XAFS study of Ti-silicalite: structure of framework Ti(IV) in presence and in absence of reactive molecules (H_2O, NH_3)

S. Bordiga[a], F. Boscherini[b], S. Coluccia[a], F. Genoni[c], C. Lamberti[a,d], G. Leofanti[c], L. Marchese[a], G. Petrini[c], G. Vlaic[e] and A. Zecchina[a,1]

[a]*Dipartimento di Chimica Inorganica, Chimica, Fisica e Chimica dei Materiali, Via P. Giuria 7, I-10125 Turin, Italy*
[b]*INFN-LNF, PO Box 13, I-00044 Frascati (Rome), Italy*
[c]*Centro di Ricerche ENICHEM ANIC di Bollate, Via S. Pietro 50, I-20021 Bollate (Mi), Italy*
[d]*INFN Sezione di Torino, via Pietro Giuria 1, I-10125 Turin, Italy*
[e]*Dipartimento di Scienze Chimiche, Via Valerio 38, Trieste and Sincrotrone Trieste SCpA, Padriciano 99, I-34012 Trieste, Italy*

Received 20 October 1993; accepted 10 February 1994

X-ray absorption at the Ti K edge (both XANES and EXAFS) of a very pure Ti-silicalite containing a small fraction of Ti(IV) substituting Si(IV), has been performed in order to study the effect of the presence or absence of ligands such as H_2O and NH_3 on the Ti(IV) coordination sphere. In particular, the effect of an outgassing treatment at 400 K and of the interaction with NH_3 has been studied and described in detail. It has been found that the Ti(IV) is fourfold coordinated in the samples outgassed at 400 K and expands its coordination sphere number under the action of adsorbates.

Keywords: zeolite; Ti-silicalite; XAFS; XANES; pre edge absorption; EXAFS

1. Introduction

Ti-silicalite, a zeolite of the pentasil family containing a small percentage of Ti substituting Si (1–2% in atoms), has shown in recent years to be an efficient and selective catalyst for oxidation reactions in solution with H_2O_2 [1–3].

The location and the structure of Ti(IV) has been investigated by means of several physical methods like XRD, UV-Vis, EPR, IR and Raman spectroscopies in order to establish the geometry and the coordination state of framework Ti(IV) and to identify extraframework Ti(IV) [4–6]. The debate is still open on the first

---

[1] To whom correspondence should be addressed.

point. In fact, even if all these mentioned techniques point towards tetracoordinated Ti substituting Si in the lattice, the state of aggregation of $[TiO]_4$ units is still debated [7,8] together with the distortion from the tetrahedral geometry.

The most important spectroscopic features associated with framework Ti(IV) in vacuum conditions can be summarized as follows [6]:

(i) IR band at 960 cm^{-1} (absent in pure and perfect silicalite): interpreted either as a mode with prevailing Si–O stretching character involving $[SiO_4]$ units perturbed by an adjacent Ti(IV) or as a stretching mode of framework Ti containing units such as $[TiO_4]$ or $[O_3TiOH]$ (or to a mixture of the two models); the recent assignment of Camblor et al. [9] and of Andrzej et al. [10] in terms of stretching modes of $Si–O^-$ groups is essentially along this line. This problem has been more recently reviewed and discussed in ref. [11], where an assignment of the finger print band in terms of stretching modes of $[SiO_4]$ groups perturbed by the presence of Ti(IV) (with little admixture of $[TiO_4]$ and $[O_3TiOH]$ vibrations) is preferred.

(ii) Raman bands at 960 cm^{-1} (strong) and at 1127 cm^{-1} (weak) (not present in pure and perfect silicalite): assigned to two Raman active modes of perturbed $[SiO_4]$ units, or to two vibrations involving $[TiO_4]$ or $[O_3TiOH]$ units embedded in the lattice (or to a mixture of the two models). The assignment is reported in detail in ref. [11].

(iii) Bands at 48000 cm^{-1}: assigned to ligand to metal charge transfer (LMCT) transitions in $[TiO_4]$ and $[O_3TiOH]$ tetracoordinated structures.

The interaction with adsorbates like H_2O, NH_3, H_2O_2 etc. selectively perturbs the IR manifestation of framework Ti(IV) (peak at 960 cm^{-1}) [4]. As the interaction with adsorbed molecules leaves all the other IR bands associated with the framework modes (1300–750 cm^{-1} interval) unchanged, this confirms that this peak is associated with Ti(IV) centres and that the adsorption occurs prevalently on them.

The interaction with the same adsorbates causes a similar effect on the Raman absorptions at 960 and 1127 cm^{-1} [11].

