

## ISOBUTENE FROM ISOBUTANOL/METHANOL MIXTURES OVER INORGANIC ACID CATALYSTS

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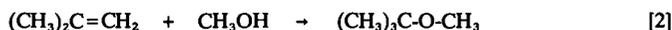
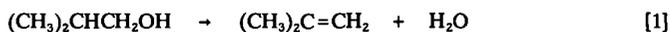
### INTRODUCTION

The increasing demand for octane boosting oxygenate compounds, particularly methyl tertiarybutyl ether (MTBE), has led to research efforts investigating alternative sources of these valuable compounds. Currently, MTBE is manufactured from methanol and isobutene *via* a liquid phase synthesis over acid resin catalysts, where isobutene is obtained as a side product from petroleum refinery FCC units (1-3). Although older FCC units can produce 8 wt% C<sub>4</sub> products in their output (4), the typical FCC refinery product slate now contains 1.4 wt% C<sub>4</sub> compounds (5), and improved processes utilizing catalytic additives such as improved ZSM-5 tend to decrease the yield of C<sub>3</sub> and C<sub>4</sub> olefins in the light ends further still (6). Thermal cracking of the isobutane in the light ends can also be carried out to obtain isobutene (5). In any case, the supply of refinery supplied isobutene is limited.

Since MTBE is now the seventh largest produced synthetic organic chemical today (7) 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 (8). Various alternatives have been sought for increasing the availability of isobutene, and one source of C<sub>4</sub> is butane from natural gas. Although, the butane content in natural gas is low, this source of C<sub>4</sub> is increasingly gaining importance. Among the processes that have been developed for the synthesis of pure isobutene is the endothermic dehydration of tertiary butanol (9).

Another possible source of isobutene for ether synthesis is isobutanol that is produced from synthesis gas. Methanol and isobutanol are the predominant products formed from H<sub>2</sub>/CO synthesis gas over alkali promoted Cu/ZnO-based catalysts (10-14). Since the two alcohols are produced together, direct coupling of these two alcohols to produce high octane ethers is also of interest. It has been shown (15,16) that over acid catalysts, the dominant reaction is direct coupling that results in the formation of methyl isobutyl ether (MIBE), a lower octane (17) isomer of MTBE. In addition to ethers, butenes were also observed, and these tended to become more abundant products over inorganic catalysts that were employed at higher temperatures than were the resin catalysts (16).

If a selective catalyst were found for converting isobutanol to isobutene with subsequent reaction with methanol, a desirable route to high octane MTBE from natural gas or coal-derived synthesis gas would be provided, as represented by Equations 1 and 2.



Such a process would alleviate isobutene dependence on petroleum feedstocks. Over the inorganic catalysts previously studied, it was shown that an equimolar mixture of methanol and isobutanol could be directly converted to a methanol/isobutene mixture in high yields with high selectivity using a sulfate-modified zirconia catalyst (16). This catalyst was found to be superior to other solid acid catalysts such as zeolites, silica-alumina and ion exchange resins. The strongly acidic zeolite H-Mordenite, on the contrary, was found to be highly selective for dehydrating the methanol in the mixture to dimethyl ether (DME) (16). No mixed ether was formed and very little dehydration of isobutanol to isobutene was seen. In the present work, the coupling and dehydration reactions were studied over H-ZSM-5 zeolite and  $\gamma$ -alumina. In addition, the pressure dependence of isobutene formation from an isobutanol/methanol mixture was examined over the  $\text{ZrO}_2/\text{SO}_4^{2-}$  catalyst.

## EXPERIMENTAL

The preparation of the sulfate-modified zirconia ( $\text{ZrO}_2/\text{SO}_4^{2-}$ ) was carried out according to the work of Hino and Arata (17).  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was added to aqueous ammonia to precipitate high surface area  $\text{Zr}(\text{OH})_4$  that was washed and dried at  $100^\circ\text{C}$  overnight. The dried  $\text{Zr}(\text{OH})_4$ , weighing 10 g was placed on a folded filter paper, and 150 ml of 1 N  $\text{H}_2\text{SO}_4$  was poured through it. The wet powder was dried at  $110^\circ\text{C}$  overnight and then calcined at  $620^\circ\text{C}$  for 3 hr. The BET surface area of this catalyst, determined from  $\text{N}_2$  adsorption/desorption data, was found to be  $60 \text{ m}^2/\text{g}$  and the sulfur content was 0.84% by weight.

The H-ZSM-5 zeolite (Mobil MZ-289) was calcined in air at  $400^\circ\text{C}$  for 2 hr prior to loading in the reactor. The Catapal-B was calcined in air at  $500^\circ\text{C}$  for 3 hr in order to activate and convert the pseudoboehmite precursor into the  $\gamma$ -alumina phase.

