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DRS UV–Vis and EPR spectroscopy of hydroperoxo and superoxo complexes in titanium silicalite

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The most important spectroscopic features in the UV–Vis of framework and extraframework Ti(IV) in titanium silicalite are briefly summarized. The spectroscopic manifestations of the complexes formed by framework Ti(IV) in presence of H_2O_2 are reported. The formation of EPR active species is also considered.

Keywords: Titanium silicalite; hydroperoxo and superoxo complexes; DRS UV–Vis and EPR spectra

1. Introduction

Titanium silicalite (TiS) is a zeolite of the pentasil family which has attracted much attention in the recent years because of its remarkable catalytic properties in oxidation reactions in liquid medium with H_2O_2 [1,2] and ammoximation of ketones and aldehydes to oxime [3,4]. Despite its great activity, the mechanisms of some reactions are still uncertain.

The location and the structure of Ti (present in small percentage, 1–2%) has been investigated by means of several physical methods like XRD, UV–Vis, EPR and Raman spectroscopies [5]. Special emphasis has been put in the distinction between framework and extraframework Ti, because only framework Ti exhibits important catalytic properties [6,7]. As the substitutional [TiO_4] group is bigger than the [SiO_4] unit, introduction of Ti into the framework is accompanied by expansion of the lattice and strain generation in the immediate vicinity of the substitutional Ti. The vast majority of tetracoordinated [TiO_4] units is exposed in the zeolitic channels, where they can interact easily with

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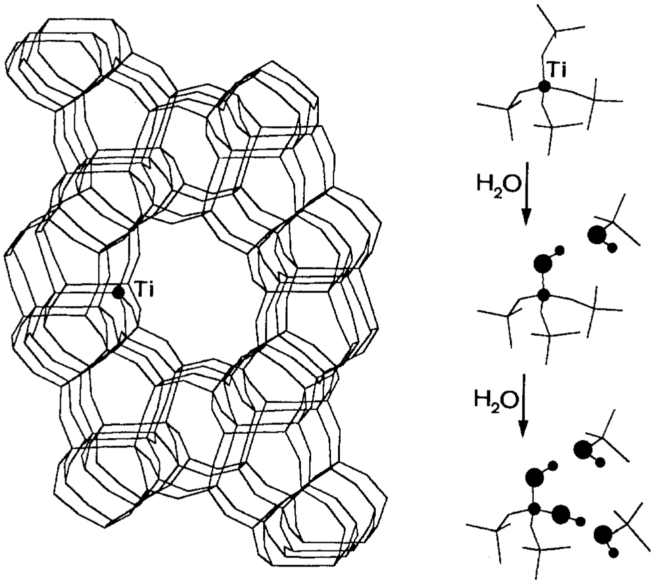


Scheme 1.

adsorbates like H_2O giving hydrolysis of one (or even more) $\geq$Si–O–Ti$\leq$ bonds following the reaction scheme 1, whereby hydrolysis of one or two $\geq$Si–O–Ti$\leq$ bonds afford a way to release the strain around the substitutional Ti.

The most important spectroscopic features of framework Ti(IV) can be summarized as follows:

(a) an optical transition at 48000–50000 cm^{-1} (in vacuum) assigned to a charge transfer (CT) in tetracoordinated [TiO_4] and [O_3TiOH] structures [5,8,9];

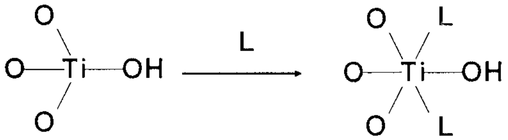
(b) an IR transition at 960 cm^{-1} associated with perturbed modes of the tetrahedral building units of the pentasilic structures. These can be either [SiO_4] units perturbed by an adjacent Ti(IV) or framework Ti containing units such as [TiO_4] or O_3TiOH [5,8,9].

When extraframework Ti(IV) is present in the form of TiO_2 microparticles it is characterized by:

(a) a broad absorption in the range 30000–35000 cm^{-1}, i.e. a frequency near to that of bulk TiO_2 (anatase or rutile);

(b) a Raman peak at 140 cm^{-1} associated with anatase microparticles.

