IV. Inorganic Catalysts for Direct Coupling of Alcohols to Ethers

A. Standard Test Screening of Inorganic-Based Catalysts

The inorganic catalysts tested in this section consisted of the following:

H-ZSM-5	MZ-289 provided by Mobil Res. & Dev. Co.
Catapal-B	Vista Chemical Co. (used to prepare γ-alumina)
H-Mordenite	Norton Zeolon-900
Montmorillonite	Aldrich K-10
Silica-Alumina	Davison Grade 980
Sulfated ZrO_2	Prepared in-house

These catalysts were chosen for their strong acidity, ability to be used at high temperatures, and ease of regenerability. Mordenite, montmorillonite, silica-alumina, and γ-alumina have long histories of use in the petroleum industry, e.g. as fluidized catalytic cracking (FCC), isomerization, and reforming catalysts. Sulfate-modified zirconia has received recent attention as a possible isomerization or alkylation catalyst owing to its very strong acidity that has been characterized as a superacid (30,31). The sulfating step has been claimed to stabilize the surface area and the tetragonal phase of zirconia, as well as forming strong Lewis and Brönsted acid sites (32).

H-ZSM-5 is a medium pore zeolite with interconnecting channels of the dimensions 5.3 × 5.6Å and 5.1 × 5.5Å. H-mordenite is a zeolite with two parallel straight channels. The larger of the channels is 6.5 × 7.0 Å and the smaller channel is 2.6 × 5.7 Å (33). Breck reports a total pore volume for mordenite of about 0.21 cm^3/g (34). The surface area of this H-mordenite is $\geq 350\ m^2/g$. Catapal-B, produced specifically for catalytic applications, is a high purity form of pseudoboehmite that is the precursor of γ-alumina. Calcination of pseudoboehmite to 500°C (for 3 hr) has been shown to result in the formation of γ-alumina, with a high surface area of typically 150-300 m^2/g, which is a solid Lewis acid, thermally stable form of alumina with a nominal molecular formula of Al_2O_3. The H-mordenite and silica-alumina catalysts were calcined at 400°C for 4 hr, while the H-ZSM-5 catalyst was calcined in air at 400°C for 2 hr prior to loading into the reactor. A sample of γ-alumina from the Fisher Scientific Company was found to be totally inactive for any reaction of the methanol-isobutanol mixture under the reaction conditions employed.

The sulfate-modified zirconia (ZrO_2/SO_4^{2-}) was prepared as described by Hino and Arata (31). Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was added to aqueous ammonia to precipitate high surface area $Zr(OH)_4$ that was washed, until free of Cl, and dried at 100°C overnight. The dried $Zr(OH)_4$, e.g. weighing ≈10 g, was placed on a folded filter paper, and 150 ml of 1 N H_2SO_4 was poured through it. The wet powder was dried at 110°C overnight and then calcined in air at 620°C for 3 hr.

The following standard test conditions were used to study the activity and selectivity of these catalysts:

Temperature	90, 125, 150, 175°C (also 200, 225, 250°C for γ-alumina)
Pressure	0.1 MPa
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

According to our standard procedure, the catalysts were diluted with 0.5 mm Pyrex beads to a total volume of 20 ml. The catalyst bed was centered in the stainless steel reactor between two glasswool plugs. The remainder of the reactor volume was filled with 3 mm Pyrex beads that served to preheat and mix the entering gas, as well as to minimize the dead volume in the reactor. The charged reactor was brought to the reaction temperature in a flow of approximately 80% He and 20% N_2. When the temperature was stabilized, the equimolar alcohol mixture was pumped into the reactor at the preset flow. The reaction was carried out at each temperature for a minimum of 6 hr. Steady state conversions of methanol and isobutanol were usually obtained within the first 2 hr time-on-stream.

The space time yields (STY) of the major products obtained over this group of inorganic catalysts as a function of reaction temperature under steady state conditions are given in Table 15. The entry "Butenes" includes iso-, *trans*-2-, and *cis*-2-butene with isobutene predominating (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 to achieve comparable conversion.

The conversions of methanol and isobutanol, over the first four inorganic catalysts, are shown in Figure 20 and Figure 21, respectively, as a function of reaction temperature. The use of standard conditions at 90°C showed very low conversion of both methanol and isobutanol for all inorganic catalysts. Only **H-mordenite** showed significant activity at this temperature, 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 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 (Figure 22). Only minor dehydration of isobutanol was seen at 150°C with >90% conversion of methanol.

