

Evidence of the Presence of Two Different Framework Ti(IV) Species in Ti–Silicalite-1 in Vacuo Conditions: an EXAFS and a Photoluminescence Study

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In a previous contribution (*J. Phys. Chem.* **1994**, 98, 4125) we reported EXAFS data collected at ADONE on a high quality Ti–silicalite (TS-1) sample (Ti = 1.47 wt %) dehydrated in a carefully controlled atmosphere at 400 K. The importance of that paper was to definitively clarify that Titanium atoms occupy silicon substitutional framework positions. However, due to the large incertitude associated with the estimated first shell Ti-coordination number ($N = 4.4 \pm 0.6$), it was not possible to clarify if only perfect "closed" $\text{Ti}(\text{OSi})_4$ sites are present or if a considerable fraction of defective "open" $\text{Ti}(\text{OSi})_3(\text{OH})$ sites must also be considered (in an ideal EXAFS measurement N is expected to be five if only open sites are present, due to the insertion of a fifth oxygen of the silanol formed in the adjacent Si center when the Ti–O–Si bridge is broken). We report more recent EXAFS data collected at LURE DCI on a high quality TS-1 (Ti = 2.03 wt %) sample: the higher photon flux of that facility and the higher Ti content of the sample has allowed us to remarkably increase the signal/noise ratio with a consequent reduction of the errors associated with the fitted parameters. The quality of the fit, performed on a wider Δk range, has also been strongly improved. Our new measurements indicate that a first shell coordination number higher than four (4.44 ± 0.25). This suggests that, even for samples dehydrated in a carefully controlled atmosphere at 400 K, a considerable fraction of sites exhibits the substitution of a bridged oxygen with two OH groups. Being the value of the error bars associated to the EXAFS analysis of fundamental importance for the solidity of our conclusions, both statistical and systematic errors associated with our measurement and data analysis have been deeply discussed. EXAFS results are also qualitatively confirmed by a parallel photoluminescence study, where the presence, in both emission and excitation spectra, of two distinct bands clearly indicates that we are dealing with two family of Ti sites characterized by slightly different environments. For both techniques, the comparison with measurements performed on the $\text{Ti}(\text{OSi}(\text{CH}_3)_3)_4$ model compound, where Ti has both the first and the second coordination shells identical to those of Ti (perfect sites) in TS-1, strongly validates our conclusions.

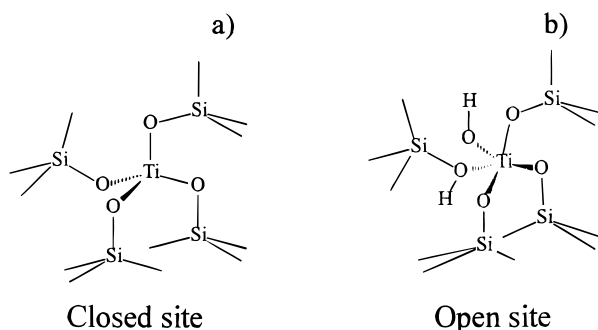
1. Introduction

Ti–silicalite (TS-1)¹ is a zeolitic catalyst very active in selective oxidation reactions utilizing H_2O_2 as oxidant (see, for

example, refs 2 and 3), and many attempts have been made to characterize the structure of Ti(IV) centers with several experimental techniques^{4–20} and theoretical approaches.^{21–28} For the time being the most common view is that Ti (IV) is incorporated as isolated center into the framework and is occupying a substitutional tetrahedral position.^{4–15,21–28} In favor of this hypothesis several XRD, IR, Raman, UV–vis, XPS, XANES,

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SCHEME 1



and EXAFS results can be mentioned. In particular: (a) The XRD measurements of Millini et al., on well manufactured TS-1, have given evidence that the unit cell volume increases linearly with the Ti loading of the sample;¹⁵ this effect can be explained only by assuming the insertion of Ti in a, or in more (already not defined), framework site(s). (b) The finger print peak at 960 cm^{-1} appearing in both IR and Raman spectra^{5,6,13} (and virtually absent in pure silicalite) is assigned to a mode with stretching character of the complex group of atoms shown in Scheme 1.

The 960 cm^{-1} band thus appears as a finger print of TS-1 and can be viewed as the ν_{as} of the (SiOTi) primary unit.^{5,6,13} Due to the higher mass of Ti (with respect to the Si) and to the polarized character of the Ti–O bond, the ν_{as} of the (SiOTi) unit has basically a $\nu(\text{Si–O})$ stretching character and hence it can be considered essentially as the $\nu(\text{Si–O})$ mode perturbed by the presence of framework Ti species. This band thus represent the direct proof that Ti atoms are framework species substituting Si in tetrahedral or nearly tetrahedral sites.

(c) The UV–vis spectra of TS-1 in vacuo is also very informative about the 4-fold coordination of the Ti, since the band at about 48000 cm^{-1} can only be explained in terms of $\text{O} \rightarrow \text{Ti}$ charge transfer transition in isolated and 4-fold, $[\text{TiO}_4]$, or nearly 4-fold, $[\text{TiO}_3\text{OH}]$, coordinated Ti species.^{6,9,12}

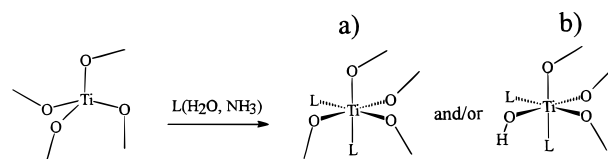
(d) The same conclusion is reached by XANES spectroscopy, because the narrow peak at 4967 eV can be only explained in terms of the Laporte allowed $A_1 \rightarrow E$ characteristic transition of the $(1s)^2 \rightarrow (1s)^1(3d)^1$ excitation in tetrahedral $[\text{TiO}_4]$ and/or nearly tetrahedral $[\text{TiO}_3\text{OH}]$, structures.^{9–12,29–31}

(e) Well manufactured TS-1 shows a well defined $\text{Ti}2p_{3/2}$ XPS peak at 459.8 eV, attributed to tetrahedral framework sites.¹⁷ Bonneviot et al.¹⁷ have also shown that, in samples where the presence of octahedral extraframework oxidic species has been proved, the XPS spectra are characterized by an additional component with a binding energy of 458.3 eV.

The assignments b–d are also based on the behavior of the corresponding spectroscopic features upon interaction, under controlled atmosphere, with extra ligands like NH_3 or H_2O . All these spectroscopies clearly indicate that the coordination sphere of Ti(IV) expands upon interaction with adsorbates and that the initial conditions are nearly totally restored upon a prolonged outgassing at room temperature.^{4–13} The ability of Ti(IV) to modify, in a reversible (or nearly reversible) way, its local environment upon interaction with adsorbates is probably the key of the catalytic ability of this important material.

