Synthesis and characterisation of microporous titanoniobosilicate ETNbS-10

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The synthesis, structural characterisation and catalytic activity in *tert*-butanol dehydration of microporous titanoniobosilicate ETNbS-10 are reported.

ETS-10 is a novel microporous framework titanosilicate consisting of 'TiO_2' rods, which run in two orthogonal directions, surrounded by tetrahedral silicate units.[1–3] The pore structure consists of 12-rings, 7-rings, 5-rings and 3-rings and has a three-dimensional wide-pore channel system whose minimum diameter is defined by 12-ring apertures. In an attempt to improve the acid characteristics of ETS-10, silicon has been isomorphously substituted by boron, aluminium and gallium.[4–6] A vanadosilicate with the structure of ETS-10 has also been reported.[7] We now wish to report the synthesis, structural characterisation and catalytic activity in the dehydration of *tert*-butanol, of niobium-substituted ETS-10.

ETNbS-10 materials with Nb/Ti molar ratios (ICP) of 0.12, 0.38 and 0.47 were prepared using a modification of the ETS-10 synthesis. An alkaline solution was made by mixing 10.00 g sodium silicate (Na_2O 8% m/m, SiO_2 27% m/m, Merck), 15.03 g H_2O, 0.80 g NaOH (Merck), 0.96 KF (Aldrich), 0.38 g KCl (Panreac), 1.02 g NaCl (Aldrich) 4.63 g $TiCl_3$ (15% m/m solution of $TiCl_3$ in 10% m/m HCl, Merck) and 1.50 g $Nb(HC_2O_4)_5$ (Niobium Products). 0.10 g seed of ETS-10 was added to the resulting gel. This gel, with a composition 5.6 $Na_2O:2.4\ K_2O:10.0\ SiO_2:TiO_2:0.30\ Nb_2O_5:266\ H_2O$, was autoclaved under autogeneous pressure for 3 days at 230 °C. The crystalline product was filtered, washed with distilled water and dried at ambient temperature, the final product being an off-white microcrystalline (2–3.5 μm) powder. The samples were characterised by powder X-ray diffraction (XRD), high-resolution and scanning electron microscopies (HREM and SEM, respectively), infrared (TFIR) and Raman spectroscopies, ^{29}Si and ^{93}Nb solid state NMR.

The ETNbS-10 samples with Nb/Ti 0.12 and 0.38 are essentially pure. SEM and powder XRD reveal that the sample with Nb/Ti 0.47 also contains some quartz ($<10\%$) and, in addition, a small amount of an unknown niobosilicate. The HREM images of this sample (not shown) and ETS-10[2,3] are very similar. The powder XRD patterns of ETS-10 and ETNbS-10 samples (not shown) are virtually identical and show no significant shift in any reflection. This is to be expected because Ti(IV) and Nb(V) have very similar ionic radii.

The total mass losses between 30 and 700 °C of ETNbS-10 (*ca.* 11%, Nb/Ti 0.12) and ETS-10 (*ca.* 12.5%) are similar. Nitrogen adsorption isotherms of ETNbS-10 and ETS-10 materials are of type I with maximum uptakes of *ca.* 0.11 and 0,12 g/g, respectively. However, due to the presence of quartz and niobosilicate dense impurities the maximum uptake of ETNbS-10 with Ti/Nb 0.47 is much smaller (*ca.* 0.06 g/g).

Fig. 1(a) shows the ^{29}Si magic-angle spinning (MAS) NMR spectra of ETS-10 and ETNbS-10 (Ti/Nb 0.47). In ETS-10 there are two types of silicon chemical environments, Si(3Si, 1Ti) and Si(4Si, 0Ti), which give the two groups of resonances at $\delta -94$ to -97 and δ *ca.* -103.7, respectively.[3] the spectrum reveals a further crystallograpic splitting of the Si(3Si, 1Ti) site. ETNbS-10 gives a ^{29}Si MAS NMR spectrum similar to that of ETS-10. However, all resonances broaden considerably and, in particular the ETS-10 peak at $\delta -103.7$, shifts slightly to low frequency. Due to this broadening, the ETS-10 line splitting at δ *ca.* -96.5 is no longer resolved. This seems to indicate the framework insertion of Nb because studies on Al-substituted ETS-10 have shown that the broadening of the ^{29}Si MAS NMR resonances is due to lattice distortion upon Al incorporation.[6] However, in ETNbS-10 Nb is likely to replace Ti and not Si. We note in passing that ETS-10 and an ETS-10 sample impregnated with niobium give very similar ^{29}Si MAS NMR spectra.

