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Conversion of methanol and isobutanol to MTBE

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Abstract

Over the resin catalyst Amberlyst 15, and under our reaction conditions, the yield of MTBE (methyl *tert*-butyl ether), from the reaction of methanol and isobutene, is at a maximum in the temperature range of 40–60°C. Slightly higher temperatures (70–90°C) are needed when using zeolite H-ZSM-5 as catalyst for the etherification reaction. When isobutanol and methanol are passed over these catalysts at temperatures below 100°C, extremely low conversions (<1% by mass) are obtained. Over the resin catalyst and at 121°C, 3.3% of MTBE+MIBE (methyl isobutyl ether) is obtained where MTBE:MIBE=1:7.4. Since the initial rate of the etherification reaction has been shown to be first order in the alkene, we investigated the dehydration reaction of isobutanol over H-ZSM-5. It was found that this reaction proceeds at temperatures above 150°C, indicating that the formation of the butenes from isobutanol proceeds at a higher temperature than the etherification reaction. Furthermore, our results with Amberlyst 15 show that the resin catalyst is unable to catalyze the isobutanol dehydration reaction within its recommended usable temperature range. A two-reactor system was therefore employed to implement the overall catalytic conversion of methanol and isobutanol to MTBE. For the dehydration step we employed a silica–alumina catalyst at 225°C, since this catalyst exhibits a higher dehydration activity for isobutanol than for methanol, as compared with γ -alumina and H-ZSM-5. The product stream from the dehydration step was then fed to reactor 2 which was loaded with the Amberlyst 15 catalyst maintained at 50°C. The two-reactor system produced a significantly higher yield of MTBE+MIBE (27.8%), with the MTBE:MIBE ratio being reversed to 11.7:1.

Key words: Amberlyst 15; etherification; isobutanol; methanol; MTBE; ZSM-5

INTRODUCTION

For the synthesis of the high-octane gasoline additive methyl *tert*-butyl ether, MTBE, the alkene precursor, isobutene, is currently obtained as a by-product of catalytic or steam cracking refinery operations [1]. It is anticipated, however, that the supply of isobutene from these sources will not be sufficient to meet future demand [2], and as a consequence, alternative routes to this branched alkene have been developed or are being investigated. These include

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the dehydrogenation of isobutane [3], the dehydration of *tert*-butanol [4] and of isobutanol [5], the exhaustive metathetical ethenolysis of branched alkenes [6] and the catalytic skeletal isomerization of the linear butenes [7]. Another route that has recently been considered is the direct coupling of methanol and isobutanol [8], which are two of the major products, along with ethanol and 1-propanol, of the catalytic higher alcohol synthesis (HAS) [9]. Klier and Herman [10] have shown that although the synthesis of MTBE from methanol and isobutanol is thermodynamically favoured, the reaction is kinetically limited. In the reaction of the binary alcohol mixture, using Nafion-H micro-saddles as catalyst, methyl isobutyl ether, MIBE, the low-octane isomer of MTBE [10], is obtained with high selectivity. With Amberlyst 15 (A15), the resin catalyst used industrially for the production of MTBE from methanol and isobutene [11], both MTBE and MIBE, at approx. a 1:4 ratio, are obtained from the reaction of methanol and isobutanol [12]. Similar high selectivities to MIBE were observed using solid inorganic acid catalysts such as mordenite, $\text{SO}_4^{2-}/\text{ZrO}_2$, silica-alumina and montmorillonite [12].

We have therefore initiated an investigation into the synthesis of MTBE from the catalytic conversion of the HAS alcohols, methanol and isobutanol, and the results of our studies obtained using a variety of acid catalysts are presented in this paper. A two-stage catalytic process for the production of MTBE from the binary alcohol mixture is described.