In particular the effect of NH_3 or H_2O on the IR and Raman band at 960 cm^{-1} is a blue shift in energy, accompanied by a decrease in intensity and broadening.¹² This indicates that the coordination of new ligands on Ti centers is accompanied by an increase of the SiO stretching character of the $\nu_{\text{as}}(\text{SiOTi})$. A new ligand (NH_3 or H_2O) to metal Ti(IV) charge transfer band

SCHEME 2



appears in the UV and the absorption-edge shifts downward to an energy typical of 6-fold coordinated Ti.^{9,11,12} In a similar way, the $(1s)^2 \rightarrow (1s)^1(3d)^1$ XANES preedge peak slightly shifts to higher energy, and its intensity is strongly reduced and broadened, becoming similar to that characteristic of a 6-fold (quasi octahedral) Ti species.^{9–12,18}

IR, Raman, UV–vis, and XANES studies are thus consistent with the view that, upon adsorption, an expansion of the sphere of Ti(IV) centers through ligand coordination, as described in the Scheme 2, is occurring.

As already indicated in our previous works,^{4–13,18} the IR, UV–vis, and XANES techniques are not able to safely distinguish between structures a and b (i.e., between the presence in the dehydrated sample of closed or open sites, see Scheme 1) or a partial presence of both. Also, the IR study of the O–H stretching in titanols present in “open” sites was not enough informative about a quantitative evaluation of TiOH species present in TS-1⁵ because the titanol band is totally overshadowed by the more abundant band of silanols present in all defective sites (hydroxyl nests) of TS-1.^{32–35}

Due to its atomic selectivity, the technique of choice for solving this problem is certainly EXAFS;³⁶ in fact, the defective site is generated from a perfect one by the rupture of a Si–O–Ti bridge and the appearance of two OH groups, basically implying the insertion of a fifth oxygen atom in the first coordination sphere of Ti. The insertion of this fifth extra ligand into the first coordination sphere of Ti is not surprising because we have already documented the high ability and the propensity of Ti atoms to increase their coordination sphere. This means that a hypothetical TS-1 containing only closed sites would give rise to a Ti first shell coordination number of $N = 4.0$, while a hypothetical sample containing only open sites would give rise to $N = 5.0$. This implies that the presence of a relative fraction x of open sites and of $1.0 - x$ of closed sites, would give rise to $N = 4.0 + x$, being $0 < x < 1.0$, in an ideal EXAFS measurement.

The most relevant problem related with this speculation consists in the experimental error bar associated with the determination of coordination number with EXAFS. In fact, if EXAFS is known to be very accurate in the bond-length determination (an accuracy of $\pm 0.01\text{ \AA}$ can be routinely achieved in a first shell analysis), the same does not hold with the coordination number, where a typical error of about 10% is normally reported. This is mainly due to the strong correlation between N and the relative Debye–Waller factor σ . This means that, for EXAFS measurements performed on a sample where the absorbing atomic species is highly diluted, such as Ti in TS-1, the discrimination between $N = 4.0$ and $N = 4.5$ can be very delicate, if not borderline. The only way to try to, at least partially, overcome this problem is to improve the signal to noise ratio of the EXAFS spectrum, which will in turn allows a fit over a wider Δk range. This improvement can be done (i) by using a more intense photon source or (ii) by using a TS-1 sample having a greater Ti content, or both. Let us stress that the second point is far to be trivial, since it is well-known the difficulty to prepare “well manufactured” TS-1 with more than 1.5 wt %.¹⁵

We here present EXAFS data collected at LURE DCI on a new synthesized TS-1 (Ti = 2.03 wt %, all framework species, as indicated by XRD, UV-vis, XPS, and XANES) which strongly improve the signal to noise ratio with respect to our previous data collected at ADONE (Ti = 1.47 wt %).⁹ The two factors allow to perform the fit over a larger $\Delta k = 4.0$ – 14.2 \AA^{-1} range, resulting in a coordination number of $N = 4.44 \pm 0.25$, which definitively rules out the model of at TS-1 based on the sole presence of perfect closed sites (Scheme 1a). The importance of this result lies in the fact that, following our starting idea summarized in Schemes 1, even for samples dehydrated in vacuo at 400 K, a considerable fraction of sites exhibit the substitution of a bridged oxygen with two OH groups.

Due to its high sensitivity to the local environment of a luminescent center, a parallel photoluminescence study has been performed to qualitatively support our EXAFS study. From photoluminescence spectroscopy two bands have been observed in both emission and excitation scans, so indicating the presence of two different families of luminescent centers, that have been attributed to two different families of framework titanium species in TS-1, in agreement with the EXAFS findings (see Discussion).

Comparison with EXAFS and luminescence spectra obtained from $\text{Ti}(\text{OSi}(\text{CH}_3)_3)_4$ model compound and with luminescence of Ti-free silicalite strongly validates our conclusions.

2. Experimental Section

TS-1 sample (Ti = 2.03 wt %) has been synthesized in EniTecnologie laboratories, following the patent in ref 1. The total insertion of Ti has been verified by parallel XRD, IR, UV-vis, XPS, and XANES characterizations (not reported for brevity); the presence of segregated TiO_2 phase or TiO_2 nanoclusters inside the channels has thus been clearly ruled out.

XAFS spectra have been performed in the transmission mode, at the EXAFS3 beam line of the DCI storage ring (operating at 1.85 GeV with a typical current of 300 mA) of LURE laboratories in Orsay (F),³⁷ using air filled ionization chambers for both incident and transmitted beams. For both detectors the gas pressure has been optimized ad hoc for each sample, maximizing the measured current within the linearity region of the device. Incident beam was monochromatized using a double crystal Si(111) (sampling step, 2.0 eV; integration time, 2.0 s/point). The energy/angle calibration was performed using a Ti foil and crystals were detuned up to one-half of the rocking curve to avoid harmonics. The EXAFS spectrum was acquired eight times under the same experimental conditions and from the eight extracted $\chi_i(k)$ ($i = 1, 2, \dots, 8$), we have computed the average $\chi(k) = (1/8) \sum_{i=1}^8 \chi_i(k)$ and the corresponding standard deviation.

As the environment of Ti in TS-1 is strongly influenced by the presence of adsorbates, EXAFS spectroscopy has been performed by using an iron cell specifically designed by authors to allow measurements under a carefully controlled atmosphere where the sample can be introduced in form of thin self-supporting wafers. This cell, equipped with two mylar windows, can be connected to a vacuum line for sample pretreatment (activation for 1 h at 400 K under a dynamic vacuum of ca. 10^{-3} Pa). This cell represents the improvement of a quartz cell successfully employed in similar experiments performed on TS-1,^{9–11} Fe-silicalite,^{11,38} and Cu^I-zeolites (ZSM-5, Mordenite, and Y),³⁹ where the security of operating in carefully controlled atmosphere was as much imperative.