The optical manifestations in the UV-Vis range (50000–40000 cm^{-1} 6–5 eV) are perturbed by interaction with adsorbates like H_2O, NH_3, H_2O_2 etc. with appearance of new bands associated with novel ligand to metal charge transfer transitions from H_2O, NH_3 and OOH ligands to Ti(IV) [12,13]. Unlike the IR and Raman experiments, these new bands show that a direct interaction of the incoming ligands with the Ti(IV) centres is occurring and hence prove that the coordination number of Ti(IV) increases upon interaction with adsorbates.

X-ray absorption spectroscopy is a powerful tool to investigate local atomic coordination in solids, liquids and molecules. A notable advantage of this technique is its chemical sensitivity, as it is possible to "tune in" to the absorption edge of the atom desired and thus to obtain chemical selective information. The development of synchrotron radiation sources has considerably improved this technique. The information which can be obtained from the interpretation of X-ray absorption spectra includes local atomic bonding parameters (bond lengths, coordination numbers and disorder factors) [14–16] and the local geometry around the absorbing atoms including bond angles [17]. For these reasons the coordination state of Ti has been often investigated by means of X-ray absorption spectroscopy at the Ti K edge and several studies have been published in recent years [7,8,18–28]. In the present paper we present an analysis of the pre edge and near edge region (XANES) around the Ti K edge and also an EXAFS determination at the local bonding parameters. We refer to the quoted papers [21–23] for a detailed description of the origins of the near edge spectral features. For the purpose of this paper it is sufficient to know the following concepts.

Ti(IV) is in a d^0 configuration corresponding to an A_{1g} or A_1 state in, respectively, octahedral or tetrahedral symmetry. The first feature in the absorption spectrum (the pre edge) corresponds to excitation of the 1s electron into empty bound states, derived from Ti and O d and p states [22].

In octahedral symmetry the final states (empty d orbitals) are T_{2g} and E_g, hence the transitions are:

$$A_{1g}-T_{2g}$$

$$A_{1g}-E_g\,,$$

which are Laporte forbidden. Consequently the pre edge absorption of Ti(oct) is expected to be rather weak.

In tetrahedral symmetry (where no inversion symmetry is present) the final states are T_2 and E and the expected transitions are:

$$A_1-T_2$$

$$A_1-E\,.$$

As in the T_2 states considerable mixing of the 3d and 4p orbitals occurs, the A_1–T_2 transition becomes allowed and is therefore particularly strong. This is the reason why tetrahedral Ti(IV) is characterized by a strong peak (A_1–T_2) overwhelming the weaker A_1–E transition. In a distorted octahedral symmetry and in other symmetries where a progressive relaxation of inversion symmetry occurs, the pre edge region is characterized by the predominance of the central peak with respect to the other two (indeed, in many cases only the central peak is observable) [18,19,21,22].

From all these considerations it is evident that analysis of the intensity, width and position of the pre edge features, can be helpful in distinguishing different coordinative situations, and their modifications under the effect of adsorbates. It is also evident that, like UV-Vis spectroscopy, XANES spectroscopy can give a direct information of the first coordination sphere of Ti(IV). Together with a detailed analysis of the pre edge region, we present the quantitative determination of the local bonding parameters from the EXAFS part of the spectrum. In order to do this we employ the single scattering formula [15,16], which is exact for the first shell contribution. In this work we have studied a very pure and well characterised Ti-silicalite sample. The effects of the adsorption and desorption of adsorbates (H_2O and NH_3) are also reported and discussed.

2. Experimental

2.1. MATERIAL AND METHODS

The synthesis procedure of Ti-silicalite is described elsewhere [29]. In Ti-silicalite sample (Ti = 1.47 wt%) Ti(IV) was nearly completely in the framework (as determined by means of several characterization methods [4,6]), only a 0.05% fraction being in extraframework position.

X-ray absorption measurements were performed at the PULS X-ray beamline of Frascati National Laboratories in Frascati, Italy. The storage ring was operated at 1.5 GeV (yielding a critical energy of 1.5 keV) and typical beam current was 40 mA. The X-ray source was monochromatized using a Si(111) channel cut monochromator. At the Ti edge the harmonics content is negligible due to the low critical energy and to the absence of the $n = 2$ reflection for Si(111). Measurements were performed in the transmission mode and the incident and transmitted flux were measured using nitrogen and argon filled ionisation chambers. For near edge spectra the estimated energy resolution was 0.6 eV and the step size was 0.2 eV; for the extended spectra (EXAFS) 2 eV steps were used, with an estimated resolution of 2 eV.

The zeolite sample, obtained as thin self supporting pellet, was placed inside a pyrex cell equipped with two mylar windows. This cell was used for both thermal treatment and gas dosages (pyrex compartment), and during X-ray measurements (between the two mylar windows). During the measurements the atmosphere surrounding the pellet was constant and carefully controlled. The cell atmosphere was varied in a fully controlled way by connecting the cell to a vacuum manifold allowing gas dosage and outgassing procedure under vacuum (10^{-2} Pa).

