Structural changes induced by dehydration in the crystalline layered silicate Na-RUB-18: a computational/experimental combined study†‡

Maria Francesca Iozzi,[a] **Chiara Bisio,**[a] **Thais Regi-Macedo,**[b] **Claudio Airoldi,**[b] **Maurizio Cossi***[a] **and Leonardo Marchese**[a]

Na-RUB-18 layered silicate ($Na_8Si_{32}O_{64}(OH)_8 \cdot 32H_2O$) is prepared following the procedure reported in the literature (ref. 1: K. Kosuge and A. Tsunashima, *J. Chem. Soc., Chem. Commun.*, 1995, 2427) and its significant structural modifications induced by progressive removal of hydration water molecules are studied for the first time by a combined experimental (TGA and variable temperature XRD and FTIR) and theoretical approach. A novel structure of a partially de-hydrated Na-RUB-18 obtained upon heating at 75 °C under inert gas flow, which leads to a reversible phase transformation in agreement with XRD and FTIR results, is found. TGA indicates that at this stage, two of the four hydration water molecules per Na ion are lost. Theoretical results based on DFT calculations suggest that the apical water molecules of the solvated octahedrally coordinated sodium ion, forming weak H-bonds with the silicate oxygen atoms, are removed at this stage. As a consequence of the dehydration, the silicate layers get closer, and, similarly to that observed for zeolites, the sodium ions move towards lattice oxygen atoms, to restore their coordination shell. A combination of IR spectroscopy and computational models is used to describe the vibrational properties of silanol/silanolate $(SiOH \cdots SiO)^{-1}$ bridges, which are responsible for the proton conduction of Na-RUB-18. The method described can be of general utility to refine structures which are not fully accessible to standard X-ray structure analysis.

Introduction

Hydrous layered silicates (HLS) are interesting materials with numerous and important industrial uses in the production of catalysts, paints, ion exchangers, etc.[2–4] Like many zeolites, these materials act as molecular sieves, but due to their 2D layered structure, the interlayer space can be also largely modified to accommodate a number of organic and inorganic guests, keeping in some cases the crystallinity of the silicate framework. The inner surfaces of HLS are characterized by a carpet of silanols (–SiOH) and silanolate species (–SiO⁻), with strong interactions between them.[5]

In most cases the structural features of such materials, though very important for the understanding of their properties, are not well known, due to their poor crystallinity. A notable exception is $Na_8Si_{32}O_{64}(OH)_8 \cdot 32H_2O$ (hereafter Na-RUB-18, as proposed by Gies and co-workers who first synthesized and characterized it):[6,7] this system exhibits a high stacking order of silicate layers and intercalated hydrated Na cations, and thus it can be used as a structural model for this class of materials.

Na-RUB-18 has been studied by X-ray powder diffraction (XRPD), giving a well resolved structure,[6] and by powder neutron diffraction and solid-state MAS NMR spectroscopy, to investigate the dynamic properties of the interlayer region and of the hydrogen bond network connecting silanols and silanolates of the layer surface. The crystal structure belongs to the I4₁/*amd* space group and it is characterized by a 1:1 ratio between the Q^3 and Q^4 silicon atoms (involved in silanol groups, $[SiO_4]_3$–Si–OH, and in quartz-like $[SiO_4]_4$–Si moieties respectively). Every other silanol is de-protonated, giving rise to a net negative surface charge, compensated by the intercalated cations: a clear sketch of the silicate structure, along with the hydrated Na ions accommodated in the interlayer space, is shown *e.g.* in ref. 7. The positions of hydrogen atoms could not be determined by XRPD, and were deduced from NMR spectra: in particular, the hydrogen bridges between adjacent silanols and silanolates on the surface [SiO–H···OSi]⁻ deserve to be further investigated. These H-bonds are likely to be particularly strong, as suggested by the fact that oxygen atoms are very close to each other (at a distance of 2.3 Å, according to X-ray structure analysis), and they participate in monodimensional H-bond networks, involving some of the hydration water molecules in the interlayer. Protons become delocalized over the entire crystal at temperatures close to 380 K at constant volume conditions, as shown by ¹H MAS NMR experiments, giving rise to unusual 1D proton conduction phenomena. As in other similar cases, it is a matter of debate whether the proton in the silanol-silanolate moiety is actually shared between the oxygen atoms or it is a typical H-bond: as this point depends on the local shape of the potential energy surface (single or double well along the O–H stretching), high level calculations can provide decisive information.

