Gas-phase synthesis of MTBE from methanol and *t*-butanol over the microporous niobium silicate AM-11

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The methyl *t*-butyl ether (MTBE) synthesis is demonstrated, where MTBE is produced by reacting methanol and *t*-butanol over the microporous niobium silicate AM-11 (Aveiro Manchester, structure number 11). The effect of the methanol/*t*-butanol molar ratio, weight hourly space velocity (WHSV) and time on stream (TOS) on this reaction is investigated. These experiments are carried out in the gas phase at temperatures in the range 50–100 °C and at atmospheric pressure, yielding considerable selectivity for MTBE at low reaction temperatures. The selectivity to MTBE decreases with increasing temperature due to by-products formation. There is no catalyst deactivation during a period of more than 23 h on stream at 70 °C. Using the catalyst three times has no effect on the catalyst activity and selectivity for MTBE.

KEY WORDS: methyl *t*-butyl ether; niobium silicate AM-11; catalyst activity; selectivity; gas phase

1. Introduction

Methyl *t*-butyl ether (MTBE) is a gasoline additive and a good octane-number enhancer. MTBE is traditionally made by reacting isobutene and methanol in the presence of an acidic catalyst [1,2]. The reaction is commonly carried out in the liquid phase in contact with an acidic ion exchange resin (ex. Amberlyst 15) at temperatures in the range 40–90 °C and pressures of about 10 atm. However, this catalyst shows some disadvantages, such as thermal stability and corrosive properties [3]. Alternative catalysts for the MTBE synthesis have received attention, for example, heteropoly acids [4–6] and zeolites, due to their excellent thermal stability and high selectivity towards MTBE [7–10]. In this report, an alternative synthesis route is described where MTBE is produced by reacting methanol and *t*-butanol over the as-synthesised microporous niobium silicate AM-11 [11]. The obvious advantage of this process is the direct use of *t*-butanol, a chemical produced as a by-product in a number of reaction processes such as the Halcon process (propylene oxide synthesis), where 3.5 kg of *t*-butanol is produced per kilogram of propylene oxide [12]. This alternative preparation of MTBE from *t*-butanol has already been investigated over heteropoly acids, oxide suports, HF-treated montmorillonite clays, mineral acid-activated clays [13], protonated zeolites [14], inorganic oxides such as Nb_2O_5, TiO_2, ZrO_2, Al_2O_3, SiO_2 and H_3PO_4-treated oxides [15].

As mentioned above, the reaction is catalysed by AM-11, a novel microporous niobium silicate, recently reported in the literature [11]. Though the structure of this material has not been elucidated as yet, a preliminary investigation suggests that octahedral niobium(V) and tetrahedral silicon are the main units of the AM-11 framework. The charge, associated with framework niobium is balanced by Na^+ and NH_4^+ cations and the as-prepared material possesses a substantial amount of Brønsted acidity at the internal surface whereas the external surface accommodates predominately Lewis acid centres [16]. A textural analysis indicates that AM-11 exhibits a large nitrogen uptake (ca. 0.15 g/g) whereas the accessibility of larger molecules to this structure is rather limited. This paper describes the MTBE synthesis from methanol and *t*-butanol over the microporous niobium silicate AM-11.

2. Experimental

2.1. AM-11 synthesis

AM-11 was prepared in Teflon-lined autoclaves under hydrothermal conditions, using the procedure described in the literature [15]. The AM-11 gel with a composition 1.0 $Na_2O : 1.0\ SiO_2 : 0.15\ Nb_2O_5 : 240\ H_2O$ was autoclaved for 10–15 days at 200 °C. The gel pH (after a 1 : 100 water dilution) was adjusted to 10.2 by adding an ammonia solution (25%, Merck). The crystalline product was filtered, washed with distilled water and dried at room temperature, the final product being an off-white microcrystalline powder. ICP analysis yields Si/Nb and ($Na + NH_4^+$)/Nb molar ratios of ca. 4.6 and 1.1, respectively.

