I. Background of C_5 Ether Synthesis

Due to U.S. federal legislation aimed at environmental improvements of the transportation industry, reformulated gasolines are being developed that contain lower content of aromatic hydrocarbons and increased levels of organic oxygenates. At the present time, the preferred oxygenate is methyl tertiary butyl ether (MTBE) because it compensates for the loss in octane number due to a reduction in aromatics, reduces the vapor pressure of the gasoline fuel, and provides for partial abatement of vehicle tailpipe hydrocarbon and carbon monoxide emissions (1).

Currently, MTBE is manufactured from methanol and isobutene *via* a liquid phase synthesis over acid resin catalysts, as represented by Equation 1, where isobutene is obtained as a side product from petroleum refinery FCC units (2-4). Although older FCC units could produce 8 wt% C_4 products in their output (5), the typical FCC refinery product slate now contains 1.4 wt% C_4 compounds (6), and improved processes utilizing catalytic additives such as improved ZSM-5 tend to decrease the yield of C_3 and C_4 olefins in the light ends still further (7). Thermal cracking of isobutane in the light ends can also be carried out to obtain isobutene (6). In any case, the availability of refinery supplied isobutene is limited.

$$(CH_3)_2C{=}CH_2 \ + \ CH_3OH \ \rightarrow \ (CH_3)_3C\text{-}O\text{-}CH_3 \qquad (1)$$

Since MTBE is now the seventh largest produced synthetic organic chemical today (8) and has also been the fastest growing catalytic process during the last decade, a ready supply of both methanol and isobutene is needed. Indeed, it has been predicted that due to continuing and increasing clean air restrictions, the demand for oxygenates (ethers and alcohols) in fuels could increase more than 10-fold by the year 2001 (9). To put this in perspective, the U.S. National Research Council states that the demand for oxygenates may approach 1 million barrels/day by the year 2000, a level equivalent to nearly 10% of current U.S. petroleum production (1). Various alternatives have been sought for increasing the availability of isobutene, and one source of C_4 is butane from natural gas. Although the butane content in natural gas is low, this source of C_4 is increasingly gaining importance. Among the processes that have been developed for the synthesis of pure isobutene is the endothermic dehydration of tertiary butanol (10).

Another possible source of isobutene for ether synthesis is dehydration of isobutanol, produced from synthesis gas as represented by Equation 2. Methanol and isobutanol are the predominant products formed from H_2/CO synthesis gas over alkali promoted Cu/ZnO-based catalysts (11-15). Since the two alcohols are produced together, direct coupling of these two alcohols to produce high octane ethers provides an attractive path to C_5 ethers. It has been shown (16,17) that over acid catalysts, the dominant reaction is direct coupling that results in the formation of methyl isobutyl ether (MIBE), Equation 3.

$$(CH_3)_2CHCH_2OH \rightarrow (CH_3)_2C{=}CH_2 + H_2O \qquad (2)$$

$$(CH_3)_2CHCH_2OH + CH_3OH \rightarrow (CH_3)_2CHCH_2\text{-}O\text{-}CH_3 + H_2O \qquad (3)$$

However, if a selective catalyst were found for converting isobutanol to isobutene followed by a reaction with methanol, a desirable route to high octane MTBE from natural gas or coal-derived synthesis gas would be provided. Such a process would alleviate isobutene dependence on petroleum feedstocks. The objective of this research was to develop the methodology for the catalytic synthesis of high value ethers, primarily MTBE and MIBE, from alcohol mixtures that are rich in methanol and isobutanol.

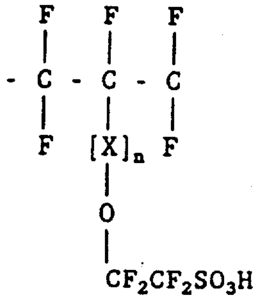
A. Selection of the Organic Resin Catalysts

Since the current commercial catalysts used for the liquid phase synthesis of MTBE from methanol and isobutene are strong acid resin catalysts, this type of catalyst was studied here for the gas phase synthesis of ethers. Task 1 of this research was centered on acid organic resins, principally those containing comparisons of the catalytic behavior of -SO_3H acid functional groups. The two general groups of these resins are

(i) polystyrene ion exchange resins, and

(ii) fluorocarbon sulfonic acid (FSA) polymers.