ªDipartimento di Scienze e Tecnologie Avanzate and Centro Interdisciplinare Nano-SiSTeMI, Università del Piemonte Orientale "A. Avogadro", Via T. Michel 11, Alessandria, Italy. E-mail: maurizio.cossi@mfn.unipmn.it
ᵇInstituto de Quimica, Universidade Estadual de Campinas, SP, Brasil

2610 | *J. Mater. Chem.*, 2009, **19**, 2610–2617

This journal is © The Royal Society of Chemistry 2009

On the other hand, XPRD and TGA show that Na-RUB-18 undergoes a large structural rearrangement upon heating, similarly to what was obtained by Brenn *et al.* for Na-ilerite, which is isostructural to Na-RUB-18.[8] Clearly, understanding the dependence of the structure on the hydration degree, and hence on the temperature, is very important in view of the proton conductive properties of the material and its potential industrial applications, besides being a very interesting chemical problem per se. However, the quality of the collected XRPD pattern (*i.e.* the crystallinity of the material) does not allow the local structure of the material at different dehydration stages, which are induced by heating, to be solved with sufficient accuracy.

The present paper deals with the hydration-dependent structural changes of Na-RUB-18, using both experimental (TG, XRPD, IR) and theoretical (semi-empirical and ab initio periodic calculations) techniques. Such a combined approach is particularly useful in this case, allowing for the first time the description of the local evolution of the structure of Na-RUB-18 as a function of the temperature and hydration degree. IR spectroscopy, on the other hand, allows the interactions involving protons to be studied, also monitoring the H-bonds as a function of the hydration degree at different temperatures: computational models are particularly useful in assisting the assignment and the interpretation of the spectra changes, linking the spectroscopic features to the atomistic description of the interlayer. From another point of view, the computed structures have to prove compatible with the experimental observations to be considered reliable models.

In the following we present first an optimized structure for as-synthesized Na-RUB-18, *i.e.* with 6 water molecules solvating each Na^+ (some of them are shared so that the H_2O/Na^+ ratio is equal to 4), giving very good agreement with the structure resolved by Gies and co-workers, and providing reliable insights about the position of hydrogen atoms, which could not be determined in Gies' work. In particular, we describe for the first time the atomic detail of the silanol-silanolate $[SiO–H\cdots OSi]^{-1}$ moiety, which is responsible for the proton conduction phenomena cited above. The IR features of both water molecules coordinated to sodium ions and silanol/silanolate couples is fully interpreted here for the first time. Then, a model is presented for the partially dehydrated material, with stoichiometry $Na_8Si_{32}O_{64}(OH)_8\cdot16H_2O$ (β-Na-RUB-18), where two water molecules per sodium ion are lost upon heating at 75 °C under inert gas flow. The structure of the latter species has never been described before, and this is the first attempt to explain the deep changes occurring in Na-RUB-18 upon dehydration: the computed structure agrees satisfactorily with the TG, IR and XRPD results.

Experimental methods

The synthesis of the Na-RUB-18 sample was performed according to the procedure described in the literature. A gel containing amorphous silica, NaOH and water (10 : 0.5 : 7 molar ratio), was prepared and crystallized at 105 °C for 9 days.[1]

Variable temperature X-ray powder diffraction (XRPD) was performed with a Thermo ARL 'XTRA-048 diffractometer (radiation Cu Kα = 1.54 Å) equipped with a Buelher high temperature stage which allowed in-situ measurements, both under controlled gas flow and under vacuum. The accessory was used in a parallel beam configuration, and the conventional incident and diffracted beam slit assembly was replaced by a parabolic mirror, which converts the divergent X-ray beam into a parallel X-ray beam,[9] and a long Soller slit (thin film collimator with angular acceptance of 0.25°) oriented perpendicular to the diffractometer plane, respectively. Diffractograms of a film of Na-RUB-18 obtained by mixing the powder with a few mL of isopropanol were collected under N_2 flow (100 mL/min) between 4 and 50° 2θ with a step size of 0.02 and a rate of 4° 2θ/min. The sample was heated at a rate of 10 °C min^{-1} and left at each equilibrated temperature for 10 min, before recording the diffractograms. The use of a parabolic mirror allowed the signal to be improved and avoided any artefacts from irregular surfaces which were formed while heating the Na-RUB-18 thin film.

Diffractograms collected after exposing the sample to water at room temperature (rt) were recorded using the same configuration, by bubbling N_2 in a beaker containing around 100 mL of water for 30 minutes.