2.2. Catalysis experiments

The gas-phase experiments were performed in a fixed-bed stainless-steel reactor at atmospheric pressure. The reactor's length and internal diameter are 16.0 and 0.5 cm, respectively, and the reactor bed measures 1.0 cm long and exhibits

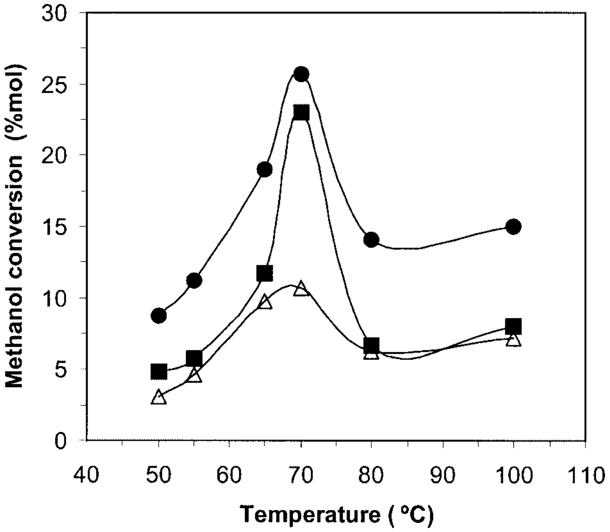

Figure 1. Conversion of methanol for different methanol/t-butanol molar ratios over AM-11; TOS = 1 h, WHSV = 0.4 h^{-1}. (●) Met/But = 1.5, (■) Met/But = 3.0 and (△) Met/But = 5.7.

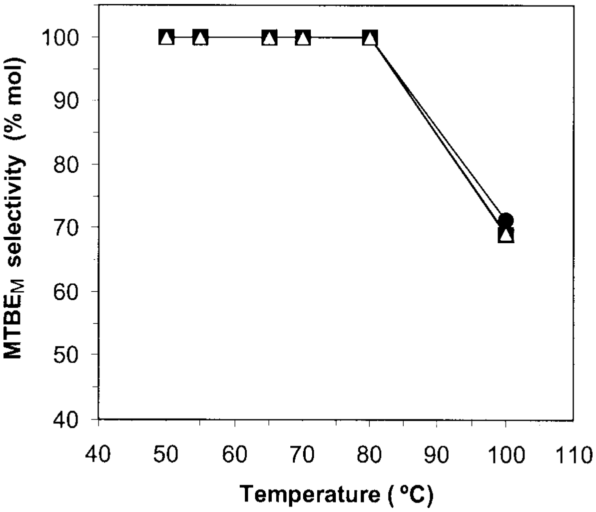

Figure 2. Selectivity for MTBE$_M$ (methanol basis) for different methanol/t-butanol molar ratios over AM-11; TOS = 1 h, WHSV = 0.4 h^{-1}. (●) Met/But = 1.5, (■) Met/But = 3.0 and (△) Met/But = 5.7.

an internal diameter of 0.5 cm. The catalyst (50 mg) was activated at 450 °C in argon with a flow rate of 2 ml min^{-1} for 3 h. The reactant mixture (methanol/t-butanol) was fed and controlled by a syringe pump and residence times were adjusted by keeping the catalyst weight constant and changing the volumetric flow rate of the reactant. The products were analysed by means of gas chromatography with a 30 m long capillary column (DP1 fused silica phase) and an FID (flame ionisation detector). Conversion and selectivity of MTBE are defined as follows in the present study [3]:

Conversion of methanol

$$= \frac{\binom{\text{molar flow rate of}}{\text{methanol at the inlet}} - \binom{\text{molar flow rate of}}{\text{methanol at the outlet}}}{\text{flow rate of methanol at the inlet}} \times 100\%,$$