**Operating Conditions.** The following standard test conditions were used to study the activity and selectivity of H-ZSM-5 zeolite and  $\gamma$ -alumina:

Temperature	90, 125, 150, $175^\circ\text{C}$ (also 200, 225, $250^\circ\text{C}$ for $\gamma$ -alumina)
Pressure	1 atm (100 kPa)
Methanol feed	1.72 mol/kg catalyst/hr
Isobutanol feed	1.72 mol/kg catalyst/hr
He (+ $\text{N}_2$ trace) flow	16.0 mol/kg catalyst/hr
Catalyst weight	5.0 g

For determining the pressure dependence of the alcohol dehydration reactions and the ether synthesis reactions over the  $\text{ZrO}_2/\text{SO}_4^{2-}$  catalyst, the gas composition was maintained while the total reaction pressure was sequentially increased. The following reaction conditions were used:

Temperature	157°C
Pressure (total)	1-62 atm (0.1-63 MPa)
Methanol feed	42.2 mol/kg catalyst/hr
Isobutanol feed	21.1 mol/kg catalyst/hr
He (+ N <sub>2</sub> trace) flow	756 mol/kg catalyst/hr
Catalyst weight	2.0 g

## RESULTS AND DISCUSSION

Reactions of Methanol/Isobutanol Over H-ZSM-5 Zeolite. The space time yields of the major products obtained over H-ZSM-5 zeolite and  $\gamma$ -alumina from methanol/isobutanol = 1/1 reactants at 1 atm with He(N<sub>2</sub>) carrier gas are given in Table 1 for a range of temperatures beginning at 90°C, along with those of two of the other inorganic catalysts, H-mordenite and  $\text{ZrO}_2/\text{SO}_4^{2-}$ , originally reported in previous work (16). The H-ZSM-5 sample was found to be active for isobutanol (i-BuOH) conversion to methylisobutylether (MIBE) and butenes as well as methanol (MeOH) conversion to dimethylether (DME). Of special note is that as the temperature was increased from 125°C to 175°C, the yield of MIBE decreased while the yield of butenes significantly increased. The activation and conversion of i-BuOH over this zeolite catalyst contrasts sharply with that of the H-mordenite studied previously. The H-mordenite sample had been found to be inactive for mixed ether formation from the methanol and isobutanol mixture over the temperature range studied, as shown in Table 1. DME was formed highly selectively and in high yield with only slight conversion of isobutanol, and this was explained in terms of "shape selectivity". Although H-ZSM-5 has smaller pores than H-mordenite, 5.3 x 5.6 Å interconnecting 5.1 x 5.5 Å vs 6.5 x 7.0 Å, respectively (19), 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. This rules out sieving as an explanation for the selectivity pattern seen in H-mordenite. The relative accessibility of the reactants to the zeolitic protons at the low temperatures employed (90-175°C) may be a factor. The intersecting channels of the H-ZSM-5 structure may allow transition state geometries or better access of isobutanol to active sites than the straight non-interconnecting channel system of H-mordenite.

Reactions of Methanol/Isobutanol Over  $\gamma$ -Alumina. The  $\gamma$ -alumina was rather inactive for the conversion of the methanol/isobutanol = 1/1 reactant mixture at the lower reaction temperatures where the other inorganic catalysts were active, and, therefore, higher temperatures (200, 225, and 250°C) were utilized. As seen in Table 1, the selectivity of  $\gamma$ -alumina was unique among the catalysts. The ethers MIBE and DME were selectively formed between 125 and 175°C, while at higher temperatures isobutene formation became more significant. Although not indicated in Table 1, small quantities of iso-octene were also

produced. It is notable that the only butene formed over this  $\gamma$ -alumina was isobutene, whereas for all of the other catalysts under reaction conditions that produce isobutene, significant amounts of the linear butenes, mostly *cis*- and *trans*-2-butene, were also produced. The molar fraction of linear butenes to all butenes formed over the inorganic catalysts, excluding  $\gamma$ -alumina, was generally about one third at 150 to 175°C. The quantities of linear butenes observed were below those calculated for thermodynamic equilibrium. Figure 1 shows the equilibrium constant ratios, i.e. ratio of each linear butene to isobutene, as a function of temperature. The selectivity of isobutanol dehydration over  $\gamma$ -alumina has been studied by several workers (20,21), and it was found that isobutene was formed with over 95% selectivity. The pronounced selectivity of the  $\gamma$ -alumina may be explained by the absence of strong Brønsted acid sites on the surface of alumina (22). The  $\gamma$ -alumina surface has been shown to contain Lewis acid sites associated with basic sites (22). It has been proposed that the acidic and basic sites act concertedly to remove, respectively, the OH<sup>-</sup> from the alcoholic carbon and an H<sup>+</sup> from the neighboring tertiary carbon of isobutanol. The presence of strong Brønsted 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 (23). Thus, the absence of strong Brønsted acidity in  $\gamma$ -alumina may explain the absence of linear butenes in the product.

