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HIGH OCTANE ETHERS FROM SYNTHESIS GAS-DERIVED ALCOHOLS

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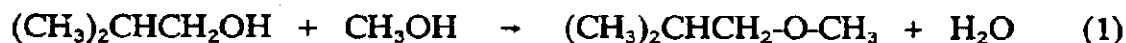
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OBJECTIVE OF THE RESEARCH

The principal objective of this research project is to synthesize fuel grade ethers, primarily high cetane methyl isobutyl ether (MIBE) and high octane methyl tertiary butyl ether (MTBE), as well as higher tertiary ethers, from H₂/CO/CO₂ coal-derived synthesis gas *via* alcohol mixtures that are rich in methanol and isobutanol (2-methyl-1-propanol). The overall scheme, as discussed at previous DOE-PETC review meetings [1,2], involves gasification of coal, purification and shifting of the synthesis gas, higher alcohol synthesis, and direct synthesis of ethers.

In the higher alcohol synthesis stage of the overall process, methanol and isobutanol are the predominant products formed from H₂/CO synthesis gas over alkali promoted Cu/ZnO-based catalysts [3-7]. The last stage of the synthesis involves direct coupling of synthesis gas-derived methanol and isobutanol that had been previously demonstrated by us [8,9] to occur over strongly acidic catalysts to yield MIBE (Equation 1) at moderate pressures and predominately 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 (Equation 2) and MIBE is minimized. This is being investigated in terms of the proper choice of reaction conditions, i.e. intermediate pressures, and acid catalysts (organic or inorganic) that are stable at temperatures under which it might be possible to promote the coupling of the two alcohols to MTBE more effectively than the reaction leading to MIBE.



The synthesis route to ethers containing the isobutyl group might also involve selective conversion of isobutanol to isobutene (Equation 3) with subsequent reaction with methanol to form MTBE. Although this route would entail the use of two catalysts, i.e. one selective for dehydration of isobutanol in the presence of methanol and another for the selective coupling of isobutene with methanol in the presence of water, such a selective process would also alleviate isobutene dependence on petroleum feedstocks. Thus, catalysts for the first step in such a process are also being investigated in this project.

Both organic and inorganic catalysts are being investigated, and the better catalysts of these classes will be subjected to complete scientific characterization and long term performance studies so that the catalysts can be further developed and optimized. 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, and
- 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 C₁-O-C₄ ether originate from coal-derived synthesis gas.

SUMMARY OF ACCOMPLISHMENTS AND CONCLUSIONS

Organic resins, including the Amberlyst-15, -35, -36, and -1010 resins and duPont Nafion-H fluorocarbon resin, have been tested in a continuous downflow stainless steel reactor for the synthesis of MIBE and MTBE from methanol and isobutanol, principally in the temperature range of 90-120°C and pressures of ambient to 1.5 MPa (220 psig). Nafion-H was an active catalyst that selectively produced MIBE and dimethylether (DME) at high pressure and isobutene at low pressures (≤ 0.1 MPa). The strongly acidic Amberlyst catalysts were more active catalysts but with lower selectivities, which could be partially controlled by reaction parameters. In general, the activity of the catalysts correlated with the content of strong acid sites and followed the trend of Amberlyst-35 > -36 > -15 > -1010 > Nafion-H. These catalysts are compared with other resins previously tested by us [1,2,10].

A wide range of strongly acid inorganic catalysts have also been tested for ether synthesis and dehydration of isobutanol. Higher reaction temperatures were found to be necessary. H-mordenite selectively produced DME from methanol/isobutanol = 1/1 mixtures at moderate temperatures, e.g. at 125°C where 80% of the methanol was converted 100% to DME, where the other inorganic catalysts that were investigated were nearly inactive. In contrast, the ZrO₂/SO₄²⁻ catalyst was hardly active at 125°C but quite actively and selectively dehydrated the isobutanol to isobutene from alcohol reactant mixtures at $\geq 150^\circ\text{C}$, e.g. at 175°C $\approx 95\%$ of the isobutanol was converted with 89% selectivity to butenes (principally isobutene), with little conversion of methanol to ethers. These two inorganic catalysts are much more selective than other oxides and zeolites previously studied [2,11].

Since the reaction pathways and products are kinetically controlled, kinetic and mechanistic studies are being carried out to provide for optimization of the ether and olefin synthesis from methanol and isobutanol. Reaction of CH₃¹³OH with ¹⁶O-containing isobutanol over the solid acid Nafion-H resin gave the two distinctly labelled C₅ ethers ¹⁶O-MIBE (a high cetane ether) and ¹⁸O-MTBE (a high octane ether). This indicates that MTBE is not derived from MIBE, the kinetically favored product, and that MTBE is formed *via* a different pathway that might involve intermediate isobutene. Modelling using computer graphics of the selective formation of DME over H-mordenite shows that the reaction is guided by a combination of selective poisoning of the large channel protons by isobutanol and a size exclusion of isobutanol in reactions catalyzed by protons located in the side pockets of the large channels.

TECHNICAL PROGRESS

1. ORGANIC RESIN CATALYSTS

During this program of research, a wide range of organic resins have been investigated for reactivity and selectivity in coupling methanol and isobutanol to form C₅ ethers. The results obtained with Amberlyst-15, Purolite C-150, and BioRad AG 50W X-2 sulfonated polystyrene ion exchange resins with divinylbenzene crosslinking and with the Nafion-H microsaddles fluorocarbon sulfonic acid (FSA) polymer were presented in the previous proceedings [2]. Using a standard test reaction with a methanol/isobutanol = 1/1 reactant mixture at ambient pressure and 90°C, the order of activity of the catalysts was determined to be Amberlyst-15 \approx Purolite C-150 > BioRad > Nafion-H. This series is not simply related to the concentration of acid groups in the resins because of other important differences, e.g. Purolite C-150 is a macroporous resin with 1.9 meq of acid groups/ml (calculated to be approximately 2.5 meq/g wet resin (as received) or about 5.5 meq/g dry resin), while the BioRad resin is a gel material with 5.2 meq H/g. Nafion-H is a fluorocarbon sulfonic acid resin with only 0.9 meq H/g of material. Amberlyst-15 is a macroreticular (macroporous) resin with an acid content of 4.7 meq H/g. Recently, additional Amberlyst resins, i.e. -35, -36, and -1010, have been obtained, and these contain strong acid groups with the appreciable acid concentrations of 5.2, 5.4, and 3.3 meq/g, respectively. Therefore, these resin catalysts have been tested and characterized.

A. Catalytic Testing of the New Amberlyst Catalysts

The new Amberlyst-35 and -36 catalysts (44 and 35 m²/g, respectively) are reported to be more acidic in terms of number of strong acid groups than Amberlyst-15, and the Amberlyst-1010 resin has a higher porosity (0.41 cm³/g) and surface area (\approx 540 m²/g) than the other three resins. Higher acidity is of great interest for alcohol coupling to ethers at low temperature. Rohm and Haas information indicates that the Amberlyst-1010 and Amberlyst-15 resins are stable to 120°C, while the Amberlyst-35 and -36 resins are more thermally stable and can be used to 140°C.

Experimental

The three catalysts were subjected to the standard test used previously for screening catalysts for ether synthesis in this laboratory. The carrier gas consisted of He containing a trace of N₂. The experimental conditions are as follows:

Catalyst weight	5.0 g dry resin
Temperature	90°C
Pressure	1 atm (0.1 MPa)
Methanol feed	1.72 mol/kg cat/hr
Isobutanol feed	1.72 mol/kg cat/hr
He + N ₂	16 mol/kg cat/hr

The temperature was also increased stepwise above 90°C to monitor the temperature dependence of the product formation.