TGA analysis was performed on a Setaram SETSYS Evolution instrument under argon (gas flow 20 mL/min), heating the samples to 500 °C with a rate of 10 °C/min.

Infrared spectra were collected on a Thermo Electron Corporation FT Nicolet 5700 Spectrometer (resolution 4 cm^{-1}). Self-supporting pellets (made with a mechanical press at 5 tons/cm^2) were placed into a special hand-made IR cell equipped with KBr windows permanently attached to a vacuum line (residual pressure: 1×10^{-6} Torr; 1 Torr = 133.33 Pa), allowing variable temperature IR measurements in flowing N_2 (100 mL/min).

Computational methods

Theoretical models of the hydrated (4 H_2O/Na^+) and partially dehydrated (2 H_2O/Na^+) structures of Na-RUB-18 were optimized with semiempirical MSINDO[10] and ab initio CRYSTAL06[11] packages. Standard parameters and basis set were used for MSINDO; the density functional B3LYP[12] was used for the ab initio calculations, along with Hay and Wadt electron core potentials (ECP) and basis set[13] for Si and Na atoms, and Pople 6-31G basis set[14] for O and H. In both cases a 2D periodic slab was modeled, instead of the full three-dimensional crystal, including in the slab two silicate layers and the intercalated Na^+ ions and water molecules: this choice makes the calculations less demanding, while retaining all the important geometrical features of the studied systems. Periodic boundary conditions were introduced through the Cyclic Cluster model in MSINDO, and with the keyword SLAB in CRYSTAL06: in the latter, the cell parameters were optimized along with the coordinates of atoms inside the unit cell.

Semiempirical calculations, cheaper though less reliable, were used to pre-screen the potential energy surface, in order to speed up the ab initio optimizations: both hydrated and partially dehydrated MSINDO structures were fairly close to the final geometries obtained with CRYSTAL06, even if some important details changed, especially in the H-bonded moieties, suggesting that the ab initio level is necessary to model accurately this system. To better estimate the silanol vibrational frequencies, some finite clusters were cut out of the periodic structures, and reoptimized with Gaussian03 at the DFT level; the B3LYP

This journal is © The Royal Society of Chemistry 2009

J. Mater. Chem., 2009, **19**, 2610–2617 | 2611

density functional was used, along with the LANL2MB ECP and basis set for Si and Na atoms, and the 6-31G(d,p) basis set for O and H.

Results and discussion

Variable temperature XRPD of Na-RUB-18 samples at different hydration stages are displayed in Fig. 1(A) and (B).

The X-ray diffractogram of the as-synthesised material (Fig. 1A, a) is characterized by reflections typical of the Na-RUB-18 structure, in agreement with the literature data.[6] It can be noticed that the thermal treatment at 50 °C (Fig. 1A, b) does not alter the structure significantly, while by heating at 75 °C (Fig. 1A, c) the basal reflection associated with the [004] plane is shifted from 7.9 to 9.2° 2θ, thus indicating a significant decrease of the interlayer distance from 11.2 to 9.5 Å. Such a process appears reversible after exposure of the Na-RUB-18 to water, as indicated by the diffraction patterns reported in Fig. 1B (curves a–c and b′–c′). Note that the diffractogram recorded at 75 °C is not sufficiently resolved to allow complete characterization of the
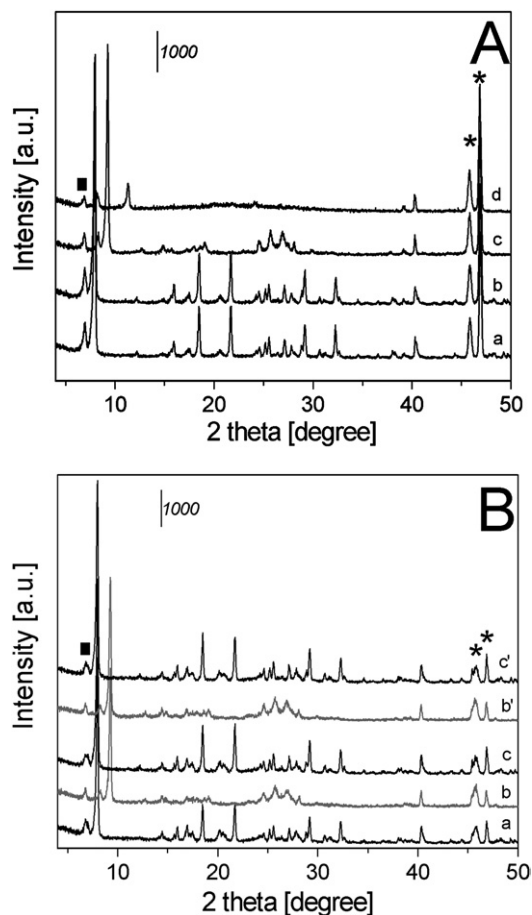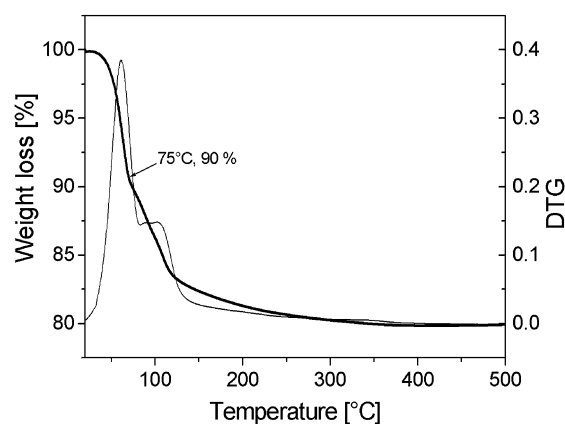