The first group contains polymeric catalysts such as Amberlyst-15, Purolite C-150, and Bio-Rad AG 50W X-2, all of which were tested for the reaction of isobutene with methanol at 75°C and 0.1 MPa to form MTBE, as well as for ether synthesis *via* alcohol coupling at 90°C and 0.1 MPa. This group of catalysts consists of sulfonated forms of polystyrene crosslinked with divinylbenzene. Amberlyst-15 and Purolite are macroreticular forms of the polystyrene type resins. The second group of FSA polymers was developed by duPont under the name of Nafion, and similar materials were subsequently developed by Dow Chemical Co. Both are copolymers of tetrafluoroethylene and fluorinated vinyl ethers that contain fluorosulfonyl groups, and the molecular structures of these are given below:



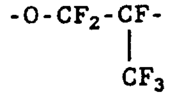
$-CF_2-CF([X]_n-O-CF_2CF_2SO_3H)-CF_2$

I. Dow Chemical Company

II. Du Pont Nafion

I; n = 0

II; n = 1, 2, 3 -- with X = $-O-CF_2-CF(CF_3)-$



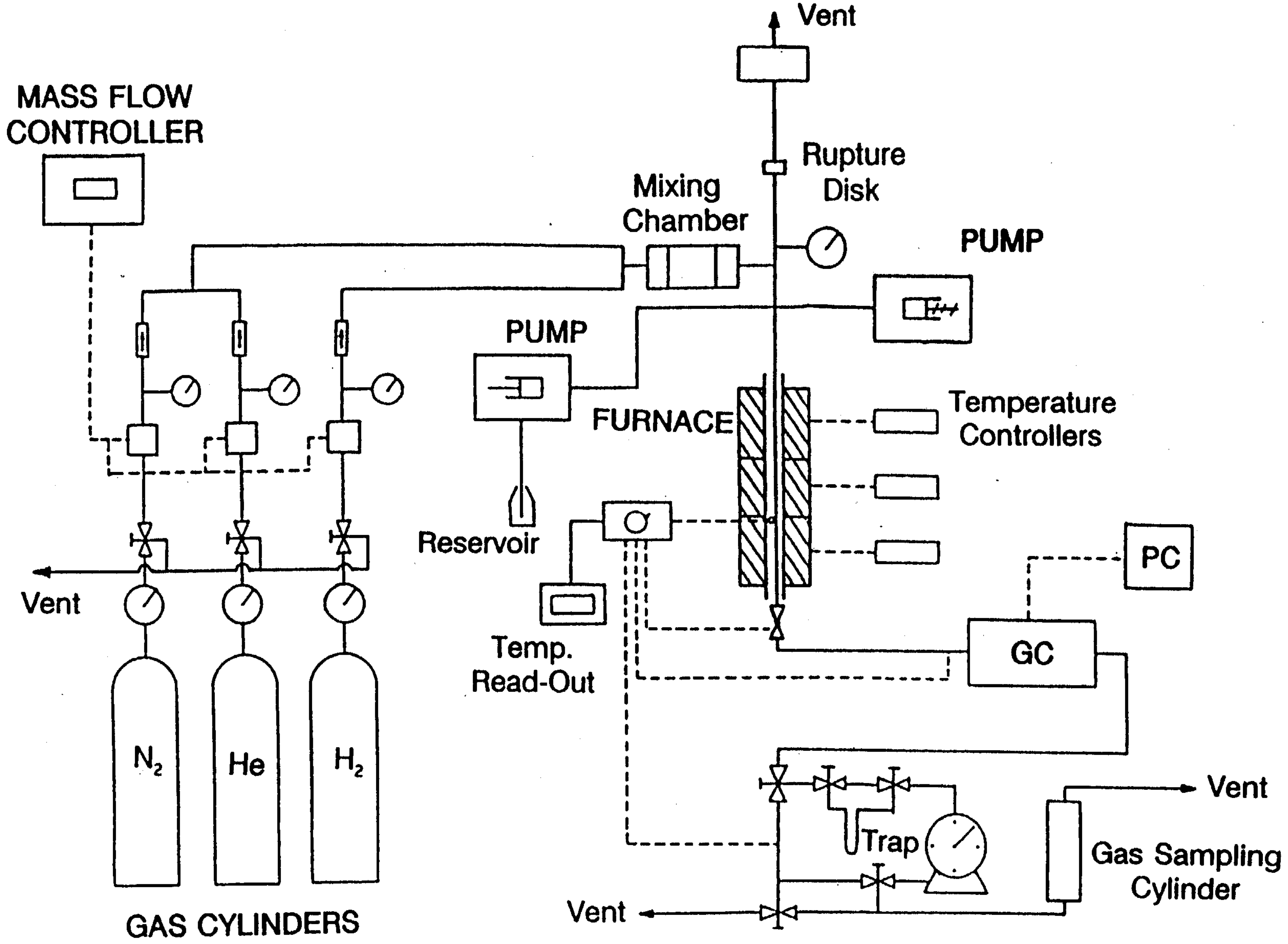
$-O-CF_2-CF(CF_3)-$

B. Experimental Testing of the Catalysts

The catalysts were tested for ether synthesis from binary methanol/isobutanol, as well as methanol/isobutene, reactant mixtures in the vapor phase in a continuous flow stainless steel bench-scale reactor system that is automated so that testing can be carried out under continuous operation at designed experimental conditions. A schematic of the reaction system is shown in Figure 1. The furnace consists of three independent heating elements and maintained a very constant steady state temperature. Typically N_2/He gas is utilized as the carrier/inlet gas, and the alcohol mixture was added at the top of the reactor *via* 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. In certain experiments, independent flows of methanol and isobutanol were employed by utilizing both pumps, and this allowed the molar ratio of the two alcohols to be easily varied during the experiments. The conversion and product composition were monitored by periodic sampling, e.g. semi-hourly, of the exit stream by gas chromatographic analysis using in-line, heated, automated sampling valves. In addition, the liquid product collected was sometimes subjected to subsequent analyses by GC, NMR, and GC/MS.

The dedicated Hewlett-Packard Model 5890 Series II gas chromatograph (HP GC) has automated heated Valco sampling valves, both thermal conductivity (TCD) and flame ionization (FID) detectors, 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 um thick methyl silicon coating) capabilities, and is interfaced and controlled by a PC data station (Gateway 2000 personal computer system) 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, that

Figure 1. Schematic of the reaction system



can produce a hard copy of each chromatogram and listing of the associated integrated peak areas.

