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Structural characterization of Ti centres in Ti-silicalite and reaction mechanisms in cyclohexanone ammoximation

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Abstract

The main results obtained by means of many physical methods (IR, Raman, UV-Vis and XAFS spectroscopies) concerning the structure of the Ti centre in titanium silicalite and the reaction intermediates in the ammoximation of cyclohexanone are concisely reviewed.

The Ti is in tetrahedral coordination in vacuo and expands its coordination sphere upon interaction with adsorbates. In the presence of H_2O and H_2O/H_2O_2 solutions one of the SiOTi bridges is hydrolyzed with formation of $(\equiv SiO)_3L_2TiOH$ ($L = H_2O$) and $(\equiv SiO)_3L_2TiOOH$ species, respectively. When NH_3 is dosed on $(\equiv SiO)_3L_2TiOOH$ structures $(\equiv SiO)_3L_2TiOO^-NH_4^+$ species are formed. These species are thought to play an important role in the ammoximation reaction. The geometries of the peroxidic species (open or bridged) are discussed also on the basis of ab initio calculations.

Keywords: Structural characterization; Ti centres; Ti-silicalite; Reaction mechanisms; Selective oxidation

1. Introduction

When the chemistry of Ti(IV) is considered in the broadest sense, it is readily realized that the number of Ti-based compounds (both molecular or in solid form) where the Ti is in four-fold coordination, is very scarce and that this metal has a very strong tendency to go into six-fold coordination. This is easily illustrated by the alkoxides $Ti(OR)_4$, which are always in the polymeric form and where each alkoxide group bridges two Ti atoms (which allows each Ti to reach the six-fold coordination with subsequent increase of stability). Only when bulky (branched) alkyl groups (R) are used (preventing polymerization), can really four-fold coordinated Ti(IV) monomeric compounds be obtained.

On the basis of these general considerations, it can be understood why the announcement of the synthesis of Ti-silicalite (TS) [1–3], a zeolitic catalyst very active in selective oxidation reactions, where (on the basis of accurate lattice parameter determinations) [2] Ti was considered to be in the framework (and hence to be very plausibly in tetrahedral coordination), has stimulated many discussions.

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In order to elucidate the structure of the Ti centre in vacuo and in the reaction conditions, several physical methods have been used, such as UV-Vis, XANES, IR, Raman and EPR spectroscopies [4–12]. EXAFS has also proved to be very informative on the coordination state of Ti, both in the presence and in the absence of adsorbates [10,11,13–15].

In this paper we review the main results obtained with these physical methods and present some new data emerging from work in progress. The structure of the Ti centre in the presence and in the absence of adsorbates, as emerging from the experimental determinations, is also compared with the results of recent ab initio calculations. The high propensity of Ti to change its coordination under the action of reactants and its ability to form peroxo species with hydrogen peroxide, without being extracted from the framework, are the key points explaining its interesting catalytic behaviour in oxidation reactions. Finally the mechanism of a partial oxidation reaction (ammoximation of cyclohexanone with H_2O_2 and NH_3) is considered in detail as a case study.

2. Experimental

Ti-silicalite samples (Ti content 1.47% wt.) were synthesized in the ENICHEM laboratories as described in [16].

Transmission IR spectra have been collected on Bruker FTIR 48 and 113V spectrometers both equipped with an MCT cryodetector, while for diffuse reflectance IR spectra an external attachment by Spectra Tech has been adapted to the Bruker IFS 48 spectrometer. Raman spectra have been obtained on a Perkin-Elmer 2000R NIR-FT Raman spectrometer equipped with an InGaAs detector and employing a Nd-YAG crystal pumped by a high pressure Krypton lamp; the adopted wavelength was 1064 nm and the output power was 1.0 W. UV-Vis measurements have been performed on a Varian Cary 5 spectrometer. The first X-ray absorption spectra (1992) have been recorded in the transmission mode at the PULS beamline of INFN at Frascati (Rome) using a Si(111) channel cut monochromator; I_0 and I_1 fluxes have been measured using nitrogen and argon filled ionization chambers respectively. Recently (September 1995) we have used the EXAFS 3 beamline of LURE at Orsay (Paris) working with air filled ionization chambers and with a double crystal Si(311) for the XANES spectra and a double crystal Si(111) for the EXAFS spectra, both detuned to eliminate harmonics.

