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 iso-butanol, from synthesis gas. Promoted commercial "zinc chromite" will be used. Promoters will be selected from Group I elements. The performance of the experimental catalysts will be evaluated at high temperatures, 623 to 673K, high pressure, 6.8 to 13.6 MPa, and 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:

I. On-line GC Analysis System Development

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, 1.0μm film) capillary column connected to a flame ionization detector (FID). This system has been calibrated with more than 20 organic compounds that 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.

II. Catalysts Evaluation

A ZnCr catalyst promoted with 3wt% Cs has been tested twice at the following conditions: total pressure = 13.9 MPa; Temperature = 648K, H_2/CO feed ratio = 2:1, GHSV = 5000 sl/kg-cat/hr, with decahydronaphthalene (Decalin) as the slurry liquid. The promoter was added by the incipient wetness method, impregnating the powder with a solution of $CsHCO_3$, drying at 125°C and then calcining at 350°C for 1 hour to decompose the carbonate. The experiments showed that the ratio of iso-butanol to methanol in the product stream was about 0.06. The slurry liquid (Decalin) did not show significant decomposition and/or alkylation during the 10 days of operation. In addition, there was no significant reduction in the BET surface area over this period.

A ZnCr catalyst promoted with 6wt% Cs has been tested at slightly different operating conditions: total pressure = 6.8 MPa; Temperature = 648K, H_2/CO feed ratio = 1:1, GHSV = 5000 sl/kg-cat/hr. Decalin was also used as the slurry liquid. This promoted catalyst was made by impregnating the powder with CsOH solution and drying at 125°C, without calcining. Compared to the 3wt% Cs promoted ZnCr catalyst, this catalyst had higher alcohols productivity. However, the ratio of iso-butanol to methanol was lower about 0.01. There was about a 20% loss of BET surface area after 8 days of operation.

The existing Haskel gas booster developed a seal leak that could not be repaired. Therefore, a new air booster (DLE 15-75 by Maxpro Technology) was purchased. This air booster has been proved to be more reliable under our experimental conditions. A test of this new compressor is planned in the near future.

III. Spent Liquid Analysis

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, it is necessary to determine the interaction of slurry liquid and catalysts. Silica gel liquid chromatography (LC) experiments were initiated to isolate the various components in the spent liquids. GC/MS and NMR analysis will then be applied to the relatively pure fractions to identify the structures of those components. The necessary experimental procedures are still being developed.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS:

The development of catalyst and process technology for producing higher alcohols, particularly 2-methyl-1-alcohols such as iso-butanol, 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. In combination with restrictions on the aromatic content of the gasoline blends, the addition of oxygenates is expected to reduce ozone forming volatile compounds, nitrogen oxide emission, and other toxic emissions from motor vehicle exhaust.

PLANS FOR THE COMING YEAR:

1. After testing the new air booster, experiments with the 6wt% Cs/ZnCr catalysts will be carried out in Decalin under normal operating pressure conditions - 13.9 MPa. Two new Cs-promoted ZnCr catalysts will be evaluated under the same operating conditions. Experiments also will be conducted with different slurry liquid, tetrohydroquinoline (THQ), tetrahydronaphthalene (Tetralin), and subject to cost and availability, decahydroquinoline (DHQ).

2. The isolation and identification of the compounds in the "spent" slurry liquid will be pursued. The results of GC/MS, H^1 and C^{13} NMR should help to identify the structure of each component. The identification of spent liquid should help to understand interactions between the slurry liquid and the catalyst that might affect the apparent catalyst activity and selectivity, and may also help to develop the mechanism(s) of any liquid degradation that may be taking place.

3. If necessary, the on-line gas chromatography 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

Journal Articles:

- Roberts, G. W., Márquez, M. A. and Haney, C. A., "Liquid/Catalyst Interactions in Slurry Reactors: Methanol Synthesis over Zinc Chromite", *Applied Catalysis A, General*, 189, 395-410, (1999)

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