Single-pot Synthesis of Methyl *tert*-Butyl Ether from *tert*-Butyl Alcohol and Methanol: Dodecatungstophosphoric Acid supported on Clay as an Efficient Catalyst

G. D. Yadav* and N. Kirthivasan

Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India

The efficacy of various solid acid catalysts and exchanged clays in a single-pot synthesis of methyl *tert*-butyl ether (MTBE) from *tert*-butyl alcohol and methanol is investigated; dodecatungstophosphoric acid (HPA) supported on K-10 clay gives the best yield with highest selectivity for MTBE.

MTBE is a useful fuel oxygenate in reformulated gasoline.[1] Of all the oxygenates, the tertiary ethers have gained wide acceptance in comparison with lighter alcohols. Despite having higher volatility, MTBE is favoured over ETBE and TAME owing to the low cost of its precursors.

MTBE is currently manufactured from isobutene and methanol over Amberlyst-15, which despite its good activity has several limitations, such as thermal instability, loss of acid sites owing to leaching and the process itself requires a considerable excess of methanol over isobutene, necessitating recycling. Several other types of catalysts have been reported such as ZSM-5, Y-zeolite, and triflic acid loaded on ZSM-5 and Y-zeolite.[2a] Chu and Kuhl[2b] have employed zeolite β, ZSM-5, ZSM-11 and rare earth exchanged zeolites Y and mordenite for the etherification of isobutene with methanol, whereas Bylina *et al.*[3] and Adams *et al.*[4] have employed ion exchanged montmorillonite such as Al^{3+} pillared clay, K-10 and K-306 clays.

Several strategies to increase production of isobutene for MTBE manufacture are being investigated.[5–7] The production of MTBE, from syngas, and the catalytic etherification and distillation in a packed bed reactor look promising.[1]

The use of *tert*-butyl alcohol in gasoline is also attractive because its properties are close to those of the oxygenate ethers and the ARCO process for the manufacture of propylene oxide from propylene leads to significant formation of *tert*-butyl alcohol. Nonetheless, a major technological breakthrough in the production of *tert*-butyl alcohol is still awaited.

The only study relevant to our work has been that of Matouq *et al.* who have used homogeneous and supported heteropolyacids.[8] It is in this context that we have studied the synthesis of MTBE from the etherification reaction of methanol and *tert*-butyl alcohol over a number of catalysts including heteropolyacids supported on clay. K-10 clay supported dodecatungstophosphoric acid catalyst has unique characteristics that have given a very high conversion and the best selectivity for MTBE.

All experiments were conducted in a 100 ml Parr autoclave. The reactants and catalyst were charged to the reactor and the temperature was raised to 85 °C. An initial sample was then drawn and the reaction was monitored by periodic GC of samples using TCD, on a Porapak-Q column (2 m × 3.2 mm). 1,4-Dioxane was used as an internal standard as well as a solvent.

Fourteen catalysts were studied (Table 1). K-10 montmorillonite, a commercial catalyst (Fluka) was used as the precursor clay for preparing the exchanged and supported catalysts. Na^+ clay was prepared by suspending 10 g of K-10 in 1×10^{-3} m^3 of saturated NaCl solution followed by washing (deionised water) until it was free from chloride ions. This was then used for the preparation of the exchanged clays.

Al^{3+} EC was prepared according to the method of Bukka *et al.*[9] ZrO^{2+} EC[10] and Cr^{3+} EC,[11] sulfated zirconia[12] and HPA–silica[12] were prepared by literature methods. Amberlyst-15 was obtained from Rohm and Hass, USA.

20 mass% HPA–clay was prepared by wet impregnating 2 g of HPA from a methanolic solution onto 8 g of clay. This catalyst was then dried at 120 °C for 1 h and calcined at 285 °C for 3 h. A similar procedure was followed for the preparation of 30 mass% HPA–silica calcined at 285 °C and 20 mass% HPA–carbon calcined at 285 °C.

K-10 is an acid activated montmorillonite clay based on the Bavarian montmorillonite Tonsil-13. It has a relatively high alumina content at 14% and surface area of 220–270 m^2 g^{-1}, compared to the natural montmorillonite and has a reduced exchange capacity of 50–60 mequiv. per 100 g. It has been reported that the acid treatment imposed on the montmorillonite in the preparation of K-10 changes its character to '25–50% clay' and the large surface area and its surface acidity arise from its remaining exchange capacity.[13,14] Dispersion of superacidic dodecatungstophosphoric acid lends it higher reactivity, (Hammett acidity values of $H_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are *ca.* −13.5).[15]

The presence of the cations in the interlayers could be judged from the increase in the activity from the precursor Na^+ montmorillonite to the respective exchanged catalysts. Furthermore, Al^{3+} and ZrO^{2+} were white whereas the Cr^{3+} exchanged clay was green indicating that exchange of chromium ions had taken place. X-Ray diffractometry analysis of these interlayered clays did not show any increase in the basal spacing. This is because the clay framework becomes rigid owing to excessive acid treatment. These results are consistent with the work of Clark *et al.*[16]

