Crystal structure of the microporous titanosilicate ETS-10 refined from single crystal X-ray diffraction data

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ETS-10 crystals up to 45 μm in size have been synthesized at 240 °C under a pressure of 80 MPa and the structure refined from single crystal X-ray diffraction data.

Microporous titanosilicates have been of interest since the discovery of important catalytic properties in titanium silicalite-1 (TS-1) in oxidation and epoxidation reactions.[1] ETS-10 is a porous titanosilicate first reported by Kuznicki *et al.*[2,3] A large number of studies have been devoted to this material owing to its interesting chemical and physical properties.[3–18] A model for the structure of the ETS-10 framework was recently proposed by Anderson *et al.* based on a detailed HREM, NMR, powder XRD and structural modeling study.[5,6] The location of the extra-framework cations and the local environments of the framework cations have also been studied by NMR, XAS and computer modeling techniques.[7,12,17] However, to date, the small crystal size of samples of ETS-10 has prevented accurate structure refinement from single crystal data, in spite of efforts to improve the syntheses.[18] The positions of the extra-framework cation sites have not yet been determined experimentally from diffraction data.

We are investigating the possibility of improving the size and crystal quality of microporous materials by using synthesis temperatures and pressures that are higher than those usually employed (⩽400 °C and ⩽200 MPa). By using this approach, ETS-10 crystals as large as *ca.* 45 μm have been obtained and successfully used to obtain single crystal X-ray diffraction data and to subsequently refine the structure.

In a typical synthesis Na_2TiF_6 (0.208 g, 1 mmol) and TPABr (0.26 g, 1 mmol) were mixed with H_2O (2.2 ml). This mixture (0.36 ml) together with sodium silicate solution (0.72 ml, Aldrich, 14% NaOH, 27% SiO_2) and 1 M NaOH solution (0.2 ml) were sealed in a Teflon tube in air. The tube was inserted into a high pressure vessel and heated at 240 °C under an applied pressure of 80 MPa for 3 days using a LECO HR-1B-2 high pressure–high temperature system. The reaction vessel was then removed from the oven and cooled to room temperature in air. The product was washed with water, filtered and air dried. Well developed tetragonal platy crystals of ETS-10 with sizes up to *ca.* 45 μm were formed together with silicalite-1 and quartz. The yield is *ca.* 20%. All of the reflections characteristic of ETS-10 were identified in a X-ray powder diffraction pattern of the multiphase product. Composition analysis of the crystals with a JEOL 8600 electron microprobe gave the atomic ratio Ti : Si = 1.00 : 5.07 which is consistent with the formula $Na_2TiSi_5O_{13}$ reported in the literature[5] and which was confirmed by our structure refinement. For many crystallites, Na peaks were observed but diminished in intensity during the microprobe measurement probably owing to the instability of the crystals under the measurement conditions. A few crystals which did not show loss of intensity of the Na peak gave Na : Si ratios ≈ 2 : 5. ETS-10 is usually prepared from gel compositions containing both potassium and sodium cations. Synthesis in the presence of Na^+ alone, however, has been previously reported.[18]

A tetragonal body centered unit cell with $a = 7.481(1)$ and $c = 27.407(5)$ Å was derived from the single crystal data measured with CCD detector. Careful checking of all of the measured frames indicated that all observed reflections were consistent with this cell. This cell corresponds to that of the ordered polymorph A (see below) predicted by Anderson *et al.*[5,6] except that the *a* axis length is halved. The halving is expected because the electron diffraction patterns of ETS-10 reported in the literature show streaking of all reflections with h,k = odd indicative of a high degree of disorder along *a*.[5,6] The unit cell observed by the single crystal X-ray diffraction is a subcell of the true unit cell. Unfortunately, our samples are very sensitive to an electron beam and consequently efforts to measure their electron diffraction patterns were unsuccessful. The powder X-ray diffraction pattern of a sample from the same synthesis is consistent with a disordered structure and differs from the calculated patterns for ordered structure models.[6] The systematic extinctions in the measured X-ray reflections based on the subcell correspond to the space group $I4_1/amd$. A disordered structure model was successfully solved and refined with this symmetry, although the converged *R* factors of the refinements are moderately high because of the structural disorder and small crystal size.†

