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HIGH OCTANE ETHERS FROM SYNTHESIS GAS-DERIVED ALCOHOLS

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HIGH OCTANE ETHERS FROM SYNTHESIS GAS-DERIVED ALCOHOLS

OBJECTIVES OF THE RESEARCH

The objective of the proposed research is to synthesize oxygenated fuel ethers, primarily methyl isobutyl ether (MIBE) and methyl tertiary butyl ether (MTBE), directly from coal-derived $H_2/CO/CO_2$ 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 methanol and isobutanol that has been demonstrated by us to occur over superacid catalysts to yield as dominant products 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 temperatures, and strong acid catalyst, e.g. an inorganic acid catalyst that is 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.

SUMMARY OF TECHNICAL PROGRESS

Three new Amberlyst solid acid resin catalysts, designated as Amberlyst-35, -36, and -1010, were obtained from Rohm and Haas. These resins were characterized in terms of accessible ion exchangeable acidities, swellabilities in water and in methanol, and surface areas. In comparison to the similar Amberlyst-35 and -36 resins, the 1010 resin had a very high surface area, low swellability, and low concentration of acid sites (≈ 3.3 meq/g).

The catalytic activities and selectivities were determined for the resin catalysts for converting a methanol/isobutanol = 1/1 reactant mixture to products. The overall activity pattern of the resins is Amberlyst-35 > Amberlyst-36 > Amberlyst-15 $\approx$ Purolite C-150 > BioRad AG 50W X-2 $\approx$ Amberlyst-1010 > Nafion-H. Amberlyst-1010 tended to form MIBE at lower temperatures and butenes > 90°C. Amberlyst-35 and -36 tended to form butenes at lower temperatures and DME at $\geq 120^\circ\text{C}$. The effect of reaction pressure on the catalysis over the amberlyst-35 catalyst was investigated at 90 and 117°C. It was observed that increasing pressure strongly decreased the space time yield and selectivity of the butenes, principally isobutene, while tending to increase the space time yield of the ethers.

The reactions of methanol/isobutanol to form ethers over the selective Nafion-H catalyst were probed by using a $\text{CH}_3^{18}\text{OH}/(\text{CH}_3)_2\text{CHCH}_2^{16}\text{OH}$ reactant. It was observed that DME consisted of $\text{CH}_3\text{-}^{18}\text{O-CH}_3$ as expected. Surprisingly, it was found that MIBE contained ^{16}O from the isobutanol, while MTBE contained ^{18}O from the methanol. These results indicate that MTBE is not formed from MIBE, i.e. no common precursor.

A study of the effect of calcination temperature on the surface area of the sulfated zirconia catalyst showed that the initial surface area can be doubled by using a lower temperature than the standard 620°C employed to-date, which might yield higher activities.

TECHNICAL PROGRESS

A. Characterization of New Amberlyst Catalysts

Three new Amberlyst solid acid resin catalysts, designated as Amberlyst-35, -36, and -1010, were obtained from Rohm and Haas. The new Amberlyst catalysts have polymeric structures that are similar to that of the Amberlyst-15 resin that was extensively studied earlier in this project. The main differences in these new catalysts compared to Amberlyst-15 are that the Amberlyst-35 and -36 resins are more thermally stable and have higher acidity, while the Amberlyst-1010 has a much higher surface area, smaller average pore size, and lower concentration of acid sites. The new catalysts were characterized by means of surface area, swelling properties, and concentration of acid sites.

Experimental: Surface Area

Surface areas were measured using a Micromeritics Gemini 2360 Surface Area Analyzer with nitrogen gas as the adsorbate at -196°C . The Amberlyst catalysts were dried at 90°C overnight under nitrogen atmosphere prior to the surface area measurements. Results were obtained as BET multipoint and Langmuir surface areas.

Results: Surface Area

Table 1 shows the results for the three Amberlyst samples. It can be seen that the Langmuir surface area results corresponded well with the values given by the manufacturer. The reason for the apparent low values determined by the BET method is not yet known. It was not specified by the manufacturer what type of surface area model was used or what adsorbate used. The surface area of the Amberlyst-15 resin used for comparison was approximately $45 \text{ m}^2/\text{g}$.

Table 1. Surface Areas of the Amberlyst Resins

Amberlyst	Manufacturer's Surface Area (m²/g)	Experimental BET Multipoint Surface Area (m²/g)	Experimental Langmuir Surface Area (m²/g)
1010	540	350	570
35	44	32	50
36	35	19	31

Experimental: Swelling Properties

To measure the swelling properties of the Amberlyst samples, approximately 1.5 g of each catalyst was mixed with 4.0 ml of solvent in a graduated cylinder. The percent swelling was measured in both methanol and water. The dry volume of the resin was taken immediately following the addition of the catalyst to the solvent. After an equilibration time of 5-10 minutes, the volume of the resin was recorded once again. This final volume was the volume after swelling. The % swelling was then calculated by taking the difference of the two volumes.

