Catalytic Isomerisation of But-1-ene to 2-Methylpropene over Solid Acids: Comparison between DAF-1 and other Shape-selective Magnesium-containing Aluminophosphates and Aluminosilicates

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Although DAF-1 is a superior isomerisation catalyst at lower temperatures [reaching some 50% of the thermodynamically limited conversion in the range 250–300°C at a weight hourly space velocity (WHSV) of but-1-ene of 3 h^{-1}] both its activity and its selectivity, as well as its longevity, are inferior to those of H$^+$-ferrierite and H$^+$-Theta-1 in the range 350–400 °C: the performance of MALPO-5, -11 and of -36 (M = Mg) is much poorer than that of DAF-1.

The quest to develop powerful new solid acid catalysts[1-3] for the conversion of n-butene (but-1-ene) 1, to isobutene (2-methylpropene, 4) is driven by three factors. First, a glut of C$_4$ alkenes results both from increased world-wide catalytic cracking of heavy oils (to yield petrol) and a concomitant increase in the steam-cracking of hydrocarbons to yield ethene (and butene by-products). Second, a clamant demand for methyl tertiary butyl ether (MTBE) as a high-octane replacement for lead derivatives in petrol: MTBE is made by the catalysed addition of methanol to 2-methylpropene.[4] And

third, the growing environmental concern about the use of corrosive liquid acids (such as 96% sulfuric acid) as catalysts for the isomerization and alkylations of hydrocarbons. Selective and active solid acids are therefore attractive as replacements; and the ever-growing family of molecular-sieve catalysts, where the proton-donating sites are distributed uniformly within their pores and cavities, offers a promising range of viable alternatives.

Here we compare the performance of a newly synthesized strong acid MALPO (a metal-containing aluminium phosphate, M = Mg) known as DAF-1[5] (Davy–Faraday-1) with MALPO-5,[6,7] -11,[6,8] -36[6,9] (M = Mg) and with the zeolites H-ZSM-5,[10] H-ferrierite[11] and H-Theta-1.[12] With the well-defined structural characteristics of such catalysts, there is scope to tailor the most promising one so as to maximize its activity towards the selective production of 4, and to minimize production of oligomeric or other products whilst sustaining (or rendering readily regenerable) the overall performance of the catalyst. Prior computational assessments[13] of the mobility and the binding energy of all four isomers (1–4) inside a number of model microporous catalysts reveal that 4 is more readily released than 1, 2 or 3 from ZSM-5 and Theta-1, but that dimerization of 4 is much more likely to occur in ZSM-5 with its intersecting channels than in the one-dimensional
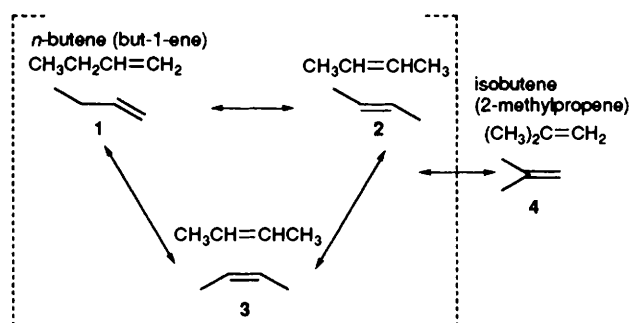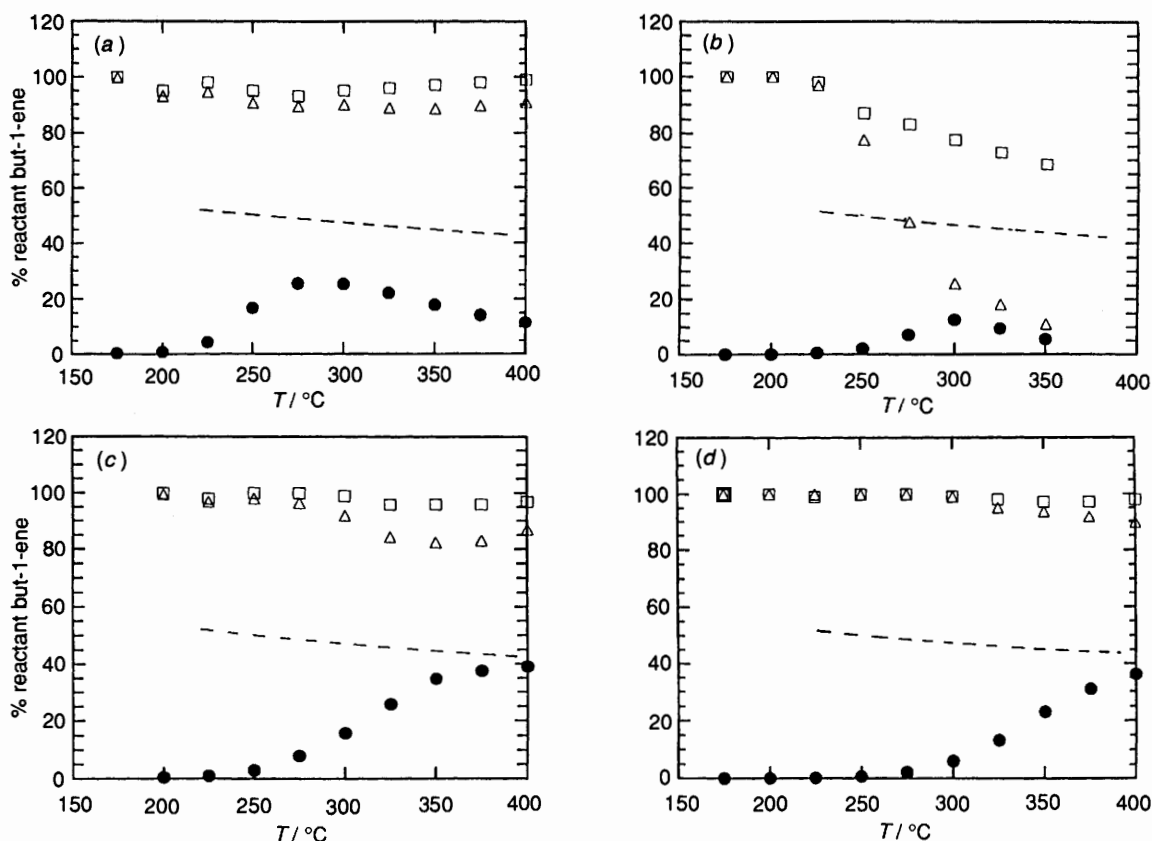
Fig. 1 Production of isobutene for (a) DAF-1, (b) ZSM-5, (c) ferrierite and (d) Theta-1. $\square$, % of the reactant hydrocarbon measured by the FID detector of the GC; $\triangle$, amount of butene isomers in the reactant stream as a percentage of the input but-1-ene; ●, yield of isobutene. The dashed line indicates the thermodynamic equilibrium level of isobutene as a function of temperature, assuming only butenes to be present. The measurements were made using a continuous stream of 10% but-1-ene in He (WHSV but-1-ene = 3 h^{-1}) over the dry catalysts.

