

Synthesis of MTBE from isobutane using a single catalytic system based on titanium-containing ZSM-5 zeolite

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A new route for the synthesis of methyl *tert*-butyl ether (MTBE) from isobutane using a single catalytic system is developed in the liquid phase; the key of the process relies on the use of a bifunctional material, Al-TS-1, capable of catalysing the oxidation of isobutane with H₂O₂ and consequently etherification with methanol.

MTBE is an useful fuel oxygenate in reformulated gasoline.¹ Among all oxygenates, the tertiary ethers have gained wide acceptance in comparison with lighter alcohols, due to good antiknocking performance and excellent physicochemical properties without producing environmentally hazardous emissions.² In this context, the global demand for MTBE will continue to rise by about 15% per year, from the current 10 to 30 MT per year by the year 2000.³ The commercial process currently used for MTBE synthesis, involves the liquid-phase reaction of methanol and isobutene at temperatures below 100 °C and pressures up to 2 MPa, over different organic resins (Amberlyst 15, LEWATIT, ...) and inorganic solid-acid catalysts especially zeolites.⁴

The availability of isobutene may cause problems in the near future due to the high demand not only for MTBE production but also for alkylation.³ By relying exclusively on isobutene produced in cracking plants (steam catalytic and fluid catalytic), the potential production of MTBE would be about 10 MT per year.³ It will therefore be necessary to resort to other sources such as *tert*-butyl alcohol (TBA)^{5,6} and isobutane as raw materials.³ Most of the isobutane is now directed to alkylation process by reacting with light alkenes (propylene, butenes and amylenes) using strong acids as catalyst, to yield alkylates with good antiknocking performances and very useful in reformulated gasoline. Alternatively, isobutane can be thermally cracked⁷ or dehydrogenated to isobutene and consequently converted into MTBE.⁸ A number of patented dehydrogenation processes are now in use,⁸ however they have some drawbacks, such as high investments and operating costs.

In this context, we have developed an alternative way of MTBE synthesis directly from isobutane over a single catalytic system based on aluminium titanium silicalites with MFI structure (Al-TS-1).^{9–11} The key of the process is the use of a bifunctional material, capable of catalysing isobutane oxidation with H₂O₂ into *tert*-butyl alcohol and consequently etherification with methanol to yield MTBE.

The experiments were carried out in a magnetically stirred batch reactor equipped with a temperature controller and pressure indicator. The reactants, except H₂O₂, and the catalyst were charged into the Teflon-lined reactor and pressurized with nitrogen to keep the mixture in the liquid phase at the reaction temperature. Once the temperature reached the set value, an aqueous solution of H₂O₂ was added slowly at *ca.* 5.0–6.5 mg min⁻¹ of H₂O₂ (50 mass%), with the temperature fixed for a predetermined time. When a two-stage process was used, once the first step was complete the temperature was increased to 100 °C and maintained for 3 h while carrying out the second step. The reaction products were analysed by gas chromatography (VARIAN 3400) on a capillary column DV-1, methyl silicone (60 m × 0.02 mm) using a flame ionization detector.

Ti-containing ZSM-5 (Al-TS-1) was synthesized following a procedure developed by our group,^{12,13} based on the method patented by Padovan *et al.*¹⁴ for TS-1 synthesis. Amorphous Al₂O₃-TiO₂-SiO₂ materials were prepared with SiO₂:TiO₂ and SiO₂:Al₂O₃ molar ratios of 40 and 160 respectively, following a two-step sol-gel method:¹¹ (a) acid hydrolysis of tetraethylorthosilicate, aluminium isopropoxide and titanium tetrabutoxide; (b) basic gelation by addition of tetrapropylammonium hydroxide (TPAOH) aqueous solution. The gel was dried and finely ground into a powdered xerogel, then this solid was wetness impregnated with the TPAOH solution, charged in Teflon-lined autoclaves and crystallized under autogenous pressure at 170 °C for 24 h. The Al-TS-1 sample so obtained presents SiO₂:TiO₂ and SiO₂:Al₂O₃ molar ratios of 76 and 160 respectively.