The refined framework structure is consistent with the structure model proposed by Anderson *et al.*[5] The TiO_6 octahedra share *trans* vertices to form TiO_5 infinite chains. These chains are each connected to two folded chains of $Si(2)O_4$ tetrahedra to form $[TiSi(2)_4O_{13}]$ columns through vertex sharing between the octahedra and tetrahedra. The columns are packed into layers parallel to the (001) plane with the columns in neighboring layers perpendicular to each other. The layers are interconnected by $Si(1)O_4$ tetrahedra which share all their vertices with the $Si(2)O_4$ tetrahedra to form a framework structure (Fig. 1, 2). In the disordered structure model based on the subcell, neighboring column positions cannot be occupied simultaneously because the resulting interatomic distances would be too short. The unoccupied column positions correspond to wide 12-ring channels. The occupancies of the column atoms [Ti, Si(2), O(3–5)] were refined to 0.50(1) and were fixed at 50% in the final refinements. Thus, each column belongs to a (001) layer that consists of parallel columns alternating with

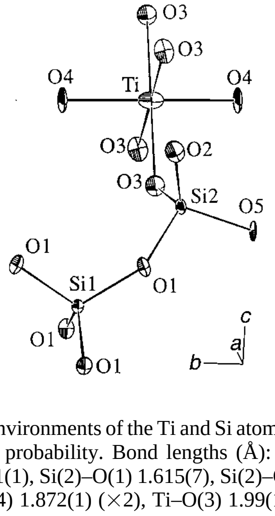

Fig. 1 Coordination environments of the Ti and Si atoms. Thermal ellipsoids are drawn with 50% probability. Bond lengths (Å): Si(1)–O(1) 1.612(7) (×4), Si(2)–O(3) 1.61(1), Si(2)–O(1) 1.615(7), Si(2)–O(5) 1.629(6), Si(2)–O(2) 1.698(4), Ti-O(4) 1.872(1) (×2), Ti–O(3) 1.99(1) (×4).

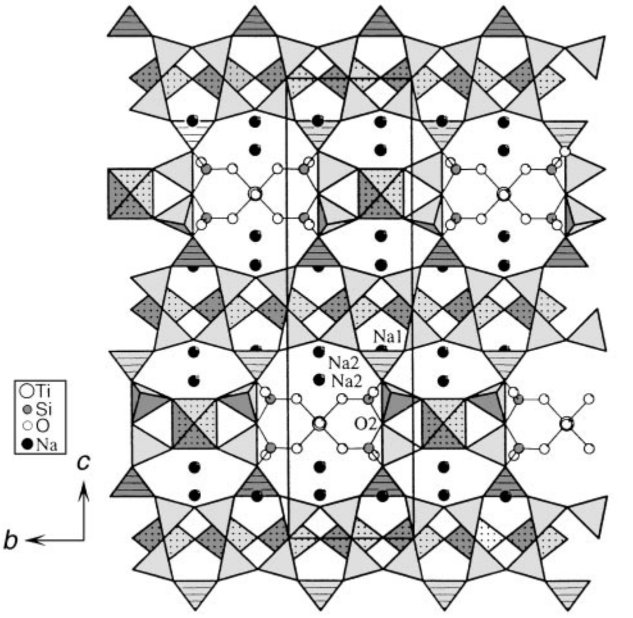

Fig. 2 Projection of the structure down (100). An ordered framework is represented with polyhedra. The $Si(1)O_4$ tetrahedra are hatched, the $Si(2)O_4$ are shaded and the TiO_6 octahedra are stippled. The non-framework Na cations are shown as filled circles.