3. Results and discussion

3.1. IR and Raman results

As is well known [2–7], TS is characterized by a medium intensity IR band at 960 cm^{-1} (Fig. 1a), which is totally absent on silicalite [7]. This band, whose intensity is proportional to the Ti content [2], is undoubtedly one of the fingerprints of this zeolitic material.

The absence of an absorption of comparable intensity in other metal-substituted zeolites [6,7], is the most plausible origin of the hypothesis that this band is associated with the stretching mode of a titanyl group anchored to the structure and protruding in the channels [12]. The in situ IR study of the response of this band towards the perturbation induced by adsorbates containing mobile hydrogen like methanol (and so capable of hydrogen bonding with the titanyl group) [4], has excluded that the correct explanation of this band can be given in terms of the vibration of a simple diatomic group.

In fact the expected hydrogen bonding interaction between the titanyl group and the methanol molecule (taken as example) should shift the $\nu(Ti=O)$ towards lower, while the opposite is observed [4] (Scheme 1). The interaction with water gives a similar result. The same is found when NH_3 is dosed. Notice how in this last case, being the hydrogen of ammonia not very prone to hydrogen bonding formation,

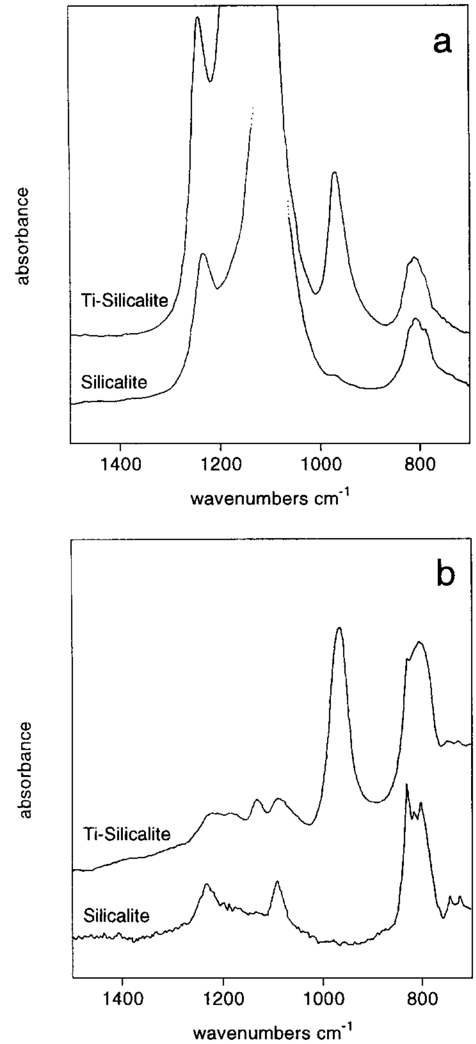
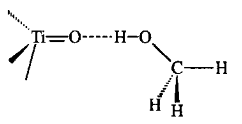


Fig. 1. Framework stretching region of silicalite and Ti-silicalite outgassed at 300 K: (a) diffuse reflectance IR spectra; (b) Raman spectra.

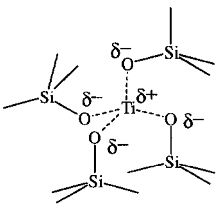
the observed perturbation must be a fortiori attributed to some other mechanism [8]. We anticipate that the common shift towards higher frequencies is better explained by the coordinative insertion of these molecules (ligands) into the coordination sphere of Ti: this is accompanied by a relaxation of the framework bonds around the site with movement of Ti towards a more external position and subsequent polarization of the TiO bonds. The implications of these experimental observations on the assignment of the 960 cm^{-1} band will become more evident in the following.

Raman spectroscopy has proved to be very informative on this point. In fact it has been shown (Fig. 1b), that the 960 cm^{-1} band is simply the strongest feature of a more complex spectrum (with components in the 1230–1080 cm^{-1} interval) associated with the presence of Ti in the structure [7]. This indicates that an explanation of the band as one of the vibrational modes of a more complex grouping of atoms (the Ti centres surrounded by four $[SiO_4]$ tetrahedra) (such as in TiO_2-SiO_2 glasses) [17–19] is much more plausible (Scheme 2).