Table 15. Product productivities (mol/kg cat/hr) over inorganic catalysts at 0.1 MPa as a function of temperature. Reactant feed was methanol = 1.72 mol/kg cat/hr and isobutanol = 1.72 mol/kg cat/hr.

	$T_{Reaction}$	DME	Butenes	MIBE	MTBE	C8 Ethers
H-Mordenite	90°C	0.060	------	------	------	------
	125°C	0.660	------	------	------	------
	150°C	0.830	0.068	------	------	0.004
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	------
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
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
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	------	------

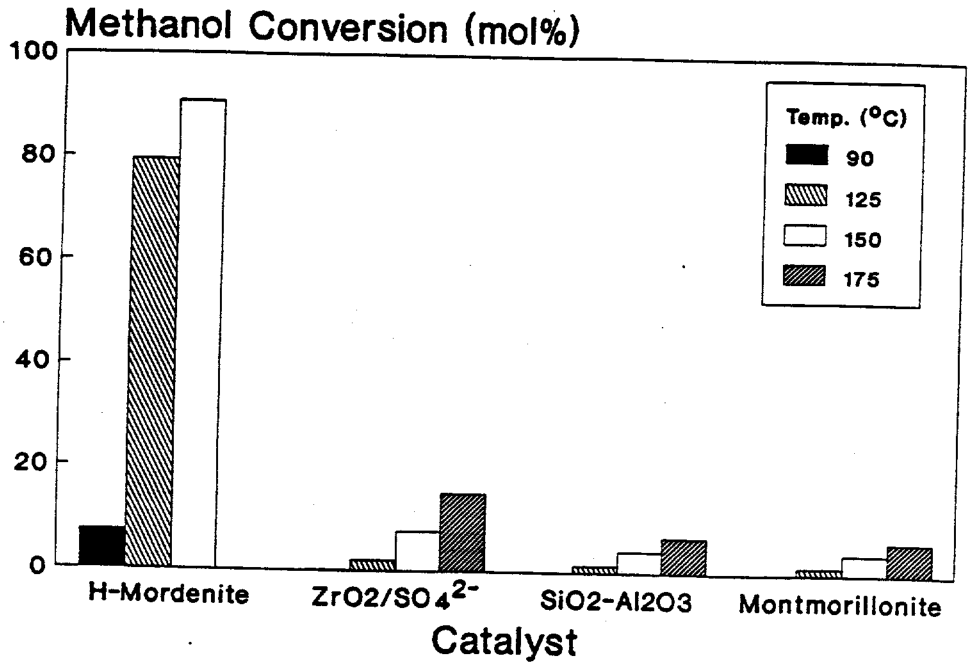

Figure 20. Conversion of methanol over four acidic inorganic catalysts under the reaction conditions given in Table 15.