12-ring channels. The O(2) site was found fully occupied because this site is located in the channel walls and is independent of the disorder. No disorder of the $Si(1)O_4$ tetrahedra was found in the refinements. As shown in Fig. 2, each $Si(1)O_4$ tetrahedron is connected to either a [100] $[TiSi(2)_4O_{13}]$ column plotted as ball-and-sticks or the one plotted as polyhedra. Since the neighboring (001) layers of columns are related by the 4_1 symmetry, there are four ways in which two neighboring layers are interconnected by the $Si(1)O_4$ tetrahedra to form an ordered double layer. Each of these ordered double layers may be considered as a stacking unit. Neighboring units can shift a half subcell along either [110] or [110] direction in order to form a framework. This gives rise to various stacking disorder possibilities. However, such stacking disorder does not cause blocking of the 12-ring channels. The hypothetical ordered polymorph A predicted by Anderson *et al.*[5,6] corresponds to simple ABAB… stacking. The structure model based on the subcell corresponds to fully disordered stacking.

The TiO_6 octahedron has site symmetry $2/m$ with the Ti–O bond lengths along the column axis (1.87 Å) being shorter than the others (1.99 Å). The $Si(1)O_4$ tetrahedron has site symmetry $4m2$ with Si–O bond length 1.61 Å. The $Si(2)O_4$ tetrahedron with Si–O bond lengths 1.61–1.70 Å and O–Si–O angles 103.3–116.8° is apparently distorted but this may be a consequence of the disorder. The –O–Ti–O–Ti– backbones of the columns are nearly linear (O–Ti–O) 180°, (Ti–O–Ti) = 177.9°. The elongated thermal ellipsoids of the Ti and O(4) atoms suggest some Ti–O bond length alternation along the chain and some tilting of adjacent octahedra in the ordered structure, as predicted from previous studies.[13,17]

The sodium cations occupy two nonequivalent positions. Na(1) is located near the $Si(1)O_4$ tetrahedra and is coordinated to eight oxygen atoms at distances 2.50–2.99 Å. The occupancy of Na(1) was found, as expected, to be nearly equal to that of the column atoms. Na(2) is split into two equivalent positions 1.67 Å apart, each of which has five coordinating oxygen atoms at 2.57–2.62 Å all located on one side of the position. The nearest oxygen atom positions on the opposite side are > 3.6 Å away. The apparent one-sided coordination implies that there are disordered space-filling species such as H_2O molecules which complete the coordination sphere of Na(2), but which can not be located by the refinements because the electron density overlaps with those of the column atoms in the subcell. Substantial water loss ($> 8\%$) below 200 °C has been reported for as-synthesized ETS-10 samples previously.[3] The splitting of the Na(2) site is related to the stacking disorder of the $[TiSi(2)_4O_{13}]$ columns.

In conclusion, we have employed a new synthesis approach to obtain ETS-10 crystals suitable for single crystal X-ray structure refinement. The structure refinement based on a disordered cell, confirms the previous structure model and provides details of the positions of both the framework atoms and extra-framework cations.

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Notes and references

† *Crystal data*: space group $I4_1/amd$, $a = 7.481(1)$, $c = 27.407(5)$ Å, colorless plate, crystal size $0.045 \times 0.045 \times 0.01$ mm. Mo-Kα radiation ($\lambda = 0.71073$ Å), $\mu = 1.1$ mm^{-1}, $2\theta_{max} = 57°$, $R(F) = 0.119/0.158$ for 426 reflections with $[I > 2\sigma(I)]$ all 532 unique reflections and 52 variables.

Intensities were measured on a SMART platform diffractometer equipped with a 1K CCD area detector using graphite-monochromatized Mo-Kα radiation at 20 °C. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 90 s frame^{-1}. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction applied on the intensities was $< 1\%$. The data were integrated using the Brucker SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The structure was solved with direct methods and refined using SHELXTL. All atom positions were refined anisotropically in the final refinements. Na(1) and Na(2) were fixed to have the same thermal parameters and a total occupancy of unity with a free occupancy ratio. CCDC 182/1236. See http://www.rsc.org/suppdata/cc/1999/973/ for crystallographic files in .cif format.

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