Selective Coupling of Methanol and 2-Methylpropan-1-ol to give 1-Methoxy-2-methylpropane (Methyl Isobutyl Ether)

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The superacid Nafion-H resin selectively catalyses the coupling of the two alcohols methanol and 2-methylpropan-1-ol to give methyl isobutyl ether.

The selective synthesis of ethers in the C_5 to C_6 range, *viz.* methyl t-butyl ether (MTBE) and methyl t-pentyl ether (MTPE), where methanol is combined with the corresponding C_4 or C_5 tertiary alkene, has received much attention in recent years[1—5] owing to the use of these ethers as effective anti-knock replacements for lead in gasoline. We now report on the synthesis of an ether related to MTBE, *i.e.* methyl isobutyl ether (MIBE), which was found to be selectively formed through the direct coupling of methanol and 2-methylpropan-1-ol (Bu^iOH) over the Nafion-H resin catalyst [reaction (1)].

$$\underset{}{MeOH} + \underset{Bu^iOH}{Me_2CHCH_2OH} \rightarrow \underset{MIBE}{MeOCH_2CHMe_2} + H_2O \qquad (1)$$

The catalyst used was a perfluorinated sulphonic acid resin having high thermal stability and acid strength in the superacid range. Nafion-H has been used by Olah and co-workers in extensive studies of alkylation reactions[6—8] and alcohol dehydration to form alkenes and ethers[6,9] in which carbenium ions were considered to be important intermediates. The coupling of MeOH and Bu^iOH to MIBE using either resins or other heterogeneous catalysts has not been reported. The absence of MTBE as a product in the present work (g.c.–mass spectrometry) suggests a mechanism not involving carbenium ions but rather the intermediacy of oxonium ions or sulphonic esters.

The reaction of MeOH with Bu^iOH was carried out in a stainless steel flow reactor under $101.3—7.6 \times 10^3$ kPa (1 atm = 101.325 kPa) total pressure, with nitrogen as a carrier gas; the reactor and mode of product analysis have been described.[10,11] Preliminary studies showed that maximum selectivity for MIBE was achieved using a mole ratio of MeOH to Bu^iOH of 2:1 and results using this molar ratio are presented here. Other products included water, Me_2O, butenes, and to a lesser extent, octenes and Bu^i_2O. We used both the regular gel form of the the resin (Nafion-H) and a porous form (Nafion-H Micro-Saddles). Both forms possessed an ion-exchange capacity of 0.9 mequiv./g and were in the fully acid form.

Figure 1 shows the effect of alcohol partial pressure ($P_{alc.}$) on the reaction rate, together with data for MeOH and Bu^iOH alone over the Nafion-H for comparison. Methanol gave only Me_2O and water, but MeOH–Bu^iOH and Bu^iOH produced both ethers and alkenes. For both methanol and the alcohol mixture, the rate increased rapidly with pressure to $P_{alc.} = 86.2$ kPa, but most dramatically for the alcohol mixture, whereas Bu^iOH showed a distinctly inverse dependence on alcohol partial pressure. Figure 2 shows the product composition as a function of alcohol pressure for the Bu^iOH–MeOH mixture, and indicates that the rapid rise of rate with increasing pressure observed in Figure 1 is due almost solely to a rapid and selective increase in the rate of MIBE formation as a function of alcohol partial pressure. Further, if the ether-forming reaction were to proceed with equal reactivity for Bu^iOH and MeOH statistically, a product ratio of MIBE : Me_2O : Bu^i_2O of 4 : 4 : 1 would be expected from the MeOH : Bu^iOH ratio of 2 : 1 employed. Remarkably however, the MIBE : Me_2O : Bu^i_2O product ratio was 19 : 9 : 1 at pressures > 150 kPa, significantly in favour of the mixed ether,