system of Theta-1. Existing patent literature indicates, for example, that H-ferrierite is also more selective than H-ZSM-5 for this reaction.[14]

DAF-1 (framework composition $Mg_{0.22}Al_{0.78}PO_4$) possesses a novel structure with two large-pore channel systems bounded by 12-membered rings, one which is one-dimensional (1D) and contains periodic supercages, while the other is linked three-dimensionally *via* medium ten-ring pores. The two channel systems are only linked by small eight-ring pores which do not allow transport of isobutene or even, according to preliminary calculations,[15] the linear butenes. Synthesis and structural details of DAF-1 are given elsewhere.[5]

The magnesium-substituted ALPOs, MgALPO-5 (Mg : P = 0.08), -11 (Mg : P = 0.08) and -36 (Mg : P = 0.12) possess 1D channel systems bounded by 12-, 10- and 12-rings, respectively. MALPO-5 and -11 samples were calcined *ex-situ* in oxygen at 550 °C according to established procedure. The catalyst samples of the above were activated by heating them in dry He at 400 °C for 2 h. Catalyst samples of the H-forms of zeolites ZSM-5, Theta-1 and ferrierite (with Si : Al ratios of 20, 30 and 10, respectively) were prepared from the ammonium-exchanged zeolites by calcination in air at 550 °C for 16 h and were activated prior to catalytic testing by heating them at 450 °C for 2 h in helium. DAF-1 and MALPO-36, however, were calcined *in situ* at 620 °C for 3 h in dry oxygen to remove the template prior to testing. A fully automated computer-controlled catalyst testing system (model 4000 Cambridge Reactor Design, UK) coupled with a gas chromatograph (Perkin-Elmer), fitted with a microsplitter and a 25 m PLOT Al_2O_3/KCl wide-bore capillary column was used for the comparison. Full details of sample preparation and experimental procedure are given elsewhere,[16] but the key points are as follows: the reaction products of a continuous input stream of 10% but-1-ene in helium [total flow 30

ml min^{-1}; WHSV(but-1-ene) = 3 h^{-1}] were monitored as the temperature was increased in steps of 25 °C, each measurement being made at the end of an isothermal step, after a reaction time of 20 min.

Under these conditions, MgAPO-5, -11 and -36 produce minor amounts of **4** (MgALPO-5 = 2% MgALPO-11 = 3.7%; MgALPO-36 = 2%), while all catalyse the facile double-bond shift. Since it is known that SAPO-11[17] (like MnALPO-31, SAPO-31 and its derivatives[18]) is a good catalyst for the isomerisation reaction, we infer that, in MgALPO-11, the acid sites related to the incorporation of magnesium must be relatively weak. The DAF-1, H-ZSM-5, H-Theta-1 and H-ferrierite catalysts all possess sufficiently strong acidity to effect the skeletal isomerization (*i.e.* to produce **4** from **1**) (Fig. 1), although the precise mechanism of the process remains unclear. DAF-1 is the most active at lower temperatures, some one-half of the maximum (thermodynamically) attainable conversion occuring at 275–300 °C. It is superior in selectivity to H-ZSM-5 at all temperatures, the latter also catalysing secondary reactions to give products of lower and higher carbon numbers. As the reaction temperature is increased above 300 °C under these conditions, the activity of production of **4** drops off over DAF-1 due to coke formation, whereas for H-Theta-1 and H-ferrierite it continues to increase, approaching thermodynamic equilibrium at around 400 °C. In addition, while the reactivity of deactivated DAF-1 can be completely regenerated by heating it in oxygen, neither ferrierite nor Theta-1 show rapid deactivation even at elevated temperatures. For example, H-ferrierite retains *ca.* 40% selectivity to **4** at 350 °C for 4 h, after which it deactivates only very slowly.

It is seen that of the Mg-containing aluminophosphates examined in the present investigation, only Mg-DAF-1 has activity for butene isomerization rivalling that exhibited by

aluminosilicate zeolites. To determine whether this comparable activity is a result of the 3D pore connectivity or the inherent acidity of DAF-1, computational as well as IR and NMR studies are currently underway.

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