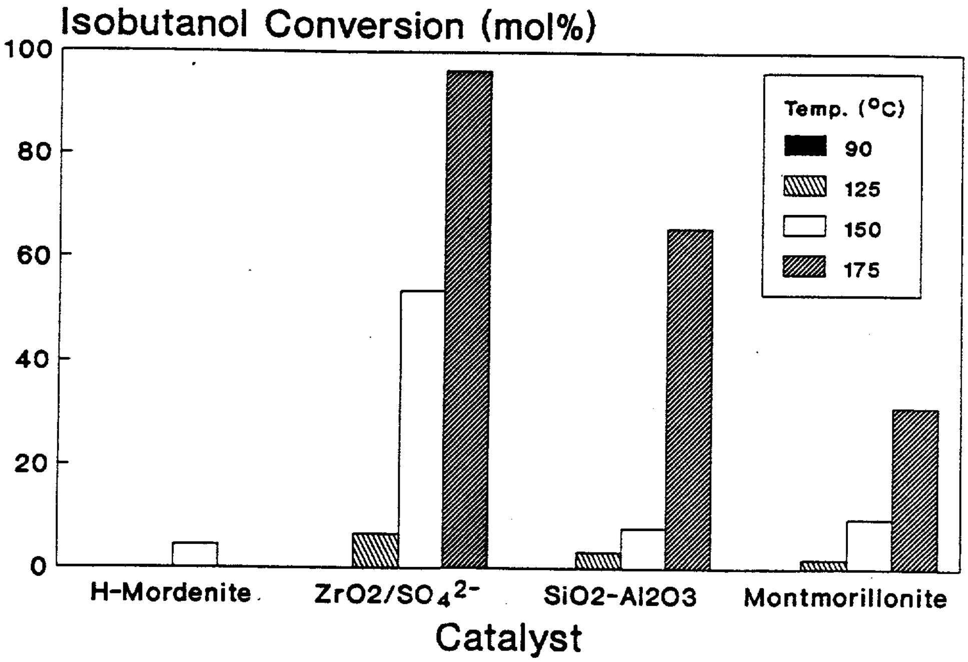

Figure 21. Conversion of isobutanol over four acidic inorganic catalysts under the reaction conditions given in Table 15.

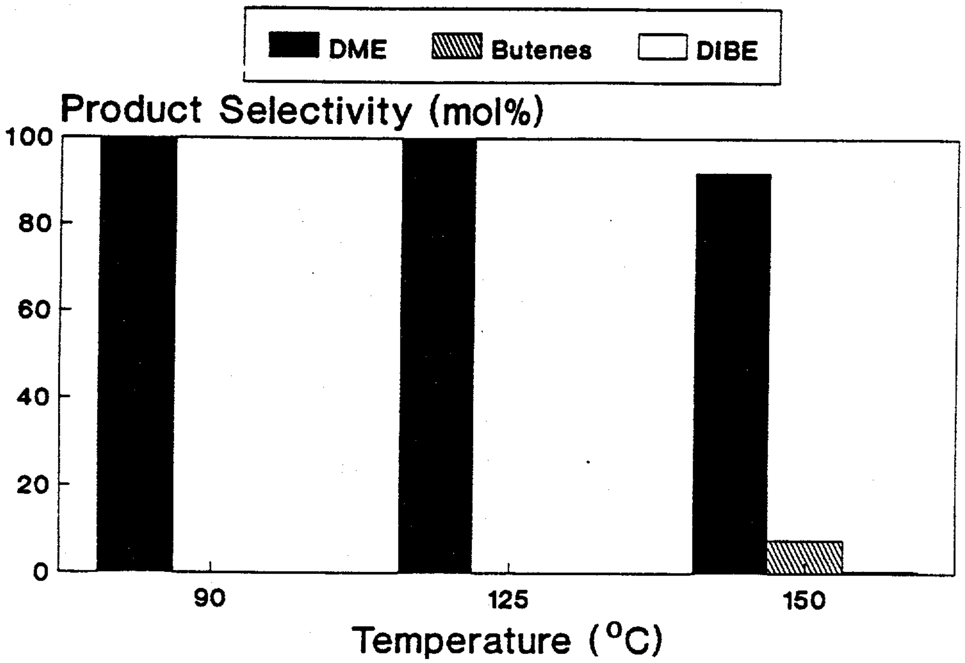

Figure 22. The product selectivity over H-mordenite from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

The sulfate-modified zirconia (ZrO_2/SO_4^{2-}) produced only methyl isobutyl ether at 90°C, but the yield was very low (Table 15). However, at higher temperature isobutanol was fairly selectively dehydrated to butenes in the presence of methanol (Figure 23). Indeed, at 150°C, the sulfate-modified zirconia showed 50% conversion of isobutanol, and this increased to 95% at 175°C with over 80% selectivity to butenes, principally isobutene. At the latter temperature, a small amount of C-12 product (0.5 mol%) was observed. On the other hand, non-sulfated zirconia was found to be totally inactive for the dehydration of either methanol or isobutanol over the temperature interval tested (90-175°C).