As far as anatase and $\text{Ti}(\text{OSi}(\text{CH}_3)_3)_4$ model compounds are concerned, due to the higher Ti concentration, only four spectra

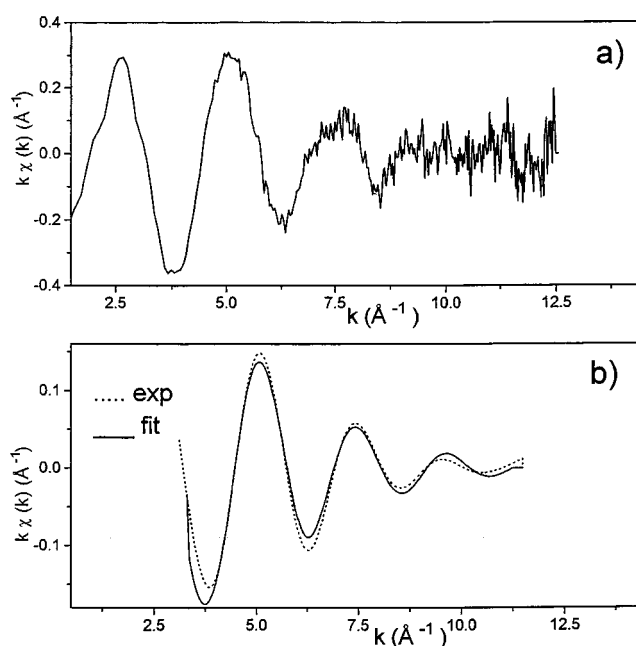


Figure 1. (a) Experimental $k\chi(k)$ (b) and quality of the fit of the old experiment performed at ADONE. These data are to be compared with the new one presented in Figure 2a and c, to appreciate the improvement of both experimental data and fit. (a) has been adapted from Figure 6 of ref 9 (note, however, that we report the $k\chi(k)$, while in the original version we reported the $\chi(k)$), while (b) has been adapted from Figure 8 of the same reference.

have been recorded. $\text{Ti}(\text{OSi}(\text{CH}_3)_3)_4$, diluted in cyclohexane, has been measured using a conventional EXAFS cell for liquid compounds already described elsewhere.⁴⁰ In the EXAFS analysis, errors were calculated at a 68.3% confidence interval. Samples homogeneity was controlled by radiographic methods.

Photoluminescence spectra have been recorded on a SPEX Fluorolog-2 spectrofluorometer equipped with a xenon UV-vis-NIR excitation lamp, whose light is filtered before reaching the sample by an excitation monochromator; the photoluminescence emission is then selected by a second monochromator (emission monochromator) before reaching the photomultiplier. Both monochromators allows a sampling step up to 1 nm in the 250–1000 nm (40000 – 10000 cm^{-1}) spectral range. All the reported spectra have been collected with an integration time of 1.0 s per point and a sampling step of $\Delta\lambda = 1.0 \text{ nm}$, which means $\Delta\tilde{\nu} = 160 \text{ cm}^{-1}$ at 250 nm (40000 cm^{-1}) and $\Delta\tilde{\nu} = 10 \text{ cm}^{-1}$ at 1000 nm (10000 cm^{-1}).

3. Results and Error Bar Analysis

3.1. EXAFS. In a previous EXAFS study,⁹ carried out at the PULS beamline of Frascati National Laboratories the coordination number of Ti(IV), in absence of weakly adsorbed water molecules was found to be slightly larger than four (4.4 ± 0.6). However, as the associated error bar was ± 0.6 , a clear conclusion about this point was not possible. This large error bar was mainly due to the lower photon flux available: as a matter of fact in that experiment we were able to observe only three EXAFS oscillations significantly above the noise, being the fourth at about 9 – 10 \AA^{-1} scarcely visible. This has allowed us to perform the fit only over a $\Delta k = 3.1$ – 12.2 \AA^{-1} range, resulting in a considerable correlation between the fitted parameters N and σ . Figure 1 reports the experimental $k\chi(k)$ and the quality of the first shell fit of our previous data for sake of comparison with recent results.

3.1.1. Standard EXAFS Analysis. In this work, we present EXAFS data collected using the higher photon flux available

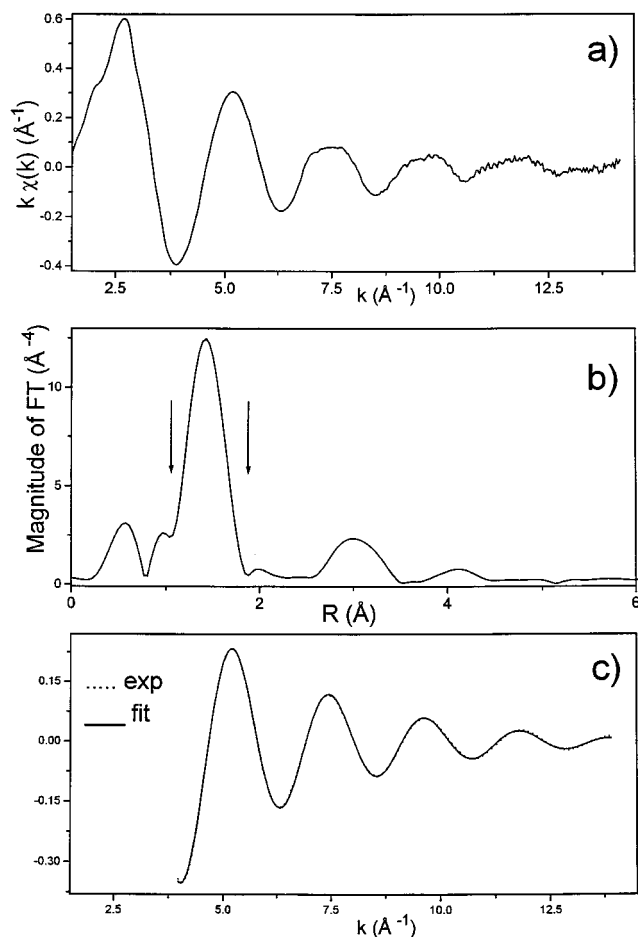


Figure 2. (a) Experimental $k\chi(k)$ averaged over eight TS-1 spectra. (b) modulus of the k^3 weighted FT in the range 3.3–14.2 \AA^{-1} without any phase correction. (c) Back-FT filtered over the first shell in the 1.07–1.84 \AA range (dashed line) and best fits (full line).

at the DCI storage ring at LURE (see Experimental Section) and we report results characterized by error bars reduced by a factor of about 2. Figure 2a shows the averaged $k\chi(k)$ function obtained estimating the atomic contribution by a polynomial fit (fifth degree) and then subtracted from experimental data following the procedure proposed by Lengeler and Eisenberger⁴² (the preedge being modeled with a line). By a simply comparison with experimental $k\chi(k)$ reported in Figure 1a, the improvement of the signal/noise ratio is evident, being now the fifth oscillation (maximum at about 12 \AA^{-1}) clearly visible. Figure 2b reports the k^3 weighted FT computed in the range 3.3–14.2 \AA^{-1} ($\Delta k = 10.9 \text{\AA}^{-1}$) using a Kaiser window with $\tau = 2.5$ (no phase correction has been adopted). EXAFS analysis was performed following standard procedures⁴¹ using Michalowicz programs.^{43,44} The EXAFS spectrum was acquired eight times under the same experimental conditions, and extracted $\chi(k)$ have been averaged before the EXAFS data analysis. Standard deviation calculated from the averaged spectra was used as an estimate of the statistical noise for the evaluation of the error associated with each structural parameters. Data analysis were obtained in the frame of single scattering curved wave approximation extracting the experimental phase shift and amplitude functions from anatase model compound (four planar and two axial oxygen atoms at 1.93 and 1.97 \AA , respectively, simulated as six equivalent nearest neighbors at 1.943 \AA). The first shell contribution was then filtered in the range 1.05–1.85 \AA ($\Delta r = 0.80 \text{\AA} \rightarrow 2 \Delta r \Delta k / \pi = 5.55$) and modeled as the Ti–O coordination shell, resulting in a first coordination shell formed

