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ADVANCE CONCEPTS FOR THE CONVERSION OF SYNGAS TO LIQUIDS

Quarterly Report #8

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Executive Summary

Large pore Metal Substituted Aluminophosphate Molecular sieves, (H-MAPO-5, H-MnAPO-5, H-CoAPO-5 and H-MAPO-36) were evaluated for the conversion of ethanol in a continuous flow fixed microreactor. At 400°C, high conversion levels were observed. Ethylene and diethyl ether were the two major products obtained however the catalysts were more selective for ethylene under the reaction conditions. At 500°C ethylene was the only product detected. The low concentration of acid sites combined with the possibly mild acid strengths of the molecular sieves were speculated to be possible reasons for the absence of higher hydrocarbons from the reaction products. Trends for the catalytic behavior of the various catalysts were unpredictable due to a number of reasons. Among these are (1) differing levels of divalent metal substitution (2) varying amount of extraframework species which can have tremendous negative impact on catalytic performance (3) differing levels of H⁺ exchange and (4) differing levels of crystallinity and thermal stability.

1.0 Introduction

The basis of this research project concerns the use of Microporous Metal Substituted Aluminophosphate Catalysts (MeAPO) for the conversion of syngas-derived organic species to useful hydrocarbons and oxygenated organic compounds. This report summarizes research activities for the period October 1, 1996 to December 31, 1996.

2.0 Experimental procedures for studies on the catalytic activities of MeAPOs for the conversion of alcohol

Procedures for the preparation of MeAPO catalysts used in the following studies were detailed in Quarterly Report #5 (October 30, 1995 - January 31, 1996). Details on the catalytic reactor were reported in Quarterly Report #7 (April 1, 1996 - June 30, 1996). The catalytic

conversion of ethanol was evaluated using selected large pore MeAPO catalysts. For catalytic experiments, each run was done with a fresh quantity (1.0 g) of catalyst, heated in the reactor in a stream of nitrogen for between two and three hours. This heating is reported to clean the channels of the molecular sieves of guest species such as water and carbon dioxide and to activate the protons attached to the interior of the channels. The carrier gas was set to a flow rate of 20 cm³/min, and the ethanol space velocity (WHSV) was set at 6.47 g of feed/g of catalyst/hr. The reaction products were sampled at 1 hr intervals. The analysis of reaction products were done using calibration standards diethyl ether, ethylene, ethanol, 99 mol % n-propane and/or 99 mol % n-butane. The conditions for the gas chromatographic analysis were as follows: Porapak Q, 80/100, 4ft x 1/8 inch metal, injector temperature: 200°C, detector temperature: 200°C, initial oven temperature. 40°C for 5 mins., column temperature programme 150°C at 15°C/min.

Results and Discussion

At 400°C, the conversion of ethanol on MeAPOs gave ethylene and diethyl ether as two major components and only minor traces of higher hydrocarbons were observed. Figures 1. shows the percent conversion of ethanol at 400°C vs time on line. H-CoAPO-5 and H-MnAPO-5 gave 80-85% conversion and their activities remained essentially constant for up to 350 minutes on line. H-MAPO-5 was next which showed a gradual decrease from 75% at 36 minutes to 55% at 350 minutes. H-MAPO-36 show a peculiar behavior minimizing its percentage conversion 40% at 100 minutes on line, thereafter increasing to its starting percentage of 54%. The order of catalytic activity in terms of percentage conversion is therefore H-CoAPO-5 = H-MnAPO-5 > H-MAPO-5 > H-MAPO36.

With regards to the reaction products at 400°C, the catalysts showed greater selectivities for ethylene compared with diethyl ether (Figure 2 and 3). H-MAPO-5 showed significant increase in the yield of ethylene with time on line. On the other hand both H-CoAPO-5 and H-MnAPO-5 both showed rapid decline in the ethylene yield with time. This is possibly resulting from deactivation of the catalysts. H-MAPO-36 gave relatively low concentration of ethylene

at less than 20%. The selectivity of the catalysts for ethylene was in the order MAPO-5 > MnAPO-5 = CoAPO-5 >>MAPO-36

Diethyl ether was the only other product observed in major concentration. Compared with the others, H-MnAPO-5 gave highest concentration of diethyl ether, the amount of which decline rapidly with time (Figure 3). H-CoAPO-5 was next, whereas diethyl ether formation on H-MAPO-36 and H-MAPO-5 was comparatively low.

The conversion of ethanol was effected at 500°C to assessed whether the reaction would go beyond ethylene formation. All catalysts studied gave < 99% conversion with ethylene been the only hydrocarbon detected. With the exception of MAPO-36 diethyl ether was not observed and the percentages ethylene obtained (between 53% and 60%) were greater than that at 400°C. As a control the sodium exchanged form of CoAPO-11 was also used as a catalyst at this temperature but gave < 15 % conversion to 9% ethylene. This suggest that the catalytic activities of the MeAPOs were due to the the presence of the acid sites.

Summary

It seems however that the low levels of acid sites combined with the possibly mild acid strengths prevented the desired extent of reaction from taking place. The catalysts all remained highly selective for ethylene and diethylether formation. Trends for the catalytic behavior of the various catalysts were unpredictable due to a number of reasons. Among these are (1) differing levels of divalent metal substitution (2) varying amount of extraframework species which can have tremendous negative impact on catalytic performance (3) differing levels of H⁺ exchange and (4) differing levels of crystallinity and thermal stability.

