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XAFS Study of Ti–Silicalite: Structure of Framework Ti(IV) in the Presence and Absence of Reactive Molecules (H₂O, NH₃) and Comparison with Ultraviolet–Visible and IR Results

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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 for Si(IV) has been performed in order to study the effect of the presence or absence of ligands such as H₂O and NH₃ on the Ti(IV) coordination sphere. In particular, the effect of an outgassing treatment at 400 K and of the interaction with NH₃ 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 with action of adsorbates. The process is partially reversible at room temperature. The pre-edge absorption of a well-manufactured Ti–silicalite has been compared with a Ti–silicalite containing extraframework Ti and with other reference compounds such as anatase and amorphous SiO₂/TiO₂. Further information has been obtained from EXAFS determination of first-shell bonding parameters.

Introduction

Ti–silicalite, a zeolite of the pentasil family containing a small percentage of Ti substituting for Si (1–2% in atoms), has attracted much attention in recent years for its properties as an efficient and selective catalyst for oxidation reactions in solution with H₂O₂.^{1–3}

The active species are thought to be framework-isolated Ti(IV) sites, while extraframework Ti(IV) does not contribute to the catalytic properties of the zeolite. For this reason a characterization method able to distinguish between the two types of titanium becomes necessary in order to select a material with the highest catalytic performance.

The location and the structure of Ti(IV) have 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 point. In fact, even if all these mentioned techniques point toward framework Ti as a tetracoordinated species substituting for Si, the state of aggregation of [TiO]₄ units is still debated^{7,8} together with the distortion from the tetrahedral geometry. Moreover, as it is known that the coordination state strongly depends upon the presence of adsorbates, the characterization of the sample in the absence and presence of different types of molecules is desirable. Thus, it is vital to understand how framework titanium species

(which should be inactive, being shielded by four oxygen neighbors) can change their coordinative state during the catalytic process and so act as catalytic centers.⁹

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

(i) The IR band at 960 cm^{−1} (absent in pure and perfect silicalite) can be interpreted either as a mode with prevailing Si–O stretching character involving [SiO₄] units perturbed by an adjacent Ti(IV) or as a stretching mode of framework Ti containing units such as [TiO₄] or [O₃TiOH] (or a mixture of the two modes); the recent assignment of Cambor et al.¹⁰ and of Andrzej et al.¹¹ 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 12 where an assignment of the fingerprint band in terms of stretching modes of [SiO₄] groups perturbed by the presence of Ti(IV) (with little admixture of [TiO₄] and [O₃TiOH] vibrations) is preferred.

(ii) Raman bands at 960 cm^{−1} (strong) and at 1127 cm^{−1} (weak) (not present in pure and perfect silicalite) can be assigned to two Raman active modes of perturbed [SiO₄] units or to two vibrations involving [TiO₄] or [O₃TiOH] units embedded in the lattice (or to a mixture of the two models). The assignment is discussed in detail in ref 12.

(iii) Bands at 48 000 cm^{−1} are assigned to ligand to metal charge transfer (LMCT) transitions in [TiO₄] and [O₃TiOH] tetracoordinated structures.

Extraframework Ti(IV) under aggregated form is revealed by the following:

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(i) An optical transition in the 40000–30000-cm⁻¹ range is assigned to a (LMCT) band in [TiO₂]_n clusters. The minimum amount of Ti(IV) in TiO₂ microparticles which can be detected with this method is 0.03%.⁶

(ii) Raman bands at 140 cm⁻¹ (very strong) and at 395, 514, and 638 cm⁻¹ (very weak) reveal that the minimum amount of anatase phase which can be detected by this method corresponds to 0.5%, if a single channel analyzer is used.⁶ However, if a multichannel analyzer or a FT-Raman instrument is used, the sensitivity toward separate TiO₂ phases can be at least 10 times larger.

The interaction with adsorbates like H₂O, NH₃, H₂O₂, 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) centers and that the adsorption occurs prevalently on them. The perturbation of this band cannot, however, be assumed per se as a proof that ligands are directly interacting with Ti(IV) via formation of direct chemical and coordinative bonds.

The interaction with the same adsorbates causes a similar effect on the Raman absorptions at 960 and 1127 cm⁻¹.¹²

The optical manifestations in the UV–vis range (50000–40000 cm⁻¹, 6–5 eV) are perturbed by interaction with adsorbates like H₂O, NH₃, H₂O₂, etc., with appearance of new bands associated with novel ligand to metal charge transfer transitions from H₂O, NH₃, and OOH ligands to Ti(IV).^{9,13} Unlike the IR and Raman experiments, the appearance of these new bands in the UV–vis shows that a direct interaction of the incoming ligands with the Ti(IV) atoms is occurring, and this proves that the coordination number of Ti(IV) increases upon interaction with adsorbates. On the other hand, the new observed manifestations cannot be explained in terms of perturbations of the preexisting LMCT bands caused by interactions not directly involving the Ti(IV) atoms (like H-bonding or van der Waals interaction). In fact, it is known that small perturbations involving the second Ti(IV) coordination sphere have little influence on electronic transitions in the UV–vis.¹⁴ It is evident that UV–vis spectroscopy is a very useful tool as it gives direct information on the chemical events occurring in the first coordination sphere of Ti(IV).