**Pressure Dependence of Ether and Olefin Synthesis Over Sulfated Zirconia.** The effect of reactant pressure on the activity and selectivity of the dehydration of a methanol and isobutanol mixture to butenes and ethers was studied. Nunan et al. (15) had previously studied this reaction over the very strongly acidic ion-exchange resin Nafion-H. It was shown that the rate of butene production decreased and the rate of ether production, mostly MIBE and DME, increased with increasing alcohol pressure. Their kinetic studies indicated that over Nafion-H, dehydration of isobutanol to isobutene required two acid sites. As a consequence, at higher pressures isobutanol inhibited its own dehydration. In studying the pressure dependence of these reactions over  $\text{ZrO}_2/\text{SO}_4^{2-}$ , the reaction conditions chosen in the present study are similar to those of Nunan et al. (15), and conversions were kept well below 10%.

The space time yields of the products of the reaction of methanol and isobutanol over  $\text{ZrO}_2/\text{SO}_4^{2-}$  are presented in Figure 2 as a function of alcohol pressure. Isobutene production decreased strongly with increasing pressure and ether production increased somewhat with increasing pressure. These results are similar to those observed with the Nafion-H resin catalyst (15), and this suggests that the same catalytic functions and properties are occurring on  $\text{ZrO}_2/\text{SO}_4^{2-}$  as were found for Nafion-H. The effect of pressure was reversible, i.e. when alcohol pressure was decreased to its original value, isobutene production increased and ether production decreased to their original rates. Even with the ratio of methanol to isobutanol of 2/1, it is clear that at low pressures isobutanol is selectively dehydrated to isobutene with little conversion of methanol to DME or MIBE.

It is apparent from Figure 2 that the reaction pressure hardly affected the yields of the ethers but that low pressures were needed to maximize the selective dehydration of isobutanol to isobutene. It is also evident from Figure 1 that low temperatures are needed when pathways exist (*via* carbenium ion chemistry with Brønsted acids) for the formation

of linear butenes in order to minimize the linear butenes and maximize the proportion of isobutene in the product stream.

## CONCLUSIONS

A route to the precursors of MTBE, viz. methanol and isobutene, from the products of higher alcohol synthesis from synthesis gas over alkali-promoted Cu/ZnO catalysts, i.e. methanol and isobutanol, can be made in one step *via* selectively dehydrating isobutanol in the alcohol mixture to isobutene over a sulfate modified zirconia,  $ZrO_2/SO_4^{2-}$ , catalyst at moderate temperatures and pressures (e.g. selectivity was  $\approx 88\%$  at  $157^\circ C$  with methanol/isobutanol = 2/1 under the reaction conditions in Figure 2 and  $89\%$  at  $175^\circ C$  with methanol/isobutanol = 1/1 under the conditions in Table 1). On the other hand, the H-ZSM-5 zeolite displayed a selectivity toward isobutene plus linear butenes of  $77\%$  at  $175^\circ C$  under the reaction conditions given in Table 1, and the selectivity of  $\gamma$ -alumina toward isobutene, with no detectable linear butenes, was  $53\%$  at  $250^\circ C$ . In contrast, H-mordenite selectively produced DME from the methanol/isobutanol mixture.

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## REFERENCES

1. Chase, J. D. and Galvez, B. B., Hydrocarbon Process., **60**(3), 89 (1981).
2. Chase, J. D., in "*Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals*," ed. by R. G. Herman, Plenum Press, New York, 307 (1984).
3. Hydrocarbon Process., **68**(11), 96 (1989); and Satterfield, C. N., "*Heterogeneous Catalysis in Industrial Practice*," 2nd Ed., McGraw-Hill, Inc., New York, 260 (1991).
4. Haggin, J., Chem. Eng. News, **67**(23), 31 (1989).
5. Monfils, J. L., Barendregt, S., Kapur, S. K., and Woerde, H. M., Hydrocarbon Process., **71**(2), 47 (1992).
6. Krishna, A. S., Hsieh, C. R., English, A. R., Pecoraro, T. A., and Kuehler, C. W., Hydrocarbon Process., **70**(11), 59 (1991).
7. Chem. Eng. News, **70**(15), 17 (1992).
8. Chem. Eng. News, **70**(19), 26 (1992).

