A XANES and EXAFS Investigation of Titanium Silicalite

Peter Behrens,*[a] Jürgen Felsche,[a] Sabina Vetter,[b] Günter Schulz-Ekloff,[b] Nils I. Jaeger[b] and Wilhelm Niemann[c]

[a] *Fakultät für Chemie, Universität Konstanz, Postfach 5560, D-7750 Konstanz, Germany*
[b] *Institut für Angewandte und Physikalische Chemie, Universität Bremen, D-2800 Bremen 33, Germany*
[c] *Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark*

XANES and EXAFS investigations of titanium silicalite-1, a microporous material with the structural features of zeolite ZSM-5, show that a large part of the titanium is coordinated octahedrally and probably occupies framework positions, a local environment that provides an explanation for the extraordinary catalytic properties of this material.

Titanium silicalite-1 (TS-1), first prepared by Taramasso *et al.*,[1] is a material with the structural features of the medium pore zeolite ZSM-5 (MFI structure type) and the formula $Ti_xSi_{1-x}O_2$ where x is restricted to a narrow range of $0 < x \leq 0.025$. TS-1 is an efficient catalyst for the oxidation of organic compounds with hydrogen peroxide and is already being employed in an industrial process.[2–4] Although TS-1 has been characterized extensively with respect to structure and catalytic activity,[1,3,5–7] the coordination of the Ti atoms in this material is still debated. Several measurements indicate a framework incorporation of Ti and thus are interpreted in terms of isomorphous substitution of Si by tetrahedral Ti. Powder X-ray diffraction[1,5] (XRD) shows a Vegard-law type dependence of the lattice parameters on Ti content and orthorhombic symmetry for TS-1 instead of monoclinic symmetry as observed in template-free silicalite-1 and ZSM-5 samples; the catalytic properties[6] of TS-1 are different from those of physical mixtures of silicalite-1 and TiO_2. However, IR and UV–VIS spectroscopic data have been interpreted by the presence of octahedrally coordinated Ti in framework positions.[7] To learn more about the coordination of Ti in TS-1, we have performed an X-ray absorption spectroscopic study at the Ti K-edge.

TS-1 was prepared following the procedure described in the patent of Taramasso *et al.*[1] from a gel containing tetraethyl silicate, tetraethyl titanate, water and tetrapropylammonium

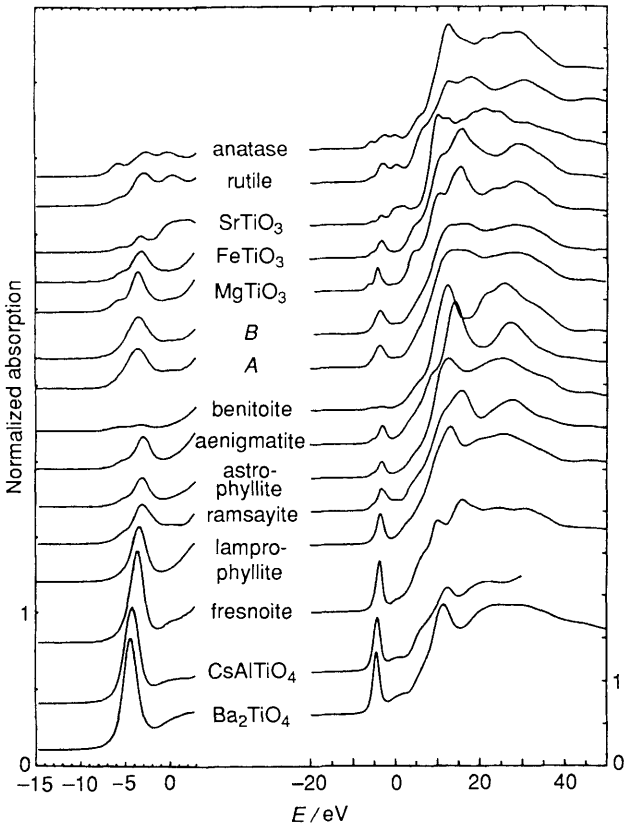

Fig 1 Ti K-edge XANES spectra of the as-synthesized sample *A* and of calcined TS-1 (*B*) together with those of reference compounds. The edge jump has been normalized to unity. The zero-point of the energy (*E*) scale was fixed at the first inflection of the K-edge of metallic Ti.

