HIGH OCTANE ETHERS FROM SYNTHESIS GAS-DERIVED ALCOHOLS

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OBJECTIVES OF THE RESEARCH

The objective of the proposed research is to synthesize high octane ethers, primarily methyl isobutyl ether (MIBE) and methyl tertiary butyl ether (MTBE), directly from $H_2/CO/CO_2$ coal-derived synthesis gas *via* alcohol mixtures that are rich in methanol and 2-methyl-1-propanol (isobutanol). The overall scheme involves gasification of coal, purification and shifting of the synthesis gas, higher alcohol synthesis, and direct synthesis of ethers.

The last stage of the synthesis involves direct coupling of synthesis gas-derived methanol and isobutanol that has been demonstrated by us to occur over superacid catalysts to yield methyl isobutyl ether (MIBE) at moderate pressures and a mixture of methanol and isobutene at low pressures. MIBE is an isomer of MTBE and a process is proposed whereby MTBE from the two alcohols is maximized and MIBE is minimized. This will be achieved by the proper choice of reaction conditions, i.e. intermediate pressures, and of inorganic acid catalysts that are stable at temperatures higher than 200°C, at which the carbonium ion reaction coupling of the two alcohols to MTBE is more effective than the oxonium ion or ester reaction coupling to MIBE.

Both organic and inorganic catalysts will be investigated, and the better catalysts of these classes will be subjected to long term performance studies. The long term performance studies of the combined process will extend to 1000 hr and detailed analytical data for all products will be provided. The project is divided into the following three tasks:

Task 1. Synthesis of High Octane Ethers from Alcohol Mixtures Containing Predominantly Methanol and 2-Methyl-1-Propanol over Superacid Resins

Task 2. Inorganic Catalysts for the Synthesis of High Octane Ethers from Alcohols

Task 3. Long Term Performance and Reaction Engineering for Scale-Up of the Alcohols-to-Ethers Process

The expected result of the proposed research is a novel process for producing ethers, in particular MTBE, in which all five carbons of the unsymmetric C_1-O-C_4 ethers originate from coal-derived synthesis gas.

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SUMMARY OF TECHNICAL PROGRESS

The testing of strongly acidic catalysts for the conversion of a mixture of methanol and isobutanol to ethers and hydrocarbons was continued. Under standardized test conditions the catalysts tested this quarter were: phosphotungstic acid supported on zirconia ($\text{PW}_{12}/\text{ZrO}_2$), "niobic acid" ($\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$), and an iron and manganese doped sulfate-modified zirconia ($\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$). The overall activity of these catalysts followed the order of $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-} > \text{PW}_{12}/\text{ZrO}_2 > \text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ with the $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst approaching $\text{ZrO}_2/\text{SO}_4^{2-}$ in both activity and selectivity for isobutene production.

The effect of the presence of water on the reaction of methanol and isobutanol over $\text{ZrO}_2/\text{SO}_4^{2-}$ was determined to be insignificant. At 157°C and a feed of 2/1 molar ratio methanol/isobutanol, the production of isobutene was unaffected by the addition of 0.05 and 0.10 parts of water to the 2/1 alcohol feed.

Surface areas have been determined for $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$, niobic acid, and phosphotungstic acid on silica. After calcination, the surface area for $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ was found to be 83 m²/g. Niobic acid and phosphotungstic acid on silica ($\text{PW}_{12}/\text{SiO}_2$) were found to have surface areas of 118 and 218 m²/g, respectively. ¹H NMR was used to determine if and how much 1-butene was present as a product when isobutanol is dehydrated over sulfate-modified zirconia. It was found to be present in small amounts, ≤3% of the product stream.

TECHNICAL PROGRESS

A. Results of Standard Tests Using Supported Heteropolyacid, Nb_2O_5 , and $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ Catalysts

The screening of very strong solid acids as catalysts for the conversion of MeOH/i-BuOH mixtures was continued. New catalysts tested were (i) 20 wt% phosphotungstic acid supported on ZrO_2 ($\text{PW}_{12}/\text{ZrO}_2$), (ii) niobic acid ($\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$), and (iii) an iron and manganese doped sulfate-modified zirconia ($\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$). The preparation and pretreatment of these new catalysts follows.

Preparation

Supported heteropolyacids are used as heterogeneous catalysts in several industrial applications. They are reported to possess strong acidic character, as well as unique selectivity characteristics in hydration/dehydration reactions. The use of zirconia-supported phosphotungstic acid, designated herein as $\text{PW}_{12}/\text{ZrO}_2$, for the standard reaction of a 1/1 molar MeOH/i-BuOH mixture was investigated.

