Rational design of a solid acid catalyst for the conversion of methanol to light alkenes: synthesis, structure and performance of DAF-4

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By careful choice of the appropriate organic template, new shape-selective solid acid catalysts—framework-substituted microporous aluminium phosphates ($AlPO_4$) that are structurally analogous to the mineral levyne—are designed, synthesised and characterised; they convert methanol preferentially to ethene and propene.

Brønsted acidity may be conferred upon an otherwise neutral solid such as $AlPO_4$ in three ways: by incorporation of (i) lower-valent metal ions in place of Al^{III} in the so-called $AlPO_4$ framework (thereby forming MeAPOs, Me = Mg, Co, Zn, *etc.*); (ii) a tetravalent ion (especially Si^{IV}) in place of P^{V}, thereby creating SAPOs; or (iii) a combination of these substitutions to yield MeAPSOs.[1–3] Many distinct $AlPO_4$ structures are now known in which substantial variation in the framework may be effected.[4–6] However, although several 'designed' microporous MeAPO solids have been prepared recently,[7–10] there is still a pressing need both to understand more about the fundamental factors that govern such syntheses[11] and to create novel solid acids for a variety of industrially important reactions.[12] In meeting this challenge, we have adopted two approaches: design by experiment based on chemical intuition,[2,7,13] and design by computer[11,14] in which, for a given target solid, an appropriate algorithm is used to build up within the desired cavity of the target microporous catalyst the template molecule to be used in its chemical synthesis.

Success in synthesising new microporous acids arises from a suitable choice of constituents of the nutrient gel from which the templated solid crystallises during hydrothermal treatment. *N,N*-diisopropylethylamine, for example, yields CoAPO-18[2] when cobalt acetate is added to mixtures (in appropriate amounts) of $Al(OH)_3$ and H_3PO_4; cyclohexylamine is the template of choice for the production of CoAPO-44,[1] and decamethonium ions yield DAF-1.[7] Our aim in this work was to synthesise both cobalt- and silicon-containing solid acids (based on $AlPO_4$) in which the cavities are somewhat different from those in CoAPO-18 or SAPO-18.

We considered it desirable to 'create' cavities that were slightly smaller in one direction than in CoAPO-18, and larger in the other so as to secure the shape-selectivity that would prevent the methanol yielding heavier alkenes upon dehydration. With our knowledge that a 1,4-diaminocyclohexane template gives rise to a porous layered $AlPO_4$ structure,[13] we reasoned that 1,2-diaminocyclohexane would favour the formation of a microporous solid with 8-ring windows (*i.e.* eight oxygen atoms lining the window), as in the chabazitic materials SAPO-34, CoAPO-18 and CoAPO-44, but significantly different in its cavity shape. However, because 1,2-diaminocyclohexane was found to be unstable under the hydrothermal conditions of synthesis, we chose instead the more stable 2-methylcyclohexylamine as template (these templates are spatially similar because the CH_3 group occupies almost the same space as a protonated NH_2). Crystallisation from a gel of composition xCoOn : $(1-x/2)Al_2O_3$: $y SiO_2$: $(1-y/2)P_2O_5$: $25H_2O$: $1.0C_7H_{15}N$, where x = 0–0.4 and y = 0–0.2, under autogenous pressure for 7 days at 200 °C resulted in the production of the desired solids, which we designate DAF-4 (Davy Faraday number four—DAF-1 was described in ref. 7). DAF-4 may be prepared as a CoAPO (with up to as much as 20 atom% of Co^{II} replacing Al^{III}) or as SAPO or CoAPSO variants.

Good quality crystals enabled the structure of the templated solid to be solved by four-circle diffractometry.†,[15] A companion computational study[14] predicted 1,2-substituted cyclohexane templates for the cage structure present in DAF-4; *de novo* design was employed in which a template molecule is 'grown' computationally to fit a specified microporous framework. These solid acid catalysts may also be synthesised using tropine (a cycloheptanol having an *N*-methyl bridge, which is dimensionally similar to 2-methylcyclohexylamine) as the structure-directing template molecule. Tropine as a template has the great advantage of shortening the synthesis time to *ca.* 20 h, as opposed to 7 days for 2-methylcyclohexylamine.

