

Sorbate–framework interactions as an aid to vibrational mode assignment: FT-Raman studies of ETS-10

Sunil Ashtekar,^a A. M. Prakash,^b Larry Kevan^b and Lynn F. Gladden^a

^a Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge, UK CB2 3RA

^b Department of Chemistry, University of Houston, Houston, Texas 77204, USA

p-Xylene–framework interactions enable identification of Ti–O stretch and three-membered ring structures in the FT-Raman spectrum of ETS-10.

In recent years there has been increasing interest in the application of Raman spectroscopy and, in particular, FT-Raman techniques to the study of the structure of molecular sieve materials and adsorption processes within them.^{1–3} However, the characterisation of aluminosilicate frameworks using FT-Raman spectroscopy remains limited by the intrinsically weak Raman effect associated with these materials. Further, there exists controversy as to the ability of the technique to identify specific structural units such as three-membered rings (3MR) within aluminosilicate and related frameworks. In this study we exploit the effect of sorbate–framework interactions on the frequency of the Raman bands characteristic of the framework structure to assign bands to specific stretches and structural units. In so doing we identify specific bands associated with 3MR structures. The framework structure considered here is the microporous titanosilicate ETS-10 which consists of corner-sharing tetrahedrally coordinated silicon and octahedrally coordinated titanium linked through bridging oxygens. The structure consists of 12-, 7-, 5- and 3-membered rings.^{4,5} The main pore system is a three-dimensional 12-membered ring channel network and displays a considerable degree of disorder. Every titanium atom is connected to four silicon and two titanium atoms. Each TiO₆ unit carries a –2 charge that is balanced by extraframework cations such as Na⁺ and K⁺. [TiO₆]^{2–} units are part of the 7- and 3-membered ring channels.

The ETS-10 sample used in the present work was synthesized using the procedure reported by Anderson *et al.*⁴ Phase purity was checked by powder X-ray diffraction, which confirmed the absence of any TiO₂ impurity. Contamination of the sample with ETS-4 and AM-1 phase impurities was below that reported for the sample studied by Anderson *et al.*⁵ Electron microprobe analysis performed on a JEOL JXA-8600 spectrometer showed that the Si/Ti ratio was 5 : 1, consistent with the previously reported composition of ETS-10.⁵ The pure ETS-10 sample was calcined overnight at 500 °C in air prior to the FT-Raman experiment. A further sample containing 0.5 mmol *p*-xylene (g dry ETS-10)^{–1} was also prepared; *p*-xylene was chosen because it demonstrates significant changes in polarisability during interaction with the ETS-10 framework whilst still being small enough to move easily within the micropore structure. The *p*-xylene/ETS-10 sample was prepared by evacuating the calcined ETS-10 material at 10^{–6} Torr at 200 °C for 12 h, the required sorbate loading was then introduced using a gravimetric technique. The sample was then equilibrated at 65 °C and held at this temperature for 12 h to ensure that the adsorbate was evenly distributed within the ETS-10 framework. Raman measurements were performed at room temperature on a Nicolet-Magna-IR 750 spectrometer equipped with a Raman module and an InGaAs detector. A Nd:YAG laser was used operating at a power of 200 mW at an excitation wavelength of 1064 nm. The resolution was 4 cm^{–1}. For each spectrum, 4000 scans were co-added giving a data acquisition time of *ca.* 2 h.

Fig. 1 shows the FT-Raman spectrum of ETS-10. A very high signal-to-noise ratio, consistent with the absence of a high fluorescence background, is observed indicative of the absence of any organic impurity as expected given that ETS-10 does not require an organic template for its synthesis and is synthesised in an environment totally free of organic species. Reviews of previously published Raman studies of aluminosilicate frameworks show the most prominent band to occur in the region between 300 and 550 cm^{–1} followed by weaker bands in the 700–900 and 1000–1200 cm^{–1} regions.⁶ Bands in the 300–550 cm^{–1} region have been assigned to the motion of an oxygen atom in a plane perpendicular to the T–O–T (T=Si, Al) bonds.^{1,2,7} The spectrum of ETS-10 exhibits a very strong peak at 726 cm^{–1} along with a small peak to its low frequency side at 639 cm^{–1}. Given that silicates have a relatively low Raman scattering cross-section, we assign the strong band at 726 cm^{–1} to the Ti–O stretch of the [TiO₆]^{2–} rod structure present in the framework. This band was not observed in the FT-Raman spectrum of Ti-silicalite-1 (TS-1); we also note that the bands seen in the present study are not characteristic of the anatase or rutile phases of titania.⁸ The spectrum also contains bands of low intensity at 987 and 1104 cm^{–1}, generally ascribed to the asymmetric stretching vibration of the Si–O bond.³ Bands at 307, 427 and 539 cm^{–1} are assigned to the various T–O–T, O–T–O bending and skeletal deformation modes of the framework. The band at 539 cm^{–1} lies to higher frequency of the bands in the 470–510 cm^{–1} region characteristic of framework structures containing rings with four or more T atoms (T = Si, Al). Previous literature suggests that this band,