Fig. 2 TGA/DTG analysis of Na-RUB-18 in argon flow (100 mL/min).

new structure obtained after heating, besides indicating the interlayer distance decrease.

On the other hand, the heat treatment at 100 °C (Fig. 1A, d) results in a collapse of the Na-RUB-18 structure. Further hydration does not restore the original structure (XRPD data not shown for the sake of clarity). This behaviour of Na-RUB-18 is similar to that described in the literature by Schwieger and co-workers for sodium ilerite.[8] TGA analysis was then performed in order to quantify the amount of water molecules lost during the dehydration process at increasing temperature (Fig. 2). The sample was left under N_2 flow at rt for 30 minutes to remove the excess of water adsorbed on the RUB-18 external surface.

As shown by TGA analysis, the Na-RUB-18 is characterized by three main weight losses, the first one located between 40 and 75 °C, with maximum at 65 °C, the other one between 75 and 120 °C, while a less pronounced weight loss is located in the 120–300 °C range.

Water molecules are almost completely removed upon heating at 100 °C, as found by IR spectroscopy (vide infra). The overall amount of water molecules (i.e. by considering both water bound to sodium ions and water derived by condensation of silanols) lost at 300 °C is around 20%, which means a H_2O/Na ratio equal to 4 in agreement with the stoichiometry of hydrated Na-RUB-18 ($Na_8Si_{32}O_{64}(OH)_8 \cdot 32H_2O$) reported by Gies and co-workers.[7] The weight loss at 75 °C is ca. 10%, which means that at this stage each sodium ion loses 2 water molecules. The sample at this stage is therefore partially dehydrated, and will be named β-Na-RUB-18. Looking at the structure proposed for the solvated octahedrally coordinated sodium, it is likely that the apical water molecules, which are not shared with adjacent sodium ions and are believed to form weaker bonds with the silicate oxygen atoms, are lost at this stage: the selective desorption of apical water has been argued also on the basis of ^1H MAS-NMR spectra recorded on both as-synthesized and partially dehydrated samples,[7] and it can be better described with the optimized theoretical models presented below.

By increasing the temperature to 120 °C, the weight of the sample is further reduced by 6%, as a result of the removal of water molecules remaining bound to sodium ions or coming from a process of condensation of structural silanols, that begins to collapse at around 100 °C, as evidenced by XRD (Fig. 1A). The condensation phenomena are completed at ca. 300 °C.

Fig. 1 (A) Variable temperature XRD patterns of Na-RUB-18 at rt (a), 50 °C (b), 75 °C (c) and 100 °C (d). (B) X-Ray diffraction patterns of Na-RUB-18 collected in N_2 flow at rt (a) and after heating the sample at 75 °C for 30 minutes (b) and after subsequent exposure to water at rt for 30 min; (c) XRD patterns collected after a second heating cycle at 75 °C for 30 min and subsequent hydration step at rt are also reported (curves b′ and c′, respectively). * indicates reflections typical of the Pt/Rh support. ■ indicates an unknown impurity phase.

2612 | J. Mater. Chem., 2009, **19**, 2610–2617

This journal is © The Royal Society of Chemistry 2009

The above results show that around 75 °C Na-RUB-18 undergoes a deep structural modification (*i.e.* phase transformation), due to the loss of two water molecules per ion, and that the resulting arrangement is still crystalline even if more disordered than the as-synthesized silicate. The disorder of β-Na-RUB-18 leads to XRPD not suitable to solve the structure, for this reason computational models can be of great help to describe the actual structural changes occurring when two water molecules are removed from the Na^+ solvation shell.