Amberlyst-35 and -36 were obtained from the manufacturer in a wet form, and they were dried overnight at 90°C to remove water before the swelling experiments were carried out. Amberlyst-1010, according to the manufacturer's data, contained less than 2% water and was not dried further.

Results: Swelling Properties

Table 2 shows the results obtained from the swelling experiments. All three catalysts swelled more in water than in methanol. Amberlyst-35 and -36 were very similar in their swelling properties, but Amberlyst-1010 swelled significantly less. One possible reason for

Amberlyst-1010 not swelling as much is that this resin has appreciably smaller average diameter of its internal pores ($\approx 50 \text{ \AA}$) than the Amberlyst-35 and -36 resins. This indicates more cross-linking and a more rigid polymer network.

Table 2: % Swelling of Amberlyst Resins in Water and Methanol

Amberlyst	% Swelling in water	% Swelling in methanol
1010	25	22
35	58	50
36	52	42

Experimental: Concentration of Acid Sites

The ion exchange capacities provided by the manufacturer were verified by titration of the Amberlyst samples in water with 0.498 M sodium hydroxide. Amberlyst-35 and -36 resins were dried at 90°C in air overnight prior to titration, while the Amberlyst-1010 was used as received. The pH was continuously monitored throughout the titration with a pH meter, providing an acid-base titration curve, where the inflection point gave the end point.

Results: Concentration of Acid Sites

Table 3 includes both the manufacturer's value of the ion exchange capacities and the experimental ion exchangeable H^+ concentrations in meq/g of the dry resin, as well as the % difference involved in the experimental results. It is seen that the experimental values obtained in this laboratory agree very well with the manufacturer's specifications. Again, the Amberlyst-35 and -36 resins had very similar properties, whereas the Amberlyst-1010 had a much lower concentration of acid sites.

Table 3. Ion Exchange Titrations

Amberlyst	Manufacturer's meq/g	LU Experimental meq/g	% Difference
1010	3.3	3.25	1.5
35	5.2	5.22	0.4
36	5.4	5.30	1.8

B. Catalytic Testing of the New Amberlyst Catalysts

The new Amberlyst-35 and -36 catalysts are reported to be more acidic than Amberlyst-15, and the Amberlyst-1010 resin has a higher porosity ($0.41 \text{ cm}^3/\text{g}$) 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 N_2 . The experimental conditions are as follows:

Catalyst weight	5.0 g dry resin
Temperature	90°C
Pressure	1 atm (0.1 MPa)
Methanol feed	$1.72 \text{ mol/kg cat/hr}$
Isobutanol feed	$1.72 \text{ mol/kg cat/hr}$
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.

Results

In Tables 4-6, the conversion at 90°C and at some higher temperatures are reported.

Table 4. 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 5. 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 6. 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

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 5). However, with reference to Table 6, 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 10% of methanol and 10% of isobutanol at 90°C [1]. Conversions of all polymer resins tested (at 90°C) during this project (see also, Reference 1) are listed in Table 7. The overall order of activity follows the sequence Amberlyst-35 > Amberlyst-36 > Amberlyst-15 $\approx$ Purolite C-150 > BioRad AG 50W X-2 $\approx$ Amberlyst-1010 > Nafion-H.

Table 7. 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

Selectivity data obtained at the reaction temperatures shown in Tables 4-6 are represented in Figures 1-3. Under the reaction conditions employed, 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. Amberlyst-1010 formed

Figure 1: Selectivity for
Amberlyst 1010 in Mole % of Products

Figure 2: Selectivity for
Amberlyst 35 in Mole % of Products

Figure 3: Selectivity for
Amberlyst 36 in Mole % of Products

MIBE, DME, and butenes (mainly isobutene) at 90°C, but butenes were favored at temperatures above 90°C. Amberlyst-35 mainly formed butenes at 90-110°C, but at 120°C and above DME was predominantly formed (Figure 2). Amberlyst-36 showed a similar selectivity pattern, with butenes being the favored products at 100 and 110°C and DME being the dominant product at 120 and 130°C (Figure 3). Figures 4-9 present the data as % yield of the products. Figures 4-6 give the % yields with respect to the methanol reactant, whereas Figures 7-9 give % yields with respect to isobutanol (fractional conversion times % selectivity). The trends observed in these plots are the same as for the selectivities in Figures 1-3.

