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November 29, 1993

Dr. Arun C. Bose
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Subject: CONTRACT NO. DE-AC22-90PC90042
OXYGENATED OCTANE ENHANCERS: SYNGAS TO ISOBUTYLENE
TECHNICAL PROGRESS REPORT NO. 9

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Dear Arun:

Enclosed is the ninth quarterly report for the subject contract covering the period from April 1, 1993 to June 30, 1993. This report has been reviewed by both UOP and DOE-PETC, and has also been approved by the Chicago Office of Patent Counsel for the DOE. Copies of this report are being also sent to the Document Control Center.

If you have any questions, please contact me at (708) 391-2398.

Regards,

Hemant Gala
Development Specialist II
Diversified Growth and Contracts R&D

Enclosure

CC: Document Control Center, U.S. DOE - PETC (9 Copies)

CONTRACT TITLE AND NUMBER:
Development of a Catalyst for Conversion
of Syngas-Derived Materials to Isobutylene
DE-AC22-91PC90042

Contractor:
UOP
50 E. Algonquin Rd.
Des Plaines, IL 60017-5016

Date: November 11, 1993
Quarterly Report No. 9
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Author:
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Contract Period: March 15, 1991 to September 14, 1994

QUARTERLY TECHNICAL REPORT

The goal of this program is to develop a catalyst and a process for the conversion of syngas to isobutylene. However, due to the low conversion and selectivity generally experienced by the industry in direct conversion of syngas to isobutylene, indirect conversion via branched C_4 alcohol intermediates is being explored. The objectives of the current program are to develop a catalyst and process for the conversion of syngas to isobutanol and to evaluate the commercial potential of the new process. The research program underway at UOP will identify and optimize key catalyst and process characteristics.

This report covers the preliminary testing of methanol synthesis catalysts alone and in combination with basic metal oxides. It is well known that the addition of basic components, in particular alkali, to conventional methanol synthesis catalysts promotes the production of higher alcohols(1). However, these additives also reduce the activity of the methanol synthesis function and require the use of temperatures that result in poor catalyst stability. The objective of this work is to determine whether the activity and selectivity of this type of catalyst can be improved by separating the methanol synthesis and base functionalities. A Cu/Zn/Al co-precipitated metal oxide catalyst has been tested in combination with SiO_2 as an inert reference and MgO and two Mg/Al Metal Oxide Solid Solution (MOSS) materials as basic co-catalysts. The latter combinations afford higher CO and H_2 conversions, but produce DME instead of higher alcohols. This suggests that the Mg-containing metal oxide samples might have some residual acid sites that are capable of dehydrating methanol. Future work will investigate ways to eliminate this activity. The pilot plant performance of the lab-prepared Cu/Zn/Al sample for methanol synthesis is comparable with that of a commercial Cu/Zn/Al water-gas shift (WGS) catalyst.

Two preliminary preparations of high temperature alcohol synthesis catalysts, co-precipitated Zn/Cr and K/Zr/Zn/Mn oxides, have also been evaluated. These two tests gave primarily light hydrocarbons and CO_2 with low to negligible alcohol yields. Further work is need to develop an acceptable high temperature catalyst testing procedure and prepare additional catalyst samples.

MASTER

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OPC ON November 15, 1993.

EXPERIMENTAL

Catalysts

Cu/Zn/Al oxide catalysts were prepared by co-precipitating an aqueous solution of nitrate salts with sodium carbonate at 50°C and pH 7. After extensive water washing, the precipitate was dried at 110°C for 12 hours, sized to 20-40 mesh and calcined at 400°C in air for 2 hours. A high sodium sample was also prepared by drying and calcining a portion of the precipitate after only partial water washing. A commercial Cu/Zn/Al oxide catalyst (ICI 52-1, a low temperature WGS catalyst) was used as received after sizing to 20-40 mesh.

A Zn/Cr oxide catalyst was prepared by similar co-precipitation procedure. After washing and drying, the catalyst was calcined at 500°C in air for 2 hours.

A Zr/Zn/Mn oxide catalyst was prepared by co-precipitating an aqueous solution of nitrate salts with potassium hydroxide at 50°C and pH 7. The solid was washed with 2L H_2O, dried at 110°C for 16 hours, sized to 20-40 mesh and calcined at 400°C in air for 2 hours.