The tetracoordinated (presumably unstrained) O_3TiOH structures can undergo ligand insertion reaction following the scheme:



$$(\mathrm{O})_3\mathrm{Ti{-}OH} \xrightarrow{\mathrm{L}} (\mathrm{O})_3(\mathrm{L})_2\mathrm{Ti{-}OH}$$

Positive evidence of the transformation of fourfold coordinated Ti into sixfold coordinated species has been recently obtained by means of UV–Vis reflectance of TiS fully immersed in H_2O and in ammonium hydroxide solution [7]. In the latter case the formation of an ammonium salt is not excluded.

It is well known that the immersion of TiS in H_2O–H_2O_2 mixtures leads to a yellow color ascribed to a peroxo titanium species. In the present letter we report about the spectroscopic manifestations of complexes formed in presence of H_2O_2. The formation of EPR active species is also considered.

2. Experimental

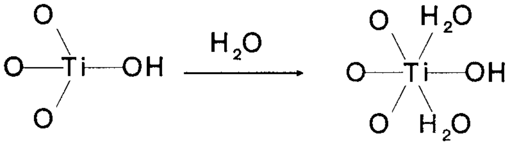
Titanium silicalite (Ti = 1.47 wt%) has been synthesized in the ENICHEM ANIC laboratories as reported in ref. [1] and characterized by means of XRD, UV–Vis diffuse reflectance, IR and Raman techniques. The DRS UV–Vis spectra have been carried out on a Varian Cary 5 spectrophotometer. During the measurements the powder was in full immersion in the liquid phase, but spectrum 1 in fig. 1a was taken in vacuum after outgassing the sample at 393 K for 4 h. This treatment does not appreciably alter the framework/extraframework Ti ratio (in fact the final spectra in H_2O–H_2O_2 do not appreciably depend upon temperature pretreatments lower than 400 K).

The EPR spectra were obtained by a Varian E-109 spectrometer, by using a silica cell suitable for outgassing procedures; also in this case the powder was in presence of a liquid phase (H_2O_2); the quartz tube was cooled down at liquid nitrogen temperature to carry out the spectra. Varian pitch ($g = 2.0028$) was used for g values calibration.

3. Results and discussion

In fig. 1a the spectra of TiS in vacuum (1), TiS in H_2O (2) and TiS in H_2O–H_2O_2 (3) are reported for sake of comparison. TiS in vacuum shows the usual strong peak at 48000–50000 cm^{-1} characteristic of a CT transition involving tetracoordinated Ti(IV) in a well manufactured TiS. On the starting sample (spectrum 1) the weak absorption associated with extralattice Ti(IV) is clearly visible in the range 32000–36000 cm^{-1}. The low intensity of this band ensures that this sample is well manufactured.

Immersion in H_2O (spectrum 2) causes the shift of the Ti(IV) CT band to 43000 ± 500 cm^{-1}; this is due to ligand additions that transform tetracoordinated Ti(IV) complexes into esacoordinated ones, as shown below:

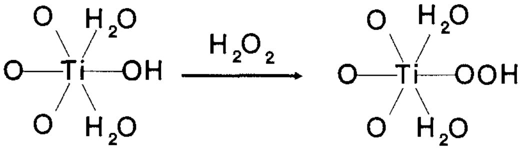


If for sake of simplicity the transition is considered to be associated with an electron transfer from OH to Ti(IV), the change of the CT frequency can be explained by the simple relation

$$\Delta\bar{\nu} = 30 \times 10^3 \, \Delta X_{\mathrm{opt}}(\mathrm{Ti(IV)})$$

where $\Delta X_{\mathrm{opt}}(\mathrm{Ti(IV)})$ is the difference between the optical electronegativity of Ti(IV) fourfold and sixfold coordinated. From the observed $\Delta\bar{\nu}$ we can infer that $\Delta X_{\mathrm{opt}}(\mathrm{Ti(IV)}) = 0.2 \pm 0.03$: this figure is in good agreement with what is known from the literature [10]. The increased ability to accept one electron from a ligand during a CT transition is the consequence of the more ionic character of Ti(IV) in sixfold coordination with respect to the tetracoordinated one. The previous considerations apply also for structures containing more than one titanol group (for instance those derived from hydrolysis of two $\gtrdot$Si–O–Ti$\lessdot$ bridges).