EXPERIMENTAL

The catalytic experiments were conducted in stainless steel tubular fixed-bed flow microreactors with an I.D. of 15 mm [13]. Methanol and isobutanol (A.R., Merck) were introduced into the reactors using a Sage syringe pump at the flow-rates indicated in the text. Brooks mass flow controllers were used to regulate the flows of isobutene and nitrogen. All reactions were carried out at ambient pressure and nitrogen was used as carrier gas at a flow-rate of 20 ml/min. Analyses of the reaction products were carried out using an on-line gas chromatograph fitted with a Porapak Q column. For the separation of MTBE and MIBE, a DB-1 capillary column was used and for the separation of the butene isomers, a Plot fused silica $\text{Al}_2\text{O}_3/\text{KCl}$ capillary column. Catalytic activities were determined at 20 min on-stream and the results are reported in terms of mass percentages of species (feed and products, excluding water) observed in the product streams. In those cases where only the percent of products is given, the balance is the unreacted feed. For the two-reactor system, the product stream from reactor 1 was first passed through a condenser before it was sent to reactor 2, in order to remove the water produced in the dehydration step, thus minimizing the formation of *tert*-butyl alcohol [1,14].

Amberlyst 15 was purchased from Rohm and Haas, the silica-alumina was obtained from Harshaw (Si-235-1T) and the γ -alumina originated from La-

porte. The ZSM-5 sample with a $\text{SiO}_2/\text{Al}_2\text{O}_3 = 60$ was prepared in our laboratories using a previously published method [15]. Prior to use, the resin catalyst was washed with water/methanol mixtures as described in ref. 16.

RESULTS AND DISCUSSION

The results in Fig. 1 show that the etherification reaction of methanol and isobutene to form MTBE proceeds readily at low temperatures over the resin catalyst Amberlyst 15. Under our reaction conditions, maximum yield of MTBE is observed in the range of 40–60°C. From Fig. 1 we can also observe that slightly higher reaction temperatures are needed to carry out the reaction when zeolite H-ZSM-5 is used as catalyst [17,18]. With the zeolite catalyst, the yield of MTBE is at a maximum between 70 and 90°C.

Under similar reaction conditions, we examined the conversion of methanol and isobutanol again using Amberlyst 15 and zeolite H-ZSM-5 as catalysts. An excess of methanol was used in these experiments. With the resin catalyst, and up to its maximum recommended usable temperature of 90°C [19,20], only extremely low conversions were observed (0.2% by mass MTBE+MIBE, see Table 1). At higher temperatures, up to 121°C [10], the conversion to MTBE+MIBE increased to 3.3% where the ratio of MTBE:MIBE was found to be 1:9. From these results we can conclude that the resin catalyst, up to its maximum usable temperature and at even higher temperatures, does not catalyze the MTBE synthesis reaction to any significant extent when the reactants are methanol and isobutanol. The coupling of the alcohols gives MIBE

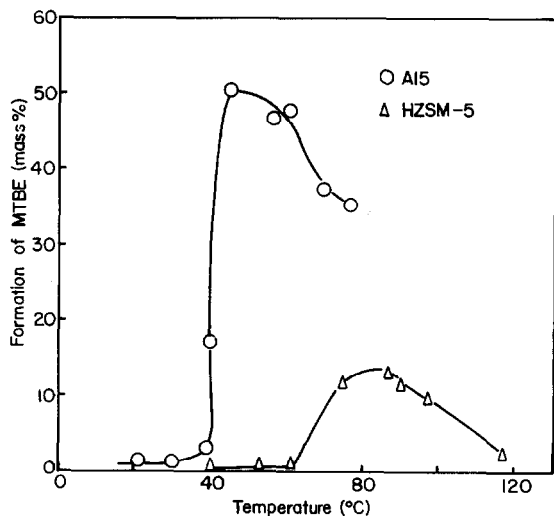


Fig. 1. Plot of percent MTBE produced versus reaction temperature (total MHSV = 3.9, methanol:isobutene mol ratio = 1.3:1).

TABLE 1

Conversion of methanol and isobutanol over A15 and H-ZSM-5 catalysts as a function of temperature^a

Catalyst	A15			H-ZSM-5	
	84	100	121 Yield ^b	75	100
Temperature (°C)					
Products					
DME	-	-	3.5	-	-
C ₄ ⁻	0.05	0.3	3.7	-	0.2
<i>tert</i> -Butanol	-	-	0.05	-	0.1
MTBE + MIBE	0.2	0.7	3.3 ^c	0.01	0.4 ^d
DIBE ^e	-	0.02	0.1	0.02	-
Other HCs ^f	0.1	0.1	0.2	0.6	1.74

^a Total MHSV = 1.6 h⁻¹, methanol:isobutanol mol ratio = 2.3:1.