The alcohol mixture was injected into the carrier gas stream at the top of the furnace preheater section of the stainless steel reactor, by means of a Gilson high pressure pump. Later experiments, in particular those with inorganic catalysts, used a ISCO high pressure piston pump provided by Air Products and Chemicals, Inc. Product analysis was achieved by utilizing an on-line GC system with in-line automated sampling valves. The dedicated Hewlett-Packard Model 5890 Series II gas chromatograph (HP GC) has two automated heated Valco sampling valves, both thermal conductivity (TCD) and flame ionization (FID) detectors, and both packed column and capillary column (a 25 m x 0.32 mm ID wall coated open tube (WCOT) capillary column with a chemically bound 5.0 μm thick methyl silicon coating) capabilities, and is interfaced and controlled by a PC data station using a complete package of menu-driven chromatographic software (Chrom Perfect) from Justice Innovations, Inc. At the same time, the GC is interfaced with a Hewlett-Packard Model 3396 Series II recorder/integrator, which can also produce a hardcopy of each chromatogram and listing of the associated integrated peak areas.

Results

In Tables 1-3, the conversion at 90°C and at some higher temperatures are reported. Amberlyst-1010 showed moderate conversion of both methanol and isobutanol. The Amberlyst-35 and -36 catalysts showed high and similar conversions at all of the reaction temperatures, but Amberlyst-35 tended to be somewhat more active than Amberlyst-36. No deactivation of the Amberlyst-35 catalyst was observed (Table 2). However, with reference to Table 3, some deactivation can be seen for Amberlyst-36, as evidenced upon lowering the reaction temperature back to 90°C after carrying out the process at higher reaction temperatures. In comparison with Amberlyst-35 and -36, Amberlyst-15 converted about 9% of methanol and 10% of isobutanol at 90°C [2]. Conversions of all polymer resins tested (at 90°C) during this project (see also, Reference 2) are listed in Table 4. The overall order of activity follows the sequence Amberlyst-35 > Amberlyst-36 > Amberlyst-15 ≈ Purolite C-150 > BioRad AG 50W X-2 ≈ Amberlyst-1010 > Nafion-H.

Table 1. Amberlyst-1010 Activity as a Function of Temperature

Temperature (°C)	% Methanol Conversion	% Isobutanol Conversion
90	5.0	4.2
100	8.3	8.9
110	14.4	21.3
120	23.6	42.2

Table 2. Amberlyst-35 Activity as a Function of Temperature

Temperature (°C)	% Methanol Conversion	% Isobutanol Conversion
90	16.4	15.8
100	32.1	43.9
110	42.9	63.9
120	62.0	57.1
130	70.0	57.9
90	17.0	15.7

Table 3. Amberlyst-36 Activity as a Function of Temperature

Temperature (°C)	% Methanol Conversion	% Isobutanol Conversion
90	12.3	10.2
100	25.9	30.0
110	42.0	63.1
120	56.7	53.1
130	63.4	57.9
90	10.7	6.8

Table 4. Activity of Polymeric Resin Catalysts at 90°C

Catalyst	% Methanol Conversion	% Isobutanol Conversion
Amberlyst-15	9.1	10.2
BioRad AG 50W X-2	4.9	5.4
Nafion-H	1.4	1.4
Purolite C-150	9.2	9.9
Amberlyst-1010	5.0	4.2
Amberlyst-35	16.4	15.8
Amberlyst-36	12.3	10.2

Under the reaction conditions employed in these tests, the catalysts were generally rather non-selective, especially at the lower temperatures. At higher temperatures (e.g. $\geq 120^{\circ}\text{C}$), one product was more dominant than the others. For example, Amberlyst-1010 formed MIBE (34 mol%), DME (28 mol%), and butenes (27 mol%--mainly isobutene) at 90°C , but butenes (56 mol%, with 22 mol% MIBE and 13 mol% DME) were favored at temperatures above 90°C . Smaller quantities of MTBE, DIBE, and DTBE were also formed at all temperatures, and the selectivity toward these tended to decrease as the temperature was increased. The butene product is given as the sum of isobutene and the linear *trans*-2-butene and *cis*-2-butene. The 2-butenes were minor products over the organic resins at the low reaction temperatures that were utilized, e.g. 88-91% of the total was isobutene except for Nafion-H where the linear butenes were generally not detectable.

The Amberlyst-35 and -36 resins showed a different selectivity pattern. In particular, the Amberlyst-35 resin mainly formed butenes at lower reaction temperatures, e.g. 46-48 mol% selectivity to butenes at $100\text{-}110^{\circ}\text{C}$, accompanied by 21 ± 1 mol% DME and 19 ± 2 mol% MIBE. However, at 120°C and above, DME became the predominant product formed, e.g. at 130°C the selectivities toward DME, butenes, and MIBE were 57, 26, and 4 mol%, respectively. All other products were very minor products at 120 and 130°C . Amberlyst-36 showed a selectivity pattern similar to that of Amberlyst-35 at all temperatures. With respect to %yields (fractional conversion times % selectivity) of the products, the Amberlyst-35 catalyst gave 29 %yield of butenes relative to isobutanol conversion at 110°C and 40 %yield of DME respect to conversion of the methanol reactant at 130°C . The corresponding %yields over the Amberlyst-36 resin, were 29 and 36 % yields, respectively.

B. Pressure Dependence Study of Amberlyst-35

The reaction of methanol and isobutanol over a Nafion-H catalyst has previously been shown to be very sensitive to the total pressure [9,10]. To investigate the pressure dependence of the synthesis reaction over Amberlyst-type catalysts, the active Amberlyst-35 resin was chosen. The pressure dependence study was carried out at the two reaction temperatures of 90 and 117°C .

Experimental

The experiment was carried out using the following conditions:

Catalyst weight	1.0 g dry catalyst
Temperature	90 and 117°C
Total pressure at 90°C	0-79 psig (0.65 MPa)
Total pressure at 117°C	0-180 psig (1.3 MPa)
Methanol feed	10.4 mol/kg cat/hr
Isobutanol feed	5.2 mol/kg cat/hr
He + N ₂	185 mol/kg cat/hr

This includes the standard temperature of 90°C and pressure of 0.1 MPa, but it is noted that the methanol/isobutanol reactant ratio = 2, which over the Nafion-H resin produced the optimum productivity toward MIBE while exhibiting a low selectivity toward DME [9,12].