TABLE 1: EXAFS Results for First Shell Bonding Parameters^a

fit variable	fit on the $\chi^{\text{fil}}(k)$ obtained from the averaged $\chi(k)$	average over the eight fits of the single $\chi_i(k)$	fit on the $\langle \chi^{\text{fil}}(k) \rangle$ obtained by averaging the single filters $\chi_i^{\text{fil}}(k)$
R (\AA)	1.793 ± 0.007	1.793 ± 0.003	1.792 ± 0.003
N	4.44 ± 0.25	4.46 ± 0.09	4.43 ± 0.11
$\sigma \times 10^{-2}$ (\AA)	5.4 ± 0.3	5.4 ± 0.1	5.4 ± 0.3
ΔE (eV)	$+0.1 \pm 0.4$	$+0.1 \pm 1.0$	-0.1 ± 0.4

^a N : Ti coordination number. R : Ti–O bond length. σ : mean square relative Ti–O displacement, the corresponding value for anatase model compound, from which phases and amplitudes have been extracted, being arbitrarily been fixed to $\sigma_{\text{anatase}} = 7.0 \times 10^{-2} \text{\AA}$. ΔE : energy shift of the Ti K-edge photoelectron edge. For N , R , σ , and ΔE , corresponding mean values and standard deviations have been computed in three different ways: following the standard procedure,⁴¹ performing the fit on the filter obtained from the averaged $\chi(k)$ (first column); performing eight different fits on the single $\chi_i^{\text{fil}}(k)$ and then applying the conventional laws of statistic (second column); performing the fit on the filter $\langle \chi^{\text{fil}}(k) \rangle$ obtained as average of the single filters $\chi_i^{\text{fil}}(k)$ (third column).

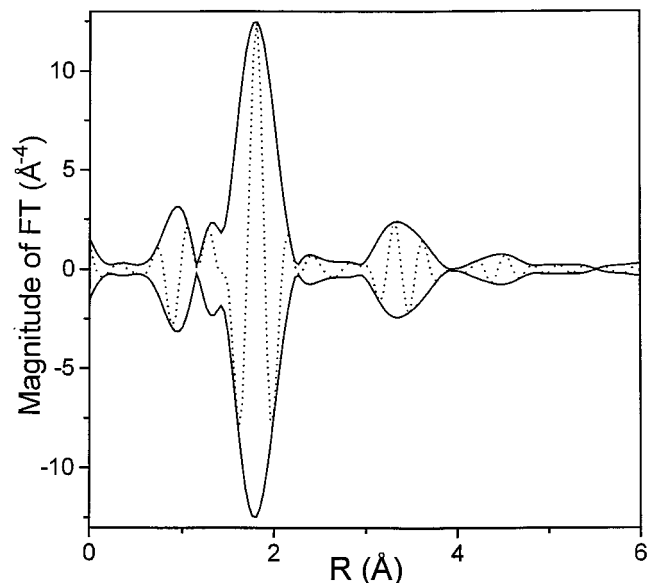


Figure 3. Modulus and imaginary part of the phase corrected k^3 weighted FT in the range 3.3–14.2 \AA^{-1} .

by 4.44 ± 0.25 oxygen atoms at $1.793 \pm 0.007 \text{\AA}$. The quality of the fit, performed in the $\Delta k = 4.0$ – 14.2\AA^{-1} range ($2\Delta r \Delta k / \pi = 5.19$), is reported in Figure 2c: it is much better than that previously reported in ref 9 (see Figure 1b). All details of this fit are summarized in the first column of Table 1.

Because the expected coordination number for a perfect site is four, from the same experimental data, we have also performed a three-parameter fit by keeping N fixed to 4.0. The quality of the former fit is better than that of the latter; however, this is always the case when an additional parameter is introduced in the fit, since it increases the flexibility of the fit function. In order to check if the additional fitting parameter brings a statistically significant improvement of the fit we have performed an F -test,⁴⁸ the importance of which for EXAFS analysis has already been discussed by Joyner et al.⁴⁹ and by Freund.⁵⁰ The F -test accepts the fit with four free parameters within a confidence level greater than 95%.

Figure 3 reports the k^3 weighted phase corrected FT of the experimental $\chi(k)$: the symmetry of the imaginary part with respect to the maximum of the modulus is noticeable and

TABLE 2: EXAFS Results for First Shell Bonding Parameters (N , R , σ , and ΔE , See Table 1) for the Fits Performed on the Eight Single Filter $\chi_i^{\text{fil}}(k)$ Values^a

fit variable	$\chi_1^{\text{fil}}(k)$	$\chi_2^{\text{fil}}(k)$	$\chi_3^{\text{fil}}(k)$	$\chi_4^{\text{fil}}(k)$	$\chi_5^{\text{fil}}(k)$	$\chi_6^{\text{fil}}(k)$	$\chi_7^{\text{fil}}(k)$	$\chi_8^{\text{fil}}(k)$
R (Å)	1.795	1.792	1.793	1.787	1.793	1.795	1.794	1.792
N	4.58	4.55	4.44	4.33	4.43	4.50	4.36	4.51
$\sigma \times 10^{-2}$ (Å)	5.8	5.6	5.4	5.0	5.2	5.7	5.0	5.5
ΔE (eV)	+1.2	+0.1	+0.3	-0.8	-1.6	+1.0	+0.8	-0.4

^a The eight progressive numbers indicate the chronological order of the acquisition.

indicates that only oxygen atoms are present in the first coordination shell of Ti atoms.^{46,47}

In order to prove beyond any doubt that the statistical errors associated with our data allow us to affirm that the coordination number is significantly greater than 4, in the next paragraph, we have evaluated for all fitted variables (N , R , σ , and ΔE) both mean values and standard deviations using two other statistical approaches.