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)^{15,16} 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. A full theoretical analysis of the XANES region requires the calculation of the cross section in the “full multiple scattering” regime. Although this is now possible in many cases with semiquantitative agreement with experimental results, here we shall relay only on the comparison among the spectra of samples investigated with those obtained on reference compounds. This method is known to yield reliable information on the local geometry around the absorbing atom.

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.

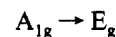
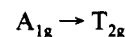
TABLE 1: XANES of Ti(IV) in Alkoxides

sample	peak position, ^a eV	ΔFWHM, eV	intensity, %	ref
Ti(OAm) ₄	2.8 ± 0.2	1.7	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

^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.

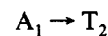
Ti(IV) is in a d⁰ configuration corresponding to A_{1g} or A₁ states in, respectively, octahedral or tetrahedral symmetry. The first feature in the absorption spectrum (the pre-edge) corresponds to excitation of the 1s electron into empty bound states, derived from Ti and O d and p states.²²

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



which are Laporte forbidden. Consequently, the pre-edge absorption of Ti(oct) is expected to be rather weak. It is a matter of fact that in anatase three very weak peaks are observed, two of them certainly associated with A_{1g} → T_{2g} and A_{1g} → E_g transitions and the third (at lower energy) of uncertain origin.

In tetrahedral symmetry (where no inversion symmetry is present), the final states are T₂ and E and the expected transitions are



As in the T₂ states, considerable mixing of the 3d and 4p orbitals occurs and the A₁ → T₂ transition becomes allowed and is therefore particularly strong. This is the reason why tetrahedral Ti(IV) is characterized by a strong peak (A₁ → T₂) overwhelming the weaker A₁ → 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}

To confirm the previous hypotheses, we report here, for sake of comparison, the data related to the Ti(OR) alkoxides which can be reasonably considered as the closest homogeneous analogues of the Ti(IV) structures hypothesized to be present in Ti-silicalite (Table 1).

From Table 1 it can be observed that on passing from fourfold-coordinated Ti(IV) in monomeric Ti(OAm)₄ (where the bulky *tert*-amyl oxide groups prevent oligomerization and hence preserve the tetrahedral symmetry) to Ti(IV) pentacoordinated in oligomeric Ti(OEt)₄ and in Ti(Obu)₄, the intensity of the single pre-edge peak diminishes by a factor of about 2.5 with broadening. The case of Ti(OPr)₄, where Ti(IV) is in a distorted fourfold coordination, is also important because it represents a clear example of how distortion from pure tetrahedral coordination can have an influence on the intensity of the peak. However, it also shows that an intensity decrement of about 2.5 times can be observed only when an increase of the coordination state is occurring. Identical considerations on the intensities derive also from inspection of the XANES spectra of SiO₂-TiO₂ glasses and Ti(IV) in cordierite obtained from refs 18–20. It must be recalled that in all these cases the pre-edge peak remains single (only a broadening being observed) without evidence of the crystal field splitting effect observed on TiO₂ anatase. From all these considerations it is evident that analysis of the intensity, width, and position of the pre-edge features can be helpful in distin-

guishing 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-characterized Ti-silicalite sample (hereafter indicated as [TSA]). This zeolite is compared to a second sample of Ti-silicalite (hereafter indicated as [TSb]), which is known from Raman and UV-vis data to contain a small but meaningful amount of extraframework titanium (in the form of microparticles of anatase) and to other reference compounds such as anatase and an amorphous SiO₂/TiO₂ sample.

The effects of the adsorption and desorption of adsorbates (H₂O and NH₃) are also reported and discussed.

Experimental Section

Materials. The synthesis procedure of zeolites samples (Ti-silicalite) is described elsewhere.²⁹ Two types of Ti-silicalite samples have been used ([TSA] and [TSb]). In the [TSA] (Ti = 1.47 wt %) sample, Ti(IV) was completely in the framework (as determined by means of several characterization methods.^{4,6} In the [TSb] (Ti = 1.94 wt %) sample, Ti(IV) was partially extraframework, as anatase.^{4,6} The amorphous compound SiO₂/TiO₂ (Ti = 1.77 wt %) has been obtained by hydrolyzing a mixture of Ti and Si organic compounds. The reaction product was calcined at 773 K for 4 h. UV-vis data indicate that in this compound no anatase phase is present. Anatase, which was used as a reference compound for octahedral Ti, was commercial grade. Its structure has been checked by X-ray diffraction.

Methods. 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 ionization 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 samples and the amorphous compound, obtained as thin self-supporting pellets, were placed inside a Pyrex sample cell. The pellets were located between two Mylar windows, which allow X-ray transmission measurements, and were moved to a different position inside the sample cell, approximately 20 cm apart, to undergo thermal treatments at variable temperatures. The cell can be located inside the beamline sample chamber and connected to a vacuum ($p = 10^{-2}$ Pa) manifold allowing in situ outgassing procedures at increasing temperature and gas dosage. In the case of anatase, a sample suitable for X-ray absorption was obtained by making a fine suspension of the powder in acetone and subsequently filtering it onto a polyacetate membrane.