2.2. DATA ANALYSIS

All the XANES spectra we show were background subtracted with a linear function in the energy range 4900–4960 eV; subsequently the spectra were normalized to unity in the continuum at 5100 eV, in order to make a meaningful comparison of the intensity of the pre edge features.

The main characteristics of the pre edge absorptions (peak positions, full width half maximum (FWHM) and intensity) were obtained using the band fitting program ASYMGRAD [30]. The fitting was carried out assuming for the experimental peaks a Lorentzian shape, see eq. (7) in ref. [30].

The EXAFS spectra were analyzed according to standard procedures [16]. The pre edge region was subtracted with a polynomial function, then the EXAFS spectrum was extracted by fitting the absorption coefficient with a cubic spline curve, finally the EXAFS was normalized by $J[1-\frac{8}{3}(E-E_0)/E_0]$, where J is the jump height. A preliminary analysis of spectra was performed by inspection of the Fourier transform, which yields an intuitive picture of local bonding around the excited atom. To perform the Fourier transform the EXAFS was multiplied by k^3 in the range $k = 2$ to $k = 12$ Å and a Hanning window was used. Quantitative analysis was performed by fitting the Fourier filtered signal of the first shell with a theoretical signal, using a non-linear least squares routine [31] (MINUIT subroutine of the CERN library) and minimization of a χ^2 type function.

The single-electron single scattering EXAFS theory [16] was applied by using the following equation:

$$k[\chi(k)] = \sum_i \frac{N_i}{R_i^2}[f_i(k)]\mathrm{e}^{-2\sigma_i^2 k^2}\,\mathrm{e}^{-2R_i/\lambda_i(k)}\sin[2kR_i + \phi_i(k)]\,. \tag{1}$$

In our calculation the variable i runs only over the first shell neighbour atoms. N_i is the number of atoms in the ith scattering shell at a distance R_i from the absorbing atom. σ_i is a coefficient related to thermal and static disorder. $\lambda_i(k)$ is the electron mean free path. The value of $\lambda_i(k)$ was found by fitting the spectrum of anatase (our reference compound of known structure: six nearest oxygen neighbours at 1.95 Å) and then was kept fixed in the subsequent fits. $f_i(k)$ and $\phi_i(k)$ are the amplitude and the phase shift functions respectively. In our simulations the theoretical curves obtained from McKale et al. [32] were used. These parameters when checked on TiO_2 (our model compound) gave the following results: $N = 6$; $R = 1.95$; $\sigma^2 = 0.0084$; so they have been considered adequate for Ti-silicalite.

Errors on the local bonding parameters were found by varying each parameter (N, R, σ^2) until the fitting function increased by $\sqrt{2}$ while varying the other parameters. This method takes account of the correlation between parameters, which is especially severe for N and σ^2 with weak backscatterers, such as O (as our case).

3. Results and discussion

3.1. XANES

3.1.1. Effect of the surrounding atmosphere on the XANES spectra of Ti(IV)

Spectrum 1 in fig. 1 corresponds to the Ti-silicalite sample outgassed at 300 K for a few seconds (in this condition the water molecules coordinated to the titanium are not completely removed); spectrum 2 corresponds to the sample outgassed at 400 K for 30 min. Both the pre edge spectra are characterised by one, well defined and intense peak. From the comparison of the two spectra, the following conclusions can be drawn:

(i) Upon the outgassing treatment the peak position shifts from 3.2 to 2.9 eV (the zero of the energy scale was taken at 4964.2 eV, which corresponds to the maximum of the first peak of a titanium foil K edge).

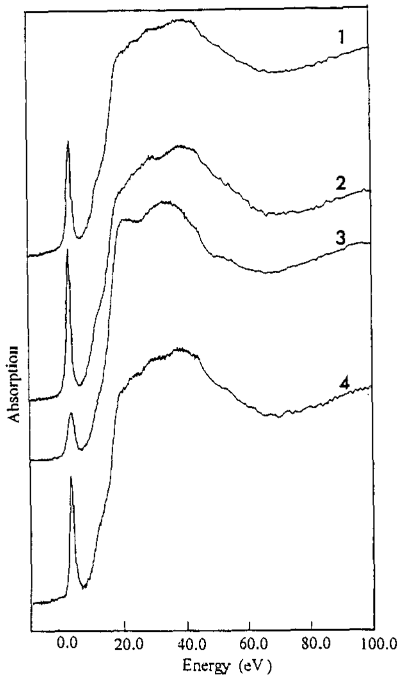

Fig. 1. XANES spectra of [TS]: effect of outgassing in vacuo and of NH_3 adsorption followed by desorption. (1) [TS] outgassed at 300 K; (2) outgassed at 400 K: (3) after dosage of NH_3 (equilibrium pressure of 10^4 Pa); (4) effect of pumping at room temperature for 10 min. (The zero of the energy scale was taken at 4964.2 eV which corresponds to the maximum of the first peak of a titanium foil K edge.)