A lab-prepared Mg/Al MOSS was made from a layered double hydroxide prepared by the method of Reichle(2). The layered double hydroxide was activated by calcination at 450°C for 6 hrs. At this temperature, the layered double hydroxide is converted to a MOSS. A commercial Mg/Al MOSS sample was obtained from Alcoa (Sorbplus) and used as received after sizing to 20-40 mesh. An MgO sample was prepared by extrusion of Maglite D MgO from Marine Magnesium Corp., drying, crushing to 20-40 mesh and calcination at 450°C in air for 6 hours. SiO_2, as 20-40 mesh granules, was prepared by crushing and sizing Davison Grade 05 silica gel.

Catalytic Testing Procedure

The catalytic testing of catalyst mixtures containing Cu/Zn/Al oxide was accomplished as follows. The Cu/Zn/Al oxide component and either the basic co-catalyst or silica, as an inert, were mixed in a 1:1 weight ratio as 20-40 mesh granules. This catalyst mixture (6g total) was loaded into a 3/8" I.D. stainless steel reactor. After pressure testing at 1500 psig with N_2, the catalyst was reduced with 2% H_2/N_2 at 250°C, 0 psig, 0.20 scf/hr for 6 hours. After purging with N_2, plant pressure was raised to 1100 psig and temperature to 300°C. Synthesis gas (47/47/6 mole% $CO/H_2/Ar$) was cut-in at 2250 hr^{-1} CO GHSV and lined-out at a temperature of 310°C. All of the tests described in this report were 16 hours in length. The testing of Zn/Cr oxide (Run 114) and K/Zr/Zn/Mn oxide (Run 119) catalysts was identical except for the use of a 450°C process temperature.

Data Analysis

CO and H_2 conversions were determined by analysis of the product gas after the condensation of any liquid products at 0°C. An argon internal standard (6% of feed) was employed. Selectivities are based on moles of carbon from CO converted to each product, including CO_2. The results given in Table 1 and 2 are from a representative product analysis between 8 and 16 hours on stream.

RESULTS AND DISCUSSION

Comparison of Commercial and Lab-Prepared Cu/Zn/Al Catalysts

A lab-prepared Cu/Zn/Al methanol synthesis catalyst has been used for the screening of basic metal oxide co-catalysts for the promotion of higher alcohol synthesis. In order to the establish the suitability of this catalyst, it has been compared with a commercial Cu/Zn/Al catalyst, ICI-52-1, a low temperature WGS catalyst. These two materials were evaluated at comparable conditions in the fixed bed pilot plant. Table 1 shows that the lab-prepared catalyst has slightly higher activity and selectivity than the commercial sample. These results indicate that the lab-precipitated catalyst is suitable for use in further catalyst development.

Testing of Cu/Zn/Al Catalyst with Basic Metal Oxide Co-Catalysts

Three combinations of Cu/Zn/Al methanol synthesis catalyst and basic metal oxide co-catalyst have been evaluated in pilot plant testing. The basic co-catalysts have consisted of two Mg/Al MOSS samples (one lab-prepared and one commercially obtained) and MgO. Table 2 shows the results of these pilot plant tests. All of the tests using the basic co-catalysts show an increase in CO and H_2 conversion; however, dimethyl ether (DME) is the new product being formed. DME is an undesired by-product that does not lie on the pathway from methanol to isobutanol. It is well known that even mild acid catalysts, such as gamma alumina, can dehydrate methanol to DME. Therefore, this result suggests the presence of some acid sites on the Mg/Al MOSS and MgO materials. The addition of alkali to these materials will be examined in the future as an approach to eliminating any residual acidity.

Testing of Zn/Cr Oxide Catalyst

A Zn/Cr co-precipitated catalyst has been prepared and tested in the pilot plant. This catalyst showed very poor performance. The results are summarized in Table 1. Light hydrocarbons and CO_2 were the primary products observed, virtually no alcohols were produced. Hydrocarbons and CO_2 are typical products arising from reactions on the reactor walls Therefore, the use of a reactor coated with an inert lining, such as porcelain, may be necessary. Alternatively, a lower testing temperature (400°C instead of 450°C) may also be necessary to reduce side reaction on the reactor walls. Blank reactor testing will be done to identify suitable conditions that minimize these side reactions. Due to the lack of any activity for alcohol production with this catalyst, the Zn/Cr catalyst preparation procedure will also be re-examined.