The UV-vis reflectance spectra were carried out in a Varian Cary 5 spectrometer on a powdered [TSA] sample in a suitably designed quartz cell, allowing in situ outgassing procedure under vacuum ($p = 10^{-2}$ Pa) and gas or liquid dosage.

The IR spectra were obtained on a Bruker IFS 48 FTIR spectrometer. The [TSA] sample was in the form of a thin film deposited on a Si plate inserted in a suitable cell allowing in situ outgassing procedure and gas dosage.

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 at 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 Lorentian 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, and then the EXAFS spectrum was extracted by fitting the absorption coefficient with a cubic spline curve. Finally, the EXAFS was normalized by $J[1 - (8/3)(E - E_0)/E_0]$, 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 $k = 2\text{--}12 \text{ \AA}^{-1}$, 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 nonlinear least-squares routine³¹ (MINUIT subroutine of the CERN library) and minimization of a χ^2 -type function.

The single-electron single scattering EXAFS theory¹⁶ was applied by using the following equation:

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

In our calculation the variable i runs only over the first-shell neighbor atoms. N_i is the number of atoms in the i th 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-neighbor oxygens at 1.95 Å) and then was kept fixed in the subsequent fits. The $f_i(k)$ 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.

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 backscatters, such as O (as our case).

Results and Discussion

XANES. *Effect of the Surrounding Atmosphere on the XANES Spectra of Ti(IV).* In Figure 1 two spectra of very pure Ti-silicalite [TSA] are reported. Spectrum 1 corresponds to the 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 characterized by one, well-defined and intense peak. From 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). (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

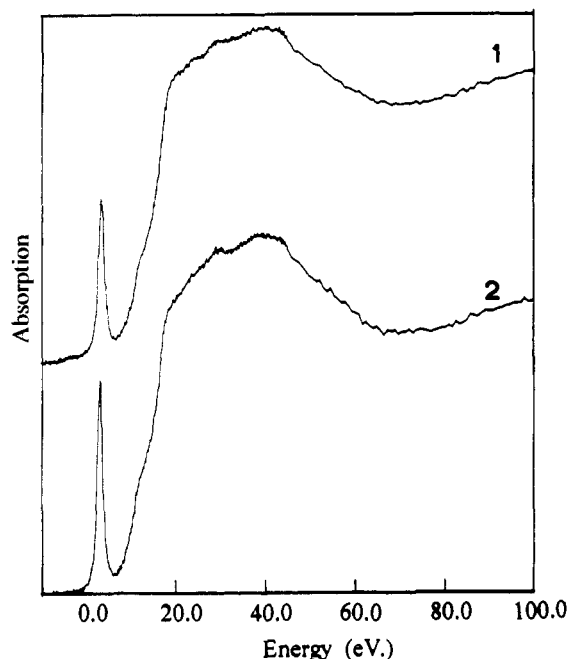


Figure 1. XANES spectra of Ti-silicalite: (1) [TSa] outgassed at 300 K; (2) [TSa] outgassed at 400 K. (The zero of the energy scale was taken at 4964.2 eV, which corresponds to the maximum of the first peak of a titanium foil K edge.)

TABLE 2: XANES of Ti(IV) in Tetrahedral Coordination

sample	peak position, ^a eV	ΔFWHM, eV	intensity, %	ref
TSa outg. at 300 K	3.2 ± 0.2	1.7	56	this work
TSa outg. at 400 K	2.9 ± 0.2	1.4	75	this work
Ba ₂ TiO 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
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 Energy values have been calculated as in Table 1.

coordination sphere as a consequence of the sample treatment (H₂O removal).

Comparison of our data with those reported in literature relative to Ba₂TiO₄ (considered as the model compound for Ti(IV) in tetrahedral coordination) and other compounds^{20,22} where Ti(IV) is certainly in the tetrahedral coordination is very informative. All such data are summarized in Table 2, together with results concerning three Ti-silicalite samples previously described in the literature.^{7,8,25,26}

From Table 2 it is evident that the similarity of the data of [TSa] (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 for Si(IV) in the pentasilic structure as shown schematically in Figure 2 (see the exploded view in inset a).

As already hypothesized,^{6,9,13} the Ti–O–Si bridges can be partially hydrolyzed without destroying the four-fold coordination, and XANES spectra are also consistent with the parent structure [OHTiO₃], which can be obtained from the previous [TiO₄] by the hydrolysis of one Ti–O–Si bridge, as shown in inset b of Figure 2. Another important observation is that the spectrum is influenced by the state of hydration; in fact, the presence of H₂O (as in the [TSa] sample outgassed at 300 K) induces an intensity decrease of the pre-edge absorption and a broadening of the peak. This indicates that XANES measurements should be preferably made under controlled atmosphere.