Selectivity of MTBE on the basis of methanol (MTBE$_M$)

$$= \frac{\text{molar flow rate of MTBE at the outlet}}{\binom{\text{molar flow rate of}}{\text{MTBE at the outlet}} + 2\binom{\text{molar flow rate of}}{\text{dimethyl ether at the outlet}}} \times 100\%,$$

Conversion of t-butanol

$$= \frac{\binom{\text{molar flow rate of}}{t\text{-butanol at the inlet}} - \binom{\text{molar flow rate of}}{t\text{-butanol at the outlet}}}{\text{molar flow rate of } t\text{-butanol at the inlet}} \times 100\%,$$

Selectivity of MTBE on the basis of t-butanol (MTBE$_B$)

$$= \frac{\text{molar flow rate of MTBE at the outlet}}{\binom{\text{molar flow rate of}}{\text{MTBE at the outlet}} + \binom{\text{molar flow rate of}}{\text{isobutene at the outlet}}} \times 100\%.$$

3. Results and discussion

Figure 1 illustrates the conversion of methanol in the temperature range 50–100 °C with various methanol/t-butanol molar ratios. For all methanol/t-butanol molar ratios, a notable increase in methanol conversion is observed in the temperature range 50–70 °C followed by a decay at higher reaction temperatures. This decay may relate to the extensive dehydration of t-butanol leading to the formation of water which, in turn, poisons some of the acid sites. Furthermore, the methanol/t-butanol molar ratio seems to have a considerable effect on the methanol conversion, which may relate to methanol residence times; i.e., high methanol/t-butanol molar ratios means shorter residence times for methanol and lower conversion.

Table 1
Methanol and t-butanol conversion, and selectivity for MTBE$_M$ and MTBE$_B$ (mol%) for different WHSV[a] at 65 °C and methanol/t-butanol = 3.0.

WHSV (h^{-1})	Conversion methanol	Selectivity MTBE$_M$	Conversion t-butanol	Selectivity MTBE$_B$
0.4	11.7	100	57.8	41.2
2.0	5.9	100	26.0	38.1
6.0	3.2	100	25.0	37.3

[a] WHSV is defined as (t-butanol + methanol (mass rates))/(mass of catalyst).

As shown in figure 2, the selectivity for MTBE as a function of methanol conversion remains at 100% up to 80 °C whereas a decrease in MTBE selectivity is found at 100 °C. At higher reaction temperatures, the striking decrease observed in MTBE selectivity appears to be due to the formation of dimethyl ether; this suggests that the dehydration of methanol is clearly favoured over the alkylation reaction at these reaction conditions. Table 1 shows the results obtained at different WHSV. At 65 °C, increase in WHSV has no significant effect on the selectivities for MTBE whereas the conversions of both, methanol and t-butanol decrease markedly. These results indicate that long residence times favour the yield of MTBE.

Due to the higher reactivity of t-butanol, a very different pattern of conversion is found. Figure 3 depicts the conversion levels of t-butanol in the temperature range 50–100 °C with various methanol/t-butanol molar ratios. For all methanol/t-butanol molar ratios, a constant increase in

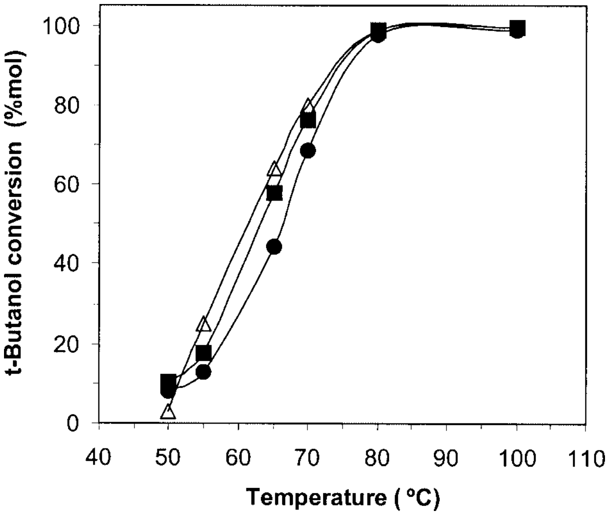

Figure 3. Conversion of *t*-butanol for different methanol/*t*-butanol molar ratios over AM-11; TOS =1 h, WHSV = 0.4 h^{-1}. (●) Met/But = 1.5, (■) Met/But = 3.0 and (△) Met/But = 5.7.