To explain in simple words the origin of the main band appearing in both IR and Raman spectra, it is useful to start from the IR and Raman spectra of silicalite in the 1350–750 cm^{-1} stretching region [6,7]. The IR and Raman spectra of silicalite show complex but nevertheless well separated absorptions in two distinct regions (1350–1000 and 800–700 cm^{-1}). In the first region the IR absorption is strong while the corresponding Raman is weak; in the second region the opposite occurs. Essentially the same pattern is also shown by amorphous silica. This observation indicates that this common spectroscopic behaviour is basically reflecting the spectroscopic properties of a common primary building unit. Two primary units can be chosen: the $[SiO_4]$ and/or the (SiOSi). In fact the silicalite framework can be consid-



Scheme 1.



Scheme 2.

ered as constituted by $[SiO_4]$ tetrahedra linked through the edges to form a tridimensional $[SiO_4]_n$ array or constituted by the linking of the even smaller (SiOSi) primary units. In this last case the framework is viewed as $(SiOSi)_n$. The two approaches are equivalent.

(i) The stretching modes representation of isolated $[SiO_4]$ groups is:

$$\Gamma_{\text{stretch}} = A_1(\text{R}) + T_2(\text{IR}) \quad (1)$$

The separation between the frequency of the IR active, triply degenerate, T_2 mode and the frequency of the IR inactive and Raman active A_1 mode is dictated by the interaction constant between the four SiO oscillators of the same tetrahedron. Moving from the isolated tetrahedron to the unit cell (constituted by 96 tetrahedra), 96 × 3 modes and 96 × 1 modes (all IR active) deriving from the original T_2 and A_1 modes will be generated forming two complex but nevertheless well separated absorptions (corresponding to a total 96 × 4 figure). If these absorptions maintain, at least partially, the IR and Raman activities of the original T_2 and A_1 modes, the complex envelopes in the 1300–1100 and 800–700 cm^{-1} ranges are readily justified.

(ii) The stretching modes of the isolated (SiOSi) groups are:

$$\Gamma_{\text{stretch}} = B_2 + A_1 \quad (2)$$

corresponding to the asymmetric (B_2) and to the symmetric (A_1) stretchings. Although both are formally IR active, the first mode is expected to give the strongest band in the IR. The frequency separation of the two modes is dictated by the interaction constant between the SiO oscillators belonging to adjacent tetrahedra. Following the procedure illustrated before, moving from the isolated (SiOSi) group to the unit cell, two envelopes will be generated, the first one (with strong IR activity) deriving primarily from the asymmetric mode, the second one (less intense in the IR, but stronger in Raman) deriving from the A_1 mode.

Coming back to the assignment of the strong band at 960 cm^{-1} observed in the IR and Raman spectra of TS, we can proceed as follows:

(i) Following the tetrahedral units scheme, the band can be essentially attributed to the stretching modes of the (Si–O) groups of the tetrahedra linked to the Ti centre pointing directly versus the Ti. This mode contains only a small admixture of ν(Ti–O) and consequently can be considered as a mode of silicalite perturbed by the presence of Ti.

(ii) Following the scheme based on the SiOSi unit, the 960 cm^{-1} band is essentially deriving from one of the two absorptions of the SiOTi group embedded in the silicalite frame (the ν_{asym}). As the two atoms are not equivalent, the ν_{asym} occurring at higher frequency is basically a ν(Si–O) with little admixture of ν(Ti–O).

Both approaches lead to the common conclusion that the main band is essentially a stretching mode with prevailing ν(Si–O) character and small or moderate admixture of ν(Ti–O) of the structure illustrated in Scheme 2. On this basis the effect of methanol, water and ammonia absorption on the 960 cm^{-1} band is understood on the basis of a further decrease of the admixture of the TiO stretching character subsequent to the TiO bond polarization and weakening caused by the insertion of ligands into the coordination sphere of Ti. In other words the band acquires a more pronounced $Si\text{–}O^{\delta-}$ stretching character.