9. Abraham, O. C. and Prescott, G. F., Hydrocarbon Process., 71(2), 51 (1992).
10. Klier, K., Herman, R. G., and Young, C.-W., Preprint, Div. Fuel Chem., ACS, 29(5), 273 (1984).
11. Klier, K., Herman, R. G., Nunan, J. G., Smith, K. J., Bogdan, C. E., Young, C.-W., and Santiesteban, J. G., in "*Methane Conversion*," ed. by D. M. Bibby, C. D. Chang, R. F. Howe, and S. Yurchak, Elsevier, Amsterdam, 109 (1988).
12. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C.-W., and Herman, R. G., J. Catal., 116, 195 (1989).
13. Nunan, J. G., Herman, R. G., and Klier, K., J. Catal., 116, 222 (1989).
14. Herman, R. G., in "*New Trends in CO Activation*," ed. by L. Guzzi, Elsevier, Amsterdam, 265 (1991).
15. Nunan, J. G., Klier, K., and Herman, R. G., J. Chem. Soc., Chem. Commun., 676 (1985).
16. Klier, K., Herman, R. G., Johansson, M. A., and Feeley, O. C., Preprint, Div. Fuel Chem., ACS, 37(1), 236 (1992).
17. Spindelbaker, C. and Schmidt, A., Erdoel, Erdgas, Kohle, 102, 469 (1986).
18. Hino, M. and Arata, K., J. Chem. Soc., Chem. Commun., 851 (1980).
19. Meier, W. M. and Olson, D. H., "*Atlas of Zeolite Structure Types*," Butterworths & Co. Ltd., Cambridge, 102 (1988).
20. Knozinger, H. and Scheglila, A., J. Catal., 17, 252 (1969).
21. Herling, J. and Pines, H., Chem. & Ind., 984 (1963).
22. Peri, J. B., J. Phys. Chem., 69, 231 (1965).
23. Kotsarenko, S. and Malysheva, L. V., Kinet. Katal., 24, 877 (1983).

**TABLE 1. Yields over Inorganic Catalysts  
(mol/kg cat/hr)**

Pressure 1 atm  
 Methanol feed 1.72 mol/kg catalyst/hr  
 Isobutanol feed 1.72 mol/kg catalyst/hr  
 He + N<sub>2</sub> flow 16.0 mol/kg catalyst/hr  
 Catalyst weight 5.0 g

	T <sub>Reaction</sub>	DME	Butenes	MIBE	MTBE	C <sub>8</sub> ether
H-Mordenite *	90°C	0.060	----	----	----	----
	125°C	0.660	----	----	----	----
	150°C	0.830	0.068	----	----	0.004
ZrO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> *	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	1.29	0.049	0.007	----
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	----	----

\* Reference 16.

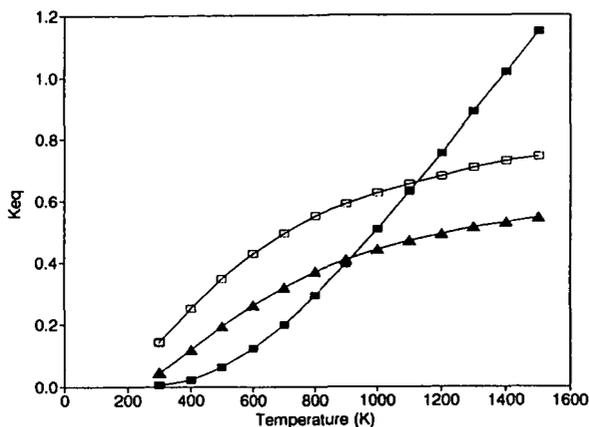


FIGURE 1. The dependence of the calculated equilibrium constants, i.e. mole ratio of linear butenes to isobutene, on the reaction temperature for the conversion of isobutene into 1-butene (■), cis-2-butene (▲), and trans-2-butene (□), beginning at STP conditions.

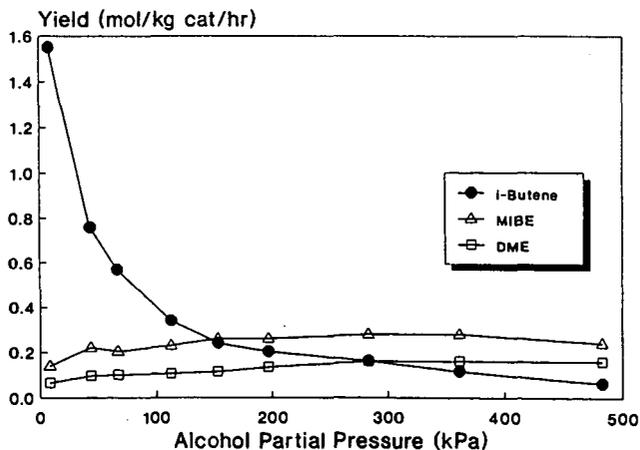


FIGURE 2. Variations of the product yields with the total alcohol partial pressure (methanol/isobutanol = 2/1) over the  $ZrO_2/SO_4^{2-}$  catalyst at 157°C. The reaction conditions are described in the Experimental Section.