Phosphotungstic acid with a formula of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, thus designated as PW_{12} , was obtained from Fisher Scientific, Co. This compound is also sometimes referred to by others as tungstophosphoric acid or 12-polytungstophosphoric acid. An aqueous solution consisting of 1.68 g of phosphotungstic acid in 5.5 ml of distilled water was prepared. The $\text{Zr}(\text{OH})_4$, 6.72 g, prepared from hydrolyzed $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, was impregnated with this solution, with constant mixing, to make a 20% loading of phosphotungstic acid by weight. The impregnated zirconium hydroxide, $\text{PW}_{12}/\text{Zr}(\text{OH})_4$, was placed in a 100°C oven overnight. The dried sample was then calcined to 300°C for 3 hr. This calcination temperature was chosen because it is below the decomposition range reported for heteropolyacids.

"Niobic acid", actually hydrated niobium oxide ($\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$), was calcined at 200°C for 2 hr. Literature indicates that high surface area and strong acidity are maintained only with low calcination temperatures such as this (1).

Recently, an iron and manganese doped sulfate-modified zirconia catalyst ($\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$) has been reported to possess stronger and more populous acid sites than $\text{ZrO}_2/\text{SO}_4^{2-}$ (2). This catalyst was also reported to be many times more active for the low temperature isomerization of butane.

The $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ catalyst was prepared according to the method described in Ref. 2. This involved first dissolving 73 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in *ca.* 100 ml of distilled water. About 700 ml of aqueous ammonia was added, and the solution was stirred for 2 hr. The Zr(OH)_4 formed was filtered and washed with distilled water until free of chloride ion. This solid was put in an oven at 100°C overnight to dry. The solution used to impregnate the Zr(OH)_4 consisted of 1.133 g $(\text{NH}_4)_2\text{SO}_4$, 2.234 g of $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.658 g of a 51 wt% solution of $\text{Mn(NO}_3)_2$. These salts were dissolved in distilled water to make 26.5 ml that was used to impregnate 25 g of Zr(OH)_4 . The impregnated catalyst was dried in a 110°C oven overnight followed by calcination at 620°C for 3 hr. The catalyst preparation was designed to give 1.5% Fe, 0.5% Mn, and 4.0% SO_4^{2-} by weight supported on ZrO_2 .

Results

The samples were diluted with Pyrex beads, charged to the reactor, and tested using the following reaction conditions:

Temperature	90, 125, 150, 175°C, (also 200 and 225°C)
Pressure	1 atm
Methanol feed	1.72 mol/kg catalyst/hr
Isobutanol feed	1.72 mol/kg catalyst/hr
He + N ₂ flow	16.0 mol/kg catalyst/hr
Catalyst weight	5.0 g

The catalytic results for these three samples, presented as the space time yields of the major products as a function of reaction temperature, are given in Figures 1-3.

The zirconia-supported heteropolyacid catalyst, $\text{PW}_{12}/\text{ZrO}_2$, exhibited low activity and very poor selectivity, shown in Figure 1, relative to other catalysts tested previously. The space time yield of isobutene was only $0.25 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$, but the yield of DME was $0.15 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$. This means that more methanol was converted to DME than the quantity of isobutanol that was converted to isobutene. Earlier, it had been found that pure ZrO_2 was totally inactive for these reactions. Therefore, the activity of the $\text{PW}_{12}/\text{ZrO}_2$ catalyst can be attributed to the presence of the phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$).

The niobic acid catalyst was essentially inactive below 175°C . However, when higher temperatures were used, most notably at 225°C , the activity and selectivity, shown in Figure 2, approached that seen for the best catalyst tested so far, $\text{ZrO}_2/\text{SO}_4^{2-}$. At 225°C , the niobic acid catalyst produced $1.0 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ of isobutene and only $0.13 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ of DME. In comparison, the $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst produced $1.1 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ of isobutene and only $0.10 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ of DME, and this selectivity with high isobutene yield was achieved at only 175°C (3).

The catalytic results for the $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst are similar at the higher reaction temperatures employed to those of the $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst. At 175°C , the Fe- and Mn-doped catalyst produced $0.91 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ of isobutene and $0.03 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ of DME, as shown in Figure 3. However, at lower temperature, the $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst was considerably less active than the $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst. For example, at 150°C the yield of isobutene was only $0.24 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ for $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ compared to $0.61 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{hr}^{-1}$ for $\text{ZrO}_2/\text{SO}_4^{2-}$.