Results

The results shown in Figures 1 and 2 demonstrate that the formation of butenes was very sensitive to the alcohol partial pressure. A small elevation of the alcohol pressure

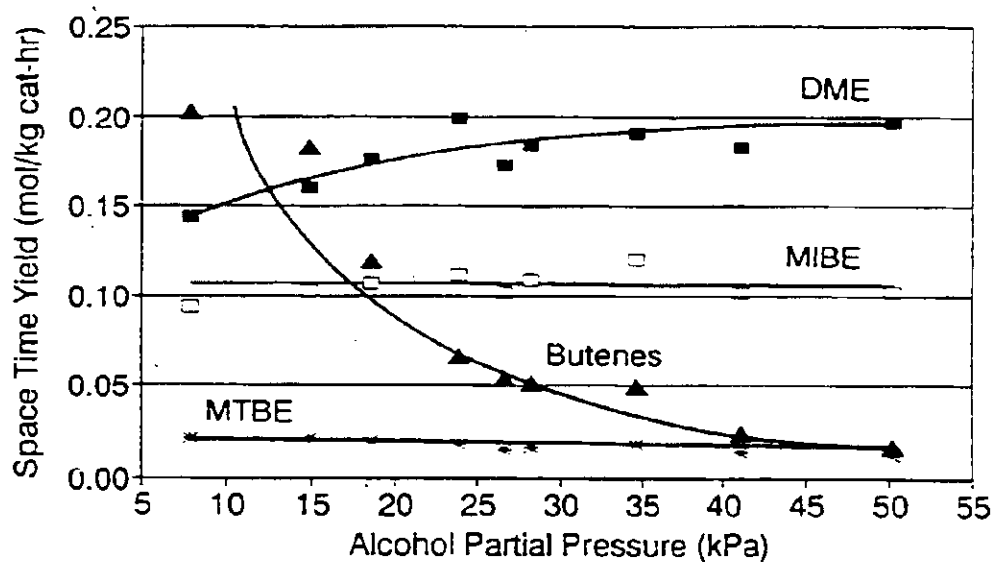


FIGURE 1. Space Time Yields of the Ethers and Butenes Formed Over Amberlyst-35 as a Function of the Alcohol Partial Pressure at 90°C.

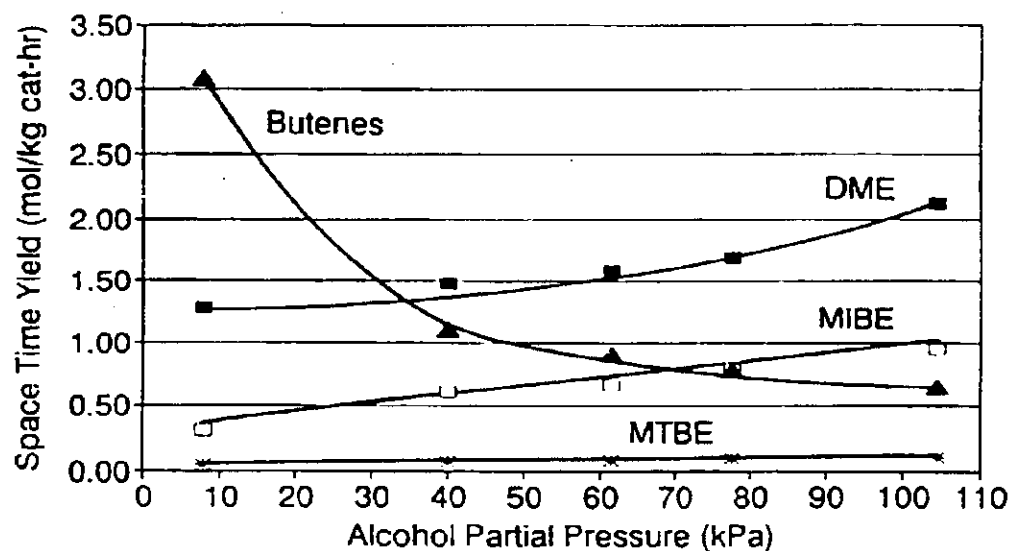


FIGURE 2. Space Time Yields of the Ethers and Butenes Formed Over Amberlyst-35 as a Function of the Alcohol Partial Pressure at 117°C.

increased. At the reaction temperature of 117°C, all of the ethers showed increasing productivities as the pressure of the reactants was increased (Figure 2). Therefore, the suppressed the formation of butenes rather drastically at both 90 and 117°C. The synthesis rates of DME, MIBE, and MTBE ethers were not significantly affected at 90°C, although there was a trend to increase the space time yield of DME as the alcohol pressure was formation and selectivity toward butenes can be suppressed by increasing the reaction pressure. This supports the dual site mechanism proposed by Nunan et al. [3,4], wherein adjacent active sites are needed for isobutanol dehydration, where one of the sites needs to be vacant. Loss of this vacant site by strong adsorption at elevated pressures would poison the reaction. These figures show that DME was the dominant product formed over the Amberlyst-35 resin under these reaction conditions and that temperature had a pronounced effect on the overall rate of formation of all of the ethers.

C. Isotope Labelling Study of Ether Synthesis Over Nafion-H

The two reactant alcohols, methanol and isobutanol, can be produced from H₂/CO synthesis gas (a non-petroleum feedstock) over base promoted Cu/ZnO catalysts [5,6,12]. Since MTBE is an oxygenated, high octane fuel additive and MIBE has a high cetane number of 53 [13], it is desirable to shift the selectivity of the alcohol coupling reaction to control MIBE or MTBE as required by fuel composition. It has been shown that in the reaction of methanol with isobutanol, MTBE is the thermodynamically favored oxygenated product but that MIBE is the kinetically favored product [1,9]. Therefore, an isotope labelling experiment was carried out to provide mechanistic insight into the manner in which methanol and isobutanol react together to form DME, MIBE, and MTBE ethers and to determine if MTBE were derived from MIBE.

Experimental

The methanol used in this experiment was purchased from MSD Isotopes and was 97.3 atom% ¹⁸O enriched. Anhydrous isobutanol was purchased from Aldrich Chemical Co., Inc., and it contained the natural abundances of oxygen isotopes, i.e. 99.8% ¹⁶O and 0.2% ¹⁸O. Nafion-H microsaddles was the catalyst employed in this study. The alcohols were mixed in a molar ratio of 1/1 and pumped into the preheater section of the reactor at the rate of 3.4 mol/kg catalyst/hr by means of a Gilson high pressure pump. The reaction took place in a gas phase tubular downflow reactor with on-line GC analysis. Conversions of methanol and isobutanol were kept below 10% to minimize any possible secondary reactions and to keep the reaction within the differential regime. Isotopic composition analysis was accomplished off-line *via* GC/MS analysis, following the trapping and condensation in a dry ice cooled cold-finger of the effluent from the reactor. The mass spectra were compared to those of reference compounds for identification of the catalytic products [14].

The experimental testing conditions that were utilized consisted of the following:

Catalyst weight	2.00 g (dry)
Reaction temperature	90°C

Total Pressure	1 atm (101 kPa)
Molar ratio MeOH:iBuOH	1/1
Methanol flow rate	1.7 mol/kg cat/hr
Isobutanol flow rate	1.7 mol/kg cat/hr
He + N ₂ flow rate	16.6 mol/kg cat/hr

Product Analysis

The molar abundances of each ¹⁶O- or ¹⁸O-containing product separated by GC were quantified *via* GC/MS analyses by comparing the most intense MS peak intensities to one another. It was observed that the most abundance fragment from both DME and MIBE was CH₃OCH₂ (with loss of the CH(CH₃)₂ part of the MIBE molecule, which was further fragmented), while from MTBE it was (CH₃)₃CO (with loss of the CH₃ group). Specifically, for MIBE analysis the peak at a mass-to-charge ratio (m/q) = 47 was normalized to the most intense peak at m/q = 45, corresponding to the CH₃-¹⁶O-CH₂ fragment [15], in order to calculate the fraction of ¹⁸O-containing MIBE relative to ¹⁶O-containing MIBE, respectively. Likewise for MTBE, the peaks at m/q = 75 and 73 [15], corresponding to the (CH₃)₃-C-¹⁸O and (CH₃)₃-C-¹⁶O fragments, respectively, were used, while the m/q = 47 peak intensity, corresponding to the CH₃-¹⁸O-CH₂ fragment, was compared to that of the m/q = 45 peak (CH₃-¹⁶O-CH₂) for DME quantification. Other less intense MS peaks were also analyzed for further verification of the analyses.

