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Healing of defects in ETS-10 by selective UV irradiation: a Raman study

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The UV–Raman spectra of a crystalline and a defective ETS-10 sample have shown that the two materials possess different stability under the laser beam. These results are interpreted in terms of a possible light-induced healing of defects in the case of the defective sample, through annealing of two vicinal TiOH groups along the Ti–O–Ti chains. Possible implications for the preparation of highly ordered materials are envisaged.

The framework of the titanosilicate ETS-10 is formed by linear chains of corner-sharing TiO_6 octahedra linked by corner-sharing SiO_4 tetrahedra. The layout of structural units generates a three-dimensional system of 12- and 7-membered ring channels, with free openings of about 8×5 and 5.5×1.5 Å in diameter.[1–3] Each TiO_6 octahedron carries a net negative charge of -2, that is compensated by exchangeable charge-balancing cations (Na^+ and K^+ in the as-synthesised form),[4] allocated in five different crystallographic positions.[5–7] In the ideal structure of ETS-10, the Ti–O–Ti chains run in two perpendicular directions of the crystal. They are isolated from one another and have the same length as the microcrystals. Following this picture, TiOH groups should only emerge at the external surface of the crystals, where the Ti–O–Ti chains are ended and hydroxyl groups saturate dangling bonds of titanium ions. However, the real material usually presents stacking disorder along the *c* crystallographic axis[1,2] which, together with point defects (*e.g.*, titanium vacancies), can cause breaks in the Ti–O–Ti chains, with subsequent formation of TiOH groups also at internal positions. Thus, as the number of such defects increases, the average length of the Ti–O–Ti chains is shortened and the distribution of chain lengths among the material becomes wider.

Quantification of the concentration of defects in ETS-10 is a difficult subject, so that comparison between different samples is not straightforward. It is, however, interesting to evaluate the amount of defects in ETS-10, as it has been pointed out that the presence of defects leads to materials having a greater photoactivity than highly crystalline ETS-10.[8,9] In particular, UV–Vis spectroscopy using H_2O_2 as probe molecule has been shown to be a useful technique for the quantification of defects in ETS-10.[9] Another technique that can be useful for the quantification of defects is Raman spectroscopy. Indeed, Southon and Howe[8] have recently presented a Raman study of a series of ETS-10 samples having an increasing concentration of defects. These authors concluded that both the position and the broadness of a Raman active band at *ca.* 725 cm^{-1} (that is attributed to the Ti–O stretching mode of the Ti–O–Ti chains)[10–13] are suited as indicators of the average chain length of the Ti–O–Ti chains and, consequently, of the concentration of defects in the sample. Their perfect ETS-10 presents an intense and sharp band at a Raman shift of 724 cm^{-1}. On moving to more defective materials, this band undergoes a progressive broadening and is blue shifted up to 50 cm^{-1} in their more defective sample.

The Raman spectra of ETS-10 that can be found in the literature have been obtained with laser excitation lines of 1064,[11] 633,[8] and 488 nm.[10,12] These spectra, however, cannot be directly compared, as they have been recorded on different samples. This has prompted us to start a systematic Raman study using different excitation laser lines, ranging from 244 to 1064 nm (*i.e.*, from UV to near-IR sources) and using always the same ETS-10 samples. In doing so, additional information coming from changes of the excitation wavelength can also be evaluated. Moreover, the Raman spectrum of ETS-10 using a laser excitation line in the UV region has never been reported up to now. In this study we adopted a He/Cd Laser (excitation line at 325 nm) coupled with a Renishaw Micro-Raman System 1000. Our attention will be focused on the parallel characterisation of well-crystalline and defective ETS-10 samples (prepared *via* mild acid treatment with HF, as described elsewhere),[9] as well as on the comparison between their Raman spectra. The results obtained from this comparison will be tested against our previous conclusions derived from UV–Vis spectroscopy using H_2O_2 as probe molecule.[9] The whole set of results will be reported elsewhere (manuscript in preparation).

