Electron transfer bands of titanium sites in dehydrated silicalites and in TiO_2–SiO_2 gel

Do Trong On, Loic Le Noc and Laurent Bonneviot*

Department of Chemistry, CERPIC, Laval University, Ste Foy, Québec, Canada G1K 7P4

The diffuse reflectance UV spectra of dehydrated titanium silicalites of MFI structure are consistent with the presence of both open [$Ti(OH)(OSi)_3$] and closed [$Ti(OSi)_4$] tetrahedral titanium sites, the closed sites seem to be the only ones occurring in TiO_2–SiO_2 silica gel.

The microporous titanium silicalites of MFI and MEL structures, TS-1 and TS-2, are active for the catalytic oxidation of alkanes into alcohols and ketones using hydrogen peroxide as oxidant.[1,2] By contrast, these so-called oxyfunctionalization reactions do not occur on Ti modified ZSM-48, β-silicalites, mesoporous MCM or amorphous SiO_2 materials which, for most of them, catalyse olefin epoxidation and hydroxylation of aromatics among other oxidation reactions involving H_2O_2.[3–7] Strikingly, all these materials exhibit very similar characteristics such as an IR band at 960 cm^{-1} assigned to Ti–O–Si bridges[8,9] and tetrahedral [TiO_4] sites according to extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) at the Ti K-edge.[10,11] These materials are characterized by a ligand-to-metal electron transfer (LMET) band at 48 000 cm^{-1} assigned to the TiOH group of [$Ti(OH)(OSi)_3$] sites.[11,12] In comparison, it arises at 32 000–36 000 cm^{-1} for TiO_2 anatase. Besides, in TS-1, the 960 cm^{-1} band intensity linearly scales the Ti content up to a maximum incorporation level of 1.8% above which anatase is formed and has been characterized by Raman and XANES.[9,10] The extraframework anatase phase does not account for the catalytic performances since it is inactive for the reactions invoked here. Hence, the morphology of the internal channels of the host silicalite matrix and/or the nature of the sites might explain the specific activity of TS-1 and TS-2.[4] The purpose of this communication is to demonstrate that at least two types of framework sites are present in dehydrated TS-1 and one of them in titanium silica gel according to their UV characteristics.

Three titanium silicalites [0.5], [1.0] and [1.5]TS-1 with Ti/(Ti + Si) atom ratios of 0.005, 0.010 and 0.015 were synthesized from a gel containing a mixture of tetraethoxysilicon(IV), tetraisopropoxytitanium(IV) and tetrapropylammonium hydroxide in propanol. Water was added dropwise under vigorous stirring and propanol removed before hydrothermal crystallization for 4 days in a Teflon-lined stainless steel autoclave at 175 °C. The solids were filtered, washed and calcined at 500 °C. The XRD spectra recorded on a Rigaku D-Max IIIVC X-ray spectrometer revealed an orthorhombic MFI structure for all the silicalites and a crystallinity of 95 ± 5%. This latter estimation is based on the area of the characteristic triplet in the range 2θ 21.5–25.5°. The solids exhibit the characteristic features of TS-1 without extraframework Ti species. The 1.5% TiO_2–SiO_2 gel was prepared by acid hydrolysis of tetramethoxysilicon(IV), and diisopropoxybisacetylacetonatotitanium(IV) in isopropyl alcohol using a 1 mol dm^{-3} HCl solution. The gel was dried off in a rotavapor and calcined at 500 °C. The chemical analysis was performed by flame atomic absorption spectroscopy. The reflectance UV–VIS spectra were measured on pellets using a Perkin-Elmer lambda 5 spectrometer equipped with a diffuse reflectance attachment provided by Harricks. The pellets were equilibrated with a water-saturated atmosphere at 25 °C or dehydrated at 450 °C. The silicalite S-1 was taken as diluent and reference for the reflectance measurements, R_∞, after which the Kubelka–Munk function [eqn. (1)] was applied.

$$F(R_\infty) = (1 - R_\infty)^2/2R_\infty \qquad (1)$$

The dehydrated [0.5], [1.0] and [1.5]TS-1 diluted by 2, 4 and 6 times respectively, exhibit similar spectra of comparable intensity within 10%, in a range where $F(R_\infty)$ closely matches the true absorption. The spectra mainly consist of a strong peak and a shoulder at *ca.* 50 000 and 44 000 cm^{-1}. The hydrated pellets also exhibit a strong peak of slightly lower intensity at 49 000 cm^{-1} and a shoulder at about 44 000 cm^{-1} [Fig. 1(*b*)]. These observations are consistent with previous findings except that only the average position was reported (see above).[11,12] The main difference between the samples resides in a tail at about 36 000 cm^{-1} of increasing importance when the titanium content increases. The UV–VIS spectrum of each TS-1 silicalite was independently simulated using three Gaussian functions whose characteristics were very similar from one spectrum to another. For more consistency, the actual simulation was performed by simultaneously fitting all the spectra with a single set of Gaussian functions. This led to excellent fits (Fig. 2). The two main Gaussian curves at 50 200 and 44 060 cm^{-1} (full linewidth at half-height, FLWH: 8725 and 5530 cm^{-1}, respectively) are of equal relative intensity (±5%) for the three TS-1. By contrast, the third Gaussian at 40 290 cm^{-1}, FLWH of 6440 cm^{-1}, has an increasing importance at higher titanium loading accounting for a different titanium site than the first Gaussians. The UV–VIS spectrum of the dehydrated 1.5% TiO_2–SiO_2 gel exhibits a broad band in the region of the third Gaussian peaking at 40 900 cm^{-1} that shifts at 39 700 cm^{-1} for hydrated samples [Fig. 1(*a*) lines]. With respect to the samples dilution and their Ti content, the bands in the gel are about five times less intense than in TS-1. The Gaussian fits for the latter bands and those of hydrated TS-1 were far less satisfying