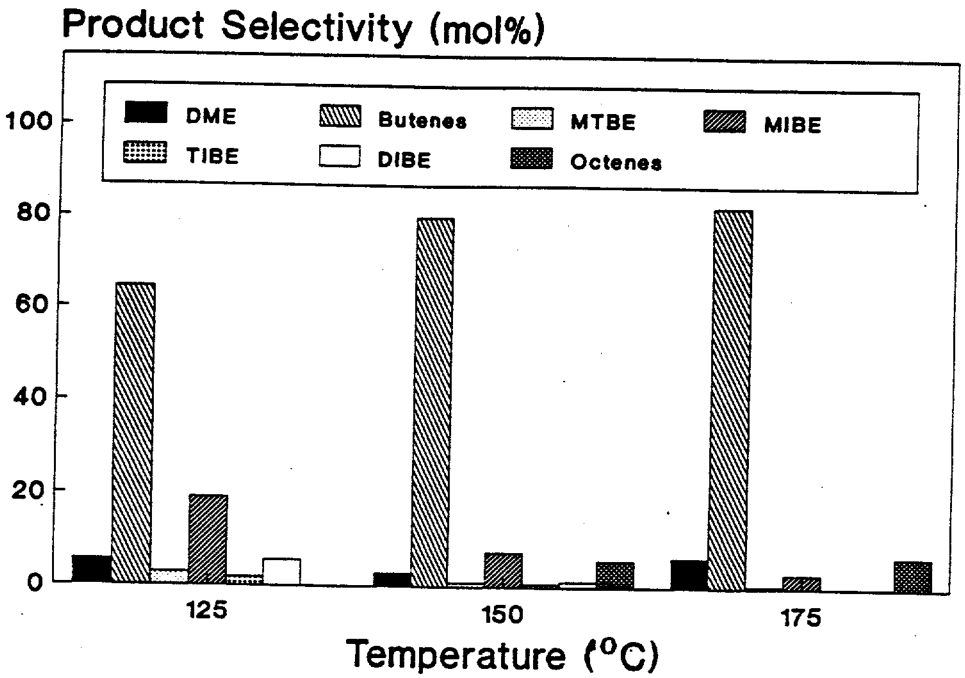

Figure 23. The product selectivity over the sulfated zirconia catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

Silica-alumina and montmorillonite showed no catalytic activity at 90°C, as indicated in Figures 20 and 21. However, at 175°C the two catalysts achieved 63% and 30% conversion of isobutanol, respectively, but ethers were not the dominant products. Montmorillonite showed poor selectivity toward any product at 125°C (Figure 24), but at higher temperature butenes were the dominant products. Silica-alumina was also mostly selective to butenes (Figure 25). In contrast, γ-alumina showed no significant conversion of isobutanol or methanol in this temperature range studied, i.e. 90-175°C.

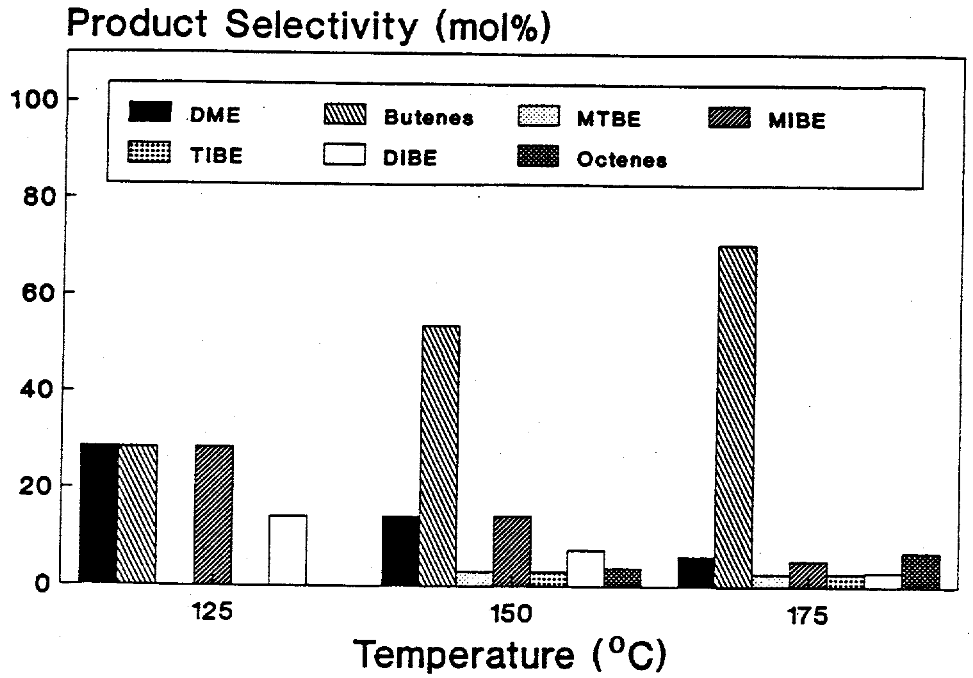

Figure 24. The product selectivity over montmorillonite from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