On the basis of the data reported in Table 1, these effects are indicative of interaction of H₂O ligands with the Ti(IV)

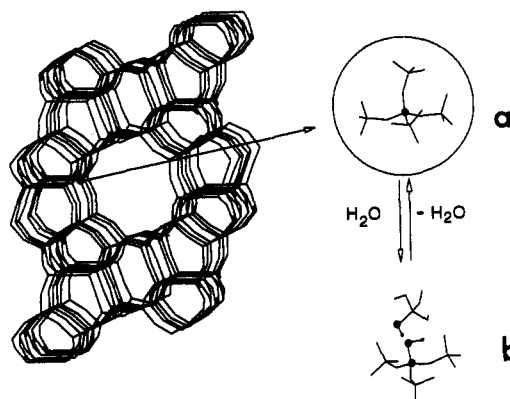


Figure 2. Silicalite framework where [TiO₄] is substituting for a [SiO₄] building unit. Inset a: [TiO₄] unit surrounded by four [SiO₄] units (the Ti(IV) center is represented by a black ball). Inset b: after water hydrolysis of a Ti–O–Si bridge shown in a inset a (black balls indicate Ti(IV) and hydroxyl groups).

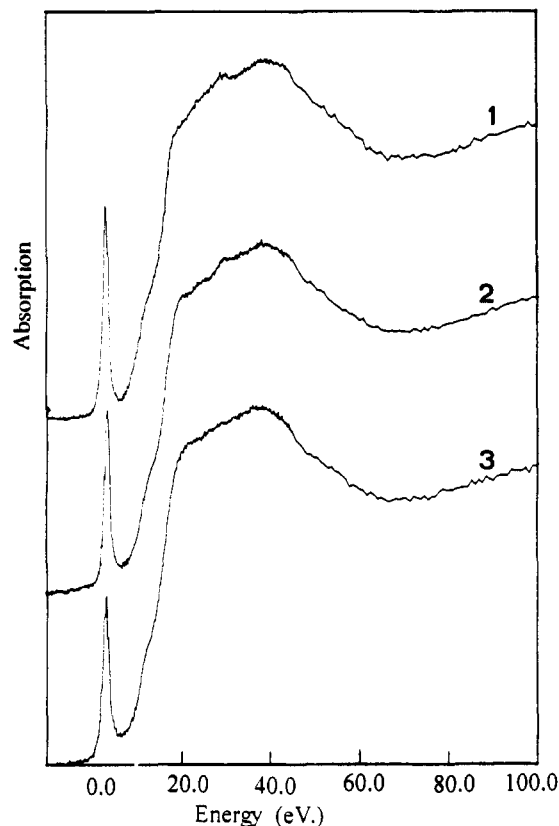


Figure 3. XANES spectra of Ti-silicalites and SiO₂/TiO₂ outgassed at 400 K: (1) [TSa]; (2) [TSb]; (3) SiO₂/TiO₂. (Energy scale as in Figure 1.)

coordination sphere. This result cannot "per se" be considered as evidence of the insertion of the H₂O into the Ti(IV) coordination sphere (with subsequent increase of the coordination number). In fact, the intensity decrement of the XANES peak can be interpreted either in terms of distortion of tetrahedral symmetry or in terms of incomplete insertion of H₂O in the coordination sphere of Ti(IV). It is most interesting to notice that Lopez et al.^{25,26} are in favor of the second interpretation. This ambiguity will be solved when the interaction with NH₃ will be discussed (vide infra).

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

XANES Spectra of Ti(IV) in Different Oxidic Compounds Containing a Comparable Amount of Ti(IV). In Figure 3 and Table 3, the spectra of [TSa] (spectrum 1), [TSb] (spectrum 2),

TABLE 3: Ti(IV) in Different Oxides

sample outg. 400 K	peak position ^a eV	ΔFWHM, eV	intensity, %
TSa	2.9 ± 0.2	1.4	75
TSb	3.2 ± 0.2	1.5	64
SiO ₂ /TiO ₂	2.9 ± 0.2	1.7	58

^a Energy values have been calculated as in Table 1.

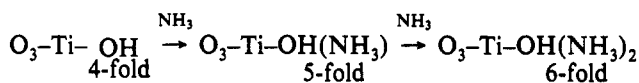
and an amorphous compound SiO₂/TiO₂, (spectrum 3) are compared. All the samples were outgassed at 400 K for 30 min in order to eliminate adsorbed water.

We notice the following: (i) All spectra are characterized by a strong peak centered around 2.9–3.2 eV, indicating that in all samples a large fraction of Ti(IV) is tetracoordinated. (ii) Spectrum 1 is characterized by the smallest FWHM and by the highest intensity of the pre-edge peak. This indicates that this sample contains the highest percentage of Ti(IV) in nearly perfect tetrahedral coordination. (iii) The lower absorption and the increased FWHM observed for spectrum 2 indicate that, in this sample, besides tetracoordinated Ti(IV), there is also Ti(IV) with a higher coordination state (notice that a fraction of anatase is present, noticed by means of UV-vis and Raman spectroscopies.⁶ (iv) Spectrum 3 is characterized by an absorption which is very similar, as far as the intensity value is concerned, to that observed in spectrum 2. However, the larger FWHM and an asymmetry at higher energy (more clearly visible when exploded views are adopted) indicate that we are dealing with a system with a significant disorder of the titanium–oxygen distances and Ti–O–Si angles (which is not surprising for an amorphous compound).

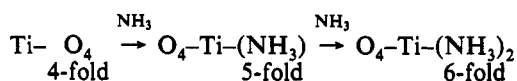
Interaction of [TSa] with NH₃. Figure 4 illustrates the effect of NH₃ adsorption (equilibrium pressure of 10⁴ Pa) and desorption on the spectra of the [TSa] outgassed at 400 K. The spectrum of anatase is also shown for the sake of comparison (spectrum 4). The relevant data are reported in Table 4.