3.1.2. Non standard EXAFS Analysis and Statistical Errors.

From the eight independent absorption spectra mentioned above, we have extracted eight independent EXAFS signals, indicated as $\chi_i(k)$, being $1 \leq i \leq 8$. For each independent $\chi_i(k)$, we have followed the same procedure outlined in the previous paragraph for the averaged $\chi(k)$ so obtaining eight independent radial distributions and eight independent first shell filters $\chi_i^{\text{fil}}(k)$. This procedure has allowed us to perform on each of the eighth experimental filters the first shell fit, as previously described for the filter obtained from the averaged $\chi(k)$. Values obtained for each fitted variable (N , R , σ , and ΔE) in the eight independent fits are summarized in Table 2. The average values and corresponding standard deviations, as obtained by using the canonical laws of statistic applied to the results coming from a repeated experiment, are reported in the second column of Table 1. Note that all average values are fully comparable with those obtained using the standard procedure (compare with the first column of the same table). This does not hold for standard deviations which (with the sole exception of that related with ΔE) seem to be excessively underestimated with this method.

A second “nonstandard” approach that we have applied to our data consists in performing the same procedure that standard analysis does on the extracted $\chi_i(k)$ ⁴¹ on the Fourier filtered first shell signals: from the eight $\chi_i^{\text{fil}}(k)$ spectra we have computed the average $\langle \chi_i^{\text{fil}}(k) \rangle$ first shell filter as $(1/8) \sum_{i=1}^8 \chi_i^{\text{fil}}(k)$. From the so obtained $\langle \chi_i^{\text{fil}}(k) \rangle$ spectrum and the corresponding standard deviation we adopted the standard fit procedure, resulting in the values reported in the last column of Table 1. For all fitted variables, the mean values obtained with this approach are fully comparable with those obtained with the two previous methods, while, as far as standard deviations are concerned, they are even smaller; this relative underestimation of the error bars is particularly relevant for the coordination number and R . Probably the average procedure performed on the filters $\chi_i^{\text{fil}}(k)$ benefits of the double Fourier transform used to obtain each $\chi_i^{\text{fil}}(k)$ from the corresponding $\chi_i(k)$. This has the ability to decrease both low and high frequency noise present in the $\chi_i(k)$ spectra. Consequently the fact that averaged filter $\langle \chi_i^{\text{fil}}(k) \rangle$ is more “clean” than the filter obtained from the averaged $\chi(k)$ (used when the standard procedure is adopted) is so not surprising.⁴³ For the purposes of this work, the two “nonstandard” approaches represent an important support to the data obtained using the standard one. On this basis it is now very reasonable to conclude this paragraph by affirming that the mean value of the Ti first shell coordination number is about 4.4 and that the value $N = 4.0$ can be discarded within a confidence level greater than 68.3%. This means that, assuming that sites

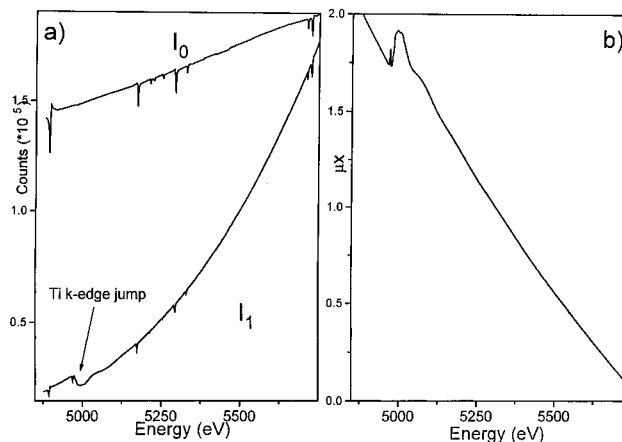


Figure 4. (a) experimental I_0 and I_1 currents for the first spectrum of TS-1. (b) corresponding absorption spectrum.

represented in Scheme 1 are the only representative substitutional sites for Ti in well manufactured TS-1, and if statistics are the only significant source of error of our EXAFS data,⁵¹ we can conclude that, in a dehydrated TS-1, both open and closed sites are present, in a nearly equivalent fraction.

It is worth mentioning that at the ninth XAFS conference (Grenoble, France, August, 1996),¹⁸ we already suggested that the Ti coordination number in TS-1 should be significantly greater than 4. However, the reported EXAFS datum $N = 4.45 \pm 0.30$ was obtained from a previous experiment,⁵² where only three equivalent spectra were collected. In that case only standard data analysis was reported. It is evident that the statistical evidence of the present study is much more solid.

3.1.3. An Attempt to Evaluate the Importance of Systematic Errors. The previous conclusion ($N > 4$) are solid only if systematic errors are not important. In the present paragraph this limitation is removed and systematic errors in both X-ray absorption measurements and EXAFS data analysis are considered.

As far as the measurements are concerned, a common origin of systematic errors in the amplitudes of the EXAFS oscillations (i.e., in the determination of both coordination numbers and the Debye–Waller factor) is related to (i) sample homogeneity, (ii) harmonic rejection, and (iii) systematic poisoning of water.

(i) In this experiment, the homogeneity of the sample was controlled by radiographic methods. The quality of the sample preparation can be appreciated in Figure 4, where both I_0 and I_1 currents and the corresponding $\mu x = \ln(I_0/I_1)$ are reported. Let us notice that, from a simple inspection, the quality μx is emerging by simply considering that some important anomalies (“glitches”), clearly visible on both I_0 and I_1 currents (some of them having an intensity greater than the Ti K-edge jump), are totally compensated in the computation of μx (see also the extracted $k\chi(k)$ reported in Figure 2a).

(ii) The harmonic rejection has been performed (see Experimental Section) by detuning the crystals at one-half of the rocking curve and using air filled ionization chambers. Being

3.62 keV, the critical energy of the spectrum emitted by a bending magnet of the LURE DCI machine, the ratio between the fundamental flux at 5–6 keV (Φ_0) and that of the first transmitted harmonic at 15–18 keV (Φ_a) is smaller than $\Phi_0/\Phi_a \approx 2 \times 10^{-1}$. Moreover, the detection efficiency of air filled ionization chambers is much greater for the fundamental photons than for those of the third harmonic: $\mu_0/\mu_a \approx 3 \times 10^{-2}$.⁵³ This means that, by detuning the crystals at one-half of the rocking curve, the actual effect of harmonics on the counts of both I_0 and I_1 ionization chambers can be considered smaller than 10^{-3} (i.e., a figure without any significant influence on the EXAFS data analysis⁵⁴).