Results and Discussion

The space time yields of the products are given in Table 5, and it is seen that MIBE is the principal products, while similar but smaller quantities of DME and isobutene were also formed. Analyzable quantities of MTBE were also formed.

TABLE 5
Space Time Yields of Products Formed by the Reaction of ¹⁸O-Methanol and ¹⁶O-Isobutanol over Nafion-H at 90°C and 101 kPa.

<u>Product</u>	<u>Space-Time-Yields</u> <u>(mol (kg catalyst)⁻¹ hr⁻¹)</u>
MIBE	0.0140
DME	0.0045
Isobutene	0.0037
MTBE	0.0010
C ₈ -Ether	trace

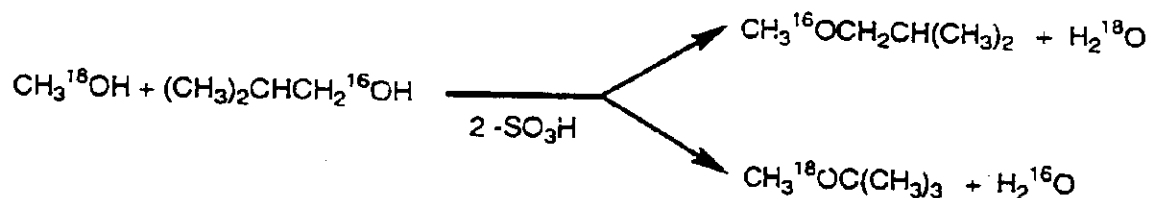
Isotopic composition of each of the oxygenates formed was determined by mass spectrometry as described. The results of these analyses are presented in Table 6. The oxygen-containing products ¹⁶O-MIBE and ¹⁸O-MTBE were found with over 90% selectivity.

The isotopic composition of DME of $\approx 92\%$ ^{18}O indicates that isotopic scrambling of methanol did not occur to a significant extent over the catalyst.

TABLE 6
Isotopic Composition (mol%) of Oxygen-Containing Products From the Reaction of ^{18}O -Methanol and ^{16}O -Isobutanol over Nafion-H at 90°C .

<u>Isotope</u>	<u>MIBE</u>	<u>MTBE</u>	<u>DME</u>
$\%^{18}\text{Oxygen}$	5.9	97.2	91.8
$\%^{16}\text{Oxygen}$	94.1	2.8	8.3

These results can be summarized as follows:

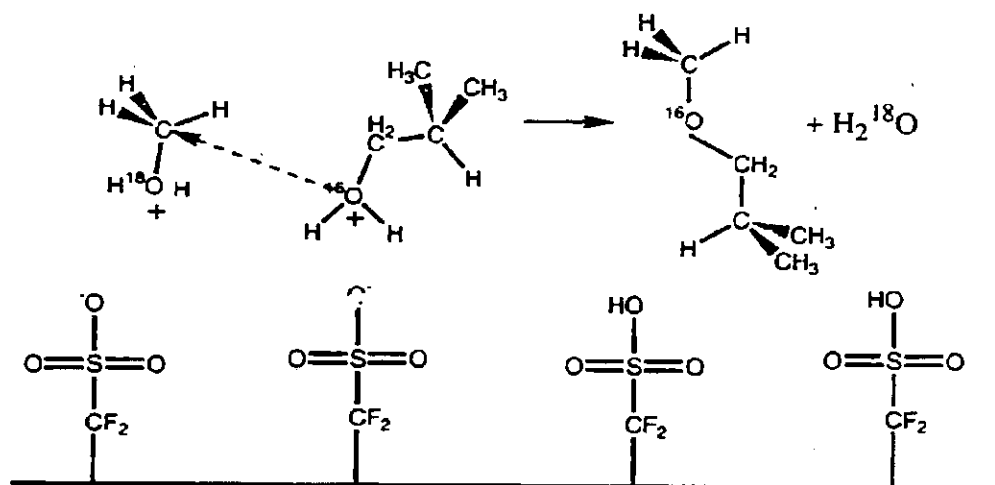


It is evident from these results that MIBE derived its oxygen from isobutanol, while MTBE obtained its oxygen from methanol. This result demonstrates that MIBE and MTBE are not formed from a common intermediate and that MTBE is not the product of isomerisation of MIBE. Moreover, MIBE is produced by a kinetically controlled pathway that is mechanistically more efficient than that leading to the thermodynamically more stable MTBE. These isotope discriminating reactions, taken in conjunction with those of the prior kinetic analyses [9], support a reaction scheme for MIBE that has mechanistic features of a $\text{S}_{\text{N}}2$ solution-phase reaction, but exhibits distinctly different kinetics unique to surface catalysed reactions in which both alcohols are activated by being adsorbed on the acid sites of the Nafion-H catalysts. This results in kinetics that show self-poisoning of the reaction by either alcohol at its high concentration, contrary to the kinetics of $\text{S}_{\text{N}}2$ reactions in solutions in which the rate is proportional to the concentrations of both reactants [15]. In fact, the surface-catalysed four-center reaction (involving two SO_3H surface groups and the two alcohols) exhibits a maximum rate at optimum concentrations of the reactant alcohols, which falls off when either alcohol is in excess as a negative power of the partial pressure of the excess reactant [9].

The specific mode of bonding of the alcohols to the sulfonic acid sites is not resolved in full detail but the current ^{18}O label flow rules out the formation of isobutyl ether or isobutyl carbenium ion put forward as a possibility earlier [9], as in this case isobutanol would lose its oxygen and MIBE would gain ^{18}O from methanol, contrary to experiment. A likely type of bonding is *via* oxonium of the alcohols, with methanol oxonium suffering a rear attack by isobutanol that is just leaving its bonded state on the neighboring sulfonic group by proton elimination; the ^{18}O -labelled H_2O is then the leaving group from methanol and the MIBE produced retains ^{16}O from isobutanol, as shown in Scheme 1. The reverse

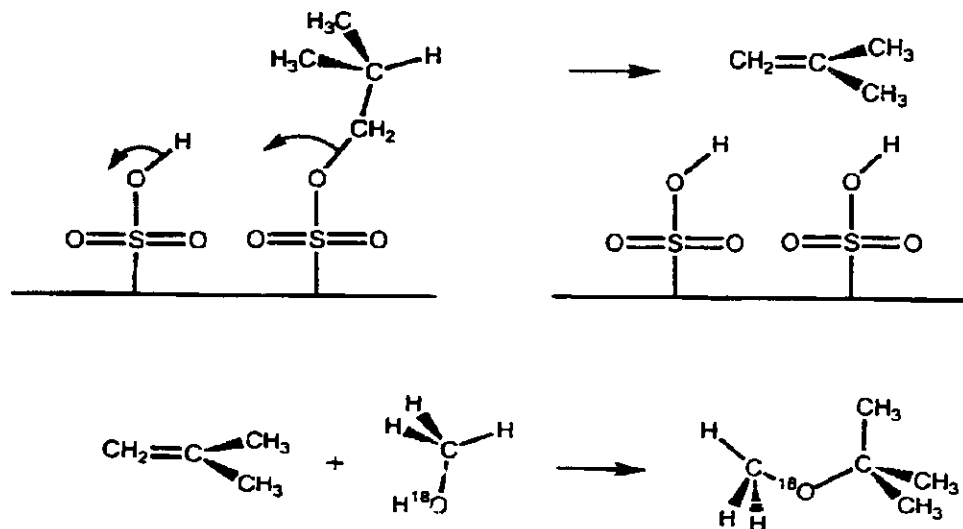
attack of isobutyl oxonium by methanol is sterically hindered, in analogy with steric hindrance of the attack of isobutyl group by ethoxide in the related S_N2 reactions of alkyl halides [15].

