Synthesis and characterisation of microporous titano-borosilicate ETBS-10

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The synthesis and structural characterisation of microporous titanosilicate ETS-10 containing boron in the framework (ETBS-10) are reported.

Microporous titanosilicates known as ETS contain six-coordinate framework titanium atoms and are, thus, fundamentally different from other zeolite-type solids. The framework of ETS-10, the most prominent member of this new family, consists 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 aluminium and gallium on sites which avoid Ti–O–Al(Ga) linkages.[4–6] We now wish to report the synthesis of boron-substituted ETS-10. Establishing the insertion of a light element, such as boron, in the framework of a zeolite-type material is, by no means, a trivial task. In order to gather as much evidence as possible for the substitution of silicon by boron in the framework of ETS-10 we have used a multi-technique approach.

ETBS-10 materials were prepared using a modification of the ETS-10 synthesis.‡ The samples were characterised by bulk chemical analysis (ICP), powder X-ray diffraction (XRD), high-resolution and scanning electron microscopies (HREM and SEM, respectively), FTIR and Raman spectroscopies, ^{29}Si and ^{11}B solid state NMR.

All ETBS-10 samples studied contain a single phase. The HREM images of this phase (not shown) are very similar to those previously reported for ETS-10.[2,3] The powder XRD patterns of ETS-10 and ETBS-10 samples (not shown) are almost identical, the only difference being a slight shift of the ETS-10 reflection at 2θ 24.63° to lower d-values when the boron content increases (2θ 24.72° for Si/B = 32). This is a first indication that the smaller boron atom replaces silicon in the structure of ETS-10.

The Raman spectrum of ETS-10 [Fig. 1(*a*)] contains a strong and sharp band at *ca.* 730 cm^{-1} associated with the TiO$_6$ octahedra. ETBS-10 samples display similar spectra [Fig. 1(*b,c*)] but this band broadens and shifts to higher frequency as the boron content increases. Similar effects have been observed with aluminium [Fig. 1(*d*)] and gallium (not shown) substituted ETS-10 samples. Hence, Raman spectroscopy provides further indication of the framework boron insertion.

Fig. 2 shows the ^{29}Si magic-angle spinning (MAS) NMR spectra of ETS-10 and ETBS-10 samples with different boron contents. 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 δ −94 to −97 and δ *ca.* −103.7, respectively.[3] The spectrum reveals a further crystallographic splitting of the Si(3Si, 1Ti) site. As the amount of boron in ETBS-10 increases, a new peak grows at δ *ca.* −99 and all the resonances broaden considerably. Owing to this broadening, the ETS-10 line splitting at δ *ca.* −96.5 is no longer resolved. This

further suggests that boron has been incorporated into the framework of ETS-10. Indeed, detailed studies on aluminium-substituted ETS-10 have shown that the broadening of the ^{29}Si MAS NMR resonances (and concomitant loss of the δ *ca.* −96.5 line splitting) is due to lattice distortion upon Al incorporation.[3] At present we cannot give a detailed assignment of the ETBS-10 peak at δ *ca.* −99. However, since (*i*) it becomes stronger as the boron content increases and (*ii*) we have found no evidence for the presence in our samples of any other (siliceous) phase, we believe that this resonance is given by Si–O–B environments.
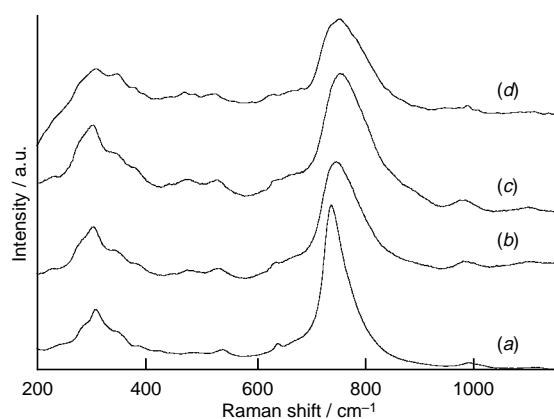

Fig. 1 Stokes shifted Raman spectra of (*a*) ETS-10, (*b*) ETBS-10 (Si/B = 45), (*c*) ETBS-10 (Si/B = 32) and (*d*) Al-substituted ETS-10 (Si/Al = 20). The spectra were measured using a Renishaw Raman imaging microscope model 2000.
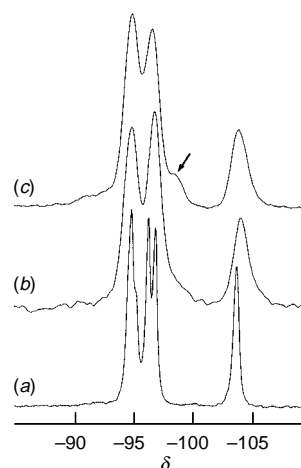