(iii) Since EXAFS measurements on TS-1 must be collected under carefully controlled atmosphere, we must be sure that the environmental condition of the sample remains unaltered during the whole experiment (i.e., for about 4 h (since a single spectrum needs an acquisition time of about 30 min)). In fact, if the quality of the vacuum in the cell degenerates with time in a significant way, incoming H_2O molecules of the poisoning atmosphere will be immediately adsorbed on Ti centers (see Introduction), with a subsequent increase of the coordination sphere of Ti and consequent progressive increase of the N values obtained from the fits performed on the single $\chi_i^{fil}(k)$ (see previous paragraph). By observing the fit parameters (in particular N) reported in Table 2 as a function of i (from 1–8), the absence of any trend with time discards poisoning as a possible source of systematic error. To be correct, this means that water has not poisoned our sample during EXAFS measurements. However the presence of a measurable amount of water before the EXAFS experiment (i.e., in a TS-1 sample activated at 400 K for 1 h) can be safely excluded on the basis of a parallel IR study. In fact, IR spectroscopy is an ideal tool to use to check the presence of H_2O in the channels of microporous materials, the bending mode of water, at about 1630 cm^{-1} , clearly detectable. Our IR study, performed on the same cells used for EXAFS measurements (where mylar windows have been substituted with KBr ones), shows that a prolonged outgassing (1 h) even only at room temperature is sufficient to remove from TS-1 all adsorbed water and that spectra of samples outgassed at higher temperatures (400, 500, 600, and 700 K) show, in the IR region of bending mode of water, no variation. Furthermore, once the eight EXAFS spectra have been collected, the TS-1 sample previously activated at 400 K was removed from the X-ray beam, further activated at 700 K for 1 h and then measured again. In such condition only four EXAFS spectra were collected and all fitted parameters (R , ΔE , N , and σ) were fully compatible with those obtained from the sample activated at lower temperature: in particular $N = 4.42 \pm 0.30$ (following standard analysis). On the basis of this discussion, we can safely rule out the presence of a measurable amount of adsorbed water in the TS-1 sample both before and during our EXAFS experiment.

As far as the data analysis is concerned, a possible origin of systematic errors is related with arbitrary choice done in extracting $\chi(k)$ from the experimentally measured $\mu\chi$, mainly related with the interval selected for the interpolation of the atomic absorption. In order to evaluate the weight of this factor, we have decided to follow a safe, although very time consuming, procedure already adopted in refs 47 and 55. We have systematically operated in the following way: from the first spectrum, $\chi_1(k)$ has been computed by simulating the atomic absorption with E^4 , E^5 and E^6 polynomial functions and by cubic splines. For all the four approaches, several different extractions have been systematically computed by changing the

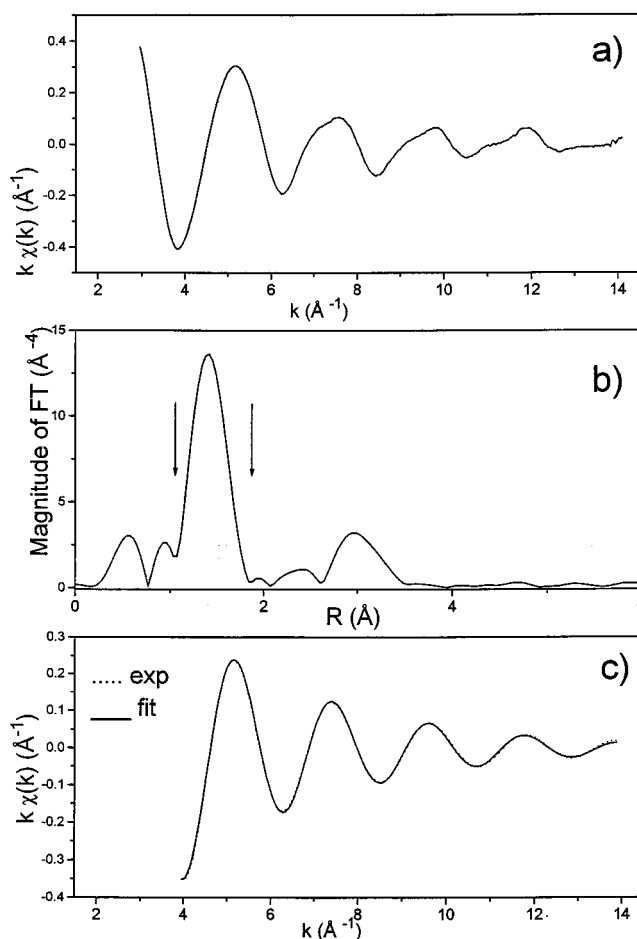


Figure 5. As in Figure 2 for the $Ti(OSi(CH_3)_3)_4$ model compound.

first point of the interval used for determining the atomic adsorption. Among all the so-obtained $\chi_1(k)$ functions, we have immediately discarded all those not *well behaved* (i.e., those showing a non-null profile at high k). By carefully superimposing the *well behaved* $\chi_1(k)$ functions, we have found that all of them are totally superimposed in the range 4–14.2 \AA^{-1} , while their feature for $k < 4 \text{\AA}^{-1}$ is extraction dependent. Among all the *well behaved* $\chi_1(k)$ functions, we have arbitrarily chosen one extracted using an E^5 polynomial function, and the same extraction procedure has been followed in a straightforward manner to obtain the remaining seven $\chi_i(k)$ functions. All fits were then performed in the extraction independent interval 4–14.2 \AA^{-1} . We can so affirm that the presence of significant systematic errors in the $\chi(k)$ extraction should be excluded.

Let us now come to the second and last possible origin of systematic errors in the data analysis that we have decided to discuss. We have proved in the past^{9,11} that phases and amplitudes extracted from anatase model compound are good to analyze the EXAFS data of TS-1. The question we raise now is the following: are they good enough to allow us to determine N in the first coordination shell with an error bar of about 5%? Alternatively, by using phases and amplitudes extracted from a model compound where titanium is in octahedral coordination to fit a material where titanium occupies a tetrahedral (or nearly tetrahedral) site, are we introducing a systematic error that, in an *ab initio* manner, removes any attempt to give a so-refined and critical result?

To answer this crucial question, we have decided to analyze, using the same phases and amplitudes extracted from anatase, the EXAFS spectrum of $Ti(OSi(CH_3)_3)_4$ compound (Figure 5), where Ti is linked to four equivalent silicon atoms through four

TABLE 3: As in Table 1 (First Column) for the Ti(OSi(CH₃)₃)₄ Model Compound

fit variable	fit on the $\chi^{\text{fit}}(k)$ obtained from the averaged $\chi(k)$
R (Å)	1.794 ± 0.006
N	4.13 ± 0.20
$\sigma \times 10^{-2}$ (Å)	4.5 ± 0.6
ΔE (eV)	-0.9 ± 0.6

bridged oxygen atoms, perfectly reproducing both first and second shell of a Ti atom in a “perfect” site of TS-1 (Scheme 1a). In this case only the standard⁴¹ data analysis has been performed on the $\chi(k)$ and results are summarized in Table 3 and in Figure 5. Being the result of the fit $N = 4.13 \pm 0.20$ we can conclude that a systematic error induced by the use of (Ti–O) phases and amplitudes extracted from anatase, although probably present, is not so important to invalidate our previous conclusions on the Ti coordination number in TS-1.⁵⁶

Summarizing the discussion outlined in this paragraph, we can conclude that, *if no other important source of systematic errors is present*, the first coordination shell around titanium in Ti–silicalite carefully outgassed in vacuo at 400 K is significantly greater than 4.

3.2. Photoluminescence. Due to the high sensitivity of Ti-based luminescent centers to the local environment, photoluminescence spectroscopy can be very useful in the discrimination between perfect “closed” Ti(OSi)₄ and defective “open” Ti(OSi)₃(OH) sites in TS-1. In this respect we will notice that Marchese et al. have recently used photoluminescence to discriminate among different kind of tetrahedral or nearly tetrahedral titanium sites in surface-grafted Ti–MCM-41^{58,59} prepared in different ways.

