

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 H₂/CO synthesis gas. The following three specific tasks have been defined:

- C 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 fluorocarbon sulfonic acid catalysts. Reaction studies involve conversion of alcohols to unsymmetrical high cetane ethers using continuous flow gas-phase reactor systems.
- C 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.
- C 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, patented by Mobil Technology Co. for paraffin isomerization, has been examined in this project 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. The ether-forming reactions obey kinetic laws consistent with a two-site catalysis whereby the precursor alcohols are adsorbed on proximal acid sites. Adsorption of pyridine and other amines followed by N 1s X-ray photoelectron spectroscopy (XPS) analysis revealed *ca* 10-12% strong Brønsted acid surface functionalities. Quantitative XPS analysis of the W/Zr ratio demonstrated a complete dispersion of WO₃ on the zirconia surface. Optical diffuse reflectance studies indicate that tungstena and sulfate dopants anchor to the zirconia surface at hydroxyl sites and change the electronic nature of the catalyst. 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.

The sodium salt of the glycoldiester of sulfuric acid has been synthesized for us by an industrial company, and we have replaced the sodium by ammonium ion using an ion exchange column and anchored the complex to the surface of zirconia. XPS and optical spectroscopy analyses to verify the successful synthesis of this catalyst precursor are being carried out before testing.

A theoretical study localized the transition state of the reactants *via* a dual-site S_N2 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 CF₃SO₃H (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-derived H₂/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

Further improvement of the strong acid tungstena/zirconia and sulfated zirconia catalysts will be sought by maximizing the concentration of proximal dual acid sites through anchoring of glycol ester precursors of tungstic acid and sulfuric acid on zirconia followed by hydrolysis.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Pertinent Article (peer reviewed)

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 *AProc. 12th Intern. Congr. Catal.-Granada, Spain,* (Studies Surface Sci. Catal. Series), ed. by A. Corma, Elsevier, Amsterdam (2000); in press.

Pertinent Conference Presentations

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

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

Klier, K., "The Transition State in Reactions Catalyzed by Polymers, Metals, and Oxides," Honor Lecture to be 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," to be 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," to be 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., 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.

Journal Issues Edited

Herman, R. G., guest principal co-editor of a special issue of Catalysis Today entitled "Advances in Clean Fuel Technology and Control of Atmospheric Emissions," issue 55(3), January 5, 2000.

Herman, R. G., guest principal co-editor of a special issue of Topics in Catalysis entitled "Catalytic Surface Centers and Mechanisms," in preparation.

Students Supported under this Grant

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