^b In mass-%. Balance is methanol + isobutanol. Percent H₂O produced is excluded.

^c Ratio of MTBE:MIBE = 1:9.

^d Ratio of MTBE:MIBE ≈ 1:9.

^e DIBE = diisobutyl ether.

^f HCs = hydrocarbons.

preferentially. Other catalytic reactions taking place are the dehydration reactions of the two alcohols to give dimethyl ether (DME) from methanol and the butenes from isobutanol, each at less than 4% by mass.

Therefore, whereas with methanol and isobutene and with A15 as catalyst, high conversions to MTBE are observed at low temperatures, with the methanol and isobutanol mixture, only extremely low conversions are obtained. A similar almost total lack of reactivity of the alcohol mixture was observed in the experiments where H-ZSM-5 was used as catalyst (see Table 1) and in the temperature range where MTBE formation is observed in the experiments using isobutene and methanol as the reactants (see Fig. 1).

In their publications [21,22], Ancillotti et al. have shown that at stoichiometric or higher alcohol:isobutene ratios, the initial rates show a zero order in the alcohol and a first order in the alkene. These authors concluded that the data agreed with an ionic mechanism whereby the protonation of the alkene by the solvated proton is believed to be the rate-determining step for the etherification reaction. This suggests that the absence of the alkene in significant concentrations in the alcohol mixture and in its product stream accounts for the low reactivities observed in Table 1, and that the presence of the isobutene is therefore a prerequisite for MTBE formation.

The dehydration reactions of isobutanol and of an isobutanol and methanol mixture, using zeolite H-ZSM-5 as catalyst, were therefore examined and the results obtained are shown in Figs. 2 and 3. With isobutanol, significant conversions to the C₄ alkenes are only observed above 150°C (see Fig. 2). At tem-

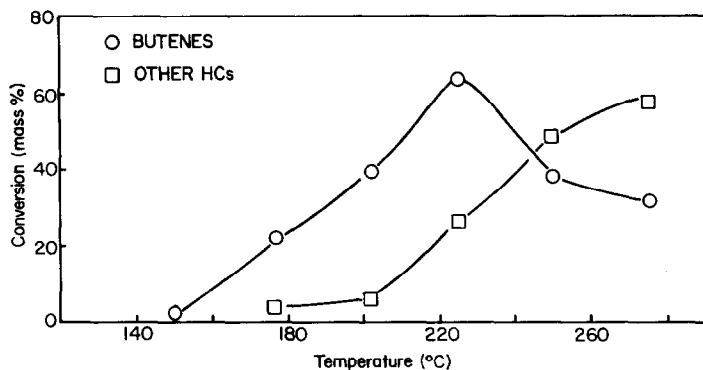


Fig. 2. Dehydration of isobutanol as a function of temperature (catalyst: H-ZSM-5, MHSV = 1.6 h⁻¹).

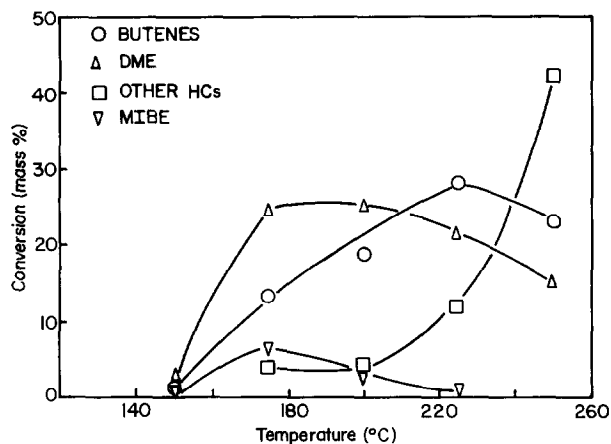


Fig. 3. Dehydration of a methanol and isobutanol mixture as a function of temperature (catalyst: H-ZSM-5, total MHSV = 1.6 h⁻¹, methanol: isobutanol mol ratio = 2.3:1).

peratures higher than 225°C, moreover, the yield of the butenes decreases drastically due to the formation of higher oligomers. In the case of the binary mixture (Fig. 3), the two dehydration products, DME and C₄⁻, are similarly observed at reaction temperatures higher than 150°C. It was also observed that at these high temperatures (over H-ZSM-5), the yield of MTBE + MIBE is still relatively low. The maximum yield of the two ethers was obtained at 175°C (6.4%, MTBE: MIBE ≈ 1:28).

