Incompletely condensed silasesquioxanes as models for zeolite defect sites: an FTIR and density functional study

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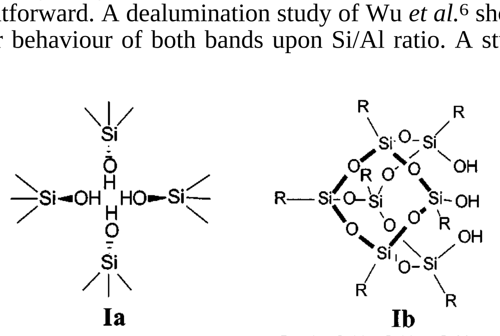
FTIR hydroxyl vibration bands in highly dealuminated zeolites could be unambiguously assigned to well defined hydroxyl clusters present at defect sites by the use of density functional calculations on incompletely condensed silasesquioxane complexes which, in addition, provided useful spectroscopic references.

Because of their defined cage like structures, it is expected that silasesquioxane complexes are not only suitable for mimicking silica surfaces[1] but can be considered as parts of zeolites as well, resembling for instance the zeolite double-four-ring (D4R). In this respect, the studies on defect sites as a part of zeolite research, in which still much is unknown about the precise zeolitic structure,[2] could profit from useful reference data obtained from silsesquioxane chemistry. Especially the assignment of zeolite defect sites by means of FTIR analysis, despite the numerous reports on these defects,[3–7] is surrounded by controversy.

In this report, we elucidated the FTIR assignment of the different possible defect sites in zeolite structures with incompletely condensed silasesquioxane complexes as references and by using computational chemistry. This powerful combination is a new approach in this field and results in a molecular level understanding of the actual hydroxyl clusters, which form the different zeolite defect sites (Fig. 1). Furthermore, a reaction of these hydroxyl clusters with different probe molecules will enable us to distinguish between defect sites located inside or outside the zeolite microporous system.

In general, the major part of the various hydroxyl bands found upon aluminium extraction out of a zeolite framework can be categorised roughly into two regions. The first is a relatively broad band between 3500 and 3560 cm^{-1} and the second, which is in most cases somewhat sharper, is present between 3680 and 3730 cm^{-1}. These bands are referred to as the 3500 and 3700 cm^{-1} bands, respectively. It is important to note that both bands can be found in various dealuminated zeolites such as ZSM-5,[3] beta,[4] faujasite[5] and mordenite,[6,7] which indicates that the different defect sites are not unique for one particular zeolite but have a more general character. The assignment of the two different hydroxyl bands which arise upon dealumination is not straightforward. A dealumination study of Wu *et al.*[6] showed a similar behaviour of both bands upon Si/Al ratio. A study by Moreno and Poncelet, however, showed a significantly different response of the 3500 and 3700 cm^{-1} bands as a function of temperature, indicating a different origin of these bands.[7]



Ia **Ib**

R = H, C_5H_9, C_6H_{11}, C_7H_{13}

Fig. 1 A two-dimensional representation of a hydroxyl nest in a zeolite (**Ia**), in comparison with the incompletely condensed silasesquioxane complex (**Ib**).

The FTIR spectrum of dealuminated mordenite clearly shows the broad band at 3500 cm^{-1} and the band around 3700 cm^{-1}, as can be seen from Fig. 2A [dealumination with nitric acid resulted in a Si/Al ratio increase from 6.7 (spectrum a) to 39 (b), 47 (c) 79 (d) and 150 (e)]. Furthermore, the Brønsted acid band around 3610 cm^{-1} is only just apparent. This band decreases with decreasing aluminium content (increasing Si/Al) and is practically gone at Si/Al = 150, as can be seen from Fig. 2A (spectrum e). Since the 3500 cm^{-1} band is shifted about 240 cm^{-1} to lower frequency compared to the isolated silanols (present at 3745 cm^{-1}) we assume that these OH bonds are highly weakened due to their mutual hydrogen bonding. Moreover, the broad appearance of this band is indicative of a strong disturbance caused by the hydrogen bridges. The shift of the 3700 cm^{-1} band is only *ca.* 40 cm^{-1} (compared to the isolated silanol band) and is considerably less broad in comparison with the 3500 cm^{-1} band. This different appearance of the 3700 cm^{-1} band implies again that this band arises from a different, but still moderately disturbed, OH species.