(ii) The intensity of the peak increases from 56 to 75%.

(iii) The full width at half maximum (FWHM) decreases from 1.7 to 1.4 eV.

All these experimental features (especially the intensity and the width) clearly indicate a significant modification of the Ti coordination sphere as a consequence of the sample treatment (H_2O removal).

Comparison of our data with those reported in literature relative to Ba_2TiO_4 (considered as the model compound for Ti(IV) in tetrahedral coordination) and other compounds [20,22] where Ti(IV) is certainly in tetrahedral coordination ($Ti[N(CH_3)_2]_4$ and $Ti(AOm)_4$) is very informative. All such data are summarized in table 1 together with results concerning three Ti-silicalite samples previously described in the literature [7,8,25,26] and with Ti(IV) compounds where Ti(IV) is in fivefold coordination ($Ti(OEt)_4$ and $Ti(OBu)_4$).

From table 1 it is evident that the similarity of the data of [TS] (sample outgassed at 400 K) with those of tetrahedral compounds, indicates that we are dealing with a structure where Ti(IV) is tetracoordinated and in a coordination symmetry close to the tetrahedral. This result confirms the mentioned hypothesis that Ti(IV) substitutes Si(IV) in the pentasilic structure. As already hypothesized [6,12,13] the Ti–O–Si bridges can be partially hydrolyzed without destroying the

Table 1
XANES of Ti(IV) in various coordination states

Sample	Peak position[a] (eV)	FWHM Δ (eV)	Intensity (%)	Ref.
TS outg. at 300 K	3.2 ± 0.2	1.7	56	this work
TS outg. at 400 K	2.9 ± 0.2	1.4	75	this work
Ba_2TiO_4	3.5 ± 0.2	1.5	82	[24]
$Ti[N(CH_3)_2]_4$	3.4 ± 0.2	2.8	83	[24]
$Ti(OAm)_4$	2.8 ± 0.2	1.6	74	[22]
$Ti(OPr)_4$	3.0 ± 0.2	1.4	50	[22]
$Ti(OEt)_4$	3.4 ± 0.2	1.5	32	[22]
$Ti(OBu)_4$	3.1 ± 0.2	2.8	30	[22]
1.6-TS-2	2.9 ± 0.2	2.0	49	[7,8]
1.9-TS-1	3.5 ± 0.2	2.3	27	[25,26]
1.9-TS-1 outg.	2.8 ± 0.2	1.5	50	[25,26]

[a] The zero of the energy scale was taken at 4964.2 eV, which corresponds to the maximum of the first peak of a titanium foil K edge.

fourfold coordination and XANES spectra are also consistent with the parent structure $[OHTiO_3]$, which can be obtained from the previous $[TiO_4]$ by the hydrolysis of one Ti–O–Si bridge. Another important observation is that the spectrum is influenced by the state of hydration: in fact the presence of H_2O (as in the sample outgassed only at 300 K) induces an intensity decrease of the pre edge absorption and a broadening of the peak. On the basis of the data reported in table 1, these effects are indicative of direct insertion of H_2O ligands into the Ti(IV) coordination sphere. In fact the intensity of the XANES peak decreases with broadening becoming very similar to that observed for pentacoordinated Ti(IV) in $Ti(OEt)_4$. More detailed discussion on the expansion of the coordination sphere will be given for the adsorption of NH_3 (vide infra). This indicates that XANES measurements should be preferably made under controlled atmosphere.

The exceedingly low intensity values of the pre edge peak observed in refs. [7,8,25,26] can be only partially accounted for by the presence of adsorbed water: the abundant presence of extraframework Ti(IV) must be invoked.

3.1.2. The interaction of [TS] with NH_3

The effect of NH_3 adsorption (equilibrium pressure 10^4 Pa) and desorption on the spectra of the [TS] outgassed at 400 K are reported in spectrum 3 and 4 respectively. The relevant data are reported in table 2.

From the XANES spectra we can see that the adsorption of NH_3 (spectrum 3) induces a deep modification of all parts of the spectrum. In particular: the sharp peak at 2.9 eV is nearly destroyed and replaced by a new, weaker and broader absorption characterised by a very large FWHM (2.5 eV) and centred at 3.4 eV. It is most noticeable that, after NH_3 interaction, the intensity has decreased by a factor of 3 which is fully consistent with an increase of the average coordination number (from 4 to 5–6).

Table 2
Ammonia adsorption and desorption on Ti(IV)

Sample	Peak position [a] (eV)	FWHM Δ (eV)	Intensity (%)
TS outg. at 400 K	2.9 ± 0.2	1.4	75
TS + NH_3	3.4 ± 0.2	2.5	24
TS + NH_3 + out.	3.1 ± 0.2	1.6	64

[a] Energy values have been calculated as in table 1.

