

Hydration Effect on Titanium Linkage to Silicalite Framework

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An EXAFS multishell analysis of a titanium silicalite with an MFI structure reveals that the double Si–O–Ti bridges formed between [TiO_x] species and the [SiO₄] framework tetrahedra are partially hydrolysed in the presence of water which results in the conversion from an edge- to a corner-sharing type of bonding between the two structural units.

The incorporation of transition metal ions into zeolite frameworks is a challenge owing to the combination of the higher stability of these ions in octahedral sites and the fact that the framework is made exclusively of tetrahedral substitution T sites. Nevertheless, some success has been achieved, in particular for titanium in silicalites of MFI (TS-1), MEL (TS-2), β or ZSM-48 structure^{1–4} producing new materials which had a unique catalytic activity in the selective oxidation of hydrocarbons.^{5–7} Based on the measured unit cell expansion as a function of the titanium incorporation level, it is widely believed that Ti⁴⁺ ions occupy regular T sites. However, a recent X-ray absorption near edge structure (XANES) study of the titanium K-edge showed that the titanium ions may occupy octahedral sites in TS-1 materials.⁸ Combining XANES and extended X-ray absorption fine structure (EXAFS), one of us showed that hydration does indeed modify the titanium environment from tetrahedral to octahedral in TS-1 materials.⁹ An EXAFS multishell analysis on TS-2 samples indicated that the [TiO_x] units were linked to

the framework [SiO₄] tetrahedra *via* an unusual edge-sharing type of binding which was not compatible with T sites.^{10,11} In this study, a multishell analysis has been applied on the same hydrated and dehydrated TS-1 samples as previously studied⁹ in order to determine the effect of hydration in terms of the evolution of the titanium local environment.

A titanium silicalite characterized by a Ti/Ti + Si ratio of 1.9 was prepared from the silicon and titanium alkoxide precursors and the appropriate template.² The samples were calcined at 773 K and stored in a dehydrated form before EXAFS measurements or rehydrated in air for several months. XRD revealed the characteristic MFI structure. The IR spectra of these materials showed the characteristic band at 960 cm⁻¹ which is attributed to titanium framework incorporation.^{1–7} The X-ray absorption data were collected in the transmission mode at LURE (France) on the monochromatized [Si(111) two-crystal channel-cut] radiation emitted by DCI. Sample preparation, analysis and presentation of the results were performed as previously described.^{10,11} The

McKale theoretical phase and amplitude backscattering functions were used for EXAFS simulation performed in the single electron–single scattering approximation. The electron inelastic mean free path, $\lambda/\text{\AA}$, was approximated by the empirical equation (1) where ξ , which is kept constant at 3.1, and Γ (always close to 1) are empirical parameters.^{10,11}

$$\lambda = (1/\Gamma)[(\xi/k)^4 + k] \quad (1)$$

Fig. 1 depicts the EXAFS oscillations and their Fourier transforms. The first FT peak is attributed to the baseline residue. The second peak contains the first oxygen neighbour contributions, the $O_{(1)}$ shell. For the hydrated sample, a beat at approximately 1.8 \AA is absent and an FT peak is apparent at about 3.2 \AA . EXAFS spectra were simulated and a satisfactory fit was achieved over a larger range than previously investigated (2.5–11.2 instead of 3–9 \AA^{-1}) by adding a silicon shell, $Si_{(1)}$, at about 2.3 \AA ; the beat at 1.8 \AA was then reproduced with reasonable fit parameters (Table 1). The introduction of a second oxygen shell, $O_{(2)}$, at about 2.0 \AA enabled the fit to include an increase of the coordination number from 4 to 5 since it is expected that hydration would

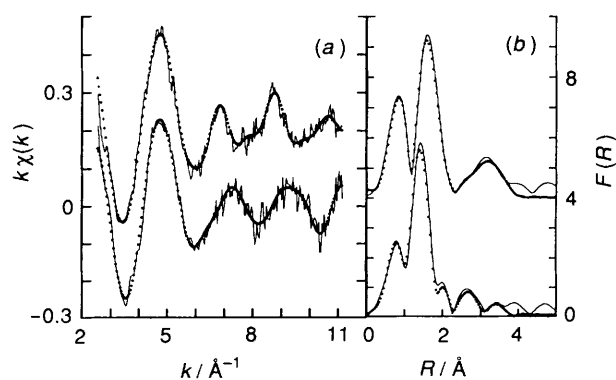
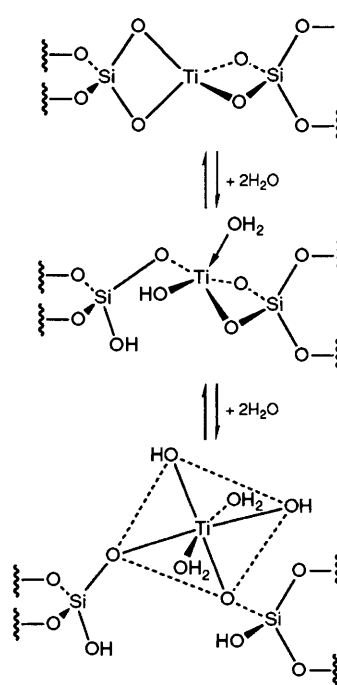


Fig. 1 Ti K-edge (a) EXAFS oscillations and (b) FT transforms of dehydrated (bottom) and rehydrated (top) TS-1: raw data (full line) and simulation on 0–3.77 \AA FT filter (dots) (offsets of +0.21 for top EXAFS lines and +4 for top FT lines)