Addition of H_2O_2 gives rise to spectrum 3 which is characterized by the strong peak at 26000 cm^{-1}; the formation of this signal is associated with a decrement of the original CT band. The formed band is undoubtedly associated with a CT from a peroxo-type species. On the basis of the structure described above, the following reaction is hypothesized



which is accompanied by consumption of hydroxyl groups and hence by a decrement of the 48000–50000 cm^{-1} band (which has, at least partially, a hydroxyl to Ti CT character).

The band at 26000 cm^{-1} is so assigned to CT transition from an hydroperoxo ligand to a Ti(IV). This assignment is in agreement with the $X_{\mathrm{opt}}(\mathrm{OOH})$ as it can be inferred from the literature [11]. In solution, the hydroperoxidic group is certainly interacting with H_2O through hydrogen bonds. Due to this interaction, the OH group in the TiOOH...H_2O species acquires substantial polarity ($\gtrdot$TiO-$O^{\delta-}$...$H^{\delta+}$...).

Fig. 1b shows the spectrum of $(NH_4)_3[Ti(O_2)F_5]$ adsorbed from an aqueous solution on silicalite which exhibits an intense absorption band at about 26000 cm^{-1}. This demonstrates that Ti(IV) peroxo species gives a band similar to that observed in spectrum 3 (in this case the observed peak is due to CT transition from a peroxo species to Ti(IV)). In the spectrum of fig. 1b it is most interesting to notice that no appreciable absorption band is present at ≈ 42000 cm^{-1}. This is due to the fact that no oxygen containing ligands (other than O_2^{2-}) are present in this complex. The CT bands originated from the fluorine occur at much higher frequencies. This observation in turn reinforces the previous assignment.

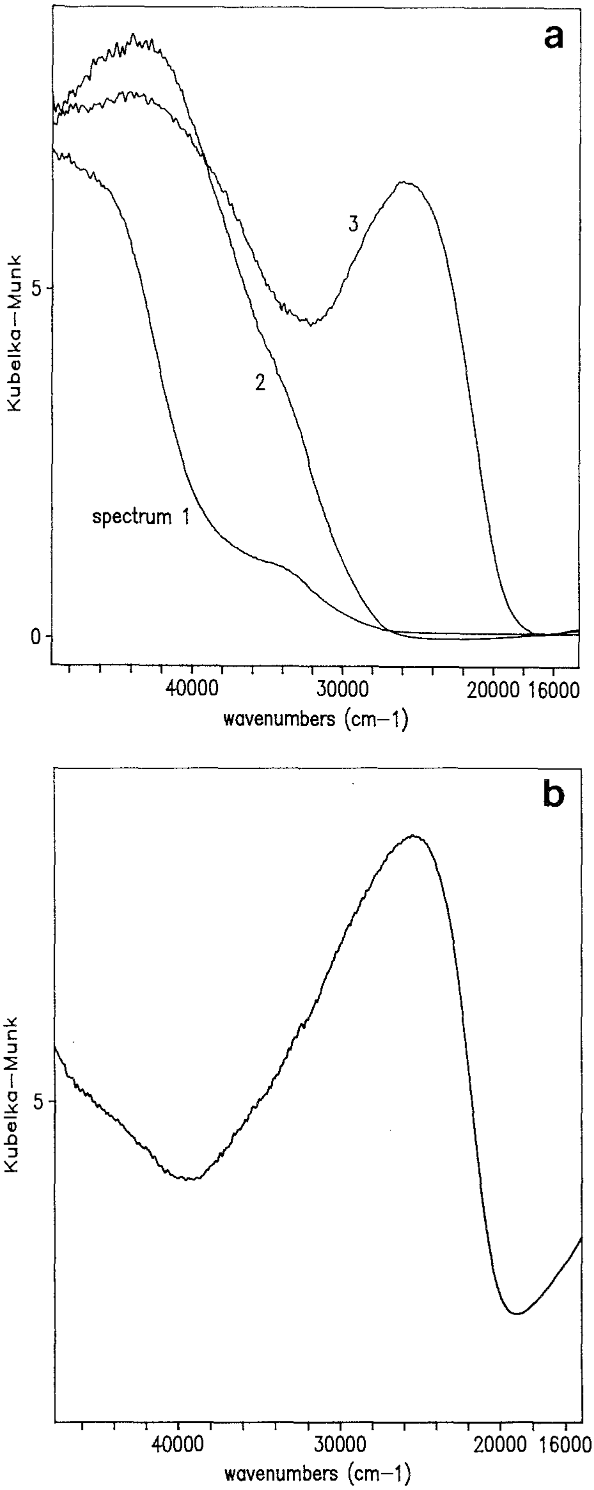


Fig. 1. DRS UV–Vis spectra of TiS: (a) in vacuum (1), in H_2O (2), in H_2O–H_2O_2 (3); (b) in $(NH_4)_3[Ti(O_2)F_5]$–H_2O.