Testing of K/Zr/Zn/Mn Oxide Catalyst

Keim and co-workers have reported that very high selectivity to isobutanol can be obtained with the use of Zr/Zn/Mn oxide based catalysts(3). A preliminary Zr/Zn/Mn co-precipitated metal oxide sample has been prepared and tested to follow-up on these reports. This initial material had a high alkali content (14.7 wt.% K) which is substantial higher than those reported by Keim. No palladium was added to this first sample, so that metal oxide activity alone could be evaluated. Table 1 summarizes the results of the pilot plant testing of this material. A small amount of alcohols, virtually all methanol, was observed in the product. Hydrocarbons and CO_2 were the major products, similar to that seen with the Zn/Cr catalyst. This again indicates that a better high temperature screening procedure needs to be developed. Future work will also include the preparation of additional catalyst samples with alkali contents below 1.0 wt.% K, with and without impregnated Pd.

CONCLUSIONS

A lab-prepared co-precipitated Cu/Zn/Al methanol synthesis catalyst has been shown to have performance comparable with a commercially obtained Cu/Zn/Al WGS catalyst in the pilot plant screening test. Three combinations of this catalyst with basic co-catalysts, consisting of either Mg/Al MOSS or MgO, have not shown any increase in higher alcohols. Rather, the co-catalysts promote the formation of DME, an undesired by-product. Further catalyst screening will investigate catalyst modifications, such as the addition of alkali to the basic co-catalysts, to prevent the dehydration of methanol to DME.

Two high temperature methanol synthesis catalysts, Zn/Cr and K/Zr/Zn/Mn, have been prepared and tested. Neither of these materials gave significant alcohol formation. The suitability of the high temperature screening procedure, particularly the presence of side reactions on the reactor walls at the 450°C temperature used, needs to be examined further. Additional samples of these catalysts will also be prepared.

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Table 1. Evaluation of Methanol Synthesis Catalysts

Run Hours on Stream	113 8-16	115 8-16	114 8-16	119 8-16
Catalyst	Cu/Zn/Al Oxide Commercial	Cu/Zn/Al Oxide Lab Prepared	Zn/Cr Oxide Lab Prepared	K/Zr/Zn/Mn Oxide Lab Prepared
Conditions				
Temperature (C)	310	310	450	450
Pressure (psig)	1100	1100	1100	1100
CO GHSV (hr^{-1})	2250	2250	2250	2250
H_2/CO (molar)	1/1	1/1	1/1	1/1
Conversions (%)				
CO	28.1	28.7	27.1	10.5
H_2	37.6	38.7	24.6	11.8
Selectivities (%)				
C_1OH	64.0	65.9	0.1	15.0
C_2OH	2.7	3.0	0.1	4.1
C_3OHs	1.1	1.4	0.1	2.5
n-C_4OH	0.6	0.7	0.1	0.5
i-C_4OH	1.0	1.3	0.1	0.0
$C_{5+}OH$	1.2	1.8	0.1	0.3
DME	1.4	4.1	0.0	0.0
C_1 HCBN	1.4	1.7	26.7	8.1
C_{2-4} HCBNs	1.8	2.3	24.8	11.2
Others	12.2	4.1	6.5	1.4
CO_2	12.6	13.7	41.4	56.9

Table 2. Evaluation of Methanol Synthesis Catalysts

Run Hours on Stream	115 8-16	116 8-16	117 8-16	118 8-16
Catalyst	Cu/Zn/Al Oxide + SiO_2	Cu/Zn/Al Oxide + Mg/Al MOSS (Lab Prep)	Cu/Zn/Al Oxide + Mg/Al MOSS (Commercial)	Cu/Zn/Al Oxide + MgO (Lab Prep)
Conditions				
Temperature (C)	310	310	310	310
Pressure (psig)	1100	1100	1100	1100
CO GHSV (hr^{-1})	2250	2250	2250	2250
H_2/CO (molar)	1/1	1/1	1/1	1/1
Conversions (%)				
CO	28.7	34.5	34.9	29.4
H_2	38.7	45.5	43.6	43.4
Selectivities (%)				
C_1OH	65.9	51.5	47.1	72.6
C_2OH	3.0	1.2	0.8	1.4
C_3OHs	1.4	0.9	0.5	0.9
n-C_4OH	0.7	0.2	0.1	0.2
i-C_4OH	1.3	1.6	0.9	1.1
$C_{5+}OH$	1.8	1.1	0.7	0.8
DME	4.1	20.4	26.3	7.0
C_1 HCBN	1.7	1.0	0.8	1.8
C_{2-4} HCBNs	2.3	0.7	0.6	1.2
Others	4.1	4.4	2.7	2.6
CO_2	13.7	17.0	19.5	10.4

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