Scheme 1

Table 1 EXAFS simulation parameters for dehydrated and hydrated TS-1^a

| Sample | Simulation parameters | Close shells | | | Proposed far shells | | | | |
|-------------------------|---------------------------------|-----------------|-----------------|------------------|---------------------|--------------------|-----------|--------------------|--------------------|
| | | $O_{(1)}$ | $O_{(2)}$ | $Si_{(1)}$ | $Ti_{(1)}$ | $Si_{(2)}$ | $O_{(3)}$ | $Si_{(3)}$ | $Ti_{(2)}$ |
| Hydrated ^b | N | 4.0 ± 1.7 | — | 1.5 ± 0.9 | — | — | — | — | — |
| | $\sigma \times 10^2/\text{\AA}$ | 8.4 ± 1.6 | — | 7.8 ± 3.3 | — | — | — | — | — |
| | $R/\text{\AA}$ | 1.97 ± 0.08 | — | 2.41 ± 0.22 | — | — | — | — | — |
| | $\Delta E/eV$ | 6.2 ± 3.2 | — | -22.4 ± 3.5 | — | — | — | — | — |
| Hydrated ^c | N | 3.3 ± 1.8 | 1.7 ± 0.9 | 0.84 ± 0.75 | (0.48) ^d | 1.0 | 4.6 | 1.64 | 2.6 |
| | $R/\text{\AA}$ | 1.93 ± 0.15 | 2.00 ± 0.17 | 2.18 ± 0.22 | 2.66 | 2.95 | 3.58 | 3.55 | 4.00 |
| Dehydrated ^b | N | 3.9 ± 1.3 | — | 2.0 ± 0.6 | — | — | — | — | — |
| | $\sigma \times 10^2/\text{\AA}$ | 4.0 ± 1.5 | — | 6.3 ± 3.2 | — | — | — | — | — |
| | $R/\text{\AA}$ | 1.89 ± 0.11 | — | 2.24 ± 0.16 | — | — | — | — | — |
| | $\Delta E/eV$ | 8.4 ± 1.19 | — | -15.8 ± 32.4 | — | — | — | — | — |
| Dehydrated ^c | N | 3.6 ± 1.5 | 0.5 ± 0.4 | 1.2 ± 0.4 | (0.2) ^d | (0.6) ^d | 1.9 | (0.8) ^d | (0.7) ^d |
| | $R/\text{\AA}$ | 1.88 ± 0.10 | 2.14 ± 0.16 | 2.26 ± 0.11 | 2.73 | 2.88 | 3.39 | 3.45 | 3.86 |

^a Accuracy calculated for nearest shells using covariant matrix and signal to noise ratio. N , σ , ΔE_0 and R are, respectively, the coordination number, the Debye–Waller factor, the energy threshold shift and the distances in a given shell X_i ; X indicates the element in a shell by its symbol, and i increments shells made of identical elements. ^b Simulation performed in the 2.5–11.2 \AA^{-1} range on a 0–2.49 \AA FT filter including baseline residue. There were 14 independent parameters and the simulation was performed on 13 parameters (5 for a baseline simulated as a fake oxygen shell^{10,11} and four for $O_{(1)}$ and $Si_{(1)}$ with $\Gamma = 1$). Fit quality (χ^2/ν) or fit residue were 0.9 or 1.1 and 9.5×10^{-3} or 5.7×10^{-3} for dehydrated and hydrated samples, respectively. ^c Simulation k range same as in ^b applied on a larger filter (0–3.77 \AA) providing 21 independent parameters. The residue was reduced more than 2 times and the fitting parameters were very close for both samples and for TS-2 samples.^{10,11} This simulation provides much less negative ΔE_0 and approximately the same σ as for the corresponding shells in simulation ^b. Substitution of Si by Ti or O atoms was performed but did not lead to satisfactory fits or to realistic positions. ^d Parentheses indicate a shell whose contribution is at the limit of significance with respect to the signal to noise ratio.

O₍₃₎, Ti₍₃₎ and Si₍₃₎ shells, whereas in the dehydrated samples only the O₍₃₎ shell is significant (Table 1). The shells involving titanium neighbours and therefore titanium clustering will be discussed elsewhere.¹³

The presence of the Si₍₃₎ shell attributed to single Ti–O–Si bridges,^{10,11} is emphasized here. It corresponds to corner-sharing between TiO_x species and SiO₄ framework tetrahedra, while the closer S₍₁₎ shell at 2.3 Å is due to double bridges, *i.e.* to an edge-sharing type of binding.^{10,11} Despite the limitations due to multiple-scattering events for almost aligned neighbours, as in the case for O and Si in single Ti–O–Si bridges, some general trends can be seen. Based on the evolution of the coordination number in the Si₍₁₎ and S₍₃₎ shells, the argument is that the double Ti–O–Si bridges are partially hydrolysed to give rise to single Ti–O–Si bridges upon hydration. The respective distances between Ti and Si in each case indicates that Ti⁴⁺ ions move backwards from Si⁴⁺ ions in the hydrated form. More detailed XPS, IR, EXAFS and XANES studies support this hypothesis as well as the partial reversal of hydration by a subsequent dehydration cycle.^{13,14}

Scheme 1 depicts how hydration could affect the titanium environment in a site whose structure^{10,11} implies a tetrahedral titanium linked to the silicalite framework *via* edge-sharing with two [SiO₄] tetrahedra. This scheme takes into account the evolution of the titanium coordination according to the increased number of oxygen neighbours (O₍₁₎ and O₍₂₎) and the symmetry evolution characterized by the Ti X-ray absorption K edges.⁹ A sequence of equilibria for a single type of site would explain an incomplete coordination saturation. Nevertheless, in accordance with the coexistence of various titanium symmetries and types of linkage to the framework;^{8–15} a mixture of non-equally water-sensitive sites is more likely to explain the results without the need to exclude an equilibrated hydration process. The complexity of this system is probably due to different titanium site locations in the silicalite framework.

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