X-Ray diffraction (XRD), thermogravimetric analysis (TGA) and *n*-C₆ adsorption measurements confirm the high crystallinity of Al-TS-1 obtained by this procedure. FTIR and diffuse reflectance (DR) UV-VIS spectroscopy reveal the incorporation of Ti into tetrahedral positions in the MFI crystalline structure whereas bulk anatase and/or extraframework Ti species were not detected. ²⁹Si and ²⁷Al MAS NMR spectroscopy indicate the presence of Al occupying tetrahedral positions in the Al-TS-1 framework, in accord with acidic properties of this material as observed by NH₃ temperature programmed desorption. The simultaneous incorporation of Ti and Al provides the Al-TS-1 samples with bifunctional properties *viz.* high catalytic activity for hydrocarbon oxygen-functionalization with H₂O₂, and acid-catalysed reactions.^{9–11}

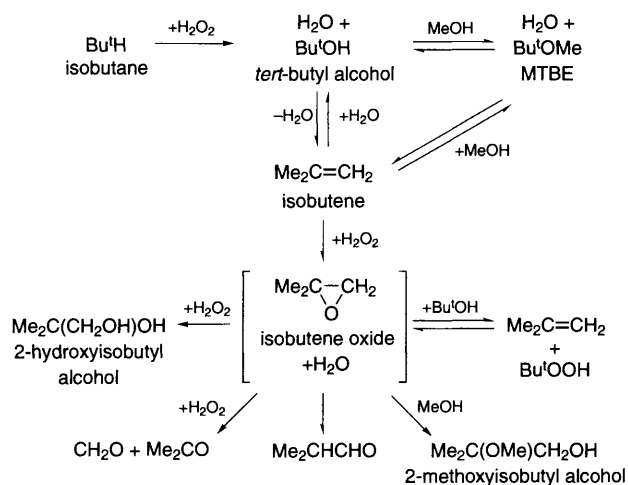
Table 1 shows the results obtained in several experiments of isobutane conversion over Al-TS-1 including the H₂O₂ yield to different products. Since the temperature for the acid-catalysed MTBE synthesis from isobutene over zeolites is usually *ca.* 100 °C¹⁵ (not higher due to thermodynamic limitations), and because this temperature is also frequently used for hydrocarbon oxidation reactions over TS-1, initial attempts to obtain MTBE from isobutane, methanol and hydrogen peroxide were carried out at 100 °C (Table 1, run 1). The H₂O₂ yield for MTBE was only 9% since at this temperature other products are formed from isobutane and methanol oxidation.

According to the obtained results Scheme 1 is proposed to describe the pathways for isobutane oxidation. The main oxidation product arising from isobutane is *tert*-butyl alcohol due to the reactivity of the tertiary carbon present in this molecule and the lack of oxidation activity in primary carbons shown by Ti-containing zeolitic materials.¹⁶ The presence of aluminium in Al-TS-1 clearly enhances the methanol oxidation as compared to TS-1,¹⁷ leading to formaldehyde (methylene glycol in aqueous solution) and formic acid, which immediately reacts with methanol to form methyl formate. Owing to the acidic properties of this catalyst, *tert*-butyl alcohol could react with methanol to form directly MTBE or could be dehydrated to yield isobutene. The alkene could react with methanol and H₂O₂ to form 2-methoxyisobutyl alcohol, as reported for TS-1.¹⁸ We postulate also the possible formation of isobutene oxide to support the presence of isobutyraldehyde, acetone, formaldehyde and *tert*-butyl hydroperoxide (and probably 2-hydroxy-

Table 1 Yields (based on H₂O₂ consumed) for different products in isobutane conversion over Al-TS-1

