Infrared Spectroscopic Investigation of Titanium in Zeolites. A New Assignment of the 960 cm^{-1} Band

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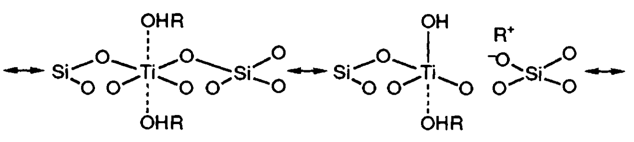
The formation of Si–O$^-$ defect groups due to the incorporation of Ti in the framework of zeolites is evidenced by means of solid-state tetraethylammonium (TEA) cation exchange; a new assignment for the infrared (IR) band in both β-Ti and TS-1 is presented.

Ti-containing zeolites, in which Ti atoms are believed to be placed in framework positions, catalyse the selective oxidation of organic compounds with H_2O_2.[1–4] However, the nature of the active centres associated to the Ti in these materials remains uncertain and a better knowledge of the incorporation of Ti is needed in order to understand the catalytic performance. Various hypotheses have been proposed to explain the mechanism of oxidation of hydrocarbons on Ti-zeolites, which involve different hypothetical framework-Ti species. One of them requires the presence of titanyl Ti=O groups which have been associated with the presence of the 960 cm^{-1} IR band,[5] which is always present in calcined Ti-zeolites. In this way, H_2O_2 can be activated through the formation of peroxy titanyl complexes that are the effective active centres. In contrast, other authors have assigned this band to the polarized Si–O$^{\delta-}\cdots$Ti$^{\delta+}$ bond,[6] and the formation of a five-membered ring involving Ti–OOH and ROH (R = Me, Si, Ti) has been proposed.[7] We report an IR investigation on a large-pore β-Ti zeolite[8] and propose a new assignment for the characteristic *ca.* 960 cm^{-1} IR band. The structural model involves a changeable Ti coordination depending on the presence of guest molecules.

β-Ti can be synthesized, as previously described,[9] by hydrothermal treatment at 408 K of aqueous reaction mixtures



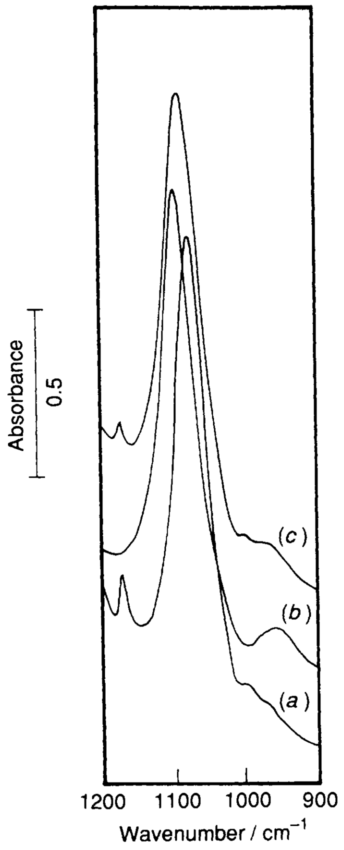


Fig. 1 IR spectra of β-Ti zeolites: (*a*) synthesized TEA–β-Ti; (*b*) β-Ti after calcination at 753 K; (*c*) sample (*b*) after solid exchange with TEA–Br

containing tetraethylammonium hydroxide, tetraethylorthotitanate, amorphous silica, and aluminium nitrate nonahydrate. The incorporation of Ti in the framework was monitored by means of chemical analysis, IR and XRD measurements.[9]

In the case of the synthesized TEA–β-Ti zeolite, two weak bands appear at 999 and 970 cm^{-1} (Fig. 1). In the case of as-synthesized TS-1 (TPA–TS-1; TPA = tetrapropylammonium) two weak bands also appear at *ca.* 1014 and 980 cm^{-1} (Fig. 2). Upon calcination, only one IR band appears at *ca.* 960 cm^{-1}, with a higher intensity than in the as-synthesized forms, for both TS-1 and β-Ti. In our opinion, if the 960 cm^{-1} band is due to the stretching vibration of the polarized Si–O$^{\delta-}$–Ti$^{+\delta}$ bond, then only one band should be observed in the as-synthesized materials which would have a similar intensity to that of the calcined material. On the other hand, no changes should occur if TEA$^+$ is exchanged on calcined β-Ti. Nevertheless, when β-Ti is partially converted in TEA–β-Ti by solid-state exchange with TEA–Br, both in a compressed pellet at 373 K, the spectrum with two weak bands at 999 and 970 cm^{-1} is partially restored (Fig. 1).