SCHEME 1. The Reaction Pathway for O^{18} -Methanol and O^{16} -Isobutanol to Form O^{16} -MIBE.



Contrary to MIBE, the MTBE contained exclusively oxygen originating from methanol and not isobutanol. Since isobutanol is dehydrated to isobutene by a parallel reaction, the origin of MTBE can be traced to a coupling of isobutene with methyl oxonium or isobutyl carbenium with methanol [16], as shown in Scheme 2. The former path is that thought to occur in the industrial acid-catalysed MTBE synthesis from methanol and isobutene [17].

SCHEME 2. The Mechanism for Isobutanol Dehydration to Form Isobutene, with Subsequent Reaction of O^{18} -Methanol to Form O^{18} -MTBE.



2. SULFATE-PROMOTED ZIRCONIA CATALYSTS

The initial testing of a strongly acidic sulfated zirconia catalyst exhibited rather high selectivity toward isobutene formation from the methanol/isobutanol reactant mixture, as reported in our previous report [2]. 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 $\text{ZrO}_2/\text{SO}_4^{2-}$, and this catalyst was also reported to be many times more active for the low temperature isomerization of butane [18]. Therefore, this catalyst was prepared and tested for the alcohol coupling reaction.

A. Preparation and Catalytic Testing of $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ Catalyst

The $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ catalyst was prepared according to the method described in Reference [18]. The preparation of the zirconia support basically followed that of Hino and Arata [19], except that first 73 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in *ca.* 100 ml of distilled water. About 700 ml of aqueous ammonia was added, and the solution was stirred for 2-4 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 ($\approx 120^\circ\text{C}$ was used for samples that were only surface doped with sulfate using 1 N sulfuric acid solution, which were washed with the H_2SO_4 solution at this point). 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 catalysts were dried in a 110-115°C oven overnight followed by calcination at 620°C for 3 hr. The catalyst preparation using the three dopants was designed to give 1.5% Fe, 0.5% Mn, and 4.0% SO_4^{2-} by weight supported on ZrO_2 .

Catalytic Testing 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 samples are presented in two forms. One presentation of the data is in the form of rate of formation of each of the products, with the units of mol of product/kg catal/hr. This is also referred to as the space time yield or the productivity. In this case, the % conversion and % selectivity of each reactant can be directly calculated if the space time yields of all significant products are plotted, as they are in this report.

The second representation of the experimental data is %yield of each of the products. This latter quantity is defined as (fractional conversion of one of the reactant x % product selectivity). Thus, for 50% conversion of isobutanol to isobutene with 75% selectivity, the %yield would be 37.5%. It can also be directly calculated from the rate of formation, i.e. %yield = (rate of formation of product/rate of reactant flow) x 100. For example, 0.645 mol isobutene/kg catal/hr under the present reaction conditions = 37.5 %yield. This last definition of %yield, as written, presumes that one mole of reactant forms one mole of product, e.g. isobutanol to isobutene (or MIBE). However, two moles of methanol can form one mole of dimethylether. In this case, it must be clear whether the %yield refers to comparisons of products containing the methyl group from methanol or molar conversions of methanol to products. As an example, the formation of 0.129 mol DME/kg catal/hr (20% conversion of methanol with 75% selectivity to DME) would correspond to a %yield of 15% because 0.258 mol of methanol/kg catal/hr would be converted to DME. If the basis were moles of products formed that contain one or more methyl groups derived from methanol, then the %yield of DME would be 7.5% ((0.129/1.72) x 100).

Results and Discussion

Sulfate-modified zirconia selectively dehydrated isobutanol from the methanol/isobutanol reactant mixture to form isobutene under the standard reaction conditions employed, but at a sequence of higher temperatures. This was a very active catalyst for isobutene formation at 175°C, as shown in Table 7. It was also selective since < 15 mol% of the butenes were linear butenes. It was found to be essential for the zirconia to be sulfated, since a test with unsulfated zirconia showed no activity over this temperature range.

TABLE 7. Space Time Yields of the Products (mol/kg cat/hr) Over the Sulfated Zirconia Catalysts from Methanol = Isobutanol = 1.72 mol/kg cat/hr Reactants at 1 atm as a Function of Temperature.

	T _{Reaction}	DME	Butenes	MIBE	MTBE	C8 Ether
ZrO ₂ /SO ₄ ²⁻	90°C	—	—	0.003	—	—
	125°C	0.006	0.067	0.020	0.003	0.008
	150°C	0.027	0.696	0.068	0.009	0.017
	175°C	0.103	1.290	0.049	0.007	—

The catalytic results for the Fe/Mn/ZrO₂/SO₄²⁻ catalyst were similar at the higher reaction temperatures employed to those of the ZrO₂/SO₄²⁻ catalyst. At 175°C, the Fe- and Mn-doped catalyst produced 0.91 mol*kg⁻¹*hr⁻¹ of *isobutene* and 0.03 mol*kg⁻¹*hr⁻¹ of DME, as shown in Figure 3. However, at lower temperature, the Fe/Mn/ZrO₂/SO₄²⁻ catalyst as prepared here was considerably less active than the ZrO₂/SO₄²⁻ catalyst. For example, at 150°C the yield of *isobutene* was only 0.24 mol*kg⁻¹*hr⁻¹ for Fe/Mn/ZrO₂/SO₄²⁻ compared to 0.61 mol*kg⁻¹*hr⁻¹ for ZrO₂/SO₄²⁻.

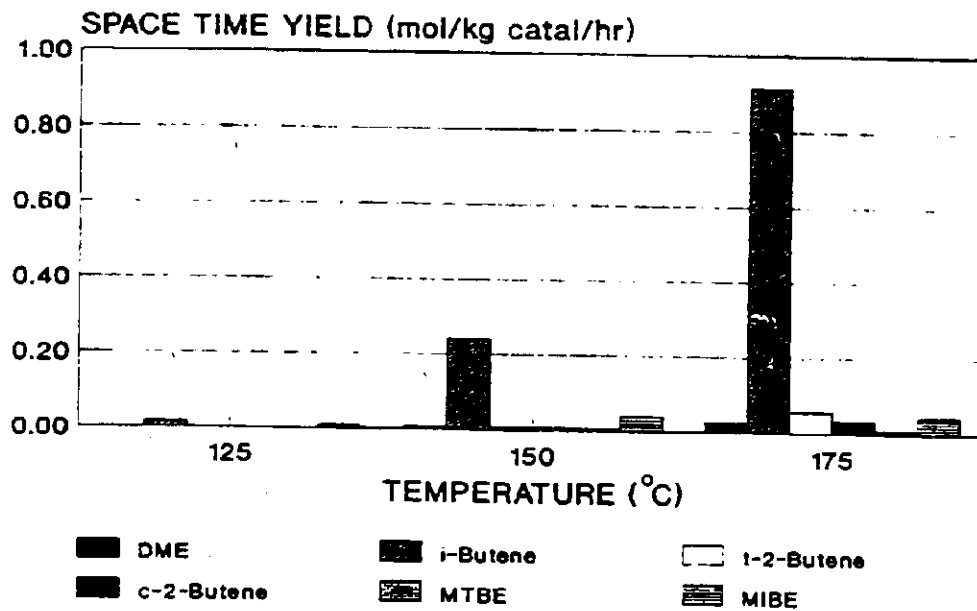


FIGURE 3. Productivity of the $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ Catalyst, Calcined at 620°C , with a Methanol/Isobutanol = 1/1 Reactant Mixture.