Incompletely condensed silasesquioxanes contain OH groups and, as such, can be used for modelling OH clusters in zeolites. Some of these complexes, which can be considered as possible models for defect sites in zeolites, are shown in Table 1. Clearly, a zeolite-like T-atom vacancy can be recognised in complex **Ib** (see also Fig. 1), whereas complex **III** represents an isolated, non-hydrogen bridged OH group at the outer surface of the zeolite, and complex **II** can be considered as a hydrated Si–O–Si bridge. The geometry of these complexes was fully optimised.† Complex **III** as a model for isolated OH groups has the highest calculated frequency for its OH stretching vibration. This frequency of 3697 cm^{-1} is in good agreement with the measured FTIR frequency for the isolated OH stretching vibration of this complex at 3705 cm^{-1} (measured in pressed KBr pellets). A shift of *ca.* 300 cm^{-1} is obtained for the

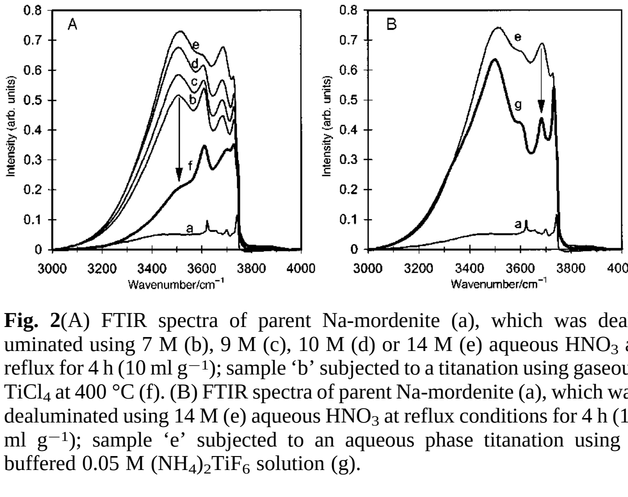


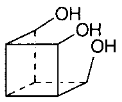
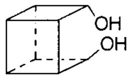
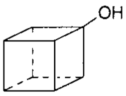
Fig. 2(A) FTIR spectra of parent Na-mordenite (a), which was dealuminated using 7 M (b), 9 M (c), 10 M (d) or 14 M (e) aqueous HNO_3 at reflux for 4 h (10 ml g^{-1}); sample ‘b’ subjected to a titanation using gaseous $TiCl_4$ at 400 °C (f). (B) FTIR spectra of parent Na-mordenite (a), which was dealuminated using 14 M (e) aqueous HNO_3 at reflux conditions for 4 h (10 ml g^{-1}); sample ‘e’ subjected to an aqueous phase titanation using a buffered 0.05 M $(NH_4)_2TiF_6$ solution (g).

calculated main bands of complex **I**, the silasesquioxane model for a zeolite T-atom vacancy, *i.e.* the actual hydroxyl nest (as plotted in Fig. 1). This shift is in good agreement with the 250 cm^{-1} shift found experimentally for the 3500 cm^{-1} band in the FTIR spectra of dealuminated zeolites (Fig. 2A). The comparable shift is a strong indication for the fact that the three membered hydroxyl nest is a reliable model for a four membered hydroxyl nest. It is important to mention the significant increase of the average OH bond distance upon hydrogen bridging, while the hydrogen bridge distance reduces to only 1.89 Å (see Table 1, complex **Ib** and **III**). Considering complex **II**, only a small shift is obtained for the OH stretching vibrations, indicative of weakly hydrogen bonded OH groups. This is confirmed by the scarcely changed OH distance and the large OH bridging distance for this complex. The small shift of the OH stretching band (22 cm^{-1} for the symmetric vibration) is in good correspondence with the measured shift of *ca.* 40 cm^{-1} for the 3700 cm^{-1} band in dealuminated zeolites. Moreover, the weaker hydrogen bridges for this type of defect site should result in a less broad signal, which is indeed obtained for the dealuminated mordenite (Fig. 2A).