An interesting property of Raman spectroscopy lies in its capacity of giving reliable spectra even with the sample fully immersed in water, or water solutions, i.e. under conditions very similar to those encountered in some partial oxidation reactions. As a consequence, this spectroscopy can allow (at least in principle) to study the structure of the complexes present in solutions, i.e. in conditions where the IR spectroscopy cannot operate. In principle it can reveal the frequency of the mode with prevailing ν(O–O) character in the peroxidic structures formed on titanium silicalite in contact with neutral and basic H_2O_2 aqueous solutions. It is thought [8,9] that these yellow coloured species (vide infra) contains TiOOH and $TiOO^-M^+$ ($M = Na^+, NH_4^+$) formed by reaction of H_2O_2 with four-fold coordinated Ti following Scheme 3.

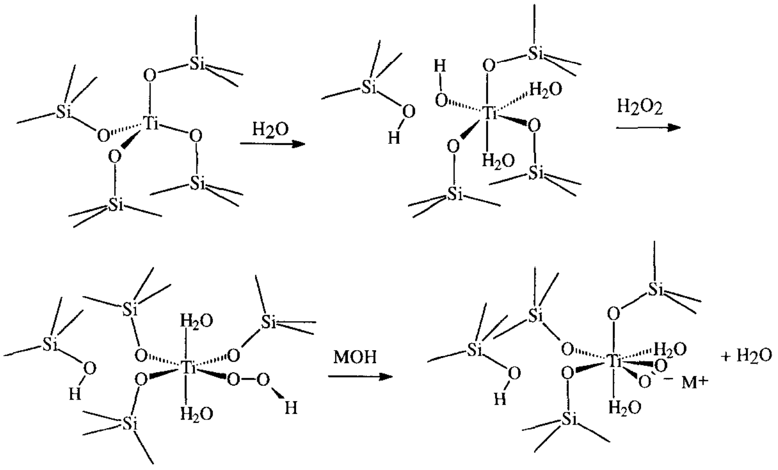
In these species, the Ti is in six-fold coordination and the TiOOH and the $TiOO^-$ moieties likely have the open and the bridged structures illustrated in Scheme 3.

On the hypothesized structure of this peroxidic species we shall return in the following. Unfortunately the peroxidic species formed under neutral conditions (vide infra), resulted too labile to resist the thermal effect of the laser beam: consequently no well defined, specific, absorption attributable to adsorbed hydroperoxo species could be observed for the sample in contact with the neutral solution (only the strong band of physically adsorbed H_2O_2 was detected).

A better situation was encountered when the peroxidic structures formed under slightly basic conditions (NaOH or NH_4OH 0.1 M solutions) were investigated. These more stable yellow species (also characterized by a different UV-Vis spectrum: vide infra) give in fact a Raman band at 840 cm^{-1}, which is assigned to the ν(O–O) mode in the salt-like $TiOO^-M^+$ peroxidic structure ($M^+ = Na^+, NH_4^+$). It is most noticeable that beside the band at 840 cm^{-1}, the Raman spectra obtained in presence of NH_4OH, distinctly show two extra bands at 985 and at 1043 cm^{-1} attributed to the oxidation products NH_2OH and nitrates. The presence of a strong peak due to hydroxylamine is specially remarkable because it plays a key role in the ammoximation reaction (vide infra) [8]. The nitrates are probably generated by further oxidation of NH_2OH under the effect of the laser beam. A second interesting observation requiring a comment concerns the transient nature of this band, which fades away after consumption of excess hydrogen peroxide. This behaviour suggests that it belongs to an active intermediate in the oxidation of NH_3 to NH_2OH and hence in the ammoximation reaction (vide infra).

3.2. UV-Vis results

This spectroscopy has played a remarkable role in the elucidation of the structure of the Ti centre both in vacuo and in presence of adsorbates or immersed in water or in diluted water solutions of hydrogen peroxide and ammonia. In particular it has added convincing evidence to the hypothesis of four-fold coordination of Ti in vacuo, and of its propensity to expand the coordination sphere in presence of adsorbates. A few important results are shown in Fig. 2a and Fig. 2b.