The catalytic results 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 (% conversion of one of the reactants x % product selectivity)/100. 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, with the usual reactant of methanol = isobutanol = 1.72 mol/kg cat/hr formation of 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).

II. MTBE Synthesis From Methanol and Isobutene over Resin Catalysts

A. Comparison of Acidic Ion-Exchange Resin Catalysts

The present commercial process for the production of MTBE involves the liquid phase addition of methanol to isobutene over the acidic ion exchange Amberlyst-15 resin in the temperature range of 50-90°C, Figure 2. A study of this reaction over several acidic ion exchange resins in the vapor phase was conducted to provide a comparison of the relative activity of other catalysts toward MTBE production. This reaction might also be important in the coupling of methanol and isobutanol in which the acid-catalyzed dehydration of isobutanol to isobutene may be followed by methanol addition to isobutene to yield MTBE. The conditions chosen for this reaction were those used by Baba et al. (18):

Catalyst Weight	0.25 g (dry)
Temperature	75°C
Total Pressure	0.1 MPa (1 atm)
N_2/He/MeOH/i-Butene	2/1/1
Total Space Velocity	2.0 mol gas/g cat/hr

The acidic ion exchange resins used in this study were Amberlyst-15, Purolite C-150, and BioRad AG 50W X-2. The Amberlyst was obtained in dry form from Rohm and Haas, the manufacturer, and was used without pretreatment. Both the Purolite and BioRad resins were originally in an extremely wet form and had to be dried at 90°C overnight prior to loading the reactor. The catalyst bed was diluted with 3 cm^3 of Pyrex beads. The results of the MTBE synthesis over these catalysts using the conditions listed above are given in Table 1, where the conversion of isobutene to MTBE is given. The most striking aspects of these results are that the macroreticular resins Amberlyst and Purolite were active while the gel-type resin BioRad was completely inactive. The macroreticular resins are characterized by a rigid structure with well-defined pores that allow easy access to internal acid sites for most liquid and vapor phase organic molecules (19). The gel type resins are produced in a manner that results in a structure that is inherently *nonporous* (19). Gel-type resins swell when exposed to liquid phase polar solvents, such as alcohols. This swelling should open the interior of the resin particle to reactants (19,20). It has been established that gel-type resins are active in liquid phase reactions, but are poor catalysts for vapor phase reactions (20,21). The MTBE synthesis results also show that the commercially used catalyst Amberlyst-15 is more active in producing MTBE on a weight basis than Purolite. Both Amberlyst-15 and Purolite C-150 were 100% selective towards MTBE formation with no trace of other products being observed.