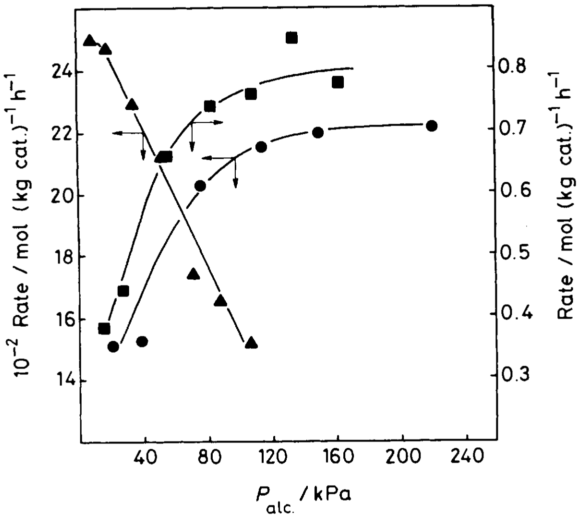

Figure 1. Effect of alcohol partial pressure ($P_{alc.}$) on the steady state reaction rates. Total pressure, 1.344×10^3 kPa; feed rate of N_2 + alcohol, 250 mol (kg cat.)$^{-1}$ h^{-1}; catalyst (Nafion-H) wt., 2.0 g. ●, MeOH; ■, MeOH–Bu^{i}OH (2:1); ▲, Bu^{i}OH.

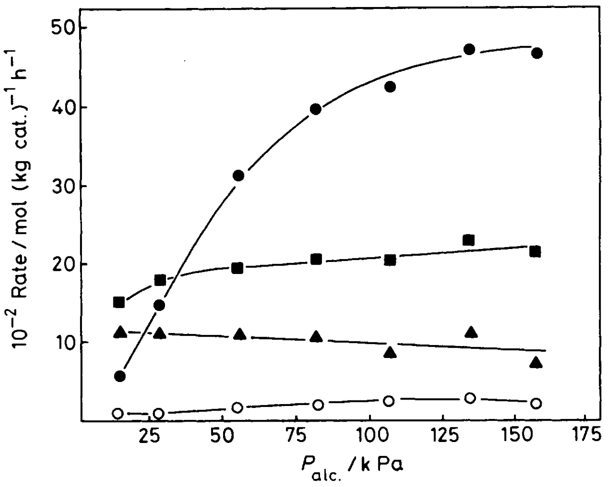

Figure 2. Effect of alcohol mixture (MeOH–Bu^{i}OH, 2:1) partial pressure ($P_{alc.}$) on the steady-state rates of conversion into: ●, MIBE; ■, Me_2O; ▲, butenes; ○, Bu^i_2O. Total pressure, 1.344×10^3 kPa; T, 396 K; feed of N_2 + alcohol, 250 mol (kg cat.)$^{-1}$ h^{-1}; catalyst (Nafion-H) wt., 2.0 g.

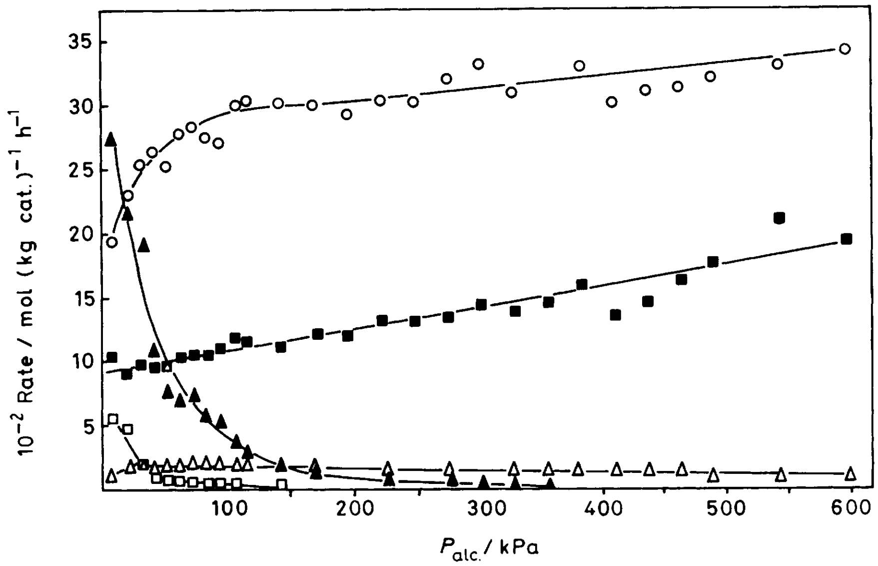

Figure 3. Variation of product yield with alcohol mixture partial pressure at a steady-state reaction rate. Reactants, MeOH–Bu^{i}OH (2:1); alcohol feed, 15.59 mol (kg cat.)$^{-1}$ h^{-1}; N_2 feed, 186 mol (kg cat.)$^{-1}$ h^{-1}; catalyst (Nafion-H Micro-Saddles) wt., 1.0 g; T, 389 K. ○, MIBE; ■, Me_2O; ▲, butenes; □, octenes; △, Bu^i_2O.