In the near edge region we also observe the formation of a peak at 13.6 eV which is very similar to those reported for compounds containing Ti(IV) pentacoordinated [22]; a clear peak in the same position is also observed in anatase sample (where Ti(IV) is in octahedral coordination). Although it is universally accepted that this region cannot be used for quantitative consideration on the coordination number, the previous observation is in qualitative agreement with our model. On the basis of the whole set of previous considerations, these spectroscopic features can be interpreted in terms of the coordination reactions shown below:

$$\underset{\text{fourfold}}{O_3{-}Ti{-}OH} \xrightarrow{NH_3} \underset{\text{fivefold}}{O_3{-}Ti{-}OH(NH_3)} \xrightarrow{NH_3} \underset{\text{sixfold}}{O_3{-}Ti{-}OH(NH_3)_2}$$

and/or

$$\underset{\text{fourfold}}{Ti{-}O_4} \xrightarrow{NH_3} \underset{\text{fivefold}}{O_4{-}Ti{-}(NH_3)} \xrightarrow{NH_3} \underset{\text{sixfold}}{O_4{-}Ti{-}(NH_3)_2}\ .$$

Similar reaction schemes have been already hypothesized on the basis of independent UV-Vis [4,12,13], IR [4] and Raman [11] investigations.

It is most noticeable that volumetric determination of the amount of adsorbed NH_3 at room temperature and under similar pressure conditions indicates that the number of NH_3 ligands per Ti(IV) centre is intermediate between 1 and 2 (which means that the coordination state of Ti(IV) is intermediate between 5 and 6). This means that in the XANES experiments not all the Ti(IV) centres reach the maximum sixfold coordination in perfect agreement with the observed decrement of the intensity.

On this basis the presence of a weak residual peak (spectrum 3 in fig. 1) can be interpreted by considering the incomplete NH_3 reaction with Ti(IV) species.

3.2. EXAFS

Fig. 2a shows the EXAFS spectra of [TS] sample outgassed at 300 and 400 K, after contact with NH_3 and after successive outgassing for 10 min at room temperature respectively. The main feature clearly emerging from all spectra, even if at high k value the noise is quite strong, is represented by the damped nature of the apparently single oscillation. As the oxygen species have this behaviour, the observed EXAFS spectra before interaction with adsorbates can basically be inter-

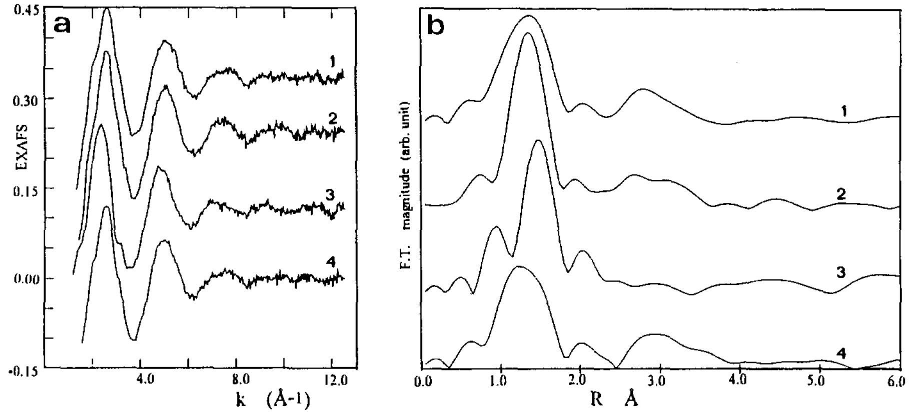

Fig. 2. (a) EXAFS of [TS] in presence and in absence of extra ligand. (1) Sample outgassed at 300 K; (2) in vacuo after a treatment at 400 K; (3) after dosage of NH_3 (equilibrium pressure of 10^4 Pa); (4) effect of pumping at room temperature for 10 min. (b) Modulus of the Fourier transform of the k^3 weighted EXAFS oscillations illustrated in (a).

preted on the basis of a coordination sphere of Ti(IV) formed only by oxygen centres. It is a matter of fact that the spectra obtained in presence of ligands (curves 1, 3 and 4) seem to be more complex than those obtained in absence ([TS] outgassed at 400 K), thus suggesting a more disordered situation (vide infra).

The Fourier transforms of the spectra 1–4 are illustrated in fig. 2b. The main characteristic clearly showing up, is undoubtedly represented by the presence of a maximum centred in the 1.2–1.4 Å interval.

Concerning the main peak the following can be commented:

[TS] outgassed at 300 K (curve 1). Although it is very broad and asymmetric at low R value, nevertheless it shows a clear maximum at 1.4 Å which, by considering the phase shift contribution due to the oxygens, indicates a surrounding first neighbour distance of about 1.8 Å. This distance is in good agreement with the known values for Ti–O bond in compounds where Ti(IV) is in fourfold coordination [18,22].