This $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ catalyst exhibited a greater selectivity in activating isobutanol relative to the conversion of methanol to products. The overall conversion levels for this sulfated catalyst at 175°C were 61.3% isobutanol to products and 6.2% methanol to products. The %yields for this catalyst are shown in Figure 4. Figures 3 and 4 demonstrate that this catalyst was quite selective for the dehydration of isobutanol to isobutene, specifically 86.6 mol% of the C_4 -containing products was isobutene and 84.4 mol% of all significant products, not including water, was isobutene.

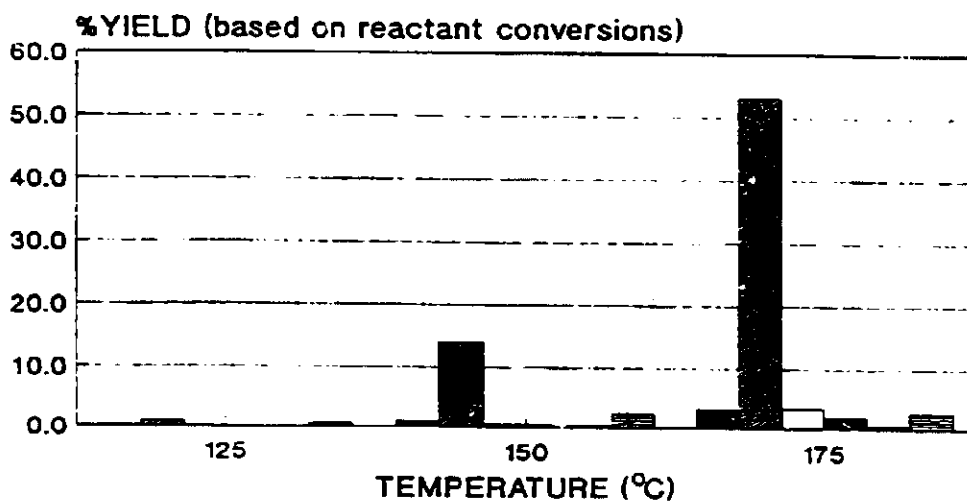


FIGURE 4. %Yield of the Products Formed Over the $\text{Fe/Mn/ZrO}_2/\text{SO}_4^{2-}$ Catalyst with a Methanol/Isobutanol = 1/1 Reactant Mixture. The Product Designation is Given in the Caption to Figure 3.

The Fe/Mn/ZrO₂/SO₄²⁻ catalyst had been tested after calcination to 620°C. Recent literature indicates that a higher calcination temperature might be beneficial for strong acid catalyzed reactions such as isomerization [7,8]. Thus, a portion of the impregnated catalyst (prepared by simultaneous aqueous impregnation of Zr(OH)₄ with SO₄²⁻, Mn²⁺, and Fe³⁺ to give 1.5% Fe, 0.5% Mn, and 4.0% SO₄²⁻ by weight supported on ZrO₂) that had been dried in a 110°C oven overnight was calcined at 720°C for 3 hr and then tested as described above.

The catalytic results for the 720°C calcined catalyst were very similar, but slightly less in terms of space time yields and %yields, as compared with the 620°C calcined catalyst. Again, it is evident that the predominant product was isobutene and that little of the methanol reactant was converted to products. At 175°C, 55.9% of the isobutanol was converted to products, with a selectivity toward isobutene of 88%. In comparison, only 5.0% of the methanol was converted to products at this temperature. Therefore, the temperature of calcination in the range utilized in these studies did not produce a significant effect on the observed activity and selectivity of the catalyst.

B. Dehydration of Alcohols to Olefins Over the ZrO₂/SO₄²⁻ Catalyst

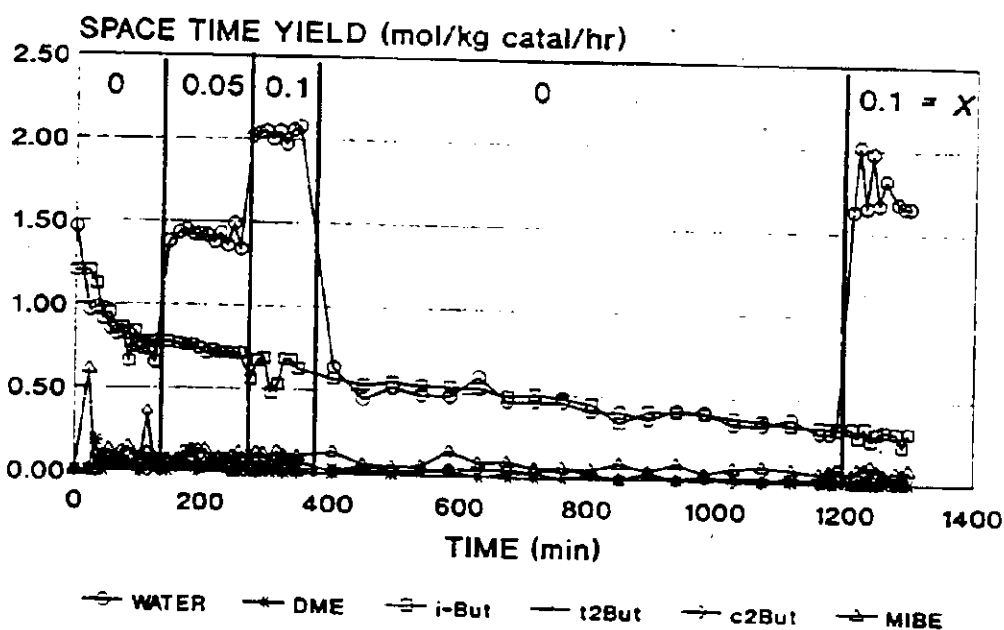
In order to compare the ability of the 1% SO₄²⁻/ZrO₂ catalyst to dehydrate linear alcohols with the dehydration of isobutanol to isobutene, a series of alcohols were individually passed over the catalyst under the usual standard reaction conditions that include an alcohol feed rate of 1.72 mol/kg catal/hr. In this series of experiments carried out at 157°C, the extent of dehydration of isobutanol to isobutene was 10.0 mol%, while those of the linear primary C₂-C₄ alcohols, ethanol, n-propanol, and n-butanol, were 3.8, 2.5, and 4.2 mol%, respectively. It is evident that the highest activity was shown by the isobutanol reactant and that an appreciably greater quantity of isobutanol was converted to isobutene than observed for n-butanol to 1-butene. These results indicate that with a mixture of alcohols over this catalyst, the predominant initial reaction will be dehydration of isobutanol to isobutene, which then could subsequently couple with the other alcohols in the reactant mixture.

C. The Effect of Water on Reaction of MeOH/i-BuOH Over ZrO₂/SO₄²⁻

A major product of any conversion of the methanol/isobutanol mixture over solid acid catalysts is water. The presence of water can influence the type of acid sites present, e.g. it can often convert Lewis acid sites into Brønsted acid sites. In addition, water may also lead to a retarding effect on the reaction, as was reported for alumina earlier [2]. This latter effect may arise by competitive adsorption of water and partial blockage of active sites. In this experiment, reaction conditions were chosen where a 2/1 mixture of MeOH/i-BuOH was reacted over the SO₄²⁻/ZrO₂ catalyst at 157°C and 1 atm within the differential regime. 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 dry 2/1 MeOH/i-BuOH mixture, then to a MeOH/i-BuOH/H₂O = 2/1/0.05 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 5. The high gas hourly space velocity (GHSV) of the carrier gas ensured low conversion levels of the reactants, e.g. at 100 hr on stream the conversion of isobutanol to products was about 4 mol% (≈ 3.7 %yield of isobutene). It can be seen from Figure 5 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, which consisted mainly of isobutene.