From the results depicted in Figs. 1-3, obtained when we have used the same type of catalyst, viz. H-ZSM-5, to carry out the two reactions under consideration, viz. etherification and isobutanol dehydration, we can conclude that a higher reaction temperature is needed for the alcohol dehydration reaction

(> 150°C), compared with that required for the etherification reaction (< 100°C). These results demonstrate that the dehydration reaction of isobutanol is a more difficult or demanding acid-catalyzed reaction [23] than the reaction of the alkene and the alcohol to form the branched ether MTBE. As previously shown by Guisnet [24,25], the more difficult/demanding the acid-catalyzed reaction, the higher the temperature and/or the strength of the acid sites needed to implement the reaction.

Therefore, the inability of the resin catalyst to catalyze the relatively more difficult dehydration reaction of isobutanol to form the alkenes, at temperatures below 90°C (see Table 1), i.e. within the temperature range where MTBE synthesis from isobutene and methanol is favoured, accounts for the observed low conversions to MTBE when the binary alcohol mixture is passed over the A15 catalyst. Further, the higher alcohol dehydration temperatures (over H-ZSM-5 for example) do not favour the MTBE synthesis reaction, but favour instead the decomposition of the ether to the reactants [26] as shown in Fig. 4.

The above results suggested to us that for the overall catalytic conversion of methanol and isobutanol to MTBE, the reaction ought to proceed via an initial isobutanol dehydration step over a catalyst at a higher temperature, followed by the etherification reaction over a second catalyst maintained at a lower temperature. A one-reactor system is therefore precluded for the types of catalyst examined in this report, due to the different temperature requirements of the two reactions. From our results (Fig. 1) and those of other workers [11], the obvious choice of catalyst for the ether synthesis is of course the resin catalyst. In an effort to select a suitable isobutanol dehydration catalyst, we investigated the dehydration activity of γ -alumina, silica-alumina and H-ZSM-

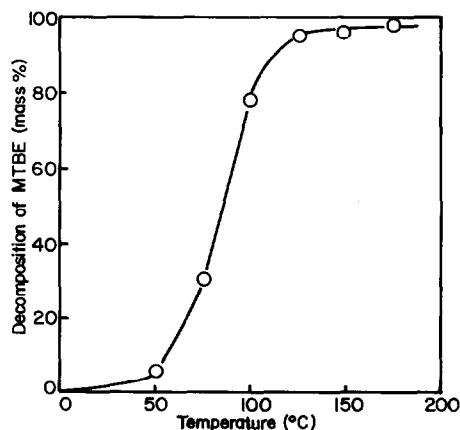


Fig. 4. Plot of percent MTBE decomposition versus reaction temperature (catalyst: H-ZSM-5, MHSV = 1.5 h⁻¹).

5. It should be noted, however, that apart from a high isobutanol dehydration activity, the catalyst has to exhibit a methanol dehydration activity that is as low as possible, since this latter alcohol has to be utilized in the subsequent etherification step.

The results for the dehydration of the alcohol mixture obtained over the above-mentioned three types of solid acid catalyst are shown in Figs. 3, 5 and 6 and the following observations can be made:

(i) With H-ZSM-5 (Fig. 3), the conversion of methanol to DME is higher than that of isobutanol to the butenes (C_4^- :DME mol ratio = 0.7:1 at 200°C).