From the XANES spectra we can see that the adsorption of NH₃ (spectrum 2) 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 characterized by a very large FWHM (2.5 eV) and centered at 3.4 eV. It is most noticeable that, after NH₃ interaction, the intensity has decreased by a factor of 3, which is even higher than that observed for Ti(OEt)₄, where the Ti(IV) is fivefold coordinated.

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 pentacoordinated Ti(IV); 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 the hypotheses of the coordinative insertion of NH₃ into the Ti(IV) coordination sphere, with subsequent increase of the coordination number. On the basis of the whole set of previous considerations, these spectroscopic features can be interpreted in terms of the coordination reactions shown below:



and/or



Similar reaction schemes have already been hypothesized on the basis of independent UV-vis,^{4,9,13} IR,⁴ and Raman¹² investigations. In fact, the transformation of a tetracoordinated Ti(IV) into Ti(IV) in five- or sixfold coordination must be associated

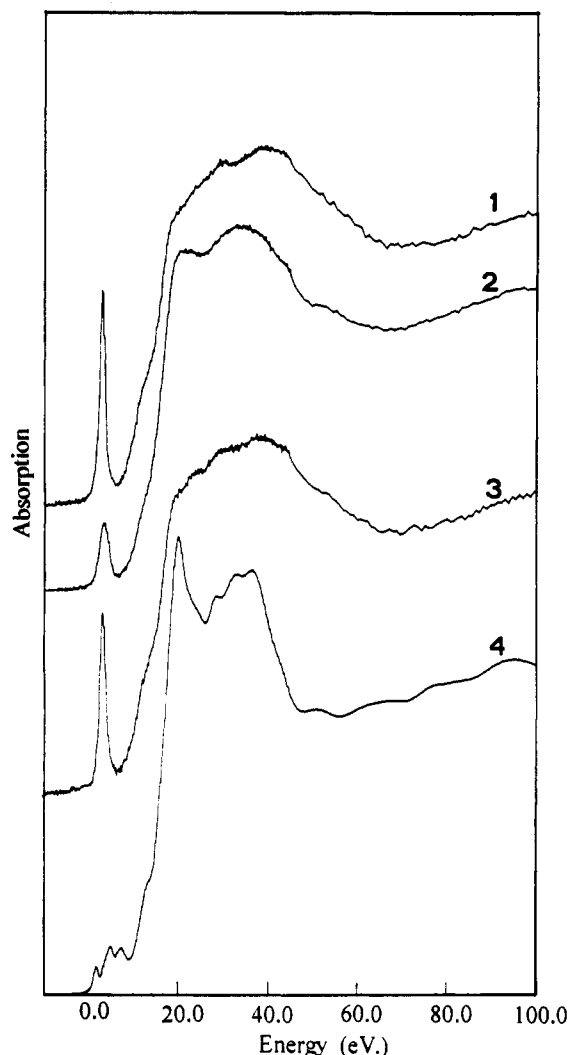


Figure 4. XANES spectra of [TSa] outgassed at 400 K, the effect of NH₃ adsorption and desorption: (1) [TSa] in vacuo; (2) after dosage of NH₃ (equilibrium pressure of 10⁴ Pa); (3) effect of pumping at room temperature for 10 min (energy scale as in Figure 1); (4) TiO₂ (anatase).

TABLE 4: Ammonia Adsorption and Desorption on Ti(IV)

sample	peak position, ^a eV	ΔFWHM, eV	intensity, %
TSa outg. at 400 K	2.9 ± 0.2	1.4	75
TSa + NH ₃	3.4 ± 0.2	2.5	24
TSa + NH ₃ + out.	3.1 ± 0.2	1.6	64

^a Energy values have been calculated as in Table 1.

with the drastic reduction of the intensity of the pre-edge adsorption; this is in qualitative agreement with our observations.

It is most noticeable that volumetric determination of the amount of adsorbed NH₃ at room temperature and under similar pressure conditions indicates that the number of NH₃ ligands per Ti(IV) center is intermediate between 1 and 2 (which means that the coordination state of Ti(IV) is intermediate between 5 and 6). This explains the drastic decrease of the intensity upon NH₃ dosage larger than that observed on passing from fourfold- to fivefold-coordinated Ti(IV). On this basis, the presence of a weak residual peak (spectrum 2 in Figure 4) can be interpreted by considering the incomplete NH₃ reaction with Ti(IV) species.

