Title: Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis in a Slurry Reactor

Author(s): George W. Roberts
E-mail: groberts@eos.ncsu.edu
Telephone: (919)515-7328
Fax: (919)515-3465
Affiliation: North Carolina State University (NCSU)
Address: Department of Chemical Engineering
Box 7905
Raleigh, NC 27695-7905

Abstract

The objective of this research is to synthesize, characterize, and evaluate promoted zinc chromite catalysts for producing 2-methyl-1-alcohols, such as isobutanol, from synthesis gas. The performance of the experimental catalysts will be evaluated at high temperatures, 573 to 673K, in a slurry reactor using a recently-discovered family of liquids that are thermally and chemically stable at reaction conditions.

Authorization to proceed with the proposed research was received from North Carolina State University on October 15, 1997. Ms. Xiaolei Sun, a graduate student in chemical engineering, was recruited to work on the project effective January 1, 1998.

Initial activity has been focused on: 1) reviewing and extending related previous work; 2) investigating methods for more comprehensive analysis of gas samples taken during catalyst-evaluation experiments and of liquid samples taken during and after catalyst-evaluation experiments, and; 3) training Ms. Sun to use the continuous stirred autoclave reactor and the associated analytical system.

Two papers were completed and submitted for publication. These papers were based on experimental data from a previous, directly-related contract with the Department of Energy. The technical content of these papers involved the thermal and chemical stability of the liquids that will be used as slurry media in the present contract. Details concerning these manuscripts can be found in the following section.

Effort was devoted to developing an analytical system that will quantify the complex mixture of products that is produced with a cesium-promoted zinc chromite catalyst. This product mixture consists of alcohols, paraffins, olefins, CO_2, dimethyl ether, and water, as well as unreacted CO and H_2. Based on the work carried out to date, it appears that the best approach will be to condense the alcohols and the heavier hydrocarbons and then analyze the uncondensed light hydrocarbons and fixed gases

using an on-line, dual-column gas chromatograph. The condensed liquid would then be analyzed off-line, using the same gas chromatograph, and using a gas chromatography / mass spectrometry (GC / MS) facility in the NCSU Chemistry Department.

Analysis of samples of the slurry liquid taken during and after the catalyst-evaluation experiments is a critical element of this research. These analyses provide information about the tendency of the liquid to hydrocrack to light hydrocarbons, and about any other reactions that might help to explain the liquid / catalyst interactions that are known to take place with the liquids and catalysts that will be used in this research. In conjunction with Professor Carol Haney of the NCSU Chemistry Department, we have begun to separate the components of the "used" slurry liquid by means of high-pressure liquid chromatography (HPLC). We have defined conditions that should allow the components associated with the four or five largest HPLC peaks to be collected. These fractions will then be analyzed by GC / MS and by nuclear magnetic resonance (NMR) spectroscopy.

The Principal Investigator visited Engelhard Corporation in Beachwood, OH to discuss the proposed research. Engelhard is the manufacturer of the parent zinc chromite to which promoters have been added. Engelhard has agreed to continue its support of the project through synthesis of experimental catalysts, and through support of the catalyst characterization effort.

Published Journal Articles, Completed Presentations and Students Receiving Support from Grant

1) Journal Articles:

Roberts, G. W., Márquez, M. A., McCutchen, M. S., Haney, C. A. and Shin, I. D., "High-Temperature Slurry Reactors for Synthesis Gas Reactions I: Liquid Thermal Stability", Ind. Eng. Chem. Res., 36, No. 10, 4143 (1997)

Roberts, G. W., Márquez, M. A. and Haney, C. A., "High-Temperature Slurry Reactors for Synthesis Gas Reactions II: Liquid / Catalyst Interactions", submitted to Ind. Eng. Chem. Res.

2) Completed Presentations:

Roberts, G. W., "Liquid-Catalyst Interactions in a Slurry Reactor for Alcohol Synthesis using "Zinc Chromite" Catalyst", Engelhard Corporation, Beachwood, OH, January 30, 1998

3) Students Receiving Support from Grant:

Xiaolei Sun, Graduate Student, Department of Chemical Engineering, North Carolina State University