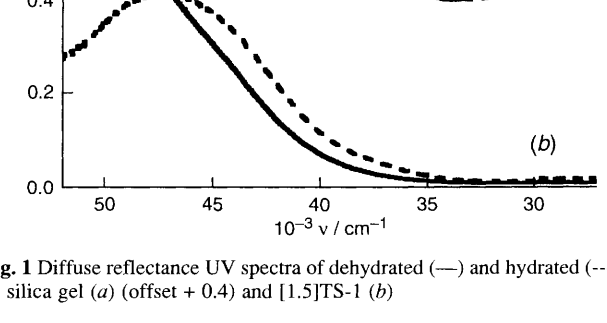

Fig. 1 Diffuse reflectance UV spectra of dehydrated (—) and hydrated (---) Ti silica gel (*a*) (offset + 0.4) and [1.5]TS-1 (*b*)

because of a large site distribution or an incomplete hydration of the sites.

In TS-1 and TiO_2–SiO_2 silica gel containing such a low loading of titanium, all the sites are made of tetrahedral [TiO_4] units according to XANES and EXAFS studies.[10,11,13,14] They must differ from the nature of the second neighbour around titanium. One excludes a titanium at the second neighbour position since it would probably lead to higher coordination numbers than four and, very different XANES features than those observed.[10,11] A multiple scattering EXAFS study clearly demonstrated the existence of Ti–O–Si bridges characterized by an average angle of about 160°.[10] Despite there being less than four silicon atoms at the second neighbour position, implying the formation of titanol TiOH group, the sites are likely substitutional and excludes our previous findings of double oxo bridges between Ti and Si.[14] There are indeed two types of silicon sites, [$Si(OSi)_4$] and [$Si(OH)(OSi)_3$], in the orthorhombic silicalites of MFI structure.[15] The [$Ti(OSi)_4$] and [$Ti(OH)(OSi)_3$] analogous structures, referred to as closed and open sites respectively, are consistent with the EXAFS and XANES characteristics and might explain the UV data.

According to optical electronegativities O.χ., an SiO^- ligand (O.χ. = 3.17)[16] coordinated to tetrahedral Ti (O.χ. = 1.85)[17] would lead to a first ligand-to-metal electron transfer at 39 600 cm^{-1}; this closely matches the characteristics of the sites in the silica gel. On the other hand, an OH ligand (O.χ. = 2.9)[16] would lead to an electron transfer at lower energy by about 8000 cm^{-1}, not observed here. Unfortunately, such a model would lead to erroneous peak positions when drastic electronic π bonding systems are at stake. The wide average Ti–O–Si angles obviously account for strong π donation effects. In a tetrahedral complex, the non-bonding d electronic levels of e symmetry, d_e becomes antibonding in the π system while the non-bonding oxygen pairs constitute the bonding counterpart, p_π. In a d^0 system, the former is the LUMO and the latter the HOMO. Hence, the first LMET (Laporte allowed), $p_\pi \rightarrow d_e$ is indeed expected to shift toward high energies for a strong π donation.[18] Therefore, the bands at 50 200 and 44 060 cm^{-1} are likely to account for LMETs of TiOSi and TiOH groups of the open sites. Accordingly, the LMET at about 40 000 cm^{-1} is assigned to TiOSi in the closed sites in both TS-1 and silica gels and falls in the predicted range because of a much smaller π donation and smaller Ti–O–Si angles likely due to a structural stress undergone by the sites.

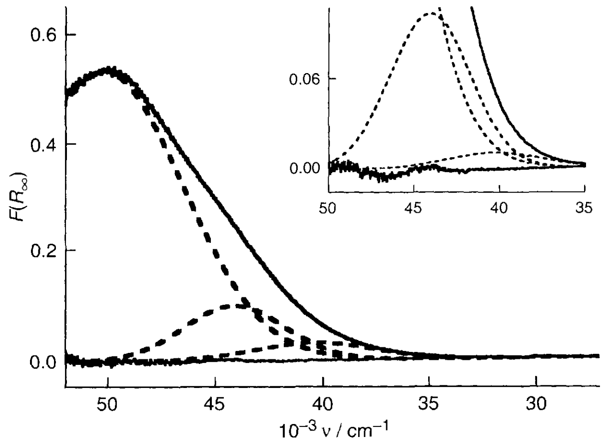

Fig. 2 Gaussian fit (---) of the UV spectra of dehydrated [1.5]TS-1 (—) and difference between fits and experimental data (lower full line); insert: details of the fit of dehydrated [0.5]TS-1

It is known that the stressed orthorhombic S-1 framework relaxes by locally breaking some Si–O–Si bridges.[15] This relaxation is more likely to occur at Ti sites in TS-1 and leads to relaxed open sites, in agreement with our very recent ^1H and ^{29}Si MAS NMR data.[19] At high Ti contents, the stabilization of a higher fraction of closed sites is consistent with the lattice expansion that diminishes the stress. A quantification of both sites is a delicate task since the absorption coefficients are unknown and are very much smaller for the closed sites than the open sites (Fig. 1).

This interpretation of the UV data sheds new light on previous studies.[8–12] It further suggests that both open and closed Ti sites coexist, the former predominate at low Ti loadings. The site distribution is related to the structural stress which is probably smaller in the amorphous titanium silica gels where the strained closed sites are preferentially accommodated.

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