Table 1 lists the results of the experiments conducted under otherwise similar conditions of mole ratio of reactants, catalyst loading (mass% of entire reaction mass), speed of agitation, temperature and reaction times. The conversions are based on *tert*-butyl alcohol which was taken as a limiting reactant with excess of methanol (1:2, Bu^tOH:MeOH). MTBE, isobutene and water were the products of the reaction. The influence of external mass-transfer resistance was verified independently

Table 1 Activities of the catalyst used for the synthesis of MTBE[a]

Catalyst	Conversion of Bu^t OH (%)	Selectivity for MTBE (%)
Na^+ Montmorillonite	21	33
Al^{3+} EC (5 mequiv. Al^{3+}/g calcined at 450 °C)[b]	24	37
Al^{3+} EC (25 mequiv. Al^{3+}/g calcined at 450 °C)	34	73
Al^{3+} EC (25 mequiv. Al^{3+}/g dried at 120 °C)	25	84
ZrO^{2+} EC	52	94
Cr^{3+} EC	44	95
Sulfated zirconia	66	93
K-10 Montmorillonite	56	70
30 mass% HPA–silica (calcined at 650 °C)	8	100
30 mass% HPA–silica (calcined at 285 °C)	55	76
20 mass% HPA–K-10 clay (calcined at 285 °C)	71	99
Amberlyst-15	74	86
20 mass% HPA–carbon (calcined at 285 °C)	0	0
HZSM-5	77	52

[a] The byproduct is isobutene. Bu^tOH (82.5 mmol), MeOH (165 mmol), 1,4-dioxane (34 g). Catalyst loading: 2.2% *m/m* of reaction mixture, *T* = 85 °C, agitation 1000 rpm, *t* = 6 h except for Amberlyst-15 for which *t* = 2 h. [b] EC = exchanged clay.

through studies on the effect of the speed of agitation and was found to be absent in all the reactions.

The comparison of results with Al^{3+} EC (5 mequiv./g of clay) and Al^{3+} EC (25 mequiv./g of clay) shows that an increase in Al content increases acidity and also the activity. However, non-calcined Al^{3+} EC (25 mequiv./g of clay) gives about the same conversion as that observed using Al^{3+} EC (5 mequiv./g of clay) calcined at 450 °C. The calcination of Al^{3+} EC increases the acidity. It is inferred that the presence of Al and H^+ in the clay increases both the Lewis and Brønsted acidic sites thereby adding to the overall acidity.

Table 1 reveals that 30% HPA on silica calcined at 650 °C was the least effective catalyst whereas 20% HPA–clay was the most efficient in terms of quantitative yields of MTBE. HPA–C did not catalyse the reaction as reported by Matouq *et al.*[8] The surface area of silica (200 $m^2 g^{-1}$) is not radically different from that of clay (235 $m^2 g^{-1}$) and hence the enhanced activity is not necessarily due to the resultant better dispersion of HPA on a larger surface but due to other factors. The calcination of HPA–silica at 650 °C might have adverse effect on the activity of the catalyst because selective sintering can reduce the access of active sites which are spread in the networks of pores. Besides, the decomposition of HPA has been reported to occur beyond 300 °C for 15% HPA supported on silica.[17,18] We have also found that HPA supported on silica and calcined at 285 °C is a better catalyst than that calcined at 650 °C. This was mainly because the sintering of the catalyst did not take place at 285 °C and hence it could catalyse the reaction more effectively; thus confirming that the absence of Al^{+3} and H^+ in HPA supported silica lowers the catalytic activity to below that exhibited by HPA–K-10.

The absence of activity of HPA–C can be explained as follows. It is not yet clear whether the interaction of HPA with carbon is physical or chemical. Nevertheless, it has been proved by Izumi and Urabe[19] that HPA once impregnated on carbon cannot be desorbed even though HPA is highly soluble in water, methanol or acetone. Also it has been reported by North[20] and Schwegler[21] that acidic HPA can form complexes with ethers and water at the catalytic centres. Owing to the possibility of such complex formation, the products will not desorb leaving no scope for further reaction to take place. It has also been found that partial exchange with cesium makes HPA a superior catalyst owing to the hydrophobic nature of cesium.[8]

K-10 montmorillonite clay alone gives conversions of 56 and 70% selectivity for MTBE, whereas 20% HPA loaded on the same clay increases the conversion to 71% with almost 100% selectivity, thus, there is a 34% increase in activity of HPA. These results can be contrasted with Amberlyst-15 which gives 74% conversion but the selectivity is reduced to 86%. Furthermore, the loss of activity from the first use to the third use in case of Amberlyst-15 was 19%; equilibrium was achieved in 2 h during the first use and in 4 h during the third use. Under similar conditions the HPA–clay catalyst showed only a 4% decrease in activity from the first use to the third use with conversions remaining almost the same. Another commercial catalyst HZSM-5 gave very high conversion of *tert*-butyl alcohol (77%) but poor selectivity for MTBE (52%).

Although Amberlyst-15 and HZSM-5 give marginally better conversion than HPA–K-10, the selectivity for MTBE is much less. Thus HPA supported on K-10 clay is a better catalyst than all others studied during this investigation.

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