Title**: PROMOTED ZINC CHROMITE CATALYSTS FOR HIGHER ALCOHOL SYNTHESIS IN A SLURRY REACTOR**

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ABSTRACT

Objective:
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. A commercial "zinc chromite" will be used, and catalyst promoters will be selected from Group I elements. 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 stable at reaction conditions. Any chemical changes in the slurry liquid over the course of the reaction will be identified and quantified.

Accomplishments to Date:
Cesium-promoted "zinc chromite" (ZnCr) catalysts have been found to produce a more complicated product distribution than unpromoted ZnCr catalysts. The product from a Cs-promoted catalyst contains C_1-C_6 alcohols, olefins and paraffins. The analytical system that had been used previously with unpromoted ZnCr catalysts was unable to separate and quantify this broad range of compounds. Therefore, a significant effort was devoted to developing an adequate on-line gas chromatographic (GC) system. After substantial consultation with column vendors and GC experts, plus experimentation with mixtures of the above compounds, a dual-column system was chosen. The first column is a 15 ft., 1/8 in OD, 60/80 Carboxen-1000 packed column connected to a thermal conductivity detector (TCD). This column is used to analyze CO, CO_2, H_2 and CH_4. The second column is a Petrocol DH 150 (150 m, 0.25 mm ID, 1.0 μm film) capillary column connected to a flame ionization detector (FID). This system has been calibrated with more than 20 organic compounds which cover the range of products that were identified in preliminary experiments. A suitable temperature program has been developed that provides a good resolution of isomers, and other compounds with similar retention times, within an acceptable analysis time.

A "blank" run was attempted without catalyst at the following conditions: total pressure = 13.9 MPa; Temperature = 648K, H_2/CO feed ratio = 2:1, with tetrahydroquinoline (THQ) as the slurry liquid. The gas booster compressor was found to have developed a seal leak during the long period of inactivity during which the analytical system was being designed and tested. The compressor is being repaired, and experiments with catalysts should be underway shortly.

The characteristics of the slurry liquid have a major influence on both the overall reaction rate and the product distribution with the unpromoted ZnCr catalyst. To understand this influence, we are attempting to isolate the compounds in the "spent" slurry liquids and to identify their structures. Through high-pressure liquid chromatography (HPLC), we found that there were at least 6 compounds in the "spent" THQ from an experiment with the unpromoted catalyst. However, since the available HPLC can only process very small samples, collecting fractions is impractical. In order to overcome this difficulty, thin-layer chromatography (TLC) work was initiated. Based on TLC plate work, a mixture of methylene chloride (CH_2Cl_2) and ethyl acetate (EtOAc) was chosen as the eluent. A silica gel liquid chromatography (LC) column is now being used for fraction collection. The initial results were not favorable due to lack of component separation, so a different eluent will be tested.

Significance to Fossil Energy Programs:
The development of catalyst and process technology for producing higher alcohols, particularly 2-methyl-1-alcohols such as isobutanol, from synthesis gas would make it possible to use coal and natural gas as raw materials for the production of the oxygenates that are used in motor gasoline, e.g., methyl tertiary butyl ether (MTBE). At present, a primary raw material for MTBE, isobutylene, is produced from petroleum as a by-product of catalytic cracking and ethylene manufacture.

Plans for the Coming Year:

1. Experiments with the first 3% Cs/ZnCr catalyst will be carried out in THQ under different operating conditions. At a total pressure of 13.9 MPa, the effect of gas hourly space velocity (GHSV) will be explored in the range of about 1000 to 5000 standard liters/kg catalyst-hr. Temperatures in the range of 598 to 673K and feed H_2/CO ratios of 1:2 to 2:1 will be evaluated. Experiments will also be conducted with decahydronaphthalene (DHN), tetrahydronaphthalene (THN) and, subject to cost and availability, decahydroquinoline (DHQ) as the slurry liquids.
2. Experiments with different Cs-promoted ZnCr catalysts will be carried out. A 3% Cs/ZnCr catalyst prepared by a different method will be evaluated, and two 6% Cs/ZnCr catalysts will also be evaluated. These catalysts have already been prepared by Engelhard Corporation (Beachwood, OH).
3. The isolation and identification of the compounds in the "spent" slurry liquid will be pursued. Isolated components will be identified by gas chromatography/mass spectrometry (GC/MS) and nuclear magnetic resonance (NMR). These analyses should help to identify interactions between the slurry liquid and the catalyst that might affect the apparent catalyst activity and selectivity, and may help to identify the mechanism(s) of any liquid degradation that may be taking place.
4. If necessary, the on-line gas chromatograpy system will be developed further, to ensure that every peak in the reaction-products analysis is identifiable and quantifiable.

PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENTS RECEIVING SUPPORT FROM GRANT

1) Journal Articles:

Roberts, G. W., Márquez, M. A. and Haney, C. A., "Liquid/Catalyst Interactions in Slurry Reactors: Methanol Synthesis over Zinc Chromite", accepted for publication in *Applied Catalysis A, General*.

2) Students Receiving Support from Grant:

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