Scheme 3.

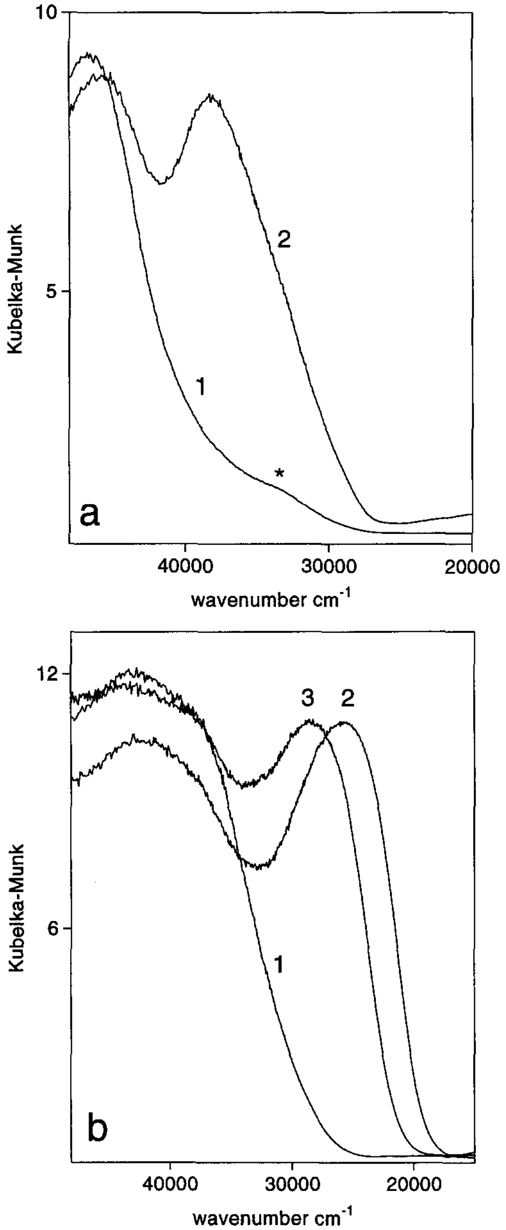


Fig. 2. UV-Vis reflectance spectra of Ti-silicalite after interaction with different adsorbates: (a) curve 1, in vacuo; curve 2, after interaction with NH_3 (100 mbar); the shoulder labelled with an asterisk is due to small fraction of extraframework Ti; (b) Ti-silicalite powder imbibed with water solutions: curve 1, pure H_2O; curve 2, H_2O_2 solution; curve 3, NH_3/H_2O_2 solution.

The spectrum in vacuo (curve 1 Fig. 2a) and in presence of gaseous ammonia (curve 2 Fig. 2a) have been interpreted in terms of ligand to metal charge transfer (LMCT) transitions in tetrahedral Ti complexes (band at ~ 48000 cm^{-1} in vacuo) and in six-fold coordinated Ti(IV) complexes (absorptions at ~ 46000 and at ~ 38000 cm^{-1} in presence of ammonia) [8,10]. The presence of a band at 48000 cm^{-1} in vacuo can be considered as characteristic of a well manufactured titanium silicalite. Any absorption appearing at lower frequency is in fact indicative of the presence of extraframework six-fold coordinated Ti species [6]. The spectrum obtained in presence of NH_3 is clear indication of the propensity of Ti to increase its coordination number in presence of ligands. The ability of reflectance spectroscopy to give reliable spectra also with the sample fully immersed in water is illustrated in Fig. 2b (curve 1), where the spectra of $(\equiv SiO)_4Ti(H_2O)_2$ and/or $(\equiv SiO)_3TiOH(H_2O)_2$ six-fold coordinated complexes are shown. The second structure is also considered because, as already discussed in previous contributions [7,8] and mentioned in Scheme 3, we do not exclude at all that, in presence of water, one of the SiOTi bridges is 'open' because of an hydrolysis reaction. The dosage of a H_2O_2 aqueous solution (curve 2, Fig. 2b) gives the strong band at 26000 cm^{-1} responsible of the characteristic yellow colour assumed by the sample [9]. This band is attributed to LMCT from a hydroperoxo ligand to the titanium centre in the structure $(\equiv SiO)_3TiOOH(H_2O)_2$ formed following Scheme 3. The effect of subsequent dosage of a NH_3 solution on the spectrum of preadsorbed H_2O_2 is shown in Fig. 2b (curve 3). In our opinion the induced shift of the peak responsible for the yellow colour of the sample, corresponds to the transformation of the open into the bridged (salt-like) species. The bridged structure is more stable than the open one: this is demonstrated by the more prolonged persistence of the yellow colour of the salt like species with respect to the linear TiOOH species formed in presence of the neutral solution.