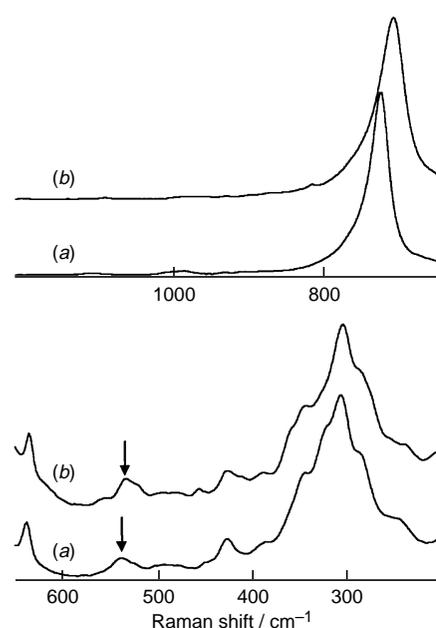


Fig. 1 FT-Raman spectra of (a) ETS-10 and (b) ETS-10 with a loading of *p*-xylene of 0.5 mmol (g dry ETS-10)^{–1}. The arrow indicates the band at 539 cm^{–1} in the pure ETS-10 spectrum.

as well as the band at 726 cm^{-1} , might be associated with 3MR structures. Assuming the correlation between average T–O–T (T=Si, Al) angle and Raman frequency to be valid,² and further that the same correlation applies to the case of the T atom being Si or Ti, a band at a frequency of 539 cm^{-1} would be consistent with a T–O–T bond angle of less than 138.1° and therefore consistent with the bond angle expected for a 3MR structure. An EXAFS analysis of ETS-10 has previously suggested a Ti–O–Si bond angle in ETS-10 of 130° .⁹ Further, Annen and Davis¹⁰ have suggested that if a band associated with a 3MR structure is observable it should occur in the frequency region of $550\text{--}800\text{ cm}^{-1}$, the particular frequency being dependent upon the type of T-atoms that are contained within the ring. However, in their work no common vibrational bands assignable to 3MR structures were observed in the range of materials studied.

Assignment of the bands at 726 and 539 cm^{-1} to 3MR structures is obtained by consideration of the FT-Raman spectrum of *p*-xylene sorbed within the ETS-10 framework. Consider first the band at 726 cm^{-1} assigned to the Ti–O stretch; the Ti–O bond being part of a 3MR structure. The sorbed aromatic is expected to associate itself with the charged species within the ETS-10 framework, and this is reflected in a shift of 16 cm^{-1} in the Ti–O stretch to lower frequency upon *p*-xylene sorption. The observed shift can be interpreted as follows. The *p*-xylene must reside within the 12-membered ring channels, and will interact through the π -electrons with the Na^+/K^+ cations which are present in order to balance the -2 negative charge associated with each Ti atom.⁹ The presence of sorbed *p*-xylene modifies the electrostatic interaction between the oxygens in the framework and the cations, thus causing the shift in Ti–O stretching frequency. We also note that there is a significant shift of the *p*-xylene C–H ring deformation mode from 1184 cm^{-1} in the pure liquid to 1193 cm^{-1} in the sorbed state, consistent with a strong sorbate–sorber interaction.¹¹ A

smaller shift in the 539 cm^{-1} band is observed again consistent with the 3MR structure, of which Ti is a constituent atom, being in close proximity to the sorbed *p*-xylene molecule; shifts in other bands are negligible.

Dr S. Ashtekar thanks BNFL for financial support. Drs A. M. Prakash and L. Kevan thank the US National Foundation and the Robert A. Welch Foundation for support. We also wish to thank Dr D. W. Lewis and Dr P. J. Barrie for their help in the preparation of this manuscript.

Footnote and References

* E-mail: Gladden@cheng.cam.ac.uk

- 1 P. K. Dutta, D. C. Shieh and M. Puri, *Zeolites*, 1988, **8**, 306.
- 2 P. K. Dutta, K. M. Rao and J. Y. Park, *J. Phys. Chem.*, 1991, **95**, 6654.
- 3 P. Knops-Gerrits, D. E. deVos, E. J. P. Feijen and P. A. Jacobs, *Microporous Mater.*, 1997, **8**, 3.
- 4 M. W. Anderson, O. Terasaki, T. Ohsuna, A. Philippou, S. P. MacKay, A. Ferreira, J. Rocha and S. Lidin, *Nature*, 1994, **367**, 347.
- 5 M. W. Anderson, O. Terasaki, T. Ohsuna, P. J. O. Malley, A. Philippou, S. P. MacKay, A. Ferreira, J. Rocha and S. Lidin, *Philos. Mag. B*, 1995, **71**, 813.
- 6 C. Bremard and D. Bougeard, *Adv. Mater.*, 1995, **7**, 10.
- 7 W. Pilz, *Z. Phys. Chem. (Leipzig)*, 1990, **271**, 219.
- 8 *The Handbook of Infrared and Raman Spectra of Inorganic Salts*, ed. R. A. Nyquist, C. L. Putzig and A. A. Leugers, Academic Press, San Diego, 1996, vol. 2, pp. 102–103.
- 9 G. Sankar, R. G. Bell, J. M. Thomas, M. W. Anderson, P. A. Wright and J. Rodia, *J. Phys. Chem.*, 1996, **100**, 449.
- 10 M. J. Annen and M. E. Davis, *Microporous Mater.*, 1993, **1**, 57.
- 11 J.-L. Guth, P. Jaques, F. Stoessel and R. Wey, *J. Colloid Interface Sci.*, 1980, **76**, 298.

Received in Cambridge, UK, 9th September 1997; 7/06563I