Incorporation of Co^{II} into the framework was confirmed using X-ray absorption spectroscopy[16–18] wherein the near-edge structure (XANES) and the EXAFS analysis[19] (see Fig. 1) both closely match other well characterised CoAPO catalysts containing tetrahedrally coordinated Co^{II}. Even DAF-4 catalysts very rich in framework cobalt exhibited high thermal stability at *ca.* 550 °C. FTIR spectroscopy confirms the substitution of Si^{IV} in DAF-4, the bridging hydroxy stretching frequency occurring at 3580 cm^{-1} (*cf.* 3573 cm^{-1} for CoAPO-

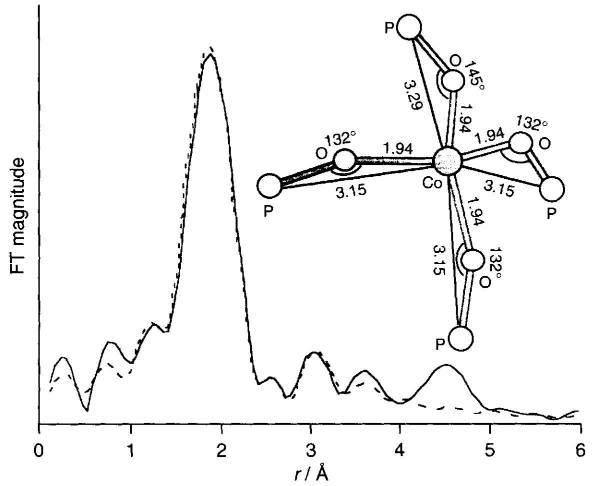

Fig. 1 Fourier transform of the raw Co K-edge EXAFS data of the as-prepared DAF-4 along with the best fit [(—) experimental data, (---) theory] obtained using the structural model shown in the inset. EXAFS data analysis[19] employing curved-wave theory and multiple scattering was performed to obtain the bond distances and angles indicated. EXAFS data were collected on station 7.1 [equipped with a Si(111) monochromator and ion chambers for obtaining data in the transmission mode] of the Synchrotron radiation source, Daresbury (2 GeV with a typical current between 130 and 250 mA).

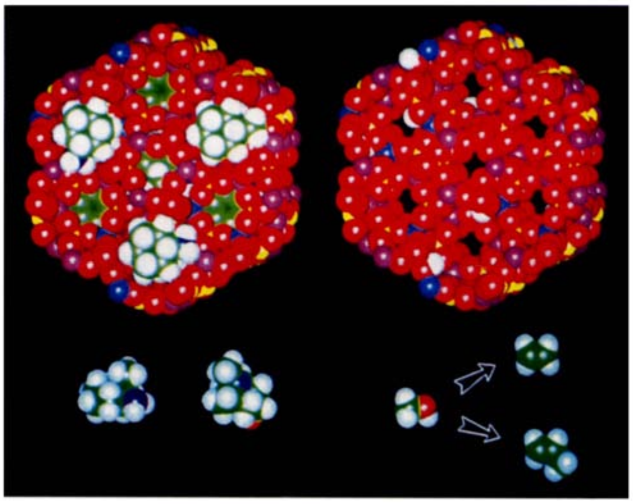

Fig. 2 Templated DAF-4 in the as-prepared catalyst (top left) and in calcined state with loosely bound protons (white) close to Co^{II} (blue) framework ions (top right). Either 2-methylcyclohexylamine or tropine (bottom left) may serve as templates in the synthesis.[14] Methanol is catalytically dehydrated, predominantly to ethene and propene.

18).[20] The CoAPO (DAF-4) catalysts are active for the conversion of methanol to light alkenes with the selective production of ethene and propene.[21–23] Typically, 0.2 g of the CoAPO catalyst with 0.5 g of powdered quartz and a WHSV of 1.29 h^{-1} exhibited a 77% conversion of methanol at 350 °C, there being a 58% selectivity towards ethene and 21% towards propene. Full details of the catalytic performance will be given elsewhere.

The archetypal DAF-4 structure that we have determined is very similar to that of the naturally occurring mineral levyne (idealised formula: $Ca_9[Al_{18}Si_{36}O_{108}]\cdot 50H_2O$)[24] which is isotypic with the previously reported synthetic materials ZK-20,[25] SAPO-35[4] and NU-3.[4] The channels of this structure, viewed normal to [001], are ellipses of dimension 3.6 Å and 4.8 Å. Fig. 2 summarises the salient features of this communication.

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Footnote

† *Crystal data* for DAF-4: $[Co_{1.65}Al_{7.35}P_9O_{36}]^-1.65[C_7H_{16}N]^+\cdot 1.05\ H_2O$, space group $R\bar{3}c$, a = 13.192(3), c = 46.149(9) Å, γ = 120°, Z = 6 (the quantity of organic template given represents the idealised amount to ensure charge neutrality). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystalloraphic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/185.

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