[TS] outgassed at 400 K (curve 2). No change is observed concerning the main peak position. The higher intensity and symmetry together with the narrower lineshape, indicate some substantial structural modification has been induced by the outgassing procedure. As the pre edge part of the spectrum is simultaneously showing an increase of the intensity and a narrowing of the XANES peak, we infer that H_2O ligands are desorbed upon outgassing at 400 K and that only the sample treated at 400 K can be used to evaluate the coordination state of Ti(IV) in absence of adsorbates.

[TS] after NH_3 contact (curve 3). NH_3 dosage affects so deeply the main peak that a second peak at 0.9 Å is observed close to the main maximum now centred at 1.5 Å.

[TS] after NH_3 contact and successive outgassing at room temperature

(curve 4). The outgassing treatment at room temperature leads to a radial distribution function similar to that illustrated in curve 1.

All these observations (together with those obtained from XANES spectra) indicate that only for [TS] outgassed at 400 K, the Ti(IV) is in a well defined coordination situation. In the remaining cases, the presence of extra ligands (H_2O and NH_3), causes a broadening of the features which are reflected in the Fourier transform curves.

The inverse Fourier transform of the radial distribution function (typical range interval $0.7 < R < 1.8$ Å) gives the EXAFS spectrum due to the first coordination sphere of Ti(IV). For the reasons discussed before more extended intervals ranging from 0.6 to 1.8 Å (curve 3) and 0.35 to 1.8 Å (curve 4) were used for the samples treated with NH_3.

Before going into detail of the EXAFS results, it is worth to recall that in Ti-silicalite containing 1–2% of Ti(IV), the intensity of the signal is intrinsically low and the experimental noise is consequently high: this suggests that signal elaboration involving more than one neighbour species (and hence more than four fitting parameters) must be made with caution. As a matter of fact the K-space available and the R-space window adopted in the inverse Fourier transform do not allow more than one shell fit (four fitting parameters) [33]. For this reason we decided to concentrate primarily our efforts on the elaboration of EXAFS signals of Ti-silicalite samples treated in vacuo at 400 K (because they are the only ones where the first coordination sphere can be reasonably considered as formed by oxygen atoms only).

The Fourier filtered signal of the first shell, can be simulated on the basis of a coordination sphere constituted by oxygen atoms disposed around the Ti(IV) centre. Fitting parameters N (number of oxygen atoms), R (nearest neighbour position in Å), and σ^2 (disorder factor in Å^2) are summarised in table 3 together with the estimated errors.

It is most noticeable that the structural data obtained for Ti-silicalites treated in vacuo at 400 K (4.4 oxygens at 1.81 Å distance and a σ^2 value of 4×10^{-3} Å^2 (which indicates a high ordered structure)) are in good agreement with those suggested by IR, UV-Vis, Raman and XANES spectroscopies. These figures are perfectly consistent with a model where Ti(IV) is randomly substituting Si in the zeolite structure, so assuming a tetrahedral oxygen coordination sphere. Although a $N = 4.4$ value seems to be too high for tetrahedral Ti(IV) species, we underline

Table 3
Fitting results for the EXAFS spectra of Ti-silicalite

Sample	$N \pm 0.6$	$R \pm 0.01$ (Å)	$\sigma^2 \pm 2$ ($10^{-3}2$)	Fit (10^{-2})
TS outg. at 300 K	5.3	1.81	9	3.2
TS outg. at 400 K	4.4	1.81	4	2.4
TS + NH_3	5.5	1.84	10	5.5
TS + NH_3 + out.	5.7	1.79	11	2.3

that + 0.4 is within the evaluated error for this variable (0.6). The presence of extra oxygens close to Ti(IV) centres derived from the Ti–O–Si bridge hydrolysis could eventually be invoked to justify a small increase of the N value.

We underline that the estimated error associated with the R variable is only 0.01 Å: this indicates that the Ti–O distance obtained from this experiment is a meaningful structural information for Ti-silicalite in absence of adsorbates. It is worth mentioning that some recent theoretical calculations by Jentys and Catlow confirm this data [34].

Extension of the same procedure to the other samples (known to contain extra ligands in the coordination sphere of Ti(IV)) still gives reasonably good fits with the exception of [TSa] in presence of NH_3 (table 3).

In this case, the fit can be improved by using a two-shell model with oxygen and nitrogen species for a total number of six. However, as too many parameters are involved we do not believe that the structural factors deriving from those simulations are totally free from artefacts. For instance comparable fit errors can be obtained by using different number of oxygens (x) and nitrogens (y) $x+y=6$ located at different distances (which is disappointing). Consequently we conclude that while our EXAFS measurements are sufficiently accurate to indicate that the coordination number is increasing upon NH_3 dosages, they do not allow detailed and safe information about the exact stoichiometry to be derived. More elaborate analyses about this point were not attempted.