In the course of the above experiments, an interesting observation has come out: indeed, the use of a 325 nm excitation laser line has produced a set of spectra on defective ETS-10 samples that depends upon the time of irradiation. These results are discussed in the present communication and they are interpreted as a light-induced healing of defects. This observation allows us to suggest a potential method for preparing highly ordered materials, by reducing their concentration of (point) defects.

The (Na,K)-ETS-10 sample used was kindly supplied by Engelhard (Iselin, NJ). This sample has been exhaustively characterised in a previous study,[9] by means of X-ray diffraction, SEM and HRTEM microscopy, UV–Vis and Ti K-edge X-ray absorption (EXAFS and XANES) spectroscopy. Starting from this material, a defective ETS-10 sample was prepared by mild acid treatment with a diluted (1 wt%) aqueous solution of hydrofluoric acid. Following this method,[9] ETS-10 samples with a very small amount of defects (involving less than 2% of the whole amount of titanium) can be prepared, without appreciable diminution of their crystallinity.

The UV–Raman spectrum of the parent ETS-10 is reported in Fig. 1a (dashed line). An intense and narrow band (with a full width at the half maximum (FWHM) of *ca.* 44 cm^{-1}) is present at a Raman shift of 724 cm^{-1}. The position and the shape of this band are completely analogous to findings by other authors using different laser excitation lines, and it has been assigned in all cases to the Ti–O stretching mode of corner-sharing titanium ions in octahedral positions. In the work of Su *et al.*[12] this band was specifically assigned to the Ti–O–Ti stretches of the octahedra along the direction of the chain, without a direct participation of the four equatorial Ti–O–Si bonds. This attribution was made on the basis that a similar band cannot be observed in the Raman spectra of other titanosilicates having TiO_6 units isolated by SiO_4 tetrahedra (*i.e.*, without Ti–O–Ti linkages). In our opinion, the great Raman intensity of the "725 cm^{-1}" band can only be explained in terms of a total-symmetric combination of anti-symmetric Ti–O–Ti stretches along the chain.

The stability of the crystalline ETS-10 sample under the laser beam is also shown in Fig. 1a. The spectra presented were obtained after increasing times of exposure to the laser beam (up

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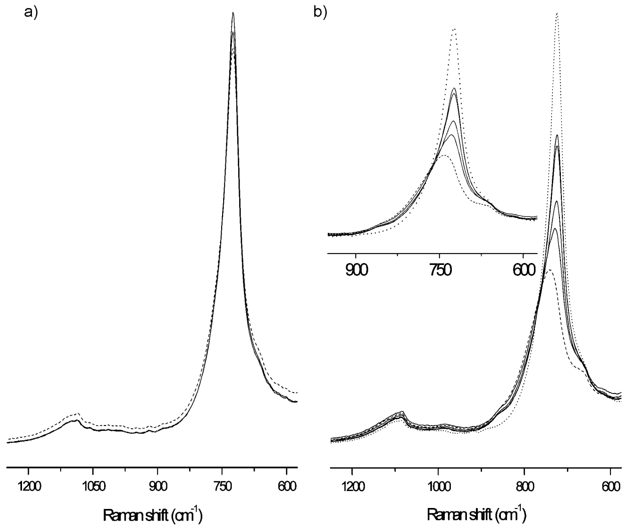

Fig. 1 UV–Raman spectra of (a) a crystalline and (b) a defective ETS-10 sample recorded in air. The dashed curve in each figure corresponds to the spectrum recorded immediately after exposure to the laser beam, while the other spectra in the series were recorded after increasing times of exposure. In part (b), the spectrum of the crystalline sample is also reported for comparison (dotted line), and an insert has been added for a better view of the 900–600 cm^{-1} spectral region.

to 1 hour) in air. Upon increasing the time of exposure, only a very small increment of the intensity of the band at 724 cm^{-1} is observed, but no appreciable changes in the position or in its FWHM are produced, so that the material can be considered as being stable under the laser beam.