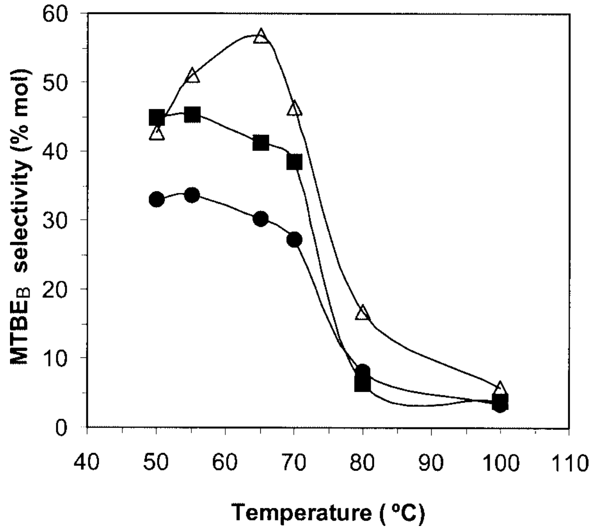

Figure 4. Selectivity for MTBE$_{\mathrm{B}}$ (*t*-butanol basis) for different methanol/*t*-butanol molar ratios over AM-11; TOS = 1 h, WHSV = 0.4 h^{-1}. (●) Met/But = 1.5, (■) Met/But = 3.0 and (△) Met/But = 5.7.

t-butanol conversion is observed up to 80 °C where 100% conversion is achieved. Due to the high reactivity of *t*-butanol, the effect of methanol/*t*-butanol molar ratio on butanol conversion is not very significant. As shown in figure 4, the MTBE selectivity, on basis of *t*-butanol conversion, decreases markedly at higher reaction temperatures and this may be due to extensive dehydration of *t*-butanol and methanol. Thus, the product distribution includes MTBE, isobutene and dimethyl ether at higher reaction temperatures whereas only MTBE and isobutene were detected at lower reaction temperatures. Figure 5 depicts the effect of both, reaction temperature and methanol/*t*-butanol molar ratio on the MTBE$_{\mathrm{M}}$ yield. The high selectivity for MTBE$_{\mathrm{M}}$ indicates that methanol conversion defines the MTBE$_{\mathrm{M}}$ yield. It follows that the effect of reaction temperature and methanol/*t*-butanol molar ratio is very similar to those on conversion and thus a very similar pattern is obtained. Figure 6 illustrates the effect of reaction temperature and methanol/*t*-butanol molar ratio on the MTBE$_{\mathrm{B}}$ yield. Whereas the effects of reaction temperature on MTBE$_{\mathrm{B}}$ and MTBE$_{\mathrm{M}}$ yield are very similar, the methanol/*t*-butanol ratio has an opposite effect. As shown in figure 6, the higher