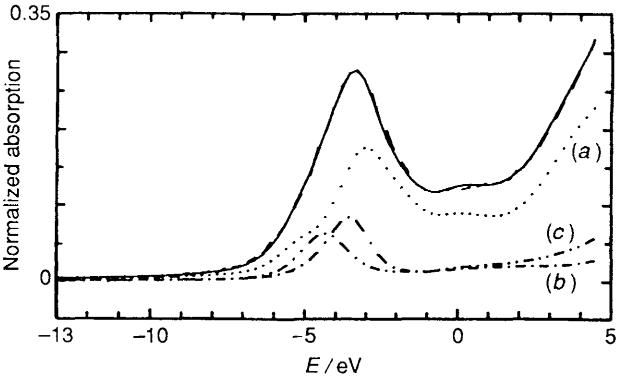

Fig. 2 Linear combination fit (——) of the pre-peak region of calcined TS-1 (– – –) using as reference spectra those of ramsayite for octahedral coordination (*a*), fresnoite for square-pyramidal coordination (*b*) and Ba_2TiO_4 for tetrahedral coordination (*c*). A fit of similar quality and with similar poportions of the three components is obtained for the as-synthesized sample.

hydroxide as a template by hydrothermal crystallisation at about 448 K under autogeneous pressure (sample *A*). Template-free TS-1 was obtained by calcination at 683 K in air (sample *B*). Powder XRD proved the samples to be pure phases. Lattice parameters for orthorhombic TS-1 are: a_0 20.089(12), b_0 19.864(9) and c_0 13.341(8) Å. Both samples were stored at ambient conditions, *i.e.* were in a hydrated state. Thermogravimetric analysis of sample *B* shows that it loses 2.5% of water in two steps. Under the conditions of the spectroscopic measurements (vacuum of about 10^{-2} Pa in order to reduce absorption of the X-rays in air) the first dehydration step occurs at room temperature.

The X-ray absorption near edge structures (XANES) of samples *A* and *B* are presented in Fig. 1 together with those of some model compounds. The thorough discussion of XANES spectra of titanium-bearing oxidic materials given by Waychunas[8] can be applied here, too. The most informative features of the spectra are the pre-edge peaks between −10 and 0 eV (the zero point of the energy scale has been fixed at the K-edge of metallic Ti), which are shown on an enlarged scale on the left side of Fig. 1. They are ascribed to 1s → 3d transitions of the excited electron and contain information about the coordination environment of the absorbing Ti atom. Compounds with tetrahedrally coordinated Ti (Ba_2TiO_4, $CsAlTiO_4$) show a strong absorption at −4.5 eV, those with square-pyramidal surrounding (fresnoite) at about −4 eV. Octahedral coordination gives less pronounced pre-edge features. If the coordination octahedron is regular, up to three peaks may be observed (anatase, rutile, $SrTiO_3$, benitoite), the central one at an energy of about −3 eV. With increasing distortion this central peak gains intensity ($FeTiO_3$, $MgTiO_3$). The titano-silicate minerals aenigmatite, astrophyllite and ramsayite contain distorted octahedral Ti. In accordance with the higher intensity and the position of its pre-edge peak, lamprophyllite contains both octahedral and square-pyramidal Ti.

The pre-edge peaks of sample *A* (TS-1 as synthesized) and sample *B* (calcined TS-1) are very similar, indicating that the calcination procedure has no significant influence on the coordination of the Ti atoms. Their height and position correspond to strongly distorted octahedral Ti. However, their width is larger than those of compounds with a uniform coordination. It may therefore be presumed that different environments of the Ti atoms coexist in TS-1 materials, with octahedral Ti dominating. This is indeed shown by a linear combination of the spectra of Ba_2TiO_4, fresnoite and ramsayite as references for Ti in tetrahedral, square-pyramidal and octahedral environment, respectively. Excellent fits of the pre-edge peaks of samples *A* and *B* are obtained (Fig. 2). The proportions of the different coordination geometries are: 10% tetrahedral, 15% square-pyramidal and 75% octahedral (with estimated errors of about 5%) for both samples. The fit procedure fails if a non-silicate compound is used for the dominating octahedral component. This indicates that Ti is in a silicate environment in TS-1.

The rise of the edge and its crest in the energy region between 0 and 10 eV are very similar for sample *A* and *B* and the titanium-silicate minerals with distorted octahedral (astrophyllite, ramsayite) or mixed octahedral–square-pyramidal (lamprophyllite) coordination. The spectra do not show any prominent shoulders or peaks like those of non-silicate compounds. This is another indication that Ti is in a silicate environment in samples *A* and *B*. The high energy parts (10 to 50 eV) of the XANES spectra, which reflect multiple scattering the excited electron experiences from neighbouring atoms, are strongly smeared out in the case of samples *A* and *B*. This corresponds to the mixed environment which is indicated by the broad pre-peak.

Samples *A* and *B* exhibit similar EXAFS oscillations (not shown here), supporting again the conclusion that the environment of the Ti atoms is the same in the as-synthesized and in the calcined sample. These oscillations are weak (in agreement with a mixed and/or distorted coordination by oxygen atoms) and their analysis is troublesome, *i.e.* the fitting procedure usually applied to obtain structural information from EXAFS data does not lead to reliable results here. Good agreement with these data is obtained by a simulation using phase-shift and backscattering amplitude functions determined on anatase, Ti–O distances as commonly observed in titanium compounds with tetrahedral, square-pyramidal and octahedral Ti coordination and the proportion of the three coordination types as obtained from our XANES analysis.

The second coordination shell around Ti is made up by a scatterer with low atomic number Z (Si).