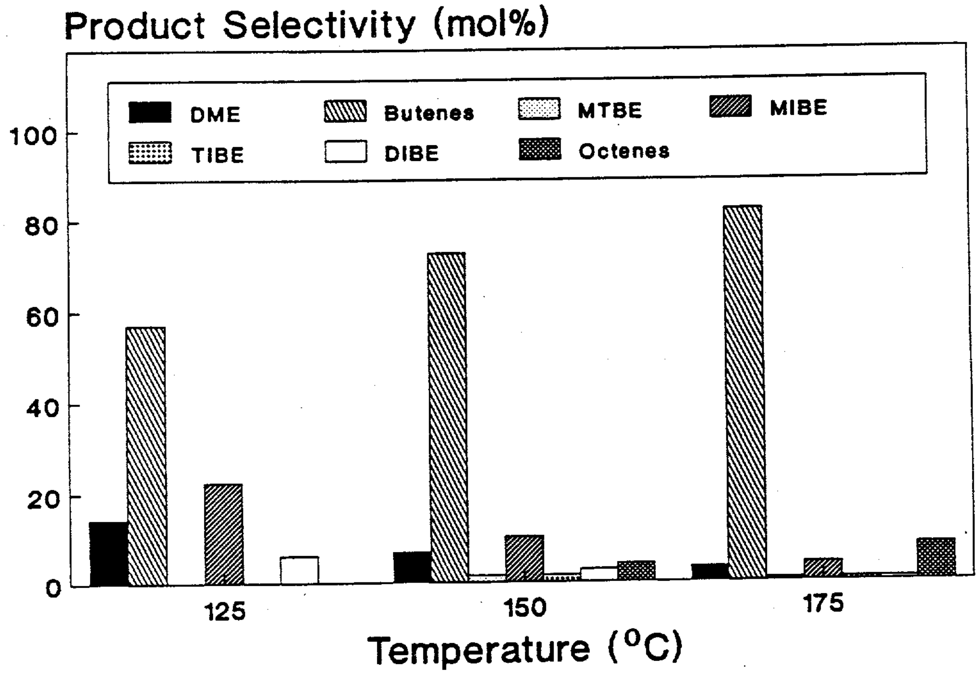

Figure 25. The product selectivity over the silica-alumina catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

The **H-ZSM-5 catalyst** was found to be active for isobutanol conversion to MIBE at 125°C, with the selectivity shifting toward butenes and DME as the reaction temperature was increased. At 175°C, ≈71% of the isobutanol was converted to products, with 77 mol% of the product being butenes. Figure 26 shows the STY of products, including the composition of the butenes, as a function of reaction temperature. As shown, a small amount of MTBE was formed over H-ZSM-5. This result contrasts sharply with that of H-mordenite, which had been found to be inactive for mixed ether formation from the methanol and isobutanol mixture over the temperature range studied. However, DME was formed highly selectively and in high yield with only slight conversion of isobutanol, and this could be explained in terms of "*shape selectivity*" of the H-mordenite. Although H-ZSM-5 has smaller pores than H-mordenite, it is very active for mixed ether formation and butene formation. This shows that the high selectivity toward DME formation observed over H-mordenite is not a general feature of acidic zeolites. The relative selectivities of H-Mordenite and H-ZSM-5 catalysts are discussed more extensively in Sections D-G of this chapter.

The **γ-alumina catalyst**, prepared from Catapal-B, was not very active at the lower temperatures where the other inorganic catalysts were active, and higher temperatures were needed to induce appreciable conversion of the reactants. However, the selectivity of γ-alumina is unique among the catalysts, as seen in Table 15 and Figure 27. The ethers MIBE and DME were exclusively and selectively formed between 125 and 175°C, while at higher temperatures isobutene formation became more important at 250°C, isobutene was the principal product. Additionally, small quantities of iso-octene were also seen. It is notable that the only butene formed over this γ-alumina was isobutene, whereas for all of the other catalysts, both organic and inorganic, that produced isobutene, there was always significant amounts of the linear butenes formed. The molar fraction of linear butenes of all butenes