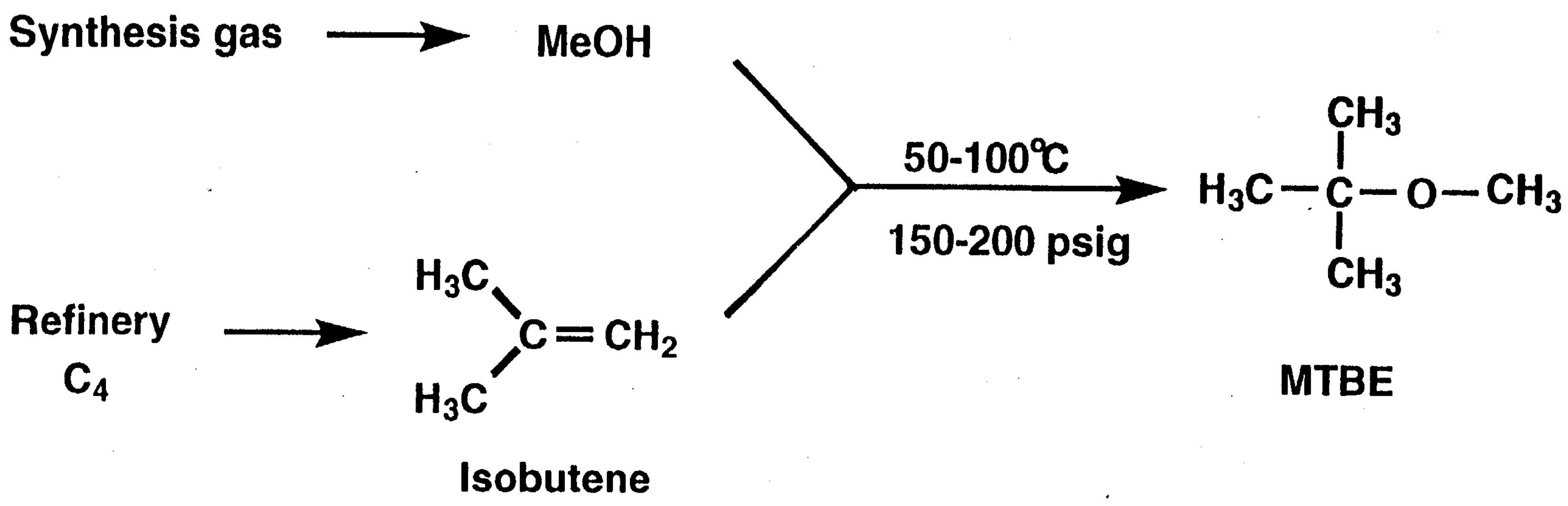
Table 1. MTBE synthesis *via* methanol and isobutene coupling at 75°C and 0.1 MPa. Total flow rates (alcohol reactants plus N_2/Hc carrier gas) for the three tests were the following: Purolite C-150 = 1950 mol/kg/hr, BioRad = 1975 mol/kg/hr, and Amberlyst-15 = 2015 mol/kg/hr.

Catalyst	**Feed Rate** (mol/kg/hr)	**Space Time Yield** (mol/kg/hr)	**Conversion** (%)
Purolite 0.2559 g	MeOH = 490 i-Butene = 485	MTBE = 76.6	15.8
BioRad 0.2587 g	MeOH = 485 i-Butene = 465	MTBE = 0.0	0.0
Amberlyst-15 0.2526 g	MeOH = 495 i-Butene = 495	MTBE = 121.4	24.6

B. Temperature Dependence of MTBE Synthesis Over Purolite C-150

After finding that Purolite C-150 was an active and selective MTBE catalyst, some additional tests were performed in order to ascertain its activity profile with respect to temperature and reactant gas hourly space velocity. The steady state activities, in terms of

Figure 2. The present commercial process for the production of MTBE



Catalyst: Amberlyst-15 (Sulfonated polystyrene ion exchange resin)

% conversion of isobutent to MTBE, of Purolite C-150 for MTBE synthesis at temperatures between 75-105°C under the same conditions as those used above are given in Table 2. The maximum productivity of MTBE was found at 85°C.

Table 2. Results of methanol and isobutene coupling over Purolite C-150 as a function of temperature at 0.1 MPa (catalyst weight = 0.26 g).

