powered engines.

## PLANS FOR THE COMING YEAR

During the next five months of this project, catalytic testing will be carried out at higher pressures to further increase the yield and selectivity of MIBE. In addition, a new catalyst will be synthesized by anchoring a dual glycol or ternary glycerol ester of a tungstic acid salt on zirconia, with the goal of maximizing the concentration of accessible proximal acid sites and producing higher space time yields of ethers.

## ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

### Pertinent Articles (peer reviewed)

Klier, K., "The Transition State in Heterogeneous Catalysis," Topics Catal. (2001); in press.

Shen, J. G. C., Kalantar, T. H., Ma, Q., Herman, R. G., and Klier, K., "Synthesis of Unsymmetrical Ethers and Branched Olefins from Alcohols over a Novel  $(\text{HO})_3\text{ZrO}_3\text{SO}-\text{CH}_2\text{CH}_2-\text{OSO}_3\text{Zr}(\text{OH})_3$ -derived Catalyst," J. Chem. Soc., Chem. Commun. (2001) 653-654.

Klier, K., Kwon, H.-H., Herman, R. G., Hunsicker, R. A., Ma, Q., and Bollinger, S. J., "Alcohol Coupling to Unsymmetrical Ethers over Solid Acid Catalysts," in "*Proc. 12th Intern. Congr. Catal.-Granada, Spain*," (Studies Surface Sci. Catal. Ser., Vol. 130), ed. by A. Corma, F. V. Melo, S. Mendioroz, and J. L. G. Fierro, Elsevier, Amsterdam, 3447-3452 (2000).

### Pertinent Conference Presentations

Klier, K., Shen, J. G., Ma, Q., and Herman, R. G., "Pincer-like Design of Acid Catalysts," at the Spring Symposium of the Catalyst Society of Metropolitan New York, Lehigh University, Bethlehem, PA, March 2001.

Shen, J. G. C., Kalantar, T. H., Ma, Q., Herman, R. G., and Klier, K., "A Novel  $(\text{HO})_3\text{ZrO}_3\text{SO}-\text{CH}_2\text{CH}_2-\text{OSO}_3\text{Zr}(\text{OH})_3$ -derived Catalyst: Synthesis, Characterization and the Catalytic Performance for MIBE Production," poster paper at the Spring Symposium of the Catalyst Society of Metropolitan New York, Lehigh University, Bethlehem, PA, March 2001.

Klier, K., Kwon, H.-H., Herman, R. G., Hunsicker, R. A., Ma, Q., and Bollinger, S. J., "Alcohol Coupling to Unsymmetrical Ethers over Solid Acid Catalysts," poster paper in the Session on Catalysis for a Better Environment at the 12th International Congress on Catalysis, Granada, Spain, July 2000.

Klier, K., "The Transition State in Reactions Catalyzed by Polymers, Metals, and Oxides," Honor Lecture, presented at the Session on Catalysis: Surface Centers and Mechanisms at the 74th ACS Colloid and Surface Science Symposium: COLLOID 2000, Lehigh University, Bethlehem, PA, June 2000.

Kwon, H.-H., Hunsicker, R. A., Herman, R. G., Klier, K., Bollinger, S. J., Butler, A. P., and Santiesteban, J. G., "Tungstena/Zirconia Catalysts for Alcohol Coupling Reactions," presented at the Session on Catalysis: Surface Centers and Mechanisms: Honoring Kamil Klier at the 74th ACS Colloid and Surface Science Symposium: COLLOID 2000, Lehigh University, Bethlehem, PA, June 2000.

Ma, Q., Klier, K., and Herman, R. G., "Studies of the Alcohol Coupling Reaction Pathway to Form Ethers Over Nafion-H," presented at the Session on Catalysis: Surface Centers and Mechanisms: Honoring Kamil Klier at the 74th ACS Colloid and Surface Science Symposium: COLLOID 2000, Lehigh University, Bethlehem, PA, June 2000.

Klier, K., "Transition States in Heterogeneous Catalysis," presented at the Conference on Catalysis in XXI Century: From Quantum Chemistry to Industry in Honor of Jerzy Haber, Cracow, Poland, May 2000.

Herman, R. G., "Synthesis and Utilization of Oxygenates for Fuels and Environmental Implications," presented at the Intertech Conference on Gas-To-Liquids Processing '99: Bringing Clean Fuels and Chemicals to Market, San Antonio, TX, May 1999.

Klier, K., "Catalysis for Oxygenates," presented at the 217th National Meeting of the American Chemical Society, Abstract No. IEC-164, Anaheim, CA, March 1999.

### **Students Supported under this Grant**

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