To check the correctness of these conclusions, in Figure 5 the effect of NH₃ dosage on the UV-vis reflectance (section a) and IR (section b) spectra is reported for sake of comparison. These spectra have been already commented on in previous contributions and explained in terms of coordination of ligands (adsorbates).^{4,9} We only remind the reader of the following:

(i) Formation of a peak at 38 000 cm⁻¹ in the UV-vis spectra with NH₃ → Ti(IV) ligand to metal charge transfer (LMCT)

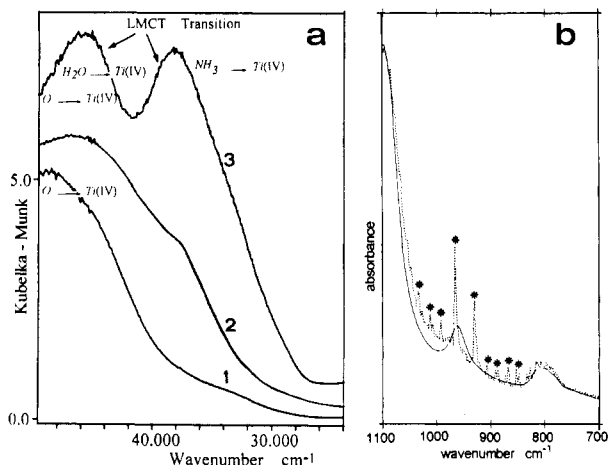


Figure 5. (a) UV-vis reflectance spectra of Ti-silicalite, effect of adsorbates: (1) [TSa] spectrum in vacuo (the band at 48 000 cm^{-1} is a $\text{OH}(\text{O}) \rightarrow \text{Ti}(\text{IV})$ (LMCT) band in tetrahedral units;⁶ (2) after NH_3 dosage (equilibrium pressure 10^4 Pa) (the new peak at 38 000 cm^{-1} is the $\text{NH}_3 \rightarrow \text{Ti}(\text{IV})$ (LMCT) transition;⁴ (3) after contact with NH_3 from 30% solution (the strong peak at 38 000 cm^{-1} has reached its maximum intensity⁹). (b) IR spectra of Ti-silicalite, effect of adsorbates: (—) [TSa] in vacuo (the band at 960 cm^{-1} is the fingerprint of framework Ti). (---) after NH_3 contact (10^4 Pa) (the band at 960 cm^{-1} is completely eroded). The peaks marked with an * are due to NH_3 in the gas phase.

character is indicative of the coordination of NH_3 ligand and subsequent expansion of the $\text{Ti}(\text{IV})$ coordination sphere. Under the adopted experimental conditions, adsorption of NH_3 from the gas phase does not lead to sixfold-coordinated $\text{Ti}(\text{IV})$ (vide supra). The maximum number of NH_3 ligands is only obtained when a higher pressure of NH_3 is dosed or by using an aqueous solution (as clearly seen from the UV-vis experiments where the $\text{NH}_3 \rightarrow \text{Ti}(\text{IV})$ (LMCT) band at 38 000 cm^{-1} reaches its maximum intensity (spectrum 3 of Figure 5a).^{13,37}

(ii) NH_3 adsorption shifts upward the 960- cm^{-1} IR and Raman peaks with weakening and broadening. Following ref 12, this has been interpreted in terms of coordination of NH_3 to $\text{Ti}(\text{IV})$, with subsequent expansion of the coordination sphere and elongation of $\text{Ti}-\text{O}$ bonds which causes the disappearance of the structural $\text{Ti}(\text{IV})$ fingerprint band.

The effect induced by NH_3 is only partially reversible at room temperature, as also documented by the XANES spectrum taken after successive outgassing for 10 min at room temperature (spectrum 3 in Figure 4), in agreement with volumetric data. In fact, a restoration of both intensity and the FWHM of the pre-edge peak (see spectrum 1 of Figure 4) and of the near edge region is not completely observed. In conclusion: four different spectroscopies give the same general answer: *the $\text{Ti}(\text{IV})$ coordination sphere expands upon adsorption of extra ligands (adsorbates) from the surrounding atmosphere.*

EXAFS. Figure 6 shows the EXAFS spectra of [TSa] 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 behavior, the observed EXAFS spectra before interaction with adsorbates can basically be interpreted on the basis of a coordination sphere of $\text{Ti}(\text{IV})$ formed only by oxygen centers. 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 their absence ([TSa] outgassed at 400 K), thus suggesting a more disordered situation (vide infra).

The Fourier transform of the spectra 1–4 are illustrated in Figure 7. The main characteristic clearly showing up is undoubtedly represented by the presence of a maximum centered in the 1.2–1.4-Å interval.

Concerning the main peak, the following can be stated:

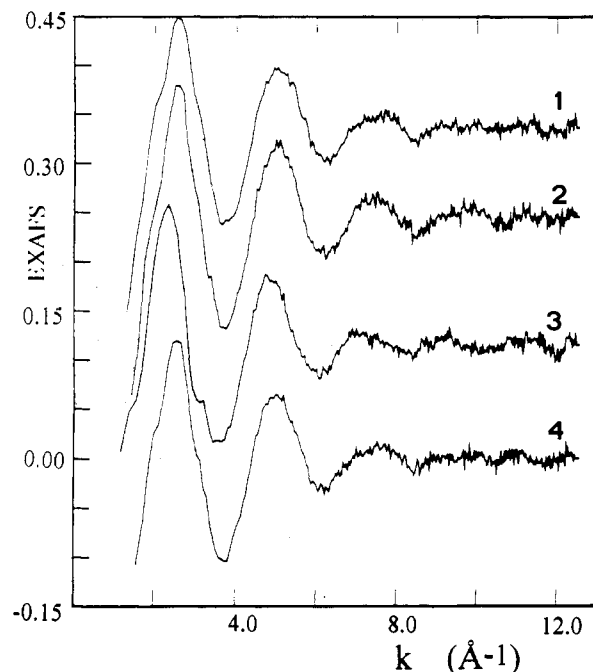


Figure 6. EXAFS of [TSa] in the presence and absence of an extra ligand: (1) sample outgassed at 300 K; (2) in vacuo after a treatment at 400 K; (3) after dosage of NH_3 (equilibrium pressure of 10^4 Pa); (4) effect of pumping at room temperature for 10 min.