Temperature	Feed Rate (mol/kg/hr)	Productivity (mol/kg/hr)	Conversion (%)
75°C	MeOH = 490 i-Butene = 470 N_2/He = 970	MTBE = 72.6	15.4
85°C	MeOH = 490 i-Butene = 470 N_2/He = 970	MTBE = 90.5	19.2
95°C	MeOH = 490 i-Butene = 470 N_2/He = 970	MTBE = 79.9	16.9
105°C	MeOH = 490 i-Butene = 470 N_2/He = 970	MTBE = 65.8	14.0

C. Space Velocity Dependence Over Purolite C-150

The effects of varying reactant space velocity on the conversion of the reactants over Purolite C-150 at 75°C are presented in Table 3. The activity of the catalyst responds quite well to changing the space velocity of the reactants. Starting with a reactant space velocity of about 500 mol/kg cat/hr, the conversion of each reactant was 36%. Approximately doubling the space velocity essentially decreased the conversion of each reactant by half, i.e. of isobutene to 15.5%. Doubling the space velocity once again decreased the reactant conversions by approximately half, i.e. of isobutene to 7.4%.

Table 3. Results of methanol and isobutene coupling to form MTBE over Purolite C-150 as a function of reactant space velocity at 0/1 MPa and 75°C (catalyst weight = 0.25 g).

Reactant GHSV (mol/kg/hr)	**Feed Rate** (mol/kg/hr)	**Conversion** (%)
Low (510)	MeOH = 245 i-Butene = 265 N_2/HE = 485	36.0
Medium (975)	MeOH = 490 i-Butene - 485 N_2/He = 975	15.5
High (1930)	MeOH = 975 i-Butene = 955 N_2/He = 1960	7.4

III. Ether Synthesis From Methanol and Isobutanol Over Resin Catalysts

A. Ether Synthesis via Coupling of Methanol and Isobutanol

This work included testing of various solid acid catalysts for the direct coupling of methanol and isobutanol to ethers. The first stage of catalyst testing involved the use of commercially available acidic ion exchange resins and is discussed below. The second stage of catalyst testing involved the use of various inorganic solid acids that included zeolites, clays, oxides, mixed oxides, and supported acid systems.

In order to study the coupling of methanol and isobutanol to ethers in a systematic manner, it was found necessary to develop a standardized set of reaction conditions. Thermodynamic calculations of the direct coupling of methanol and isobutanol indicate that low temperatures, i.e. 50-90°C, are necessary to achieve favorable selectivity to desired products, especially MTBE and MIBE (17). All of the ion exchange resins are thermally stable within this temperature range, and 90°C was chosen for the reaction temperature in order to maximize conversion. Low pressure, i.e. 0.1MPa, was utilized in these reactions in light of the findings of Nunan et al. (16,17) that indicated lower pressures favored greater isobutene formation, the precursor of MTBE. The alcohol partial pressure was chosen such that no condensation would occur within the reaction system, and this was determined empirically under reaction conditions. The ratio of methanol to isobutanol used in the feed was investigated using Amberlyst-15 as a catalyst. Initially, a molar ratio of MeOH/i-BuOH = 2/1 was used for the feed. Then the same experimental conditions were used except that the MeOH/i-BuOH ratio was changed to 1/1, which is the stoichiometric ratio of the desired reaction. The 1/1 reactant mixture yielded more ether products than the 2/1 mixture, and therefore the 1/1 molar alcohol ratio was chosen for the standard test reaction. Alcohol feed rate and total gas flow were similar to those described by Nunan et al. (16,17).

The catalyst bed was diluted to 20 cm^3 with Pyrex beads. A summary of the experimental conditions is given below:

Catalyst weight	5.00 g (dry)
Reaction temperature	90°C
Total Pressure	0.1 MPa
Molar ratio MeOH/iBuOH	1/1
MeOH flow rate	1.72 mol/kg cat/hr
i-BuOH flow rate	1.72 mol/kg cat/hr
He + N_2 flow rate	16 mol/kg cat/hr

Product Analysis

The acid catalyzed reaction of the two alcohols usually results in a complex mixture of products. The following product abbreviations are used in this report:

DME:	Dimethylether
MTBE:	Methyl tertiary butyl ether
MIBE:	Methyl isobutyl ether
TIBE:	Tertiary butyl isobutyl ether
DIBE:	Di-isobutyl ether.