Table 1. Apparent activation energies $E_A{}^{App.}$ for alcohol dehydration to ethers and alkenes. Catalyst, Nafion-H; N_2 feed, 186 mol (kg cat.)$^{-1}$ h^{-1}; catalyst wt., 2.0 g.

	Reactant $E_A{}^{App.}$/kJ mol^{-1}		
Product	MeOH[a]	Bu^{i}OH[b]	MeOH–Bu^{i}OH[c]
Me_2O	87.5	—	84.2
MIBE	—	—	84.3
Butenes + octenes	—	169.0	144.6
Bu^i_2O	—	84.7	97.0

[a] $P_{alc.}$ 146.8 kPa; T 362—388 K. [b] $P_{alc.}$ 64.1 kPa; T 380—410 K. [c] $P_{alc.}$ 101.3 kPa; T 359—402 K.

MIBE. This result indicates that one of the two alcohols is preferentially activated, *e.g.* by proton attachment to form an oxonium ion or by esterification of the resin SO_3H group, which then reacts preferentially with the second alcohol.

Good Arrhenius plots were observed for ether and alkene formation, the resulting apparent activation energies being presented in Table 1. The activation energy for ether formation is much lower than for alkene formation, thus explaining the higher selectivity for ether formation at low temperatures but also predicting an increase in alkene formation with increasing temperature. The dehydration of the alcohol mixture over Nafion-H Micro-Saddles was studied over a wide pressure and temperature range as shown in Figures 3 and 4. Again, an initial large increase of the steady-state rate of MIBE formation with increasing pressure was observed, accompanied by a substantial suppression of

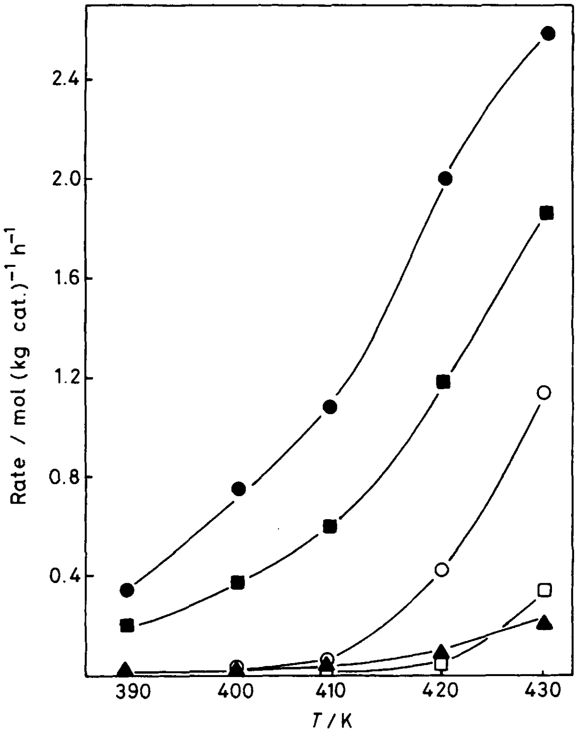

Figure 4. Effect of temperature on the reaction rate. Reactants, MeOH–Bu^iOH (2:1); alcohol feed, 15.59 mol (kg cat.)$^{-1}$ h^{-1}; N_2 feed, 186 mol (kg cat.)$^{-1}$ h^{-1}; catalyst (Nafion-H Micro-Saddles) wt., 1.0 g; total pressure, 7.582 × 10^3 kPa. ●, MIBE; ■, Me_2O; ○, butenes; □, octenes; ▲, $\text{Bu}^i{}_2O$.

alkene formation (compare Figures 2, 3, and 4). Increasing temperature increased the rates of both ether and alkene formation (Figure 4), but the selectivity for alkene formation increased rapidly at higher temperatures, as predicted by the activation energy data.

In conclusion, high selectivity for MIBE formation (42.0 mol% of product mixture at 430 K) with accompanying high yields [230 g (kg cat.)$^{-1}$ h^{-1}] can be achieved under mild conditions. Further, no catalyst deactivation was observed over the several weeks of carrying out the coupling reaction with both the regular gel and the porous forms of Nafion-H.

The authors appreciate Professor T. E. Young's suggestion that the alcohol activation may involve the sulphate ester. We thank the U.S. Department of Energy for financial assistance.

Received, 6th February 1985; Com. 165

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