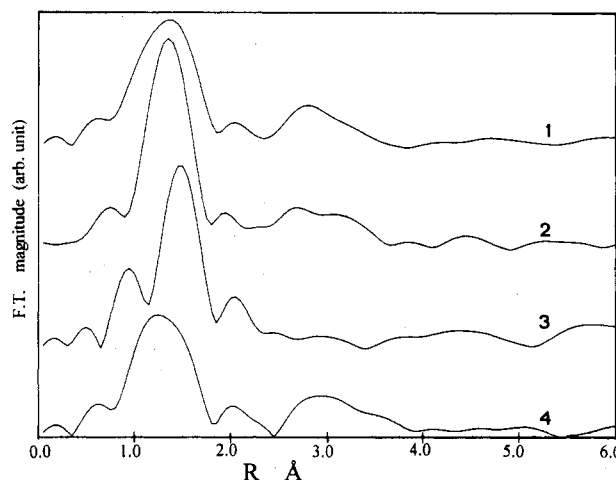


Figure 7. Modulus of the Fourier transform of the k^3 weighted EXAFS oscillations illustrated in Figure 6.

[TSa] 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-neighbor distance of about 1.8 Å. This distance is in good agreement with the known values for $\text{Ti}-\text{O}$ bonds in compounds where $\text{Ti}(\text{IV})$ is in fourfold coordination.^{18,22}

[TSa] Outgassed at 400 K (Curve 2). No change is observed concerning the main peak position. The high intensity and symmetry, together with the narrower lineshape, indicate that 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 conclude that H_2O ligands are desorbed by outgassing at 400 K and that only the sample treated at 400 K can be used to evaluate the coordination state of $\text{Ti}(\text{IV})$ in the absence of adsorbates.

[TSa] 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 centered at 1.5 Å.

[TSa] after NH_3 Contact and Successive Outgassing at Room Temperature (Curve 4). The outgassing treatment at room

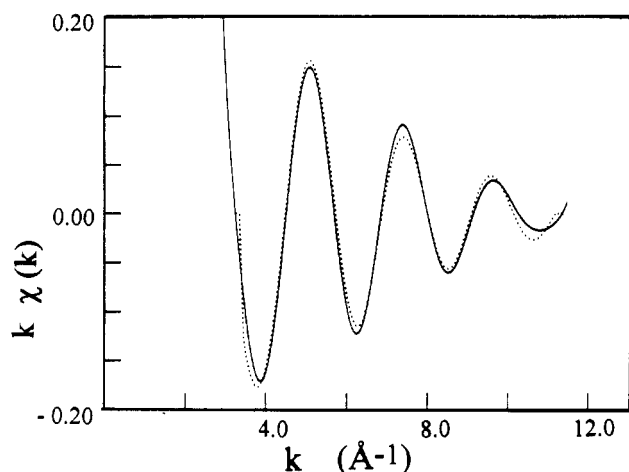


Figure 8. Inverse Fourier transform of the first-shell signal of [TSa] outgassed at 400 K (full line) and the best fit (dotted line).

TABLE 5: Fitting Results for the EXAFS Spectra of Ti-Silicalite

sample	$N \pm 0.6$	$R \pm 0.01$ (Å)	$\sigma^2 \times 10^3$ (10 ⁻³ Å ²)	fit (10 ⁻²)
TSa outg. at 300 K	5.3	1.81	9	3.2
TSa outg. at 400 K	4.4	1.81	4	2.4
TSa + NH ₃	5.5	1.84	10	5.5
TSa + NH ₃ + out	5.7	1.79	11	2.3
TSb outg. at 400 K	4.5	1.81	6	1.9

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 [TSa] outgassed at 400 K is the Ti(IV) in a well-defined coordination situation. In the remaining cases, the presence of extra ligands (H₂O and NH₃) causes a broadening of the features, which is 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 a more extended interval ranging from 0.6 to 1.8 Å (curve 3) and from 0.35 to 1.8 Å (curve 4) was used for the samples treated with NH₃.

Before going into detail of the EXAFS results, it is worth recalling that in Ti-silicalite containing 1–2 atom % 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 neighbor species (and hence more than four fitting parameters) can be made with caution. As a matter of fact, the k -space available and the R -space window adopted in the inverse transform do not allow more than a one-shell fit (four fitting parameters).³³ For this reason we decided to concentrate primarily 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).

In Figure 8 the result obtained for [TSa] outgassed at 400 K (full line) is reported. This spectrum can then be simulated on the basis of a coordination sphere constituted by oxygen atoms fourfold disposed around the Ti(IV) center. The result of this simulation (fitting range 3.1–11.2 Å⁻¹, k^2 weight) is compared (dotted line) in Figure 8 with the experimental one: the agreement between the two curves is quite satisfactory.