Let us recall that small particles of titanium oxides dispersed on Vycor glass^{60–62} or in zeolitic cavities^{63,64} or mixed titanium–silicon oxides⁶⁵ exhibit a luminescence peak at about 490 nm (≈ 20400 cm^{−1}) when excited at about 290 nm (≈ 34500 cm^{−1}). Ampo et al.^{60–65} have attributed the absorption at about 280–290 nm (≈ 35700 – 34500 cm^{−1}) to an oxygen to titanium charge transfer $O^{2-}Ti^{4+} \rightarrow (O^-Ti^{3+})^*$ transition and the emission in the 450–550 nm (≈ 20200 – 18200 cm^{−1}) range to the radiative decay process from the charge transfer state to the ground state $O^-Ti^{3+} \rightarrow O^{2-}Ti^{4+}$.

Figure 6a reports both emission and excitation photoluminescence spectra of dehydrated TS-1 collected at room temperature. The two spectra in the 250–325 nm (≈ 40000 – 30750 cm^{−1}) range represent excitation scans performed with the emission monochromator at 495 nm (≈ 20200 cm^{−1}) and at 430 nm (≈ 23250 cm^{−1}). The 11 spectra in the 400–650 nm (≈ 25000 – 15385 cm^{−1}) range represent emission scans performed with the excitation monochromator statted at 11 fixed wavelengths from 250 nm (≈ 40000 cm^{−1}) to 300 nm (≈ 33333 cm^{−1}) by step of 5 nm. These emission spectra clearly show the presence of two distinct bands at 430 nm (≈ 23250 cm^{−1}) and at 495 nm (≈ 20200 cm^{−1}). The excitation at 250 nm gives rise to an emission spectrum where the band at 495 nm is dominant with a shoulder at 430 nm; by increasing the excitation wavelength, we observe a progressive decrement of the band at 495 nm with a parallel increase of the band at 430 nm. When the excitation wavelength is 300 nm, the situation is completely reversed and the emission spectrum is characterized by a dominant band at 430 nm with a shoulder at 495 nm. The presence of an hysosbestic point at about 450 ± 5 nm (≈ 22220 cm^{−1}) clearly indicates the progressive evolution of the two luminescent Ti species. The same holds for excitation

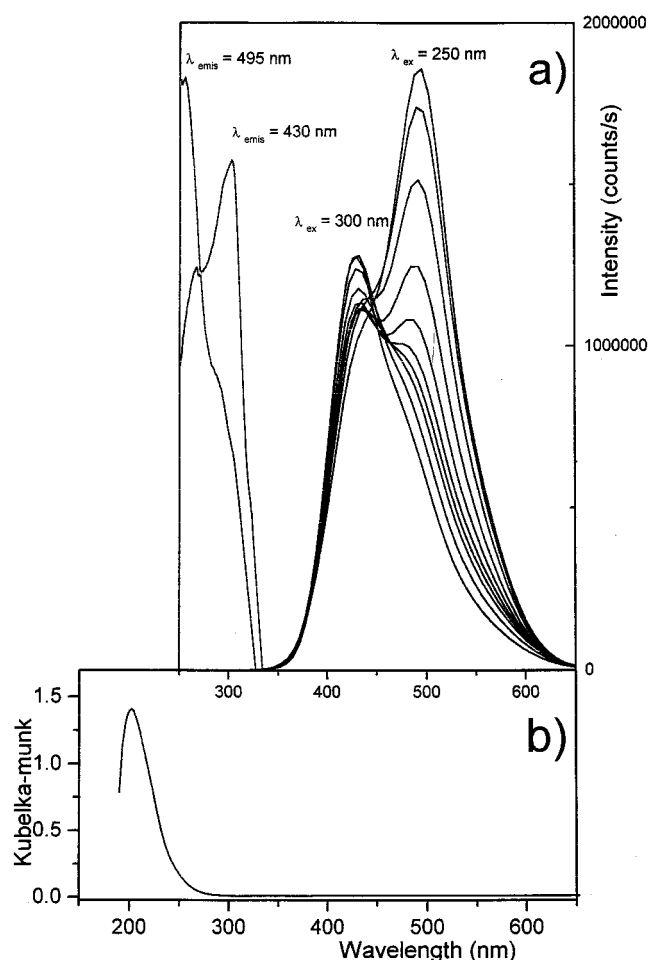


Figure 6. (a) RT luminescence spectra of dehydrated TS-1: spectra in the 250–325 nm (≈ 40000 – 30750 cm^{−1}) range represent excitation scans performed with the emission monochromator at 495 nm (≈ 20200 cm^{−1}) and at 430 nm (≈ 23250 cm^{−1}); while spectra in the 400–650 nm (≈ 25000 – 15385 cm^{−1}) range represent emission scans performed with the excitation monochromator statted at different wavelengths from 250 nm (≈ 40000 cm^{−1}) to 300 nm (≈ 33333 cm^{−1}) by step of 5 nm.

scans, which exhibit two evident peaks at 250 nm (≈ 40000 cm^{−1}) and at 300 nm (≈ 33333 cm^{−1}). Spectra reported in Figure 6a clearly show how the emission at 495 nm is preferentially activated by exciting the sample at 250 nm, while the emission at 430 nm is more active when the titanasilicate is excited at 300 nm. The presence of two close bands in both excitation and emission spectra is indicative of two slightly different families of Ti atoms which differ for their local environment, in full agreement with the EXAFS results reported in the previous section.

The same experiment performed on Ti(OSi(CH₃)₃)₄ model compound is reported in Figure 7: in this case only one band is present in both emission and excitations scans, at 500 and 250 nm, respectively. We are so able to attribute the bands at 495 nm (emission scans) and at 250 nm (excitation scans) to Ti atoms in perfect “closed” Ti(OSi)₄ sites and the bands at 430 nm (emission scans) and at 300 nm (excitation scans) to Ti species in defective “open” Ti(OSi)₃(OH) sites.