The same spectroscopic effect is observed when a NaOH aqueous solution is dosed.

The spectra of the peroxo and hydroperoxo species compare very well with those of homogeneous compounds with similar structure. It is most noticeable that the peroxo species formed in presence of excess ammonia have also transient character [8] as the associated band quickly fades away after consumption of hydrogen peroxide: this confirms their nature of reactive intermediates in the formation of hydroxylamine (vide infra).

3.3. XANES and EXAFS results

A typical X-ray absorption spectrum it the 4900–5400 eV range of titanium silicalite in vacuo is shown in Fig. 3.

This spectrum can be divided into two parts, i.e. the XANES and the EXAFS parts, both extensively investigated in the last few years [10,11,13–15], to clarify the local environment of Ti(IV). The first part correspond to the so called X-ray absorption near edge structure, while the second one correspond to the so called extended X-ray absorption fine structure. The narrow absorption at 4967 eV in the XANES region is associated with the promotion of one electron from a $(1s)^2$ fundamental configuration to an excited one as shown below:

$$(1s)^2 \rightarrow (1s)^1(3d)^1 \qquad (3)$$

As the excited configuration energy is split in two levels (E and T_2) by crystal field perturbation, two transitions: $A_1 \rightarrow E$ and $A_1 \rightarrow T_2$ are expected. While the first transition is Laporte forbidden, the second one is allowed and appears as an intense and narrow characteristic peak at 4967 eV. This peak is shown only by the very few genuine tetrahedral or quasi tetrahedral Ti species known in the literature (for instance by alkoxides $Ti(OR)_4$ where R is a branched alkyl group) [20]. The presence of this narrow peak is a further and final proof that (in vacuo) Ti is in four-fold (tetrahedral or quasi tetrahedral) coordination. We shall see in the following that the pre-edge region is very sensitive to the coordination and symmetry state of the Ti centre (because it is essentially an optical spectroscopy). While the XANES part of the spectrum corresponds to an energy range associated only with the excitation of the electron to a very high but still bound level, the EXAFS part corresponds to an energy range where a $(1s)^2$

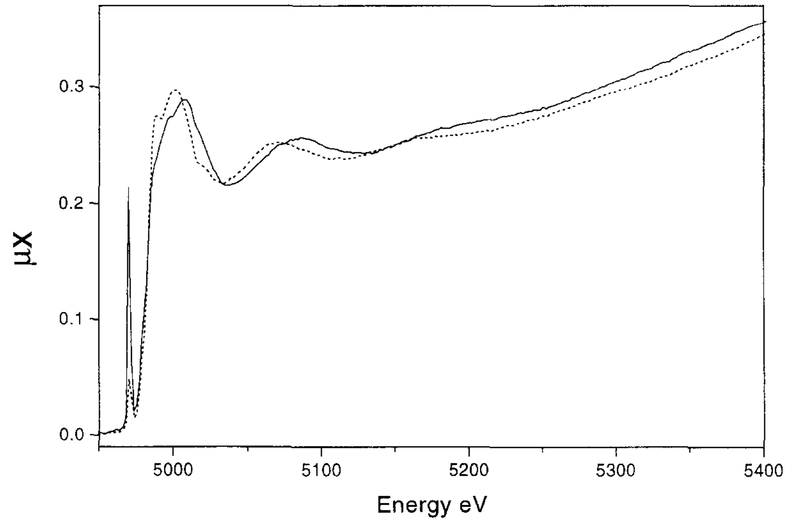
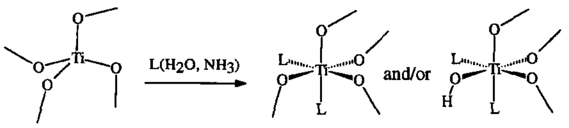