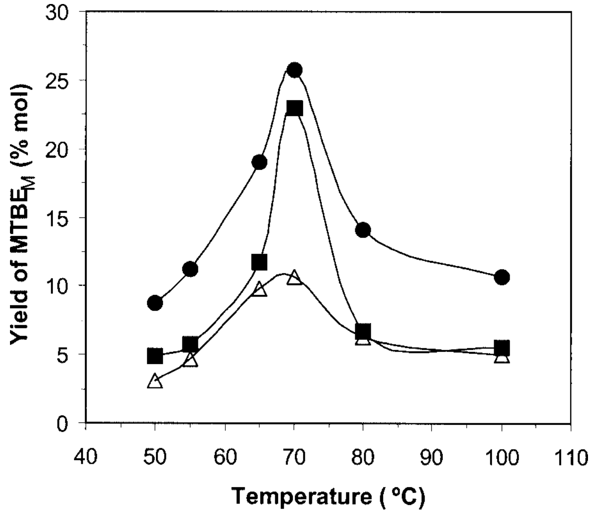

Figure 5. Yield of MTBE$_{\mathrm{B}}$ (*t*-butanol basis) for different methanol/*t*-butanol molar ratios over AM-11; TOS = 1 h, WHSV = 0.4 h^{-1}. (●) Met/But = 1.5, (■) Met/But = 3.0 and (△) Met/But = 5.7.

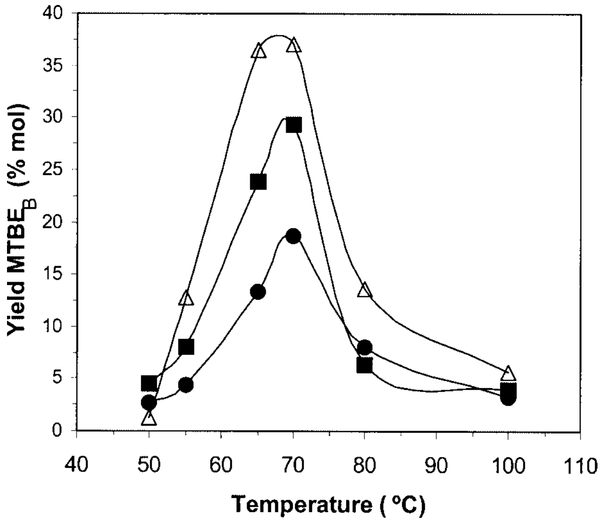

Figure 6. Yield of MTBE$_{\mathrm{M}}$ (methanol basis) for different methanol/*t*-butanol molar ratios over AM-11; TOS = 1 h, WHSV = 0.4 h^{-1}. (●) Met/But = 1.5, (■) Met/But = 3.0 and (△) Met/But = 5.7.

Table 2

Methanol and *t*-butanol conversion, and selectivity for MTBE$_{\mathrm{M}}$ and MTBE$_{\mathrm{B}}$ (mol%) on AM-11 reused three times at temperature 70 °C, methanol/*t*-butanol = 1.5 and WHSV = 0.4 $^{-1}$.

Catalyst	Conversion methanol	Selectivity MTBE$_{\mathrm{M}}$	Conversion *t*-butanol	Selectivity MTBE$_{\mathrm{B}}$
1 time	25.7	100	68.5	27.3
2 time	23.9	100	61.9	25.1
3 time	25.4	100	62.0	25.1

the methanol/*t*-butanol ratio the higher the $\mathrm{MTBE_B}$ yield. This may be explained by the fact that the excess methanol suppresses the secondary reaction of isobutene and thus promotes the selectivity and yield for $\mathrm{MTBE_B}$.

The catalyst deactivation was monitored at 70 °C, WHSV $= 0.4\ \mathrm{h}^{-1}$, methanol/*t*-butanol $= 3.0$. No loss of activity and selectivity of MTBE is observed after 23 h and when the catalyst is reused three times, the selectivity for MTBE is maintained at practically the same level (table 2), and the activity is not significantly affected.

4. Conclusions

An alternative route for MTBE synthesis is demonstrated by reacting methanol and *t*-butanol over the as-synthesised microporous niobium silicate AM-11. This process constitutes a direct outlet of the abundant *t*-butanol and achieves a considerable yield of MTBE at lower reaction temperatures (ca. 70 °C). At higher reaction temperatures, the selectivity for MTBE as a function of both, methanol and *t*-butanol is decreased because of the extensive dehydration reactions. The catalyst deactivation is insignificant and the overall catalytic performance of this material points to its potential in the MTBE technology.

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