FIGURE 1
PW₁₂/ZrO₂
MeOH/i-BuOH = 1/1

FIGURE 2
 $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$
 $\text{MeOH}/i\text{-BuOH} = 1/1$

FIGURE 3

Fe/Mn/ZrO₂/SO₄²⁻ calcined at 620°C
MeOH/i-BuOH = 1/1

B. The Effect of Water on Reaction of MeOH/i-BuOH Over $\text{ZrO}_2/\text{SO}_4^{2-}$

The major product of any conversion of the MeOH/i-BuOH mixture over solid acid catalysts is water. The presence of water can influence the type of acid sites present as well as may lead to a retarding effect on the reaction, as was reported for alumina earlier (4). In this experiment, reaction conditions were chosen where a 2/1 mixture of MeOH/i-BuOH was reacted over $\text{ZrO}_2/\text{SO}_4^{2-}$ at 157°C within the differential regime as described in the last quarterly report (5). Specifically, the conditions were:

Temperature	157°C
Pressure	1 atm
Water feed	0, 1.08, 2.16 mol/kg catalyst/hr
Methanol feed	43.3 mol/kg catalyst/hr
Isobutanol feed	21.6 mol/kg catalyst/hr
He + N ₂ flow	762 mol/kg catalyst/hr
Catalyst weight	0.4 g

The catalyst was first exposed to the 2/1 MeOH/i-BuOH mixture with no water, then to a 2/1/0.05 MeOH/i-BuOH/H₂O mixture, followed by a 2/1/0.1 mixture. The feed was again switched to the dry 2/1 mixture and then back to the 2/1/0.1 MeOH/i-BuOH/H₂O mixture. The results of this experiment are shown in Figure 4. It can be seen that the catalyst gradually and steadily deactivated with time on stream. However, the presence or absence of water in the feed did not affect the yield or selectivity of the products, mainly isobutene.

Another experiment with a fresh catalyst was carried out wherein it was first exposed to the water-containing reactant mixture and then to the dry alcohol reactant mixture. No difference in effect from the previous experiment was observed. These results differ from those observed earlier for alumina, where a strong inhibition, *ca.* 30%, in the production of DME, MIBE, and isobutene was noted (4). Those results were explained with the

FIGURE 4

$\text{ZrO}_2/\text{SO}_4^{2-}$ with and without H_2O in the reactants at 157°C and 1 atm

$\text{MeOH}/i\text{-BuOH}/\text{H}_2\text{O} = 2/1/x$ molar ratio

knowledge that alumina is known to possess strong acidity only in the form of Lewis acid sites that depend in number and strength on the degree of hydration of the surface. In the case of $\text{ZrO}_2/\text{SO}_4^{2-}$, however, Arata has shown (6) that Lewis acid sites can be converted to strong Brønsted acid sites upon exposure to low partial pressures of water, i.e. 5 torr. In the present investigation, in the "dry" runs where the only water present was that formed as a product of the reaction, the partial pressure of water was less than 1 torr. In the "wet" runs, the partial pressure of water was about 3 torr. Under high conversion conditions, the water produced during reaction can reach above 75 torr. We are currently investigating whether the state of this catalyst changes drastically in the presence of water during the course of different reaction conditions through direct spectroscopic means.

C. Surface Area Measurements

Surface areas have been determined for samples of $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ and niobic acid ($\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$), prepared as described in Section A of this report, as well as the 12-phosphotungstic acid on silica catalyst ($\text{PW}_{12}/\text{SiO}_2$) that was prepared and tested as described in the previous quarterly report (5).

Experimental

Samples were analyzed with a Gemini 2360 Analyzer instrument from Micromeritics. Surface area was determined at -196°C by using the BET multipoint technique. Points were chosen so that p/p_0 varied from 0.05 to 0.3. This yielded a linear BET-plot and accurate determination of the surface area. Samples were generally degassed at 300°C for 2 hr prior to exposure of N_2 at -196°C .

Results

Surface areas were determined for $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ samples dried at 100°C and after calcination at 620°C . The uncalcined sample of $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ was degassed at 120°C , whereas the calcined $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$, niobic acid, and phosphotungstic acid on silica ($\text{PW}_{12}/\text{SiO}_2$) catalysts were degassed at 300°C . The measured surface areas are given in Table 1. The surface area determined for calcined $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ is in good agreement with the reported value of $97 \text{ m}^2/\text{g}$ (2).

