TITLE: CATALYSTS FOR HIGH CETANE ETHERS
AS DIESEL FUELS

PI: K. Klier and R.G. Herman

STUDENTS: H.-H. Kwon (postdoctoral)
R. A. Hunsicker
S. J. Bollinger
A. P. Butler
D. Chen

INSTITUTION: Lehigh University
Department of Chemistry/ZCSS
Bethlehem, PA 18015
e-mail: kk04@lehigh.edu
phone: (610) 758-3577
fax: (610) 758-6536

GRANT NO.: DE-FG26-98FT4D113

PERIOD OF
PERFORMANCE: Sept. 1, 1998 - Apr. 20, 1999 DATE: April, 1999

ABSTRACT

OBJECTIVE

This project aims at the development of catalysts and processes for high cetane ethers from precursor alcohol mixture synthesized from oxides of carbon and hydrogen. Three specific tasks have been defined:

1. Preparation and testing of solid acid catalysts for ether synthesis. This task involves preparation of the 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. Reactor studies involve conversion of alcohols to unsymmetrical ethers of high cetane value.

2. Reaction mechanism and kinetics. This task involves the determination of reaction rates as a function of operating variables, primarily partial pressures of reactants and products and temperature. Further probe into the reaction mechanism entails ^{18}O retention from one labeled alcohol to the product ether.

3. Characterization for insight into catalyst optimization. The solid acid centers involved in the

catalytic reaction are subject to quantitative analysis of their concentration and strength through a combination of surface area measurements, X-ray powder diffraction, high resolution XPS, TPD/TGA, and optical methods.

ACCOMPLISHMENTS TO DATE

Tungstena/zirconia catalysts have been prepared and tested for the reaction of methanol and isobutanol (2-methyl-1-propanol). The catalysts were found to be active, giving rise to products methyl-isobutyl ether (MIBE), dimethyl ether (DME), isobutene (IB), and minor side products (di-isobutyl ether-DIBE and methyl-tertiary butyl ether-MTBE).

Reaction rates were examined as a function of partial pressures of methanol (P_M) and isobutanol (P_B) with the following results: increasing P_B results in self-poisoning of IB formation and increase of MIBE formation; the MIBE rate has an optimum at $P_{B,\,max}$ = 40 kPa at constant P_M = 23 kPa and T = 423 K and at $P_{M,\,max}$ = 140 kPa at constant P_B = 13 kPa and T = 423 K; kinetic analysis shows a strict compliance of all reactions involved to the dual-site Langmuir-Hinshelwood mechanism observed earlier on fluorocarbon sulfonic resins [1] in this laboratory; MTBE is a minor unsymmetrical ether product due to a favored path (S_N2) to MIBE. The ratio of sorption equilibrium constants is 3.4 in favor of isobutanol over methanol bonding to the acid sites.

Near-infrared examination of the formation of the tungstena/zirconia catalysts revealed that surface hydroxyls of ZrO_2 are utilized for anchoring of the WO_x species into a highly dispersed state. The resulting surface possesses a very low concentration of surface hydroxyls, in agreement with the Mobil result that the concentration of Brønsted acid sites on this type of catalyst is low [2]. High resolution XPS was carried out utilizing the nitrogen bases pyridine [3] (a weak base), triethylamine (a strong base), and ethylenediamine (a dibasic amine). Quantitative analysis of the N1s, W4f, and Zr3d XPS emissions revealed the following: there is a proton transfer from the catalyst surface to the nitrogen of each of these bases; the transfer to pyridine demonstrates that the acid sites are very strong; the surface concentration of these acid sites is low (N:W ˜ 0.1).

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, that can be obtained from CO/H_2-synthesized isobutanol or petroleum resources, have ideal cetane and vapor properties for immediate use in diesel-powered engines.

PLANS FOR THE COMING YEAR

- Further improvement of the tungstena/zirconia catalysts will be sought by maximizing the concentration of dual acid sites through glycol ester precursors of tungstic acid, anchored on ZrO_2 and hydrolyzed.
- A new generation of fluorocarbon sulfonic resin catalysts anchored on hydrophobic supports will be

synthesized, tested and characterized by methods already in use. Effects of water will be examined.

REFERENCES

1. Nunan, J.G., Klier, K., Herman, R.G., “Methanol and 2-Methyl-1-Propanol (Isobutanol) Coupling to Ethers and Dehydration over Nafion H: Selectivity, Kinetics, and Mechanism”, *J. Catal.*, 139, 406 (1993).
2. Chang, C.D., Kresge, C.T., Santiesteban, J.G., Vartuli, J.C., U.S. Patent 5,510,309 (4/23/1996), assigned to Mobil Oil Corp.; C.D. Chang et al., U.S. 5,382,731; U.S. 5,453,556.
3. Johansson, M., and Klier, K., "Surface Acidity (Brønsted and Lewis) by High Resolution X-ray Photoelectron Spectroscopy", *Topics Catal*., 4, 99 (1997).

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Conference Presentations

- Klier, K., "Catalysis for Oxygenates", presented at the American Chemical Society Spring 1999 Meeting, Industrial and Engineering Chemistry Division, Anaheim, CA, March 1999

Students Supported under this Grant

- H.-H. Kwon, postdoctoral fellow in Chemical Engineering, Lehigh University
- R. A. Hunsicker, graduate in Chemical Engineering, Lehigh University
- S. J. Bollinger, undergraduate in Chemistry, Lehigh University
- A. P. Butler, undergraduate in Chemistry, Lehigh University
- D. Chen, undergraduate in Chemistry, Lehigh University