Run	T/°C	t/h	Isobutane conv. (%)		H ₂ O ₂ yield ^a (%)						
			Rel. ^b	Abs. ^c	MTBE	Bu ^t OH	H ₂ C=CMe ₂	Me ₂ C(OMe)CH ₂ OH	Bu ^t OOH	CH ₂ O + HCO ₂ Me	Other
1	100 ^d	4	41.0	4.5	9.0	13.7	5.3	12.7	7.8	27.1	3.7
2	80 ^e	6	60.6	20.8	4.5	42.5	5.5	0.1	1.5	25.6	11.7
3	80/100 ^f	6/3	63.7	5.9	37.3	7.8	10.5	2.6	2.1	24.7	9.6
4	80/100 ^e	6/3	63.2	21.7	35.2	10.6	4.0	0.2	1.3	29.9	16.9
5	80/100 ^g	7/3	61.6	31.8	32.7	10.4	7.1	0.5	1.3	29.7	13.3

^a (mol Product/mol H₂O₂) × 100. ^b (mol Isobutane reacted/mol H₂O₂) × 100. ^c (mol Isobutane reacted/mol isobutane) × 100. ^d Reaction conditions; isobutane : methanol mass ratio = 2, (isobutane + methanol) : H₂O₂ (50 mass%) mass ratio = 10.9, H₂O₂ conv. = 100%, 0.6 g catalyst and addition of 6.5 mg H₂O₂ (50 mass%) min⁻¹ for 210 min. ^e Reaction conditions; isobutane : methanol mass ratio = 0.27, (isobutane + methanol) : H₂O₂ (50 mass%) mass ratio = 12.8, H₂O₂ conv. = 100%, 1.0 g catalyst and addition of 5 mg of H₂O₂ (50 mass%) min⁻¹ for 195 min. ^f Reaction conditions; isobutane : methanol mass ratio = 1.4, (isobutane + methanol) : H₂O₂ (50 mass%) mass ratio = 15, H₂O₂ conv. = 100%, 1.0 g catalyst and addition of 5 mg H₂O₂ (50 mass%) min⁻¹ for 195 min. ^g Reaction conditions; isobutane : methanol mass ratio = 0.27, (isobutane + methanol) : H₂O₂ (50 mass%) mass ratio = 7.6, H₂O₂ conv. = 100%, 1.0 g catalyst and addition of 5 mg H₂O₂ (50 mass%) min⁻¹ for 300 min.



isobutyl alcohol, although this was not detected)¹⁹ as oxidation products in the reaction.

With this scheme in mind, a temperature of 100 °C favours the dehydration of *tert*-butyl alcohol to yield isobutene and the reaction of the latter to form mainly 2-methoxyisobutyl alcohol. If the reaction temperature is decreased to 80 °C (Table 1, run 2) acid catalysis does not take place extensively and the main product is *tert*-butyl alcohol. However, we considered the possibility of carrying out the reaction at both temperatures as in a temperature gradient reactor (80 °C for the oxidation step and 100 °C for the acid-catalysis step). By comparison of the results of runs 2 and 4 in Table 1, it was concluded that the major transformation during the second step is conversion of *tert*-butyl alcohol into MTBE with only small changes in the remainder of the product distribution. From the results shown in Table 1 corresponding to runs 3, 4 and 5, the selectivity towards the different products is almost invariant as the absolute conversion of isobutane to MTBE increases from 6 to 32%, and probably this is also true for higher conversions which thus could avoid or minimize recycling of the raw compound, isobutane, in a plausible industrial application of this process.

Since H₂O₂ utilization is one of the keys in the process, the analysis of the results shows H₂O₂ yields towards MTBE of over 33% with appreciable yields for other relevant products as

regards MTBE synthesis (*tert*-butyl alcohol and isobutene). It is of note that isobutane selectivities are *ca.* 60 and 85% towards MTBE and MTBE + *tert*-butyl alcohol + isobutene respectively. Although the present results are quite promising, we are attempting to improve H₂O₂ utilization in order to compete with MTBE synthesis from isobutene obtained by isobutane dehydrogenation or thermal cracking. The relatively high cost of hydrogen peroxide can be compensated with the use of a bifunctional catalytic system which allows MTBE synthesis from isobutane to be carried out in a single reactor.

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