Since it is concluded that the two FTIR hydroxyl bands at 3500 and 3700 cm^{-1} cannot be ascribed to the same defect site, it is interesting to know where these different defect sites are located in the zeolite microporous structure. To investigate this, the two different hydroxyl clusters are reacted with different probe molecules. Well known titanium precursors are used as probes, $TiCl_4$ and $(NH_4)_2TiF_6$, usually applied in post-synthesis procedures in the preparation of titanium zeolites.[8] The latter however, used in aqueous applications, is considered to be more bulky, especially in its hydrated form. Moreover, its siliceous analogue, $(NH_4)_2SiF_6$, is reported to be almost unable to enter the mordenite 12-ring.[9] It is assumed, therefore, that also the large $TiF_6(H_2O)_n{}^{2-}$ ion hardly enters the mordenite microporous structure.

Applying the different titanium precursors to the same kind of dealuminated mordenite, results in a totally different behaviour of the two above mentioned hydroxyl defect site bands. $TiCl_4$ reacts primarily with the hydroxyl nests shown by the significant decrease of the 3500 cm^{-1} band upon titanation [Fig. 2A(*f*)]. The 3700 cm^{-1} band seems hardly affected by this titanation treatment. This result is in agreement with the spectra reported earlier of dealuminated mordenite reacted with $TiCl_4$.[8c] Correspondingly, in a report concerning the titanation of dealuminated beta, the broad FTIR band present around 3500 cm^{-1} is significantly reduced upon reaction with $TiCl_4$.[10] Using aqueous $(NH_4)_2TiF_6$ as the titanium source, however, results in the opposite behaviour. The FTIR spectrum of a dealuminated mordenite titanated with this titanium source shows mainly a decrease of the 3700 cm^{-1} band [Fig. 2B(g)]. Since the 3500 cm^{-1} band was assigned to hydroxyl nests resulting from the extraction of framework aluminium, these nests are located in the zeolite micropores. The 3700 cm^{-1} band, on the other hand, was attributed to hydroxyl pairs. Since this band is affected predominantly by the titanation with the bulky $(NH_4)_2TiF_6$, we believe that these pairs are located mainly on the outer (or mesoporous) surface of the zeolite.

Table 1 Incompletely condensed silasesquioxane complexes[a] and their calculated O–H stretching vibrations and O–H distances†

	Ib	**II**	**III**
			
OH stretching vibrations (shift in bold)[b] /cm^{-1}	3403(asym)(**294**) 3396(asym)(**301**) 3331(sym) (**366**)	3698(asym)(**-1**) 3675(sym) (**22**)	3697 (**0**)
Average O—H bond distance/Å	0.996	0.980	0.978
Average O•••H bridge distance/Å	1.89	2.62	–

[a] Lines in figures represent Si–O–Si units which are terminated by hydrogen atoms at each corner. [b] The shift is defined as the difference of the calculated vibration with the 3697 cm^{-1} vibration for complex **III**.

In conclusion, our new approach to the controversy of the assignment of the different hydroxyl bands in FTIR analysis, using silasesquioxane as models for defect sites in zeolites, is a powerful tool to clarify the different defect site structures. Based on its FTIR shift and the OH distances of the model compound **Ib**, the band at 3500 cm^{-1} must indisputably be assigned to hydroxyl nests (*i.e.* T-atom vacancies, as depicted in Fig. 1). Simultaneously, the band at 3700 cm^{-1} cannot be assigned to the same kind of hydroxyl cluster and evidence is found for the assignment of this band to a hydroxyl pair, featuring less hydrogen bonding. Regarding their location in the zeolite microporous structure, the use of titanium probe molecules shows that, in contrast to the hydroxyl nests present in the mordenite micropores, the hydroxyl pairs seem to be located primarily on the outer surface of the zeolite crystals.

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Notes and references

† *Computational details*: calculations are based on the density functional theory (DFT)[11] as implemented in the Dgauss program (version 4.0) produced by Oxford Molecular Ltd.[12] A generalised gradient approximation to the exchange (Becke)[13] and correlation (Lee, Yang and Parr)[14] was used, and applied self-consistently. The Gaussian basis sets used are of double-zeta quality and include polarisation functions for all atoms (DZVP2).[15] A second set of basis functions, the fitting basis set, is used to expand the electron density in a set of single-particle Gaussian-type functions. All geometry optimisations were carried out fully relaxed, so as to avoid introducing unnatural strain in the molecules. The second derivatives are calculated analytically in the harmonic approximation, giving a good approximation to compute vibrational spectra.

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