MeOH/i-BuOH/H₂O = 2/1/x molar ratio

FIGURE 5. The Space Time Yield Observed With the Sulfated Zirconia Catalyst at 157°C and 1 atm in the Absence and Presence of Injected Water.

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 [2]. Those results were explained with the 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 [20] 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 rather high levels. For example, over the $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst at 175°C (Figure 3), the water partial pressure generated by isobutanol dehydration corresponded to ≈ 42 torr, under non-differential reaction conditions. This approached the initial partial pressures of isobutanol and methanol reactants, which was ≈ 67 torr. Thus, perhaps additional experiments need to be carried out under differential reaction conditions, but where appreciably higher water injection rates are utilized to maintain higher levels of water partial pressures over the catalyst. 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.

D. Surface Area Measurements of Zirconia-Based Catalysts

Surface areas were determined with a Gemini 2360 Analyzer instrument from Micromeritics. The surface areas were measured 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 $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ samples dried at 100°C and after calcination at 620°C . The uncalcined sample of $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ was degassed at 120°C , whereas the calcined $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ was degassed at 300°C . The measured surface areas for the dried and the calcined samples were 219 and $83 \text{ m}^2/\text{g}$, respectively. The surface area determined for calcined $\text{Fe}/\text{Mn}/\text{ZrO}_2/\text{SO}_4^{2-}$ is in good agreement with the reported value of $97 \text{ m}^2/\text{g}$ [18].

The influence, if any, of the calcination temperature on the surface area of the synthesized singly doped $\text{SO}_4^{2-}/\text{ZrO}_2$ catalysts was also investigated. Samples calcined to 620°C were previously shown to be very active catalysts for isobutene synthesis from methanol/isobutanol mixtures [7], as well as from isobutanol alone [8]. The surface area of the sulfate-modified zirconia decreased as the calcination temperature increased, as shown in Table 8. The reduction in surface area can be attributed to sintering of the catalyst by agglomeration of small particles to form larger particles. The effect of surface area on the catalytic properties of these catalysts, as well as stability of the catalysts under reaction conditions, has not yet been investigated.

TABLE 8. Surface Area of the Sulfated Zirconia vs Calcination Temperature

Calcination Temp. (°C)	BET Single Point (m ² /g)	BET Multipoint (m ² /g)
350	225	232
455	200	205
551	146	150
620	105	108
720	36	37

E. 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 C₄ products.

Experimental

Products from dehydration of isobutanol over sulfated zirconia were collected in a N₂ (*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°C. All samples were diluted approximately 1:4 with CDCl₃. The pure butene samples were used to calibrate peak positions.

Results

Isobutene has distinctive ¹H NMR peaks at 4.65 and 1.7 ppm, whereas 1-butene has groups of peaks at approximately 5.9, 4.9, 2.1, and 1.0 ppm. The spectra of the pure butenes were compared to the spectrum of the dehydration products of isobutanol. 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 ≤3% 1-butene.

3. DME AND OLEFIN SYNTHESIS OVER ZEOLITE CATALYSTS

Alcohol coupling and dehydration reactions over six inorganic catalysts listed in our previous report [2] were considered further. The inorganic solid acid catalysts were less active than their organic counterparts at 90°C, but they exhibited appreciable activity at higher temperatures, i.e. 150-175°C. Of special interest was the contrasting behavior of H-mordenite with the H-ZSM-5 zeolite. The H-mordenite showed very high selectivity toward DME at 125 and 150°C, while the H-ZSM-5 zeolite was nearly 60% selective to MIBE at 125°C but over 75% selective toward butenes at 175°C. The H-mordenite used in this study was Norton Zeolon-900 and had a surface area of 350 m²/g as determined by us. The ZSM-5 zeolite was obtained from Mobil Research and Development Co. (Mobil MZ-289). Both the H-mordenite and the H-ZSM-5 zeolite were dried at 400°C before testing.

H-Mordenite exhibited quite different catalytic behavior as compared with all of the other the other inorganic catalysts tested, as partially shown in Table 8. In particular, it was able to selectively dehydrate methanol to form DME in the presence of isobutanol at temperatures above 90°C. Indeed, H-mordenite was the only inorganic catalyst to show significant activity at 90°C, reaching ≈10% conversion of methanol. Increasing the temperature to 125°C resulted in a large increase in methanol conversion over H-mordenite and only a minor change for the other inorganic catalysts. Further increase in temperature yielded ≈90% conversion of methanol over H-mordenite, while the other catalysts still exhibited below 20% methanol conversion. Of special interest with the H-mordenite catalyst was the product selectivity pattern that demonstrated that methanol was selectively dehydrated to dimethylether (DME) at both 90 and 125°C. Only minor dehydration of isobutanol was seen at 150°C with nearly total conversion of methanol. Reaction studies with only isobutanol (no methanol present) over H-mordenite showed low yields of butenes at 90 and 125°C, while at higher temperatures of 150, 175, and 185°C the production of butenes was significantly increased. This showed that higher temperature was needed to promote the activation of the dehydration of isobutanol over H-mordenite.

The space time yields (STY) of the major products obtained over the inorganic catalysts as a function of reaction temperature, shown in Table 9, were obtained under steady state reaction conditions. The flow rates utilized for this comparison were those employed with the organic resin catalysts. Therefore, no attempt to increase and to optimize the reactant flow rate or the space time yields was carried out. Since ≈100% conversion of the methanol occurred over the H-mordenite catalyst at 150°C to form DME, it is clear that the space time yield of DME could be greatly increased by altering the reaction conditions. The entry "Butenes" in Table 9 includes iso-, *trans*-2-, and *cis*-2-butene with isobutene predominating (always greater than 65% of the butene content). When compared with the organic resin catalysts discussed previously, it is noted that higher temperatures were required with these inorganic catalysts, and higher yields of linear butenes were produced that approached their thermodynamic equilibrium values.

Comparison of the H-mordenite catalyst with the **H-ZSM-5 zeolite** is of special interest. The latter catalyst was active in the formation of MIBE, butenes, and dimethylether (DME) from methanol and isobutanol. At 125°C, the major product was

MIBE, whereas at higher temperatures the butenes predominated. The main butene product was isobutene, but approximately one-third of the butenes were linear.

TABLE 9. Space Time Yields of the Products (mol/kg cat/hr) Formed Over H-Mordenite, H-ZSM-5 Zeolite, and Other Inorganic Catalysts from Methanol = Isobutanol = 1.72 mol/kg cat/hr Reactants in He/N₂ Carrier Gas at 1 atm as a Function of Temperature.

