Chemical Conversions using Sheet Silicates: Simple Method for Producing Methyl t-Butyl Ether

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Summary Copper-exchanged montmorillonite, in which the water of hydration of the interlamellar Cu^{2+} ions has been exchanged by methanol, readily converts 2-methylpropene into methyl t-butyl ether.

METHYL t-BUTYL ETHER (MTBE or 2-methoxy-2-methylpropane) is currently extensively used as a gasoline blending agent[1] and is prepared industrially using a range of solid catalysts such as heteropolytungstic or molybdic acids doped with phosphorous or boron,[2,3,4] various acidified ion-exchange resins,[5,6] acid alumina,[6,7] and other, mixed-metal carbonyl-compounds,[8] often at high pressures.

Prompted by our success[9] in converting alk-1-enes to di-(2-alkyl) ethers, using the interlamellar water of certain cation-exchanged montmorillonites, we investigated the feasibility of effecting a comparable synthesis of MTBE. It seemed possible that a metal-exchanged montmorillonite might catalyse the addition of methanol, rather than water, though the known, strong tendency of methanol to displace other intercalated organic compounds might have prevented the hydrocarbon molecules reaching the catalytic sites. In the event, the reaction proceeded smoothly and more rapidly than the sulphuric acid-catalysed addition of alcohols to isobutene in solution.[10]

The catalyst is prepared from bentonite (as supplied by Hopkin and Williams) by exchanging the interlamellar ions for copper by standard techniques.[11] It is important that no excess of copper sulphate be left in the bentonite from the exchanging solution, since the catalysts have then been observed to catalyse other, undesired, reactions of olefins. The presence of surplus copper salt is revealed by thermogravimetric analysis (loss of water from $CuSO_4.5H_2O$ at 250 °C). The exchanged bentonite is equilibrated (see ref. 9) in an atmosphere of 12% relative humidity at 30 °C over saturated, aqueous lithium chloride, to give a reactant with a *c*-spacing of 12·4 Å and a water content of 7·5%. When this reactant (1 g) is stirred with methanol (4 cm^3) and 2-methylpropene (4·8 g) at 95—100 °C in a closed system for 3 h, MTBE is produced in *ca.* 70% yield; small amounts of t-butyl alcohol and dimethyl ether are also produced. Many other alkenes form intercalates with this reactant, including hex-1-ene, but-1-ene, 3,3-dimethylbut-1-ene, 4-methylpent-1-ene, 2-methylpent-1-ene, 2-methylpent-2-ene, 2,4,4-trimethylpent-1-ene, and 2,4,4-trimethylpent-2-ene, but of these only the last four undergo addition of methanol to form methyl ethers. While addition of the elements of water to form bis-secondary ethers has been observed,[9] the addition of an alcohol has so far been observed only with branched alkenes to give tertiary ethers. Addition of propan-2-ol to 2-methylpropene has also been observed, but the product has not been fully characterised.

Brönsted acidity of the copper-exchanged montmorillonite is an important factor here as in numerous other reactions of sheet-silicate intercalates,[9,12] but the detailed geometry around the catalytic centre is not known. That the conversion is not a surface reaction is shown by the fact that sodium- and calcium-exchanged montmorillonites are ineffective as catalysts.

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