Table 1. Surface Areas

Catalyst	Surface Area (m^2/g)
$\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ dried to 100°C	219
$\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ calcined to 620°C	83
Niobic Acid	118
($\text{PW}_{12}/\text{SiO}_2$)	218

D. ^1H NMR to Resolve Whether 1-Butene is a Product

Our main technique to identify reactants and products is gas chromatography (GC). Isobutene is an abundant product when isobutanol is dehydrated over acid catalysts. As shown, other possible dehydration products are cis-2-butene, trans-2-butene and 1-butene. By using GC, with our present method of separation using a Cp-Sil-5 capillary WCOT column, isobutene can be separated from cis-2-butene and trans-2-butene but not from 1-butene. To resolve if and how much 1-butene is present as a product over the sulfated zirconia, ^1H NMR was utilized to further distinguish the C_4 products.

Experimental

Products from dehydration of isobutanol over sulfated zirconia were collected in a N_2 (*l*) cooled trap. The product stream was dried with molecular sieves prior to the trap to remove as much water as possible. As standards, individual samples of pure 1-butene, isobutene, cis-2-butene, and trans-2-butene were collected from their respective gas cylinders.

A 500 MHz Bruker AM500 NMR instrument was utilized for these analyses. The spectra were acquired from 0 to 8 ppm at approximately $-20^{\circ}C$. All samples were diluted approximately 1:4 with $CDCl_3$. The pure butene samples were used to calibrate peak positions.

Results

Isobutene has distinctive 1H NMR peaks at 4.65 and 1.7 ppm (Figure 5), whereas 1-butene has groups of peaks at approximately 5.9, 4.9, 2.1, and 1.0 ppm (Figure 6). The spectra of the pure butenes were compared to the spectrum of the dehydration products of isobutanol (Figure 7).

From the NMR spectra, it is concluded that 1-butene was indeed present in the product stream in a small amount. By integrating the NMR peaks at 5.9 and 4.65 ppm, the quantity of 1-butene could be determined. Neither cis-2-butene nor trans-2-butene have any peaks in this region. It was found that the product stream consist of $\leq 3\%$ 1-butene.

FIGURE 5
Spectrum of pure isobutene in CDCl_3

~~BRUKER~~

MARISTD1
DATE 21-12-92
TIME 9: 26

SOLVENT CCl_3
SF 500.135
SF0 500.130
SF02 500.130
SF2 500.135
SY 165.0
O1 7941.000
SI 32768
TD 32768
SW 6024.096
SM2 6024.096
HZ/PT .368
VD 0.0

PW 1.0
RD 0.0
AQ 2.720
RG 1
NS 15
TE 300

DE 105.3
DR 12
DW 83
FW 7500
O2 50000.000
DP 63L P0

LB 0.0
GB 0.0
NC 0
CX 20.00
CY 15.00
F1 7.500P
F2 .001P
MI .01
DC 1.000
HZ/CM 187.536
PPM/CM .375
IS 1
SA 5432.62

FIGURE 6

Spectrum of pure 1-butene in CDCl_3

HQ.DMSO
DATE 21-12-92
TIME 8:59

SOLVENT	CCl3
SF	500.135
SF0	500.130
SF02	500.130
SF2	500.135
SY	166.0
O1	7941.000
SI	32768
TD	32768
SW	6024.095
SW2	6024.095
HZ/PT	.368
VD	0.0
PW	1.0
RD	0.0
AQ	2.720
RG	1
NS	16
TE	300
DE	105.3
DR	12
DW	83
FW	7600
O2	50000.000
DP	63L P0
LB	0.0
GB	0.0
NC	-1
CX	20.00
CY	15.00
F1	7.500P
F2	.001P
MI	.01
DC	1.000
HZ/CM	187.536
PPM/CM	.375
IS	1
SR	5432.62

FIGURE 7

Spectrum of isobutanol
dehydration products

FID3 14-12-92
DATE 14-12-92
TIME 9:59
SOLVENT CDCl3
SF 500.135
SF0 500.130
SF02 500.130
SF2 500.135
SY 166.0
O1 7941.000
SI 32768
TD 32768
SM 6024.096
SW2 6024.096
HZ/PT .368
VD 0.0
PW 2.0
RD 0.0
AQ 2.720
RG 4
NS 228
TE 300
DE 106.3
DR 12
DM 83
FW 7600
O2 50000.000
OP 63L P0
LB 0.0
GB 0.0
NC 5
CX 20.00
CY 0.0
F1 8.000P
F2 .000P
MI .01
DC 1.000
HZ/CM 200.056
PPM/CM .400
IS 1
SR 5433.73

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