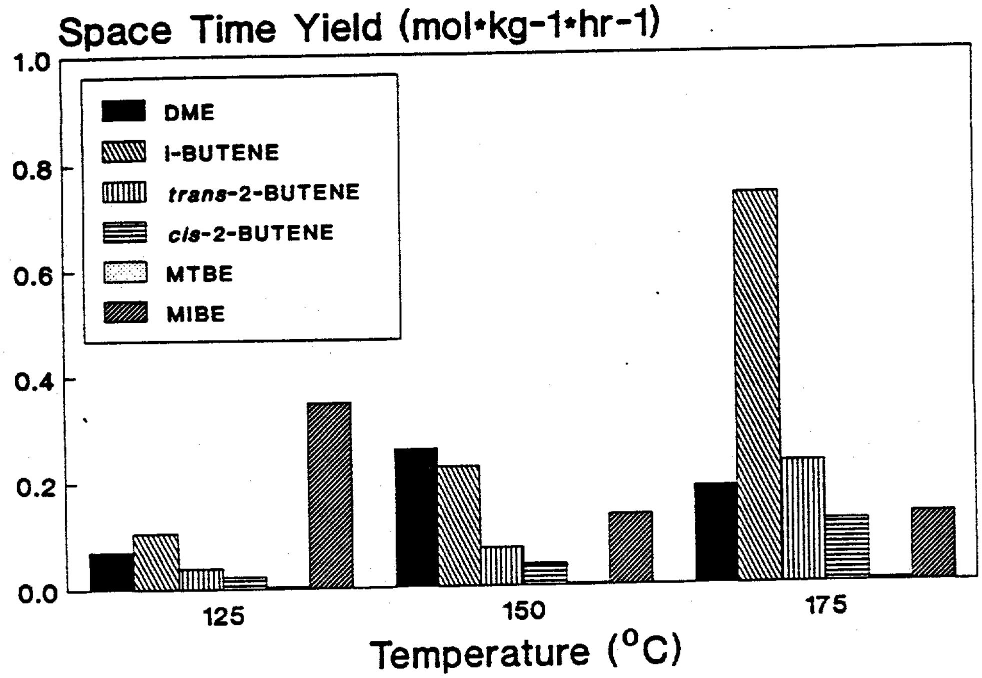

Figure 26. The product yields over the H-ZSM-5 zeolite catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

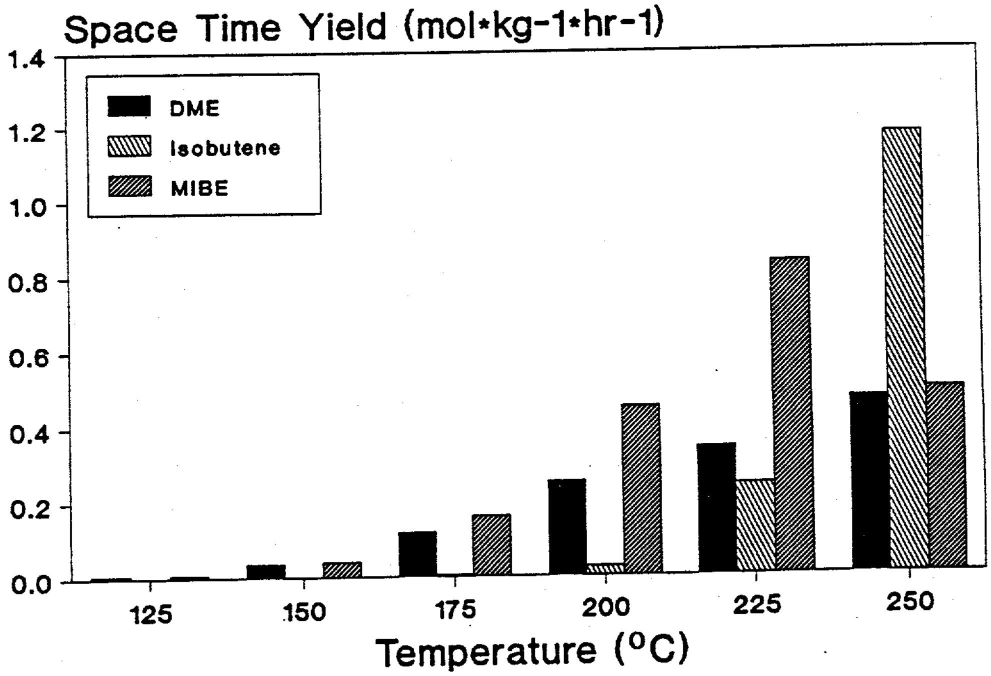

Figure 27. The product yields over the γ-alumina catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

formed over the inorganic catalysts, excluding γ-alumina, was about one-third.