Fig. 3. XAFS spectra of Ti-silicalite in vacuum (full line) and after NH_3 dosage (dotted line). NH_3 adsorption strongly modifies the titanium environment as clearly evidenced by the reported spectra both in the pre edge region (erosion and broadening of the 4967 eV peak) and in the EXAFS region where EXAFS oscillations are clearly modified. Spectra collected at Lure during experiment [22].



Scheme 4.

electron is promoted to an unbound level and hence leaves the Ti atom as a spherical wave. Waves leaving the Ti centres under the effect of the excitation and waves scattered in the opposite direction by the first shell, second shell etc. atoms surrounding the Ti centre can interfere either constructively or destructively (see, for example, [21]): this causes the appearance of the extended fine structure observed at highest energies of Fig. 3. In this fine structure, the precious information is contained concerning primarily the number and the distances of the atoms of the first coordination sphere of Ti. The analysis of the EXAFS pattern has allowed to confirm that, in vacuo, the first coordination sphere of Ti is constituted by four oxygen atoms at $d = 0.181 \pm 0.001$ nm distance [10,11]. These first shell data have been extracted from spectra collected at ADONE (a first generation synchrotron radiation machine) in 1992, where the S/R ratio was insufficient to extract reliable information from the second shell environment of Ti atoms. New measurements have been very recently performed at LURE [22] and the analysis of the second sphere contribution is now in progress in order to establish if one of the SiOTi bridges can be easily hydrolysed by the presence of water (as shown in the first part of Scheme 3).

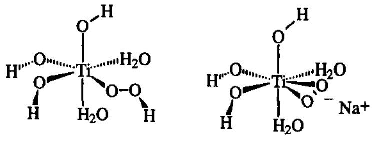
Both the XANES and EXAFS parts of the X-ray spectrum are heavily modified by the presence of adsorbates [10,11,14,15]. This is clearly shown in Fig. 3 (dotted curve), where the effect of NH_3 adsorption is shown.

The most important observation concerning the XANES part of the X-ray spectrum is the drastic reduction of the intensity of the pre-edge peak upon adsorption of NH_3 (but the same is observed when water is dosed from the gas phase). This effect finds a simple explanation in terms of ligand insertion in the coordination sphere of Ti, with formation of six-fold coordinated structures [10,11], see Scheme 4 where $L = NH_3$, H_2O and where the $(\equiv Si{-}O)_4TiL_2$ and or $(\equiv Si{-}O)_3Ti\ OHL_2$ species has distorted octahedral structure. In fact in the parent octahedral complexes the optical transitions are all Laporte forbidden. A corollary of the previous observation is that, in order to increase its coordination number, the Ti atom must migrate from the original framework position to a more external and relaxed one. This capacity of the silicalite framework to relax around the Ti centre without allowing the atom to go into an extraframework position, is likely one of the key points explaining the stable catalytic properties of the Ti centre.

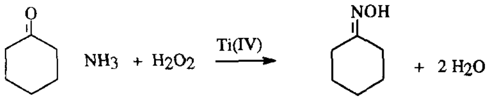
3.4. Ab initio calculations

The characterization of the Ti center and of its complexes with hydrogen peroxide is now proceeding by means of theoretical ab initio calculations on cluster models representing the first coordination sphere of Ti [23,24]. The clusters in Scheme 5 have been chosen as a first attempt to model the high-coordinated peroxo complex in the hydrogen and salt form (with Na^+).

All calculations were performed at the Hartree–Fock level with a full electron double Z basis set with polarizations functions (DZP) using the Gaussian92 program. In the case of the Ti–OO–H complex, the only minimum found corresponds to an open geometry, while in the case of the sodium salt two minima were



Scheme 5.