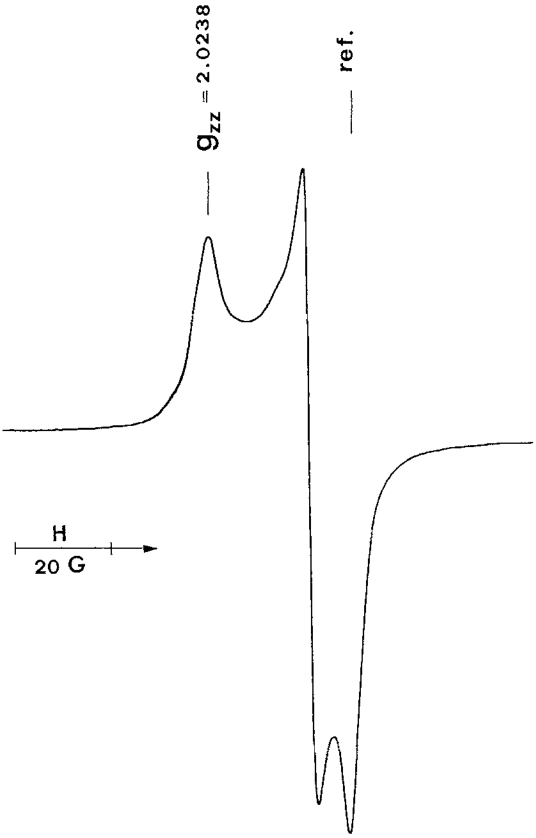
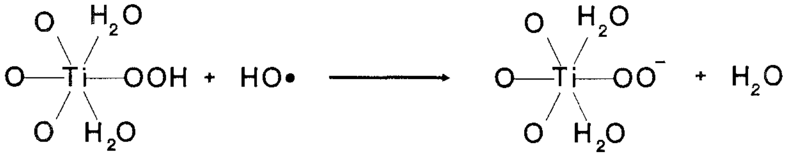


Fig. 2. EPR spectrum of TiS in presence of H_2O_2.

The great similarity between the frequencies of the Ti(IV)–O_2^{2-} CT peak in $(NH_4)_3[Ti(O_2)F_5]$ and the peak observed on TiS in presence of H_2O_2, suggests that peroxo species possibly deriving from H_2O_2 interaction with double hydroxylated Ti centres, could not be spectroscopically distinguishable from the most aboundant hydroperoxidic ones.

In presence of H_2O_2, TiS gives an intense and anisotropic EPR spectrum (fig. 2), characterized by the following principal values of the g tensor: $g_{zz} = 2.0238$, $g_{yy} = 2.0099$ and $g_{xx} = 2.0030$. These parameters are in good agreement with those reported in the literature [12] for the superoxide radical ion stabilized on Ti(IV) centers of both supported and bulk titanium dioxide. The spin counting was performed comparing the intensities of the doubly integrated superoxide spectra with those recorded for various weighted amounts of $CuSO_4 \cdot 5H_2O$. The number of spin derived for the spectrum of fig. 2 is about 1×10^{18} per gram of sample. This figure can be compared with the total number of Ti ions (1.47 wt%) present in the same amount of sample which is about three orders of magnitude higher. This suggests that the formation of the O_2^- derives from a side reaction. The following path can be suggested:

$$H_2O_2 \longrightarrow 2HO\bullet$$



which involves only a small portion of Ti(IV) centres and is probably favored at high H_2O_2 concentrations. In fact, after outgassing the sample at RT the number of spin increases by one order of magnitude since the removal of water (which is more volatile) shifts the reaction to the right. Further research is in progress on this point.

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