The central-transition ^{93}Nb MAS NMR spectrum [Fig. 1(b)] of ETNbS-10 contains a broad (full-width-at-half-maximum, FWHM, *ca.* 240 ppm) asymmetric resonance at δ *ca.* 100 relative to solid Nb_2O_5. This is consistent with niobium being present in distorted octaedral coordination.[8]

Raman spectra (Fig. 2) provide perhaps the best evidence for the isomorphous substitution of Ti by Nb in the ETS-10 framework. ETS-10 gives a main strong and sharp band at *ca.* 735 cm^{-1}, assigned to the TiO_6 octahedra. As the samples Nb content increases this peak shifts slightly and broadens and, simultaneously, a band grows at *ca.* 664 cm^{-1}. The latter is typical of NbO_6 octahedra in microporous niobosilicates: titanoniobosilicate synthetic analogues of the mineral nenadkevichite give a similar band at 668 cm^{-1},[8] while a recently reported niobosilicate (AM-11) gives a band at 687 cm^{-1}.[9] The FTIR spectrum of ETS-10 (not shown) displays bands at 446, 550 and 746 cm^{-1}, associated with the TiO_6 octahedra. As the Nb content of the samples increases the intensity of these bands decreases, while a new band at 918 cm^{-1} is seen. This is a

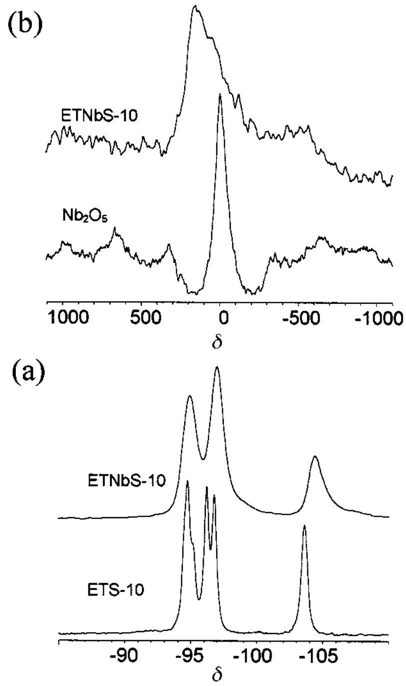

Fig. 1 (a) ^{29}Si MAS NMR spectra of ETS-10 and ETNbS-10 (Nb/Ti 0.47). (b) ^{93}Nb MAS NMR spectra of Nb_2O_5 and ETNbS-10 (Nb/Ti 0.47). The ^{29}Si and ^{93}Nb spectra were recorded at 79.5 and 97.84 MHz on a Bruker MSL 400P spectrometer using spinning rates of 5 and 32 kHz, respectively.

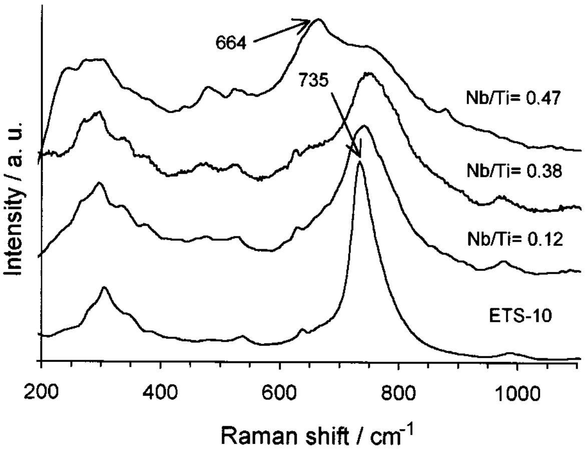

Fig. 2 Stokes-shifted Raman spectra of ETS-10 and ETNbS-10 materials (the Nb/Ti ratios are depicted). The spectra were measured using a Renishaw imaging microscope model 2000.

further indication that Nb replaces Ti in the ETS-10 framework.

A preliminary characterisation of the acid–base properties of ETNbS-10 was performed by means of *tert*-butanol dehydration. The main product of this catalytic process is isobutene an essential ingredient in methyl *tert*-butyl ether (MTBE) synthesis. The product distributions for ETNbS-10 and (for comparison) ETS-10 are given in Table 1. It is apparent that the former dehydrates *tert*-butanol to isobutene with remarkably high activity and selectivity. This finding coupled with the large pore volume of this material point to its potential in catalysis. These results are in accord with a recent study on *tert*-butanol dehydration over AM-6, ETS-10 and Al-substituted ETS-10 which has shown that the basic sites are responsible for the excellent catalytic performance of the materials.[10]

Table 1 A comparison between the catalytic performance of the ETS-10 and ETNbS-10 materials under identical reaction conditions[a]

	ETS-10	Ti/Nb = 0.12	Ti/Nb = 0.47
Conversion	44.0	71.2	99.7
Isobutene	43.56	65.0	95.0
C_5–C_9	0.44	6.2	4.7

[a] Catalyst activation at $T = 400$ °C and $P = 1$ atm for 3 h. WHSV = 2 h^{-1}, TOS = 60 min. $T = 250$ °C, Ar carrier gas flow 30 ml min^{-1}.

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