C. 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 [2,3]. 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.

Figure 4: % Yield for Amberlyst 1010
Relative to Methanol Conversion

Figure 5: % Yield for Amberlyst 35
Relative to Methanol Conversion

Figure 6: % Yield for Amberlyst 36
Relative to Methanol Conversion

Figure 7: % Yield for Amberlyst 1010
Relative to Isobutanol Conversion

Figure 8: % Yield for Amberlyst 35
Relative to Isobutanol Conversion

Figure 9: % Yield for Amberlyst 36
Relative to Isobutanol Conversion

Results

The results shown in Figures 10 and 11 demonstrate that the formation of butenes was very sensitive to the alcohol partial pressure. A small elevation of the alcohol pressure 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 increased. At the reaction temperature of 117°C, all of the ethers showed increasing productivities as the pressure of the reactants was increased (Figure 11).

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

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 was purchased from MSD Isotopes and was 97.3 atom% ^{18}O enriched. Anhydrous isobutanol was purchased from Aldrich Chemical Co., Inc., and it contained the natural abundances of oxygen isotopes, i.e. 99.8% ^{16}O and 0.2% ^{18}O . 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

Figure 10: STY versus Alcohol Partial Pressure for Amberlyst 35 at 90 C

Figure 11: STY versus Alcohol Partial Pressure for Amberlyst 35 at 117 C

cold-finger of the effluent from the reactor. The mass spectra were compared to those of reference compounds for identification of the catalytic products [4].

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 (0.1 MPa)
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

Via GC/MS analyses, the molar abundances of each ¹⁶O- or ¹⁸O-containing product separated by GC were quantified 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 [5], 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 [5], 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.

The oxygen-containing mixed ether products were found to be ¹⁶O-MIBE and ¹⁸O-MTBE with near 100% selectivity, Figure 12. The isotopic composition of DME, formed

Figure 12

$\text{Me}^{18}\text{OH} + \text{i-BuOH}$
over Nafion-H at 90 °C

from two molecules of methanol, was found to be 92% $\text{CH}_3\text{-}^{18}\text{O-CH}_3$, indicates that even activated methanol did not isotopically scramble to any significant extent with ^{16}O on the catalyst or from water produced from isobutanol and methanol dehydration. The results shown in Figure 12 clearly show that the source of oxygen in MIBE was from the isobutanol reactant, while MTBE retained the oxygen from the methanol reactant. These results indicate that MTBE and MIBE are formed *via* different mechanisms.

Since the MIBE and MTBE products do not share the same source of the oxygen atom, MIBE cannot be the direct precursor to MTBE. The mechanism for the MIBE synthesis must be consistent with a substitution-type reaction in which an isobutoxy group adds to "methanol" and the methanol hydroxy moiety is part of the leaving group. These results are most consistent with an $\text{S}_{\text{N}}2$ -type mechanism involving surface bound species, *viz.* protonated methanol attacked by a nearby hydrogen bonded isobutanol molecule, as illustrated in Figure 13. On the other hand, protonated isobutanol predominantly eliminates water to form isobutene since attack on the protonated isobutanol molecule by a different alcohol molecule is sterically hindered, and this is consistent with the extensive literature on solution chemistry of the isobutyl group [6]. Subsequently, MTBE is most likely formed from the isobutene product (or its carbenium ion precursor) and methanol, e.g. ^{18}O -methanol in our experiment to form the ^{18}O -labelled MTBE, as illustrated in Figure 14.

E. BET Surface Area Studies of Sulfate-Modified Zirconia

The objective of these experiments was to determine the influence, if any, of the calcination temperature on the surface area of the synthesized $\text{SO}_4^{2-}/\text{ZrO}_2$ catalysts. 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].

Figure 13

S_N2 Mechanism for hydrogen bonded i-BuOH + MeOH oxonium ion to MIBE

Figure 14

Mechanism for i-BuOH dehydration to i-butene

Subsequent reaction of Me^{18}OH with i-butene to MTBE

Experimental

The preparation of the $\text{SO}_4^{2-}/\text{ZrO}_2$ sample was carried out according to the method described by Hino and Arata [9], which is briefly described as follows:

1. Zirconium hydroxide ($\text{Zr}(\text{OH})_4$) was prepared by hydrolyzing zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) with aqueous ammonia solution (NH_4OH), and the solution was stirred and digested for 4 hr.
2. The sample was then filtered, washed with distilled water, checked for the absence of Cl^- with AgNO_3 , and dried at 118°C overnight.
3. The treatment of the catalyst with sulfate was performed by pouring 1 N sulfuric acid onto a filter paper containing the catalyst, and the catalyst was dried overnight at 114°C in air.
4. Samples of the catalyst were then calcined in air at different temperatures for 3 hr. After weighing into analysis tubes, the samples were degassed at 300°C for 3 hr, and the measurement of BET surface area was conducted with a Gemini 2360 Surface Area Analyzer.

Results

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, will be investigated in the next period of this project.

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

Calcination Temp. (°C)	Langmuir (m ² /g)	BET Single Point (m ² /g)	BET Multipoint (m ² /g)
350	379	225	232
455	334	200	205
551	248	146	150
620	181	105	108
720	58	36	37

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