This is not the case for the defective ETS-10 sample. Indeed, the initial Raman spectrum of this sample (Fig. 1b, dashed spectrum) presents a broad band (FWHM = 81 cm^{-1}) at a Raman shift of 741 cm^{-1} (*i.e.*, 17 cm^{-1} blue shifted with respect to the band found in highly crystalline ETS-10, see the inset for a better view). Upon increasing the time of exposure to the laser beam (up to 220 min in the last spectrum of the series), this band is progressively narrowed (final FWHM = 55 cm^{-1}) and shifted towards lower Raman shifts, down to 724 cm^{-1}. For comparison, the spectrum of a crystalline ETS-10 is also included in the Figure (dotted line). A similar effect was reported by Southon and Howe, when ETS-10 samples containing an increasing concentration of defects were compared.[8] According to their conclusions, narrowing and red-shifting of the "725 cm^{-1}" band occur when the concentration of defects in ETS-10 samples diminishes (and hence, the average length of the Ti–O–Ti chains increases). Since the analogous effect is observed in our defective ETS-10 sample upon exposure to the 325 nm laser beam, we interpret the phenomenon as a diminution of the concentration of defects in our sample, probably through a light-induced healing of the existing defects.

In favour of a light-induced origin of this phenomenon, it is interesting to point out that we have not been able to reproduce the effect observed in the defective ETS-10 sample by irradiating with other laser lines (namely, 244 and 442 nm). This eliminates the possibility that the effect observed is due to a thermal effect (*i.e.*, increment of the temperature of the sample under the laser beam), or, for the same reason, to a diminution in the amount of adsorbed water. Moreover, both heating and water desorption should also be present in the crystalline sample, and it is seen that their effect (if any) is very limited in this sample. Finally, it is important to stress that the observed changes in the Raman spectrum of the defective ETS-10 are not reversible; *i.e.*, once the irradiation of the sample is interrupted (and, hence, the sample reaches again its equilibrium conditions of temperature and adsorbed water), the band is still observed at 724 cm^{-1} and has the same intensity and FWHM. This fact, again, is in opposition to a possible attribution of the observed phenomenon to changes in temperature or in the amount of water adsorbed.

An explanation for the fact that only by irradiating with a 325 nm laser source is it possible to observe the above mentioned narrowing and red-shift of the "725 cm^{-1}" band in defective samples, comes from the relative position of this laser line with respect to the band gap of ETS-10. Indeed, this laser source falls just at a slightly higher wavelength than the edge of the lower charge-transfer transition of ETS-10 (*ca*. 308 nm, measured at the inflection point), that has been attributed to the oxygens along the Ti–O–Ti chains.[14–16] Hence, when the sample is irradiated with the 325 nm laser line, the Ti–O–Ti chains are directly excited and the electronic transition (charge transfer) from the oxygens along the chain to the Ti(IV) ions takes place. Consequently, an activation of the chain is expected, that could lead to a more favourable reactivity of the TiOH groups along the chain, thus facilitating the condensation of two vicinal TiOH. As a consequence of this condensation, a broken chain (terminated with TiOH groups at both ends) could be reconstructed.

This is, however, just a hypothesis to explain the observed behaviour of defective ETS-10 samples under a 325 nm laser beam, and further experiments or calculations are needed in order to demonstrate its validity. It is important to stress that, whatever the explanation for the apparent ordering of the Ti–O–Ti chains, our results point towards potentially interesting new means for post-synthesis modifications of zeolitic materials by selective irradiation with a convenient light source, leading to materials having a lower concentration of defects. If the above hypothesis is demonstrated to be correct, the method could be used in a number of systems (namely, metal substituted zeolites), and the strategy could be that of irradiating the material with a light source falling in (or close to) its absorption edge.

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