These products are obtained by the following reactions:

$$2\ \text{MeOH} \rightarrow \text{DME} + H_2O \qquad (4)$$

$$\text{MeOH} + \text{i-BuOH} \rightarrow \text{MTBE} + H_2O \qquad (5)$$

or

$$\text{MeOH} + \text{i-Butene} \rightarrow \text{MTBE} \qquad (1)$$

$$\text{MeOH} + \text{i-BuOH} \rightarrow \text{MIBE} + H_2O \qquad (3)$$

$$\text{i-Butene} + \text{i-BuOH} \rightarrow \text{TIBE} \qquad (6)$$

$$2\ \text{i-BuOH} \rightarrow \text{DIBE} + H_2O. \qquad (7)$$

The isobutene shown in some of the above reactions originated from the isobutanol reactant:

i-BuOH $\rightarrow$ i-Butene + H_2O. (2)

The acid catalyzed dehydration of isobutanol was studied previously by several workers and is known to result in a mixture of butenes, i.e. isobutene, 1-butene, *cis*- and *trans*-2-butene (22,23). It will be shown herein that among these butenes, isobutene is the dominant product formed. Mechanistically, reactions 2-5, and 7 may involve oxonium ion intermediates. Reactions 1, 2, and 6 may require carbenium ions to be formed. These intermediates will be considered later in this report from a perspective of the dominant reaction pathways that operate to control the selectivity of the synthesis reactions that yield ethers and olefins.

Activity and Selectivity of Ion Exchange Resins

The results of the standard test over the four ion exchange resins at steady state activity are shown in Table 4 in terms of the conversions of the reactant alcohols. In this test the microsaddles (MS) form of Nafion-H was used.

Table 4. Activities of the resin catalysts in the MeOH + i-BuOH standard test.

Catalyst	Methanol Conversion (%)	Isobutanol Conversion (%)
Amberlyst-15	9.1	10.2
BioRad	4.9	5.4
Nafion MS	1.4	1.4
Purolite C-150	9.2	9.9

All catalyst testing runs reached steady state conversion levels after the first hour of reaction. All catalysts studied were most selective for MIBE production. Relative overall activity followed the order Amberlyst-15 ≈ Purolite C-150 > BioRad > Nafion MS. One interesting observation is that the BioRad AG 50W x-2 resin was quite active in the reaction between methanol and isobutanol but was observed to be inactive for methanol and isobutene conversion (cf. Table 1). The presence of isobutanol at a temperature much below its boiling point may allow it to be absorbed enough by the BioRad gel resin to cause swelling of the polymer matrix. This would render the active sites in the interior of the resin particle to be accessible. This evidently did not occur with gas phase isobutene, which possibly explains the sharp differences in the activities of this resin with different reactants. Product selectivities for the different catalysts are illustrated in Figure 3. Water is, of course, the major product of these dehydration reactions, but it is not included in the selectivity analysis. The butenes are shown as the sum of isobutene and the linear *trans*-2-butene and *cis*-2-butene, where 88-91% of the total was isobutene except for Nafion where the linear butenes were not detectable. Under the standard reaction conditions, Nafion appears to be the most selective catalyst for MIBE production. The other catalysts produce significant amounts of MTBE, along with the other ethers TIBE, DIBE, and DME. The higher selectivity of Nafion towards MIBE formation may be due to the distinctly different nature of the acid sites of Nafion. The fluorosulfonic acid groups of Nafion contrast with the sulfonic acid groups of the other ion exchange resins tested in this study.

Figure 4 gives the ratios of MTBE to isobutene, MIBE to DME, and MIBE to MTBE produced over the catalysts and illustrates the effectiveness of the catalysts for MIBE formation. In addition, a low MTBE/isobutene ratio in the case of Nafion MS suggests that even when isobutene is formed in relatively high concentrations in the presence of excess methanol, it is difficult to produce MTBE under these reaction conditions.