In fact we think that in our case (characterized by low Ti(IV) concentration and strong noise) it is a better choice to use the simplest single shell modellization (and then to compare it with the results obtained by means of different and independent physical methods) rather than to trust the results of further manipulation (especially when mathematical procedures using many fitting parameters are necessarily involved).

As regards the data concerning [TS] sample with H_2O adsorbed into the channels ([TS] outgassed at 300 K), in presence of NH_3 and after successive outgassing at room temperature, a comparison of N, R and σ^2 indicates:

N – The coordination number increases in presence of H_2O and more distinctly in presence of NH_3. The high estimated error (0.6) found for this variable does not enable further consideration. This is mostly due to the low intrinsic accuracy of the variable N as obtained by EXAFS spectra of Ti–O pairs (restricted R range available). Although these results are essentially qualitative they fully confirm the data derived from XANES, IR, UV-Vis and Raman spectroscopies.

R – The Ti–L (L = ligand) distances are constant in all the series but in [TS] sample treated with NH_3 where we observe an increase from 1.81 to 1.84 Å. As in this case the estimated error is very small, this change must be meaningful. The 1.84 Å figure probably is the average of the shorter Ti–O and longer Ti–NH_3 distances. This does not mean that upon NH_3 adsorption the Ti–O distance is not changing. On the contrary, we think that upon the expansion of the coordination sphere (caused by NH_3 adsorption), the Ti(IV) slightly move outwards from fourfold to fivefold and sixfold coordinative positions with subsequent increase of the Ti–O distances. From the reasons discussed before we do not try to estimate this effect in a quantitative way.

σ^2 – The presence of adsorbates (H_2O and NH_3) (or of a minor fraction of extra-framework Ti(IV)) causes an increasing of the disorder factor. In fact the smallest σ^2 value was obtained in the case of [TS] sample outgassed at 400 K again. The evaluated error for this variable is 2×10^{-3} Å^2 which is sufficiently small to make the differences among the tabled values significant. On this basis [TS] sample treated in vacuo at 400 K appears to be the most ordered system (in agreement with data obtained with IR, UV-Vis, Raman and XANES spectroscopies).

4. Conclusions

The coordinative state of Ti(IV) in Ti-silicalite, has been investigated by X-ray absorption spectroscopy.

Pre edge peak characteristics (peak position, FWHM and intensity in XANES spectra) of well manufactured titanium silicalite [TS] previously outgassed at 400 K confirms that this sample is a very pure material where nearly all Ti is fourfold coordinated and in a symmetry very close to a *perfect* tetrahedron (no data of comparable quality on Ti-silicalites have been published so far).

The experimental results also indicate that the coordination state of Ti(IV) in Ti-silicalite prepared following ref. [26] and containing a small Ti(IV) percentage, strongly depends upon the presence or absence of ligands (adsorbates). In particular, adsorption and desorption of NH_3 on [TS] investigated in situ give clear indication of increase and decrease of the coordination state of Ti(IV). These data are in qualitative agreement with previous UV-Vis, IR and Raman investigations.

The EXAFS spectra confirm that Ti(IV) in [TS] outgassed at 400 K are fourfold coordinated and that adsorption of ligands (H_2O and NH_3) leads to an increase of the coordination sphere. These conclusions must be considered as essentially qualitative.

From a more quantitative point of view the safest results are: $N = 4.4 \pm 0.6$ and $R = 1.81 \pm 0.01$ Å obtained for fully dehydrated [TS].

The comparison of the XAFS and the UV-Vis, IR and Raman spectroscopic results indicates that they can all be interpreted on the basis of *the simplest model*, corresponding to Ti(IV) in the substitutional position in the pentasilic framework.

Acknowledgement

We are grateful for excellent technical support by F. Campolungo (INFN-LNF). AZ and SB acknowledge the financial support from Consiglio Nazionale Ricerche (Progetto Finalizzato Chimica Fine II). SB and LM acknowledge the financial support from ENICHEM.

References

[1] V. Romano, E. Esposito, F. Maspero, C. Neri and M.G. Clerici, Chim. Ind. (Milan) 72 (1990) 610.

[2] G. Bellussi, A. Carati, M.G. Clerici, G. Maddinelli and R. Millini, J. Catal. 133 (1992) 220.

[3] P. Roffia, G. Leofanti, A. Cesana, M. Mantegazza, M. Padovan, G. Petrini, S. Tonti and V. Gervasutti, in: *New Developments in Selective Oxidation*, eds. G. Centi et al. (Elsevier, Amsterdam, 1990) p. 43.

[4] M.R. Boccuti, K.M. Rao, A. Zecchina, G. Leofanti and G. Petrini, in: *Structure and Reactivity of Surfaces*, eds. C. Morterra et al. (Elsevier, Amsterdam, 1989) p. 133.