However, if the titanyl group is responsible for the 960 cm^{-1} band in the calcined material, and this appeared because of cleavage of two Si–O–Ti bonds of a tetrahedral framework Ti, no bands at all should appear in the as-synthesized zeolite, and no changes would be expected after TEA$^+$ exchange of the β-Ti calcined form. This does not occur in practice (Fig. 1). Moreover, very few examples of compounds containing Ti=O groups have been unambiguously characterized.[10] One of these compounds is the titanyl diacetylacetone, in which the stretching band of the Ti=O group appears at 1087 cm^{-1}.[11] A decrease of more than 120 cm^{-1} in the stretching wavenumber of this group would mean such a decrease in the Ti–O bond order that the assignment of the band at 960 cm^{-1} to a double-bonded Ti=O group seems unlikely. Recently, Hari *et al.*[12] have reported the presence of a band at 965 cm^{-1} in the IR spectra of vanadium silicalites, *i.e.* the same wavenumber as in TS-1. This strongly suggests that these bands cannot be associated with a metal–oxygen bond. Jacobs[13] also show the existence of a band at 960 cm^{-1} in the Raman spectrum of silicalite-1, although this is less intense than in TS-1.

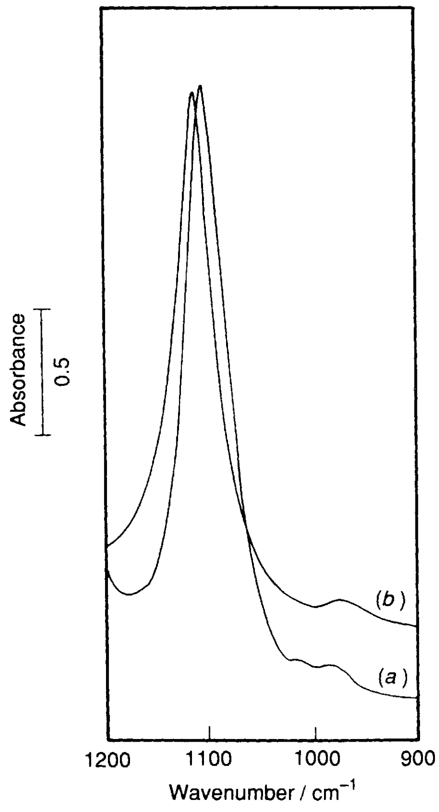


Fig. 2 IR spectra of: (*a*) TPA–TS-1 zeolite; (*b*) sample (*a*) after calcination at 753 K

We propose another assignment for the IR bands in Ti-containing zeolites, which takes into consideration a band which appears at 950–960 cm^{-1} in crushed silica, alkali silicates, and silica gels.[14–16] This band has been assigned to the stretching vibration of Si–O$^-$ groups and has also been observed in zeolites with a high concentration of defects. We have observed two weak bands at 999 and 970 cm^{-1} in β-zeolites with a very high Si : Al ratio (Fig. 1), for which the presence of a high concentration of Si–O$^-$ defects exists.[17] Since for β-Ti, either TEA$^+$ and/or H$^+$ can act as countercations for Si–O$^-$ defect groups, the bands at 999 and 970 cm^{-1} can be ascribed to the stretching vibration of Si–OR (R = TEA, H) groups. The position of the band is higher as the strength of the countercation decreases, since the Si–O$^-$ bond is weakened to a lesser extent. In both the as-synthesized and TEA$^+$-exchanged β-Ti zeolites, two bands at 999 and 970 cm^{-1} appear (Si–O TEA and Si–OH, respectively), whereas calcination gives rise to a unique and more intense band at *ca.* 960 cm^{-1} (Si–OH). For TS-1 materials, the band at *ca.* 1014 cm^{-1} corresponds to Si–OTPA groups (the higher wavenumber being due to the weaker acidity of TPA$^+$ cations).

This assignment is fully consistent with the IR experimental data from Boccuzzi *et al.*[18] and Bellusi *et al.*[7] Indeed, it has been found[7] that in TS-1, the 960 cm^{-1} band shows an oxygen isotopic shift, and no hydrogen isotopic effect was observed for this band.[7,8] When analogous isotopic experiments were performed on silica gel,[19] the band at 960 cm^{-1}, assigned to the Si–O stretching vibration[20] in surface silanol groups, an isotopic effect was observed for oxygen but not for hydrogen. These results can, therefore, be regarded as evidence to support our previous model[9] for the coordination state of Ti in β-Ti materials, in which Ti coordinates to four framework oxygen atoms, but because of its large covalent radius it can interact with one or two more ligands. This expands its coordination to a five- or six-fold one. The extra ligands can be H_2O molecular or OH^- ions, and for the latter the negative charge can be delocalized by resonance with the formation of Si–OR groups ($R = TEA^+$ or H^+). The interaction between TEA^+ and the negative framework accounts for the competition between Al^{III} and Ti^{IV} observed during the synthesis of β-Ti. The same applies for TS-1 materials where a similar competition between Ti^{IV} and Al^{III},[21] Ga^{III}[22] and Fe^{IV}[23] has been found.

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