Our results show that a large part† of Ti in TS-1 is coordinated octahedrally and is in a silicate environment. The titanium cannot be present in the form of small TiO_2 clusters. The fact that upon dehydration the amount of octahedral Ti decreases, while that of four- and five-fold Ti increases,[9] agrees favourably with framework incorporated Ti, the additional (*i.e.* non-framework) oxygen ligands probably stemming from H_2O, OH^- and silanol groups.[7] Although coordination numbers higher than four seem to be in conflict with the incorporation of Ti into a tetrahedral network structure, the flexibility of the MFI framework as it is expressed, *e.g.* by the reversible orthorhombic–monoclinic transition[10] of H-ZSM-5 or the fact that it tolerates trigonal coordinated boron atoms[11] in boron-substituted ZSM-5, may allow for such a substitution. Considering the strong dislike of Ti^{IV} for tetrahedral coordination by oxygen, the incorporation of five- or six-fold Ti into the MFI structure may be regarded as a compromise. The distortion of the structure induced by non-tetrahedral framework atoms is a straightforward explanation for the low maximum Ti content of TS-1. On the other hand, the strain imposed on five- or six-fold Ti atoms by the demand of the framework for four bonds with tetrahedral orientation may account for the extraordinary catalytic properties of this material.

We thank the Hamburger Synchrotronstrahlungslabor HASYLAB at DESY for allocating beam time and J. Ehrich, M. Fröba and R. Piffer for help with the measurements. This work was supported by the Bundesminister für Forschung und Technologie under contract 03-FE2KON.

Received, 9th November 1990; Com. 0/05045H

References

1 M. Taramasso, G. Perego and B. Notari, US Pat., 4410510, 1983.

2 A. Esposito, C. Neri and F. Buonomo, Deutsche Offenlegungsschrift 3309669, 1983; A. Esposito, C. Neri and F. Buonomo, Eur. Pat. 0102655, 1984; P. Roffia, M. Padovan, E. Moretti and G. de Alberti, Eur. Pat. 0208311, 1987; C. Neri, B. Anfossi, A. Esposito and F. Buonomo, Eur. Pat. 0100119, 1984; C. Neri and F. Buonomo, Eur. Pat. 0100117, 1984.

3 B. Notari, in *Innovation in Zeolite Materials Science, Studies in Surface Science and Catalysis*, eds. P. J. Grobet, W. J. Mortier, E. F. Vansant and G. Schulz-Ekloff, Elsevier, Amsterdam, 1988, vol. 37, p. 413.

4 U. Romano, A. Esposito, F. Masperi, C. Neri and M. Clerici, in *New Developments in Selective Oxidation, Studies in Surface Science and Catalysis*, eds. G. Centi and F. Trifiro, Elsevier, Amsterdam, 1990, vol. 55, p. 33; P. Roffia, G. Leofanti, A. Cesana, M. Mantegazza, M. Padovan, G. Petrini, S. Tonti and P. Gervasutti, p. 43; C. Ferrini and H. W. Kouvenhoven, p. 53.

5 G. Perego, G. Bellussi, C. Gorno, M. Taramasso, F. Buonomo and A. Esposito, in *New Developments in Zeolite Science and Technology, Studies in Surface Science and Catalysis*, eds. Y. Murakami, A. Iijima and J. W. Ward, Elsevier, Amsterdam, 1986, vol. 28, p. 129.

6 B. Kraushaar-Czarnetzki and J. H. C. van Hooff, *Catal. Lett.*, 1989, **2**, 43; T. Tatsumi, M. Nakamura, S. Negishi and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1990, 476; D. R. C. Huybrechts, L. De Bruycker and P. A. Jacobs, *Nature*, 1990, **345**, 240.

7 M. R. Boccuti, K. M. Rao, A. Zecchina, G. Leofanti and G. Petrini, in *Structure and Reactivity of Surfaces*, eds. C. Morterra, A. Zecchina and G. Costa, Elsevier, Amsterdam, 1989, p. 133.

8 G. A. Waychunas, *Am. Mineral.*, 1987, **72**, 89.

9 P. Behrens, S. Aβmann, J. Felsche, S. Vetter, G. Schulz-Ekloff, N. I. Jaeger and W. Niemann, in Proceedings of the VIth International Conference on X-ray Absorption Fine Structure, York, 1990, in the press.

10 E. L. Wu, S. L. Lawton, D. H. Olson, A. C. Rohrman and G. T. Kokotailo, *J. Phys. Chem.*, 1979, **83**, 2777; H. van Koningsveld, J. C. Jansen and H. van Bekkum, *Zeolites*, 1989, **9**, 253; H. van Koningsveld, J. C. Jansen and H. van Beckum, *Zeolites* 1990, **10**, 235.

11 K. F. M. G. J. Scholle and W. S. Veeman, *Zeolites*, 1985, **5**, 118.

---

† It cannot be excluded that a partial dehydration and reduction in coordination number takes place during evacuation; in TS-1 stored at ambient conditions all the Ti might be in an octahedral environment.