	T _{Reaction}	DME	Butenes	MIBE	MTBE	C8 Ether
H-Mordenite	90°C	0.060	—	—	—	—
	125°C	0.660	—	—	—	—
	150°C	0.830	0.068	—	—	0.004
H-ZSM-5	90°C	0.005	0.001	0.012	—	—
	125°C	0.071	0.169	0.350	0.004	0.003
	150°C	0.261	0.339	0.134	0.003	0.003
	175°C	0.185	1.086	0.131	0.005	0.002
Silica-Alumina	90°C	—	—	—	—	—
	125°C	0.007	0.028	0.011	0.001	0.003
	150°C	0.021	0.225	0.032	0.005	0.014
	175°C	0.039	0.943	0.049	0.007	0.016
Montmorillonite	90°C	—	—	—	—	—
	125°C	0.008	0.008	0.008	—	0.004
	150°C	0.019	0.071	0.019	0.004	0.014
	175°C	0.034	0.378	0.029	0.014	0.031
γ-Alumina	90°C	—	—	—	—	—
	125°C	0.006	—	0.007	—	—
	150°C	0.035	—	0.038	—	—
	175°C	0.118	0.002	0.160	—	—
	200°C	0.253	0.023	0.450	—	—
	225°C	0.342	0.242	0.831	—	—
	250°C	0.470	1.073	0.493	—	—

H-ZSM-5 is a medium pore zeolite with interconnecting channels of the dimensions 5.3 × 5.6 Å and 5.1 × 5.5 Å. H-Mordenite is also a porous zeolite and has elliptical 7.0 × 6.5 Å channels (12-rings with openings crystallographical running in the c-direction). However, mordenite also has a system of small channels running perpendicular to the large channels (and running in the b-direction). These small channels are sometime said to consist of 3.7 × 4.8 Å channels because they have entrances of 8-ring openings (windows) of these dimensions. However, because of the mordenite structure, about 8 Å into the small pore there is a zig-zag Y-branching of the pore structure due to twisted 8-rings. This results in a distorted window to each side of the Y-branching of some 2.6 × 5.7 Å. This is a

considerable restriction in the free diameter of the small channel pores through which reactant molecules can move, i.e. be transported to reactive sites in the small pores with subsequent diffusion of product molecules out of the small pores and the zeolite. The net result is that the mordenite structure is more realistically viewed as large channels having two rows of side *pockets*.

The main channels in both zeolites are accessible to the isobutanol reactant, which has a van der Waals diameter along the line joining the two methyl groups of 4.9 Å. The smaller channel system of ZSM-5 zeolite is also accessible to isobutanol, but this molecule is excluded from the smaller channel system of mordenite. Methanol, with a van der Waals diameter of 3.8 Å for the methyl group, has access to all channels to which isobutanol is accessible, as well as to the side pockets of mordenite.

Of pertinent interest here is the distribution of the active, strongly acidic proton in the mordenite. Using crystallography as a guide, it was found that the alkali ions (8 cations/unit cell) in dehydrated Na-mordenite [21] and Cs-mordenite [22] were the following: 1.5-2 in the large channels (designated as Type I), 2-3 in the 8-ring window openings to the small channel system (designated as Type II), and 3-4 inside the small channels (designated as Type III). A ^{133}Cs NMR investigation located the Cs^+ ions at locations that were consistent with this crystallography [23]. It is reasonable to assume that the proton distribution in dry H-mordenite will be similar except for a shift of the protons to proximal oxygens to form OH species. The small channel protons can be located in pockets off of the side of the channels. As pointed out, these pockets consist of an entrance 8-ring, a second parallel 8-ring at the distance of 3.5 Å from the first, and two fused oxygen 8-rings that form the bottom of the pocket. The pocket is 3.7 x 4.8 Å wide and ≈ 8 Å deep, and two offset antiparallel pocket systems are wedged into each other, resulting in the ≈ 2.6 Å constriction, to form the backbone structure surrounding the large channels. The cations located deepest in the pocket are symmetrically placed on the two sides of the bottom center oxygen of the pocket and are shared by pockets meeting at their bottoms from opposite sides. The pocket shape in mordenite resembles that of a chalice, or cup, from which the name of organic calixarenes of similar shape is derived. As the mordenite structure is made of channels surrounded by the fused cups, it could perhaps be appropriate to characterize this structure as inorganic crystalline polycalixarene.

The observed reaction selectivity whereby no isobutanol reacts in H-mordenite below 150°C, as shown in Table 9, indicates that the Type I acid sites located in the large channels are rendered unreactive. It is proposed that this poisoning occurs by the formation of a very strong complex between the Type I protons and isobutanol or its decomposition products. If these strong acid protons react with isobutanol to produce irreversibly bonded esters or carbenium ions or oligomeric species, they will be inaccessible for further steady state reactions with both alcohols, and only the protons located in the side pockets, which are accessible only to methanol, will be able to function as active catalytic centers. No coke formation was observed at the reaction temperatures employed. It appears that at 150°C, the Type I acid sites begin to be regenerated, as indicated by the appearance of isobutene and C_8 ether.

The high selectivity of H-mordenite to DME at low temperatures appears to be due to a combination of selective poisoning of the large channel Type I protons by isobutanol and a size exclusion of isobutanol in reactions catalyzed by the Type III protons located in the side pockets. The role of Type II protons depends on their location. Functionally, they will act as Type I if located in the large channels and as Type III if placed inside the small channel pockets. Computer graphics have been used to model

- a. the entrance of methanol and isobutanol into the large channels and of methanol into the small channels and pockets,
- b. formation of oxonium $\text{CH}_3\text{OH}_2^{\oplus}$ by reaction of methanol with the strongly acidic Type III protons,
- c. $\text{S}_{\text{N}}2$ attack on this oxonium by a second methanol molecule to form DME, and
- d. the exiting of the DME from the small channels.

These 3-dimensional molecular modelling experiments will be presented elsewhere with additional details of reactant mobilities and configurational limitations.

The self-poisoning of Type I acid sites for isobutanol reactions at temperatures below 150°C occurs even in the absence of methanol as demonstrated here. At temperatures above 150°C , the reaction products that are formed from isobutanol in the presence and absence of methanol are the same except for DME and MIBE that contain methyl groups originating from methanol. The conversion rates of isobutanol are slightly higher in the absence of methanol as compared with methanol present, but the difference is small enough to permit the conclusion that the poisoning of Type I acid sites in the large channels is due to isobutanol only and not to preferential adsorption or reactions of methanol. This is consistent with the greater basicity of isobutanol as compared with methanol that competes with it for acid sites [8,9].

Conclusions For the Zeolite Catalysts

The H-mordenite and H-ZSM-5 zeolites show distinctly different selectivity patterns from one another, and these two catalysts are much more selective than the other aluminosilicates and the γ -alumina that were tested for alcohol coupling and dehydration reactions. In particular, it has been shown that:

- (1) H-mordenite is a selective catalyst for dehydration of methanol to *dimethylether* (DME). Isobutanol is not converted to any ethers or dehydrated significantly to isobutene over H-mordenite under the conditions used. Molecular modelling with computer graphics has shown that the synthesis reaction is guided by a combination of selective poisoning of the large channel protons by isobutanol and a size exclusion of isobutanol in reactions catalyzed by protons located in the side pockets, comprising the small channel network, of the large channels.

- (2) H-ZSM-5 zeolite is active and fairly selective for the dehydration of isobutanol to butenes at high temperatures, e.g. 175°C, but it produces MIBE as the dominant product at low temperatures. However, the $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst is more active and selective for *isobutene* synthesis than is the H-ZSM-5 zeolite.
- (3) The inorganic catalysts are generally less active than the organic polymeric catalysts at 90°C, especially when compared with the Amberlyst-36 and -36 resins. However, the H-mordenite catalyst, which dehydrates methanol to DME, is more active and selective at 90°C for converting methanol to products than is the Nafion-H resin, which is selective for synthesizing *methyl isobutyl ether* (MIBE).
- (4) The product to be synthesized from a mixture of methanol and isobutanol can be control by the choice of catalyst. Reaction engineering is still being carried out to shift the product selective to *methyl tertiary butyl ether* (MTBE).

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