The selectivity of isobutanol dehydration over γ-alumina had been studied by several workers (35,36), and it was found that isobutene was formed with over 95% selectivity. The pronounced selectivity of the γ-alumina may be explained by the absence of strong Brönsted acid sites on the surface of alumina (37). The γ-alumina surface has been shown to contain Lewis acid sites associated with basic sites (37). It has been proposed that the acidic and basic sites act concertedly to remove, respectively, the OH^- from the alcoholic carbon and an H^+ from the neighboring tertiary carbon of isobutanol (35,36). The presence of strong Brönsted acid sites in the other catalysts, both organic and inorganic, has been associated with carbenium ion chemistry, which leads to rearranged products in isobutanol dehydration (38). Thus, the absence of strong Brönsted acidity in γ-alumina may explain the absence of linear butenes in the product.

B. Effect of Water on the Reaction Rate Over γ-Alumina

The effect of co-feeding water with the reactant alcohols on the reaction of methanol and isobutanol over γ-alumina was investigated. The concentration and strength of Lewis acid and base sites on the surface of γ-alumina is known to depend on the extent of hydration (32,35). Other researchers have shown that Lewis acid sites on alumina can be converted to hydroxyl groups of only weak acidity upon addition of water vapor. In order to evaluate possible poisoning of the alcohol reactions over γ-alumina by water, which is always a major product of the dehydration reactions and of the ether-forming alcohol coupling reactions, testing was repeated at the standard reaction conditions over a controlled temperature range with and without water added to the alcohol feed. In addition to the standard reaction condition, the following parameters were used:

Temperature	150, 160, 170, 180°C
Water feed	0.000 mol/kg catalyst/hr (for dry feed) 0.172 mol/kg catalyst/hr (for wet feed)

The experiment began by bringing the charged reactor to 150°C under the He and N_2 flow. The 1/1 molar anhydrous mixture of methanol and isobutanol was then pumped into the reactor at the predetermined rate. The reaction temperature was raised in 10°C intervals to 180°C, collecting data at each temperature for several hours. The reaction temperature was returned to 150°C, and the yields of products were redetermined under the dry feed conditions. Following this experiment, the dry alcohol feed was stopped and the catalyst was kept under inert gas flow until all reactants had left the catalyst bed, which occurred within about two hours. A mixture of methanol, isobutanol, and water was prepared in a molar ratio of 1/1/0.1, respectively. This wet alcohol mixture was then pumped into the reactor. The productivity data were obtained under the wet conditions at the same temperatures as for the dry reactant run. After raising the reaction temperature to 180°C, the temperature was lowered to 150°C. The productivities of the products was redetermined at 150°C, after which the wet alcohol feed was stopped. After allowing the catalyst to dry out under the inert gas flow, the anhydrous 1/1 mixture of methanol and isobutanol was again pumped into the reactor at the 150°C reaction temperature.

The space time yields of the DME and MIBE and of the isobutene and iso-octene hydrocarbons produced as a function of reaction temperature from the methanol and isobutanol reaction mixture, with and without water, are presented in Figure 28. As can be seen, the productivities of DME and MIBE were higher for the dry run than for the reaction with water present. The catalyst activity and productivity were restored to about the same values as those of the fresh catalyst when the reaction conditions were returned to the dry alcohol feed at 150°C. There was apparently very little deactivation with this catalyst. The presence of water had an inhibiting effect on the reactions, but this inhibiting effect was reversible.