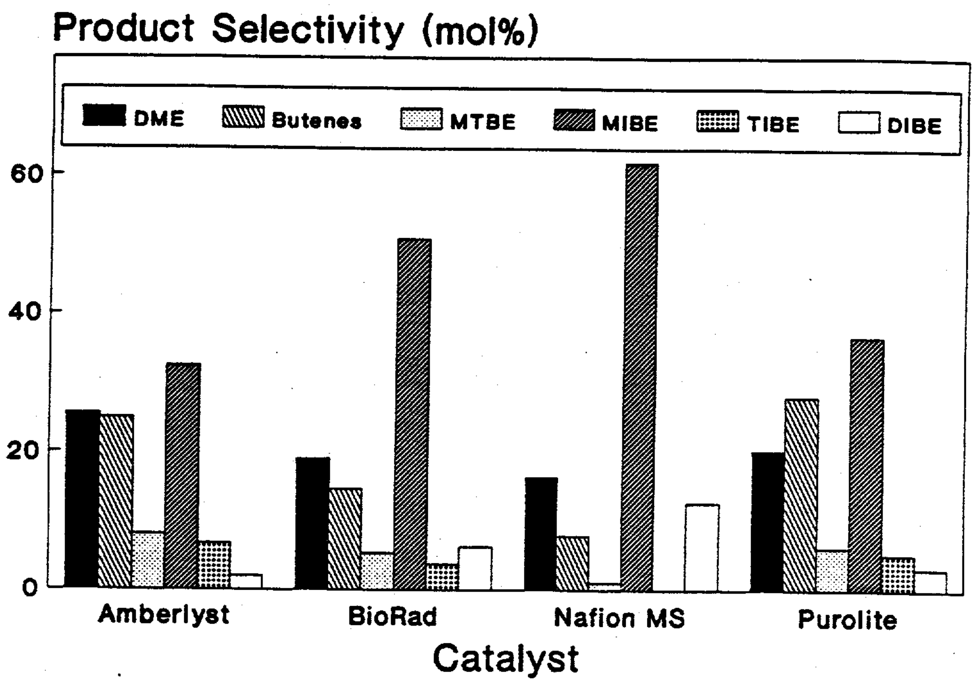


Figure 3. The product selectivities of the organic resin catalysts at 90°C and 0.1 MPa with methanol/isobutanol = 1/1 reactants.

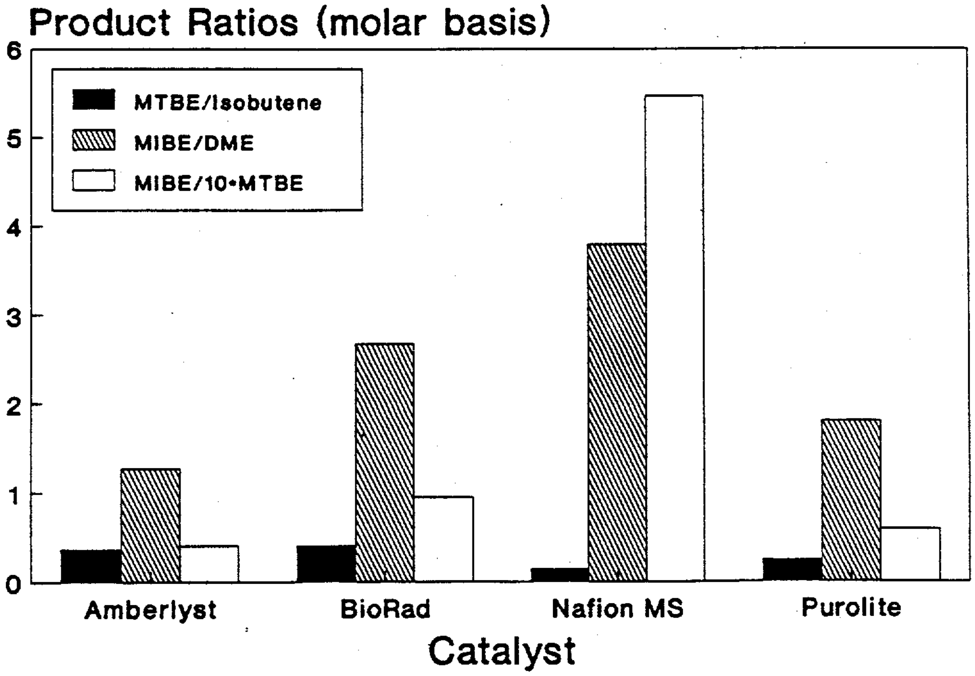


Figure 4. The product ratios of MTBE/isobutene, MIBE/DME, and MIBE/MTBE over the organic resin catalysts at 90°C and 0.1 MPa with methanol/isobutanol = 1/1 reactants.

B. High Temperature Testing of Nafion-H MS and Nafion-K

For comparison with both organic resins and the inorganic catalysts, the Nafion-H MS catalyst test was repeated under standard conditions and was extended to higher temperatures. Table 5 shows activities of Nafion-H MS at 90, 125, 150, and 175°C.