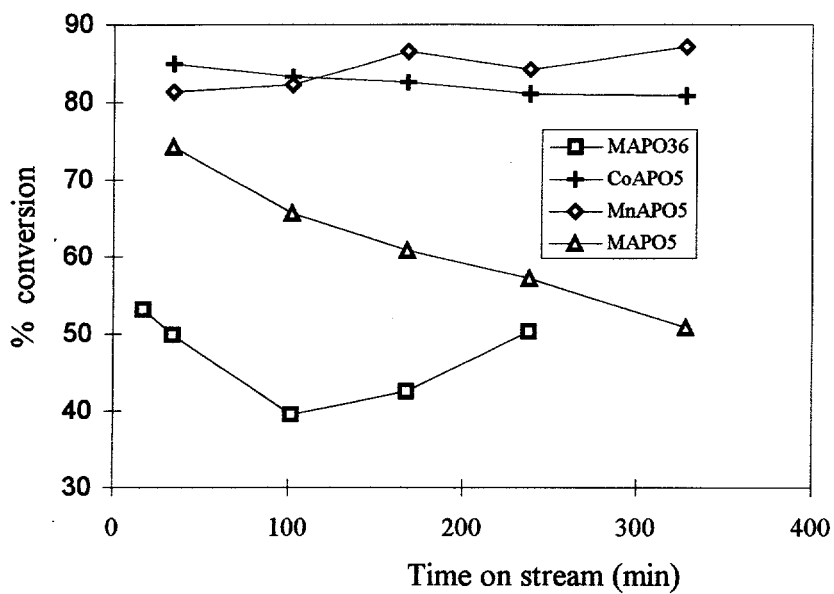


Figure 1. Conversion of ethanol on H-MeAPOs

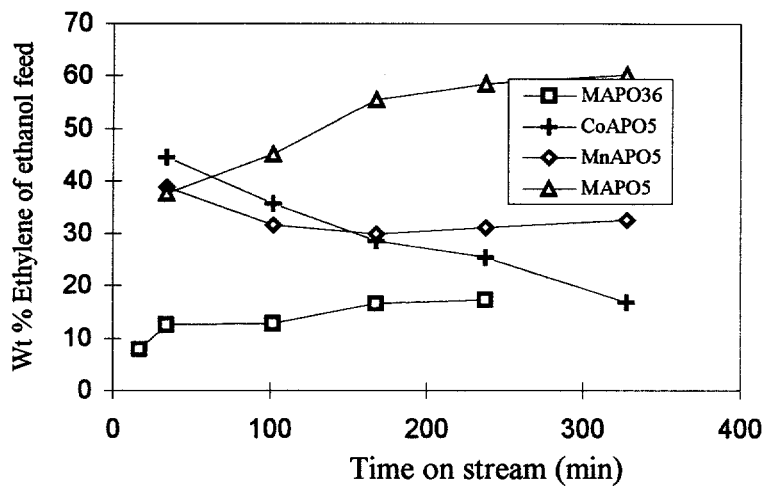


Figure 2. Ethylene formation on MeAPO-36

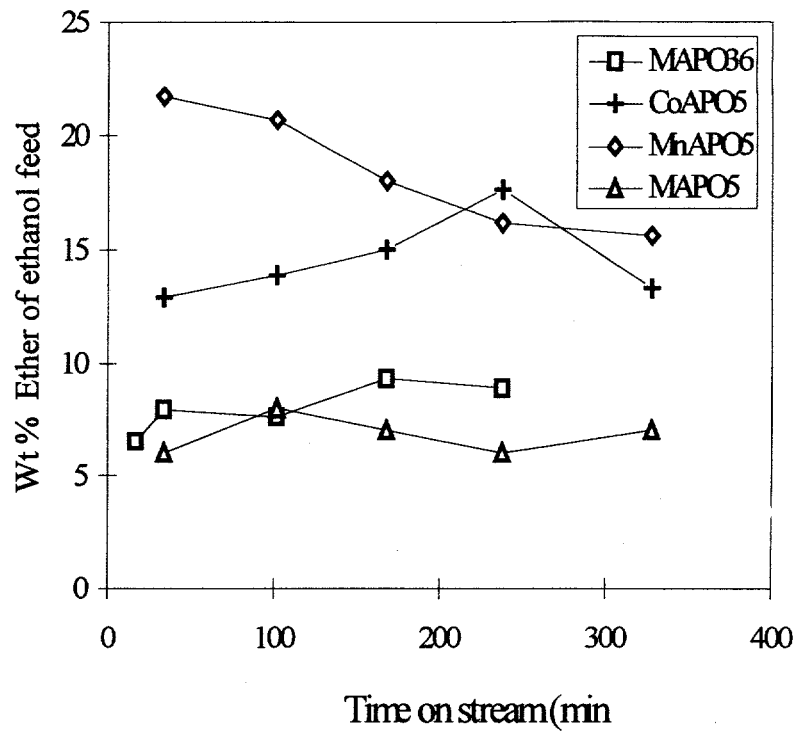


Figure 3. Diethyl ether formation from ethanol conversion