Fitting parameters N (number of oxygens atoms), R (nearest-neighbor position in Å), and σ^2 (disorder factor in Å²) are summarized in Table 5 together with the estimated errors. For the reasons discussed before these errors include correlation effects. In the same table a complete list of simulated results concerning the other spectra in Figures 6 and 7 is also reported, together with the data concerning [TSb] sample (vide infra).

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} Å², 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, assuming a tetrahedral oxygens coordination sphere. Although a $N = 4.4$ value seems to be high for tetrahedral Ti(IV) species, we underline that $+0.4$ is within the evaluated error for this variable (0.6). The presence of extra oxygens close to Ti(IV) centers derived from the Ti-O-Si bridge hydrolysis (Figure 2) 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 meaningful structural information to Ti-silicalite in the absence of adsorbates. It is worth mentioning that some recent theoretical calculations by A. Jentys and R. A. Catlow confirm these data.³⁴ These simulations are based on the lattice energy calculation using interatomic potentials including short-range interactions and long-range Coulomb's force (evaluated by the Ewald method).³⁵ A shell model has been used by the authors to represent the polarizability of the atoms.³⁶ The electronic structure of the representative clusters, containing the sites of interest, was been calculated by quantum mechanical studies.

When two Ti-silicalite samples outgassed at 400 K are obtained from two different syntheses [TSa] (a very pure Ti-silicalite sample) and [TSb] (compound with a small percentage of extralattice Ti(IV) as anatase microparticles)—are compared, no remarkable differences for N , R , and σ^2 (within the evaluated error) are observed. This observation indicates that EXAFS data on these samples cannot readily be used to discriminate well-manufactured samples from samples containing a small percentage of extraframework Ti(IV).

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 NH₃ (Table 5).

In this case, the fit can be improved by using a two-shell model with oxygen and nitrogen species for a total number of 6. However, as too many parameters are involved we do not believe that the structural factors deriving from those simulations are totally free from artifacts. For instance, comparable fit errors can be obtained by using a 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 NH₃ dosages, they do not allow detailed and safe information about the exact stoichiometry to be derived. More elaborate analysis about this point was not attempted.

In fact, we thought that in our case (characterized by low Ti(IV) concentration and strong noise) it was a better choice to use the simplest single shell-model (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).

Regarding the data concerning [TSa] sample with H₂O adsorbed into the channels ([TSa] outgassed at 300 K), in the presence of NH₃ and after successive outgassing at room temperature, a comparison of N , R , and σ^2 indicates the following:

For N , the coordination number increases in the presence of H₂O and more distinctly in presence of NH₃. 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.

For *R*, the Ti–L (*L* = ligand) distances are constant in all the series except for [TSA] sample treated with NH₃, 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 value is probably the average of Ti–O and Ti–NH₃ distances. This does not mean that upon NH₃ adsorption the Ti–O distance is not changing. On the contrary, we think that upon the expansion of the coordination sphere (caused by NH₃ adsorption) the Ti(IV) slightly moves outward from fourfold to fivefold and sixfold coordinative positions with subsequent increase of the Ti–O distances. However, from the reasons discussed before, we did not try to estimate this effect in a quantitative way.

For σ^2 , the presence of adsorbates (H₂O and NH₃) (or of a minor fraction of extraframework Ti(IV)) causes an increasing of the disorder factor. In fact, the smallest σ^2 value was obtained in the case of [TSA] sample outgassed at 400 K. The evaluated error for this variable is $2 \times 10^{-3} \text{ Å}^2$, which is sufficiently small to make the differences among the tabled values significant. On this basis, [TSA] sample treated in vacuo at 400 K again appears to be the most ordered system (in agreement with data obtained with IR, UV-vis, Raman, and XANES spectroscopies).

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 [TSA] previously outgassed at 400 K confirm that this sample is a very pure material where nearly all Ti is fourfold and in a symmetry very close to a perfect tetrahedron (no data of comparable quality on Ti-silicalites have been published so far).

XANES spectroscopy showed enough sensitivity to qualitatively recognize the presence of Ti(IV) in distorted octahedral coordination in [TSb] samples and in an amorphous SiO₂/TiO₂ (in agreement with UV-vis and Raman measurements). The experimental results also indicate that the coordination state of Ti(IV) in Ti-silicalite, prepared following ref 29 and containing a small Ti(IV) percentage, strongly depends upon the presence or absence of ligands (adsorbates). In particular, adsorption and desorption of NH₃ on [TSA], 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 [TSA] outgassed at 400 K is fourfold coordinated and that adsorption of ligands (H₂O and NH₃) leads to an increase of the coordination sphere. As stated in the text, it is not possible to fit the EXAFS spectra with more than one shell because of the limit on the number of allowed fitting parameters. It is true that this limits the information which can be obtained from the analysis, but we believe that the obtained data, even if only qualitative in some cases, are significant.

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

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.

Note Added in Proof. After the submission of this manuscript, a paper has appeared (Boyanov, B. I.; Duck, D.; Farrini, D.; Morrison, T. I.; Yang, D. S. *Catal. Lett.* **1993**, *21*, 333) which is in full agreement with our results.

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