[5] A. Zecchina, G. Spoto, S. Bordiga, M. Padovan, G. Leofanti and G. Petrini, in: *Catalysis and Adsorption by Zeolites*, eds. G. Ohlman et al. (Elsevier, Amsterdam, 1991) p. 671.

[6] A. Zecchina, G. Spoto, S. Bordiga, A. Ferrero, G. Petrini, G. Leofanti and M. Padovan, in: *Zeolite Chemistry and Catalysis*, eds. P.A. Jacobs et al. (Elsevier, Amsterdam, 1991) p. 251.

[7] D. Trong On, L. Bonneviot, A. Bittar, A. Sayari and S. Kaliaguine, J. Mol. Catal. 74 (1992) 233.

[8] D. Trong On, L. Bonneviot, A. Bittar, A. Sayari and S. Kaliaguine, Catal. Lett. 16 (1992) 85.

[9] A.M. Camblor, A. Corma and J. Pèrez-Pariente, J. Chem. Soc. Chem. Commun. (1993) 557.

[10] G.D. Andrzej, M. Turek, I.E. Wachs, D.R.C. Huybrechts and P.A. Jacobs, Zeolites 13 (1993) 365.

[11] D. Scarano, A. Zecchina, S. Bordiga, F. Geobaldo, G. Spoto, G. Petrini, G. Leofanti, M. Padovan and G. Tozzola, Faraday Trans. Chem. Soc., in press.

[12] A. Zecchina, G. Spoto, S. Bordiga, F. Geobaldo, G. Leofanti, G. Petrini, M. Padovan, M. Mantegazza and P. Roffia, in: *Proc. 10th Int. Congr. on Catalysis*, Budapest, 19-24 July 1992, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadémiai Kiadó, Budapest, 1993).

[13] F. Geobaldo, S. Bordiga, A. Zecchina, E. Giamello, G. Leofanti and G. Petrini, Catal. Lett. 16 (1992) 109.

[14] E.A. Stern, Phys. Rev. B 10 (1974) 3027.

[15] D. Sayers, E. Stern and F.W. Lytle, Phys. Rev. Lett. 27 (1971) 1204.

[16] P.A. Lee, P.H. Citrin, P. Eisenberger and B. Kincaid, Rev. Mod. Phys. 53 (1981) 769.

[17] C.R. Natali, M. Benfatto and S. Doniach, Phys. Rev. A 34 (1986) 4682.

[18] B. Gregor, F.W. Lytle, D.R. Sandstrom, J. Wong and P. Schultz, J. Non-Cryst. Solids 55 (1983) 27.

[19] M. Emili, L. Incoccia, S. Mobilio, G. Fagherazzi and M. Guglielmini, J. Non-Cryst. Solids 74 (1985) 129.

[20] T. Dumas and J. Petiau, J. Non-Cryst. Solids 81 (1986) 201.

[21] G.A. Waychunas, Am. Miner. 72 (1987) 89.

[22] F. Babonneau, S. Doeuff, A. Leaustic, C. Sanchez, C. Cartier and M. Verdaguer, Inorg. Chem. 27 (1988) 3166.

[23] T. Uozumi, K. Okada, A. Kotani, O. Durmeyer, J.P. Kappler, E. Beaurepaire and J.C. Parlebas, Europhys. Lett. 18 (1992) 85.

[24] C.A. Yarker, P.A.V. Johnson, A.C. Wright, J. Wong, R.B. Gregor, F.W. Lytle and R.N. Sinclair, J. Non-Cryst. Solids 79 (1986) 117.

[25] A. Lopez, H. Kessler, J.L. Guth, M.H. Tulier and J.M. Mopa, in: *Proc. 6th Int. Conf. X-ray Absorption Fine Structure*, New York 1990 (Elsevier, Amsterdam, 1990) p. 549.

[26] A. Lopez, M.H. Tulier, J.L. Guth, L. Delmotte and J.M. Popa, J. Sol. State Chem. 102 (1993) 480.

[27] E. Schultz, C. Ferrini and R. Prins, Catal. Lett. 14 (1992) 221.

[28] P. Behrens, J. Felsche and W. Nieman, Catal. Today 8 (1991) 479.

[29] M. Taramasso, B. Perego and B. Notari, US Patent 4 410 501 (1983).
[30] C. Lamberti, S. Bordiga, C. Cerrato, C. Morterra, D. Scarano, G. Spoto and A. Zecchina, Comput. Phys. Commun. 74 (1993) 119.
[31] F. James and M. Roos, Comput. Phys. Commun. 10 (1975) 343.
[32] A.G. McKale, B.W. Veal, A.P. Paulikas, S.K. Chan and G. Knapp, J. Am. Chem. Soc. 110 (1988) 3763.
[33] F.W. Lytle, D.E. Sayers and E.A. Stern, Physica B 158 (1989) 701.
[34] A. Jentys and R.A. Catlow, Catal. Lett. 22 (1993) 251.