Fig. 2 ^{29}Si MAS NMR spectra of (*a*) ETS-10, (*b*) ETBS-10 (Si/B = 45) and (*c*) ETBS-10 (Si/B = 32). The spectra were recorded at 79.5 MHz on a Bruker MSL 400P spectrometer using 3.0 μs radio-frequency pulses, 40 s recycle delays and spinning rates of 5 kHz.
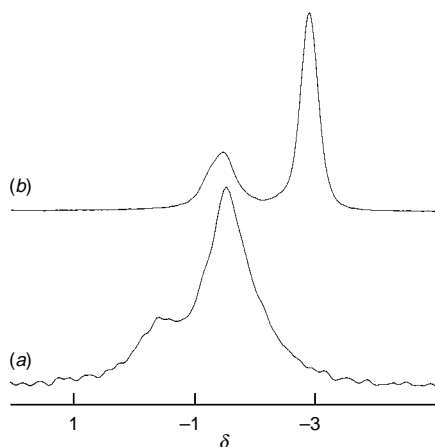
Fig. 3 (*a*) ¹H–¹¹B CP MAS and (*b*) ¹¹B MAS NMR spectra of ETBS-10 (Si/B = 32), recorded at 128.4 MHz, using 2 s recycle delays, a contact time of 1 ms and spinning rates of 7 kHz

The ¹¹B MAS NMR spectra [Fig. 3(*b*)] of ETBS-10 samples with different boron contents are similar and contain two groups of very sharp peaks (full width at half maximum, FWHM, *ca.* 78 Hz) at δ *ca.* −1.4 and −2.9. This implies that any electric field gradients created by the electronic cloud at the ¹¹B nuclei are very small and shows that boron is in tetrahedral, rather than trigonal, coordination[7,8] and, most likely, residing in the framework. Indeed, it has been reported that hydrated boron-substituted H-ZSM-5 zeolite gives a single sharp ¹¹B NMR peak at δ −3.[7] On the other hand, the local environment of any extraframework boron would, in principle, be more distorted or, at least, a dispersion of boron sites would occur leading to significantly broader ¹¹B NMR resonances. As prepared hydrated ETBS-10 and dehydrated ETBS-10 (500 °C for 2 h in air) display almost identical ¹¹B and ²⁹Si MAS NMR spectra. The parent gel gives a much broader (FWHM 360 Hz) ¹¹B resonance at δ *ca.* 1.1 (not shown). A second faint and broad peak is seen at δ *ca.* 3.2. The ¹H–¹¹B cross-polarization (CP) MAS NMR signal is very weak and the spectrum shown in Fig. 3(*a*) required the accumulation of 30 000 transients (500 for the MAS spectrum). We tentatively assign the two resonances at δ −1.4 and −0.5 to symmetric B–OH environments presumably associated with defect sites or on the surface of the crystallites. Since the former is broader than the δ −1.5 MAS NMR peak it is probably not given by the same boron site.

In order to be absolutely sure that the ¹¹B NMR spectrum of ETBS-10 does contain two separate resonances and that the peaks seen are not part of a second-order quadrupole powder pattern we have further recorded quadrupole nutation (QN)[8] and triple-quantum (3Q)[9] MAS NMR spectra. The latter (not shown) contains two ¹¹B resonances confirming the presence of two main boron sites (the peaks revealed by CP MAS are too faint to be detected). The QN spectrum (not shown) recorded with a radiofrequency, B_1, field of 28 kHz (non-selective excitation) again shows that two resonances are present. A second spectrum, recorded with B_1 = 10 kHz (small deviation from non-selective excitation) suggests that the δ −1.4 resonance has a larger quadrupole coupling constant (C_Q) and, hence, is given by a slightly more distorted boron site. However,

both C_{QS} are estimated to be very small (40–80 kHz) confirming that boron is in tetrahedral coordination.

Since ETS-10 contains corner-sharing TiO_6 octahedra and corner-sharing SiO_4 tetrahedra for every framework titanium there is an associated −2 charge. In an analogous way, when SiO_4 is replaced by AlO_4 a −1 charge is introduced. The preferred framework site for silicon substitution by aluminium in ETS-10 has been recently modelled by lattice energy minimisation and semi-empirical quantum chemical calculations on model clusters.[10] The latter technique indicates that, compared to Al–O–Si–O–Ti linkages, Al–O–Ti direct linkages result in enhanced electronic repulsion between neighbouring negative charges associated with the AlO_4 and TiO_6 sites and higher lattice strains. Thus, both electronic and strain factors influence the observed preferential aluminium siting and it is difficult to decide which one plays a more important role. At present, we are performing similar calculations to ascertain whether it is possible to decide or not which one these two factors plays a more important role in the location of boron in ETBS-10.

Notes and References

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