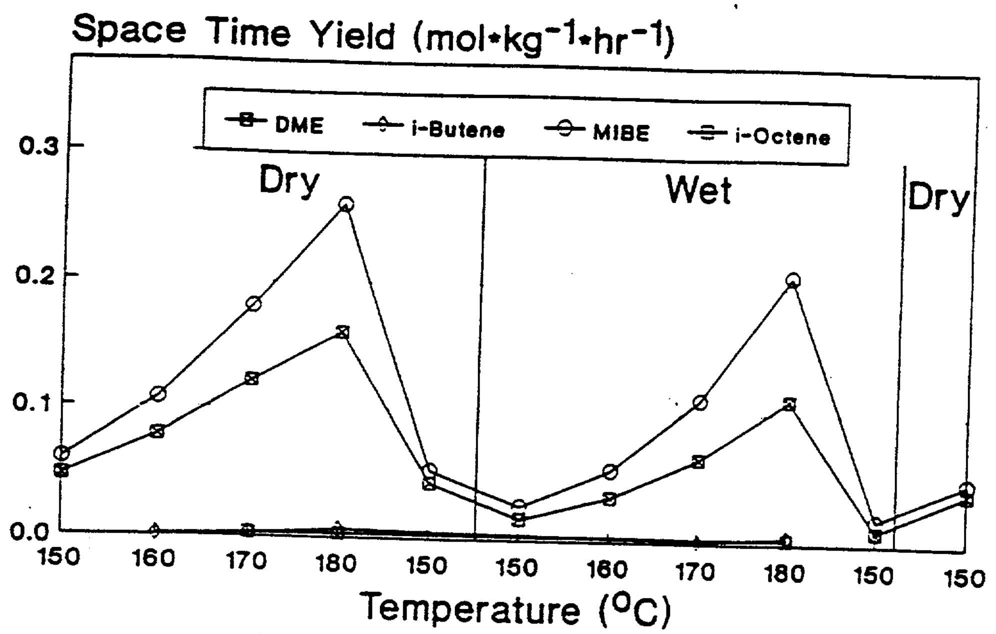

Figure 28. The effect of the methanol/isobutanol = 1/1 reactant being dry or wet on the productivity of the γ-alumina catalyst.

Conclusions From the Screening Tests

The patterns that emerge from the catalytic testing are the following:

(i) H-mordenite is a selective catalyst for dehydration of methanol to DME. Isobutanol is not converted to any ethers or dehydrated significantly to isobutene over H-mordenite under the conditions used. Evidently the pore size or shape of H-mordenite restricts the activation of isobutanol. Even though the isobutanol molecule is small enough to enter the larger channel pores of mordenite, its conversion is suppressed by one or all of the following three classic mechanisms of zeolite shape selectivity: (a) inaccessibility at low temperatures of acid centers that reside primarily in the narrow side channels of the mordenite structure (this type of size exclusion in alcohol dehydration was first studied by Weisz et al. (39), and it should be noted that acid sites in mordenite are accessible to molecules as large as 1-methyl-2-ethylbenzene at higher temperatures (40)), (b) retardation of isobutanol transport by preferential diffusion of methanol, e.g diffusive selectivity as studied by Chen et al. (41), or (c) size restrictions on the transition states involving isobutanol, isobutyl esters, and isobutyl oxonium ions, following the concept of restricted transition state selectivity in zeolites as first proposed by Csicsery (40).

(ii) Sulfate-modified zirconia is an efficient and highly selective catalyst for the dehydration of isobutanol to isobutene, with methanol dehydration to DME being suppressed. The reasons for this selectivity pattern have not been established, but it is tentatively suggested that isobutanol is more strongly bonded than methanol to the sulfate groups on the zirconia surface so that methanol activation is suppressed. The relative bonding strength of isobutanol and methanol to the sulfate-modified zirconia would have to be more markedly different than that on Nafion H because DME and MIBE are co-products with isobutene over Nafion H but not over the sulfate-modified zirconia. An alternative explanation may be dilution of acid sites, which would disfavor ether-forming reactions since they require two adjacent acid sites. Isobutanol dehydration, while also a dual site mechanism, may only require one acid functionality adjacent to a non-acid empty adsorption site.

(iii) The overall order of activities for the dehydration reactions over the inorganic acids tested is:

$$ZrO_2/SO_4^{=} > \text{H-ZSM-5 zeolite} > \text{H-mordenite} > SiO_2/Al_2O_3 > \text{H-Montmorillonite} > \gamma\text{-}Al_2O_3.$$

(iv) The inorganic catalysts are generally less active than the organic polymeric catalysts