As far as excitation scans are concerned, it is worth mentioned that the intensity of the xenon UV lamp drops down to zero in the 260–230 nm range. This means that excitation spectra at $\lambda < 250$ nm ($\tilde{\nu} > \approx 40000$ cm^{−1}) are meaningless. For this reason, in Figures 6a and 7, excitation spectra have been reported only up to 250 nm. The actual position of the maximum of the excitation band attributed to perfect “closed” Ti(OSi)₄ sites is

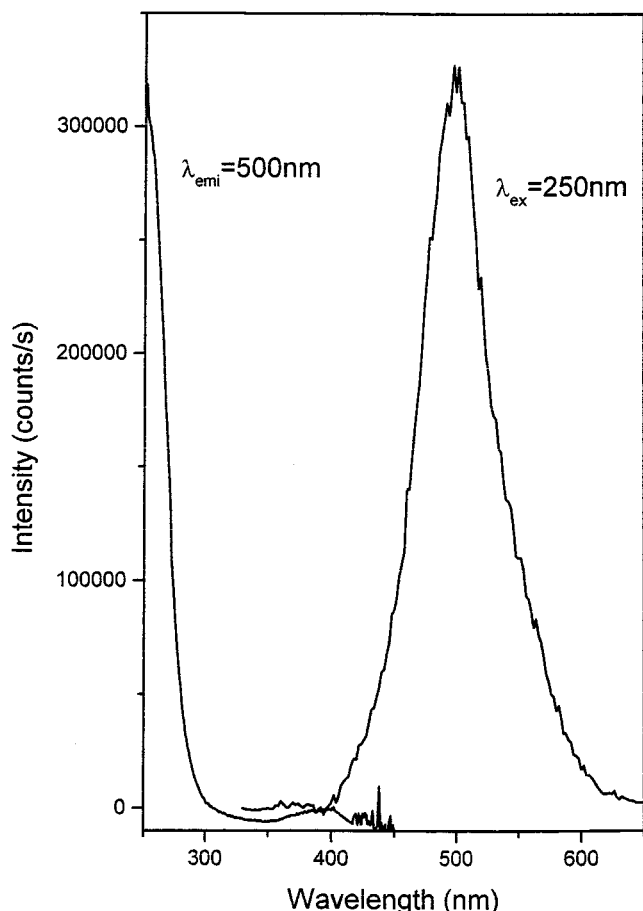


Figure 7. As in Figure 6a for $\text{Ti}(\text{OSi}(\text{CH}_3)_3)_4$ liquid model compound diluted in cyclohexane. In this case only one spectrum is reported for both emission and excitation experiments. The intensities of the bands reported in Figures 6 and 7 can not be compared since different experimental conditions have been adopted.

likely situated at lower wavelength probably close to the maximum observed in the reflectance UV–vis spectra reported in Figure 6b (i.e., near 208 nm (48000 cm^{-1})).^{6,9,12}

4. Discussion

The driving idea that has aimed this work is that Ti heteroatoms in well manufactured TS-1 samples can be located into two different type of framework sites: “closed” and “open” sites depicted in Schemes 1. In fact, this is an “old” idea that was originally suggested by our group since we were aware that on the basis of IR, Raman, and UV–vis data^{9,12,13} it was not possible to safely distinguish between them. We now think that the new EXAFS and photoluminescence data here presented allow the evolution of our starting idea from the ground of a simple, although very plausible, supposition to that of a strongly supported hypothesis.

Although strictly speaking, what we have here clearly demonstrated is only that the Ti first shell coordination number is definitively greater than four and that TS-1 exhibits two different luminescent centers, we will now show that the most plausible consequence of these observations is in favor of our original hypothesis for the reasons listed below.

(i) $N > 4$ implies that the perfect closed site (Scheme 1a) cannot be considered as the only site hosting Ti in TS-1 and that at least one additional, more highly coordinated site must be taken into account. It is worth recalling that parallel UV–vis, XRD, XANES, and XPS investigations (see Experimental

Section) rule out the presence of segregated nonframework anatase phase or of nanocluster of TiO_2 dispersed in the channels. Moreover, the fact that this sample, shows a cell volume increment, with respect to silicalite, compatible only with an insertion of 100% of Ti in TS-1 framework¹⁵ means that the additional site must be a framework one.⁶⁶ It is also worth recalling that, on the basis of the discussion debated at point iii of section 3.1.3, we can safely rule out that the increased number of Ti neighbor can be due to the presence of a measurable amount of adsorbed water in the TS-1 sample activated at 400 K for 1 h. These considerations lead us to consider that our first idea is the most reasonable way to interpret the present EXAFS result.

(ii) Coming now to the photoluminescence results, we are aware that photoluminescence spectra must be interpreted with care, because it is well-known that undesired defects or impurities can give rise to luminescent centers not related to the main chemical species present in the “ideal” crystal. For this reason, the risk of an erroneous assignment of luminescence bands is serious. As far as impurities are concerned, they can be safely excluded in the case of TS-1 because extremely high purity reactants are needed to synthesize a well manufactured TS-1.¹ This means that we do not expect the luminescence spectra reported in Figure 6 to be significantly affected by emissions coming from impurities. On the contrary, TS-1 is a very defective crystal and several T centers are missing (up to 5–8%), therefore generating a considerable number of internal silanol groups (hydroxyl nests) as clearly evidenced by IR spectroscopy.^{5,32–35} Now, if the attribution of the 495 and 250 nm bands (emission and excitation scan respectively) to Ti atoms in perfect “closed” $\text{Ti}(\text{OSi})_4$ sites comes in a straightforward manner from direct comparison with parallel experiment on $\text{Ti}(\text{OSi}(\text{CH}_3)_3)_4$ model compound, the attribution of the bands at 430 nm (emission scans) and at 300 nm (excitation scans) to Ti species in defective “open” $\text{Ti}(\text{OSi})_3(\text{OH})$ sites is more questionable. In fact, on the basis of the sole experiment reported in Figure 6, no direct evidence has been given to proof that also the second luminescent center in TS-1 is a “slightly different” Ti center and not an hydroxyl nest generated by a Si vacancy. To clarify this point, a blank photoluminescence experiment has been performed on a Ti-free silicalite^{32,33} synthesized following the same patent adopted for TS-1¹ and activated at 400 K for 1 h. Silicalite exhibit a broad photoluminescence emission in the 400–500 nm ($25000\text{--}20000\text{ cm}^{-1}$) range when excited in the 250–300 nm ($40000\text{--}33333\text{ cm}^{-1}$) interval, which intensity is more than 1 order of magnitude lower than that obtained from TS-1 measured under the same experimental conditions. This means that, in the spectra reported in Figure 6, a broad background due to defects and/or very low density of impurities is present, but it is a feature of secondary importance with respect to the two main luminescence centers that must be attributed to two Ti species in two slightly different local environments.

5. Conclusions

We have here clearly demonstrated that in “well manufactured” TS-1 the Ti first shell coordination number is definitively greater than four and that this material exhibits two different luminescent centers. These results strongly support the hypothesis that, even in the dehydrated TS-1, both perfect “closed” $\text{Ti}(\text{OSi})_4$ sites and defective “open” $\text{Ti}(\text{OSi})_3(\text{OH})$ sites are present. This result was already hypothesized in previous works from our group based on IR, Raman, and UV–vis data^{9,12,13} and is in agreement with very recent findings from Bonnevot et al.^{16,17}

6. Acknowledgment

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- (66) Please note that the term "Ti site" used in this context must be considered with a local meaning and that it must not be confused with the same term used in crystallography (12 or 24 different tetrahedral sites for orthorhombic or monoclinic silicalite). In fact, both EXAFS and photoluminescence techniques are not sensitive to long range ordering and no attempt can be done to distinguish among possible preferential crystallography substitution sites for Ti using local techniques. Our group has recently faced this problem performing Rietveld refinement on very high quality XRD data collected at the BM16 beamline at the ESRF.⁶⁷
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