Table 5. Activities of the Nafion-H MS catalyst in the MeOH + i-BuOH standard test as a function of temperature.

Temperature (°C)	Methanol Conversion (%)	Isobutanol Conversion (%)
90	1.4	1.5
125	28.2	31.6
150	60.3	99.6
175	59.3	98.2

Conversion at 90°C compared well with the previous catalytic test (Table 4). Upon increasing the temperature to 125°C, conversion increased to ≈30% for both methanol and isobutanol with methyl isobutylether (MIBE) and DME as major products. A few minor products were not identified at this temperature. At higher temperatures (150 and 175°C), methanol conversion, predominantly to DME (MIBE selectivity decreased at higher temperature), increased to ≈60%, whereas isobutanol was almost completely converted, predominantly to isobutene. It must be noted that at 150 and 175°C a large number of small unidentified peaks in the analytical gas chromatogram were seen. Upon unloading the catalyst from the reactor, the previously light yellow catalyst had changed color to black. It had a greasy "film" over it and smelled "oily". Apparently, due to its very strong acidity, Nafion-H at 150°C and above is able to catalyze extensive isomerization and oligomerization.

To probe the significance of the acid groups in the Nafion-H resin, a portion of

Nafion-H was exchanged to its potassium form, designated as Nafion-K. To achieve the ion exchange 10 g of Nafion-H was immersed in 75 ml of 1 M potassium nitrate (KNO_3) and stirred for approximately 45 min. The solution was strongly acidic dur to the exchange of H^+ for K^+. A new portion of potassium nitrate was added after the previous was decanted and the catalyst was washed with distilled water. The procedure was repeated until full exchange was reached, as determined by testing the pH of the exchannge solution. Four portions of KNO_3 were needed for total exchange of the Nafion-H. Finally, the Nafion-K resin washed in distilled water and allowed to dry overnight at 90°C.

In contrast to the results in Table 5 for Nafion-H MS, Nafion-K showed no activity at all over this temperature range. This indicates that a catalyst possessing appreciable acidity is necessary for the reactions discussed above. The tested Nafion-K also retained its light yellow color, even after being subjected to reaction conditions at 175°C, indicating the color change of Nafion-H was due to either thermal decomposition of the SO_3H groups (assuming the SO_3K group does not) or to hydrocarbonaceous deposits on the Nafion-H resin.

C. Nafion-H MS Activity Dependence on Sodium Content

The objective of this study was to further investigate the role that the concentration of acid sites has on the activity of the Nafion-H MS catalyst.

To 0.52 g of Nafion-H MS was added 5.2 ml of 0.016 M sodium chloride solution. Since Nafion-H MS has 0.89 meq H^+/g, the added sodium chloride was equivelent to 18% of the acid sites. The catalyst was left to equilibrate with the NaCl solution overnight. The pH was measured before and after equilibration, and the difference was taken to correspond to the amount of sodium exchanged into the Nafion-H MS catalyst. The experimentally determined degree of exchange was 18%. The catalyst was then washed in distilled water until a neutral pH was obtained. Following this, the sample was filtered, dried at 100°C for 3 hr, and then left to cool in air. The following experimental conditions were used for the testing of the non-exchanged catalyst and the Na^+ exchanged sample:

Temperature	90°C
Pressure	1 atm
Methanol feed	5.7 mol/kg cat/hr
Isobutanol feed	5.7 mol/kg cat/hr
Helium ($+N_2$ trace)	52.7 mol/kg cat/hr
Catalyst weight	0.5 g

Table 6 shows that both the non-exchanged and the 18% exchanged Nafion-H MS produced three major products, e.g. MIBE, DME and isobutene. In both cases, MIBE was the dominant product. The yield of MIBE only decreased 10% with the sample having 18% less acidic sites available.

Table 6. Productivity over Non-exchanged and 18% Exchanged Nafion-H MS

Compound	Productivity over non-exchanged Nafion-H (mol/kg cat/hr)	Yield over 18% Na^+ exchanged Nafion-H (mol/kg cat/hr)
MIBE	0.050	0.045
DME	0.015	0.015
Isobutene	0.009	0.013

It was shown in the previous experiment that 100% exchange of Nafion-H with potassium resulted in a 100% activity loss. Therefore, a more extensive series of experiments should be carried out with partially exchanged Nafion-H samples where 25-90% of the acid groups would be exchanged with Na^+ or K^+ and the effect on activity and selectivity would then be determined.