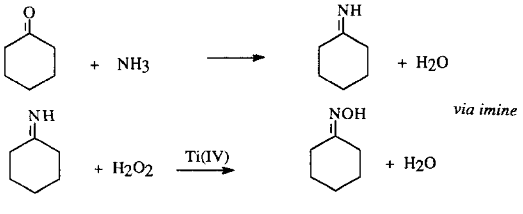
Scheme 6.

found for the open and closed Ti–(O–O)– complex, the closed one being favoured by 10.5 Kcal/mol.

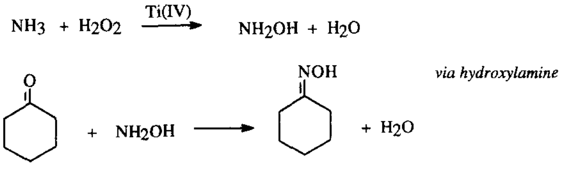
In the stabilization of these complexes, a key role is played by the ligands other than the peroxo, whose ability to bind to the Ti center is dictated by the framework geometry and flexibility. This points the need for models including part of the zeolite moiety to investigate the actual catalytic center.

3.5. *The ammoximation of cyclohexanone: a case study of an oxidation reaction mechanism*

The reaction of ammoximation of cyclohexanone with H_2O_2 and NH_3, (see Scheme 6) is an important industrial reaction because it gives cyclohexanoneoxime, a valuable intermediate for the production of caprolactame and nylon. Two reaction mechanisms have been proposed: (Scheme 7 and Scheme 8): and an interesting debate has developed on this point [8,25,26]. In the first case (Scheme 7) the role of Ti-silicalite is to catalyze the oxidation of imine intermediate [25,26] while in the second case is to promote the oxidation of NH_3 to give NH_2OH (Scheme 8) [8]. The discovery that Ti-silicalite is able to oximate also large ketonic molecules which cannot penetrate the channels (because of their dimension) is in favour of the second hypothesis (Scheme 8). This hypothesis is also confirmed by the fact that Ti-silicalite is a good catalyst for the partial oxidations of NH_3 into NH_2OH.



Scheme 7.

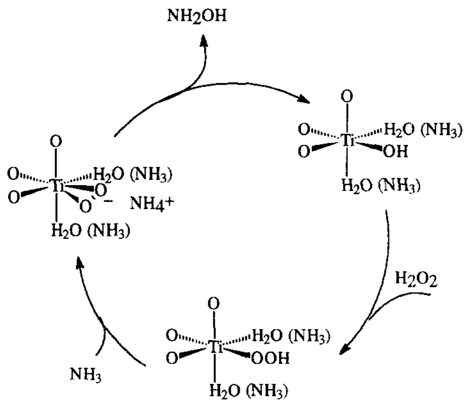


Scheme 8.

On this basis we can conclude that the mechanism in Scheme 7 plays a negligible role. We have also seen in the previous paragraphs how NH_3 and H_2O_2 molecules interact separately and together with the titanium centres to give the structures shown in Scheme 3 and that the yellow hydroperoxo ammonium salts $TiOO^-...NH_4^+$ easily decompose to give hydroxylamine.

From these observations it is possible to propose the mechanism shown in Scheme 9 for the formation of the NH_2OH intermediate on Ti-silicalite.

Following Scheme 9, the small hydroxylamine molecule can either directly interact with cyclohexanone inside the channels to give directly the oxime or can migrate towards the exterior of the microcrystal to react with larger ketonic molecules which cannot penetrate the channels.



Scheme 9.

4. Conclusions

The structure of titanium centre depends upon the absence or the presence of adsorbates. The Ti is in tetrahedral coordination in vacuo and expands its coordination sphere upon interaction with adsorbates. In presence of H_2O and H_2O/H_2O_2 solutions one of the SiOTi bridges is hydrolyzed with formation of $(\equiv SiO)_3L_2TiOH$ $(L = H_2O)$ and $(\equiv SiO)_3L_2TiOOH$ species, respectively. When NH_3 is dosed on $(\equiv SiO)_3L_2TiOOH$ structures $(\equiv SiO)_3L_2TiOO^-NH_4^+$ species are formed. These species are though to play an important role in the ammoximation reaction. The geometries of the peroxidic species (open or bridged) is discussed also on the basis of ab initio calculations.

Acknowledgements

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