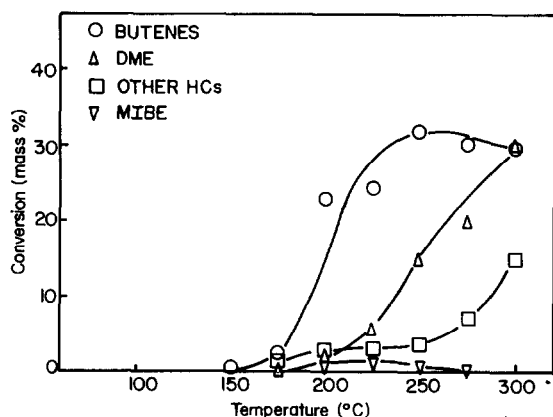


Fig. 5. Dehydration of a methanol and isobutanol mixture as a function of temperature (catalyst: silica-alumina, total MHSV = 1.6 h⁻¹, methanol: isobutanol mol ratio = 2.3:1).

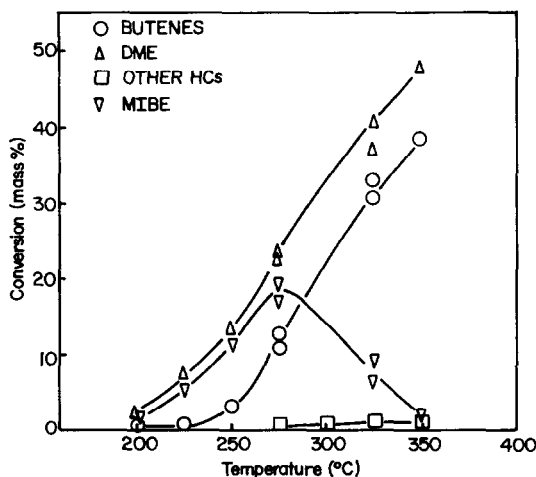


Fig. 6. Dehydration of a methanol and isobutanol mixture as a function of temperature (catalyst: γ -alumina, total MHSV = 1.6 h⁻¹, methanol: isobutanol mol ratio = 2.3:1).

TABLE 2

Composition of C₄⁻ fraction obtained from the dehydration of isobutanol with the silica–alumina catalyst

Temperature (°C)	225	250
	%	
<i>trans</i> -2-Butene	15.3	18.8
1-Butene	5.2	6.5
Isobutene	69.2	62.0
<i>cis</i> -2-Butene	10.3	12.7

TABLE 3

Typical feed and product streams from the two-reactor system^a

Compounds	Mass-%		
	Feed	Products from reactor 1 ^b	Products from reactor 2 ^c
DME	–	5.8	12.5
Methanol	49.1	50.5	23.4 ^d
C ₄ ⁻	–	35.5	32.8
<i>tert</i> -Butanol	–	0.1	1.2
MTBE + MIBE	–	2.1 ^e	27.8 ^f
Isobutanol	50.9	1.8	–
Other HCs	–	4.2	2.9

^a Using 1 g of each catalyst; total alcohol flow-rate of 2.4 ml/h; methanol:isobutanol mol ratio=2.3:1.

^b Temp. = 225°C.

^c Temp. = 50°C.

^d Methanol mass balance is deficient due to loss of the alcohol by condensation along with the water in the condenser.

^e MTBE:MIBE=1:14.0.

^f MTBE:MIBE=11.7:1.

(ii) With silica–alumina (Fig. 5), the degree of isobutanol dehydration is higher than that of methanol (C₄⁻:DME=3.6:1 at 225°C; see Table 2 for analysis of the C₄⁻ isomers).

(iii) With γ -alumina (Fig. 6), methanol is preferentially dehydrated (C₄⁻:DME=0.7:1 at 350°C).

From the above results we can conclude that the maximum C₄⁻ formation with a minimum methanol dehydration occurs with the silica–alumina catalyst. For the two-reactor process, therefore, silica–alumina was employed in the first reactor (for the dehydration step) and Amberlyst 15 in the second reactor. The results obtained, where the product stream of reactor 1 is fed to

reactor 2, are listed in Table 3. An MTBE + MIBE yield of 27.8% by mass is observed at 50°C. And most significantly, the ratio of MTBE:MIBE in this instance was found to be 11.7:1.

CONCLUSIONS

The results from the two-reactor system show that:

(i) MTBE formation from methanol and isobutanol has significantly increased.

(ii) The MTBE:MIBE ratio has been reversed from 1:9 (using the A15 catalyst only) to 11.7:1 (using the two-step process).

(iii) The necessity of the two-reactor system, for the types of catalyst discussed in this paper, has thus been demonstrated.

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