Two bi-dimensional models were used for Na-RUB-18 and β-Na-RUB-18, respectively: the former was prepared cutting two silicate layers with the intercalated ions and water molecules from the structure resolved in ref. 6, and saturating with hydrogen atoms all the $Si-O^-$ groups on the top and bottom faces: the resulting 2D unit cell is $Na_4Si_{32}O_{72}H_{12} \cdot 16H_2O$. The partially de-hydrated model was obtained by removing the apical water molecules from the hydrated one, so that the unit cell is $Na_4Si_{32}O_{72} \cdot 4H_2O$. Slab models describe well all the relevant features of the interlayer region, with a considerable saving of computational effort with respect to 3D structures; all the geometry optimizations were performed releasing the symmetry constraints (so that all systems were considered in the P1 group), in order to leave the maximum freedom to the atoms motion. The CIF files of the optimized slabs (*vide infra*) are available as ESI.‡ The 2D model of the fully hydrated Na-RUB-18 was first optimized at the semiempirical MSINDO level, then refined at the DFT level with CRYSTAL06. The resulting structure is depicted in Fig. 3, and the main geometrical parameters are listed in Table 1 along with their experimental counterparts: the slab periodicity is described by the lattice parameters $a = 7.6256$ Å, $b = 15.3816$ Å, $\gamma = 90.1302°$, and the optimized interlayer distance is 11.48 Å. As expected, each ion is coordinated to six water molecules,
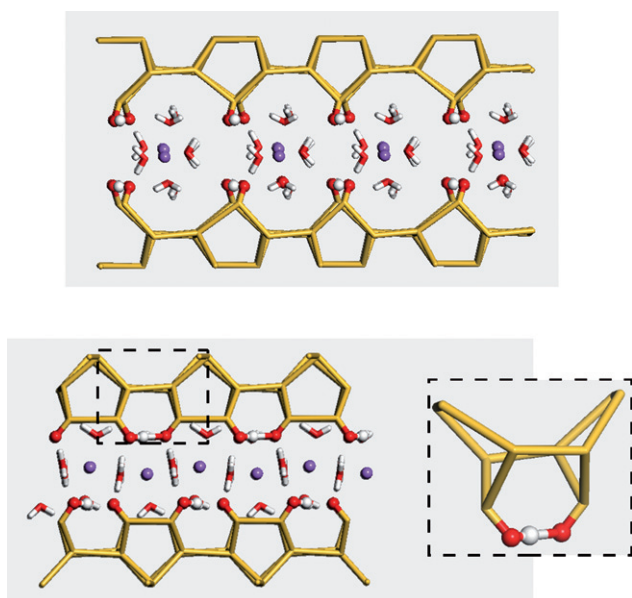

Fig. 3 Optimized structure for the 2D model of the hydrated Na-RUB-18 ($Na_4Si_{32}O_{72} \cdot 16H_2O$), viewed from the two periodic directions; the oxygen atoms in the silicate structure are not indicated for clarity, as well as the silanol groups saturating the top and bottom external surfaces. Inset: detail of the silanol-silanolate bridge.

Table 1 Experimental and computed distances (Å) of as-synthesized Na-RUB-18. See Fig. 4 for labelling

Distance	XRD	Model
$Si^1 \cdots Si^1$	3.17	3.22
$Si^2 \cdots Si^2$	3.10	3.17
Si–O (avg.)	1.61	1.66
$O^1 \cdots O^2$	2.30	2.46
$O^1 \cdots H$		1.39
O^2–H		1.07
$Na \cdots O^1$		3.90
$Na \cdots O^2$		4.65
$Na \cdots O^{ap\ 1}$ ($Na \cdots O^{ap\ 2}$)	2.25 (2.34)	2.29 (2.52)
$Na \cdots O^{eq}$ (avg.)	2.57	2.51

forming octahedra with four equatorial molecules shared with the adjacent solvation shells, and two apical molecules: equatorial water molecules are strongly H-bonded to oxygen atoms of silanol-silanolate pairs (remember that every other silanol group is deprotonated, so that the surface of the silicate is actually covered by silanol-silanolate pairs with a net negative charge), while apical molecules are involved in weaker H-bonds with oxygen atoms of the Q^4 sites of the silicate framework. This strongly suggest that the apical water molecules are lost first upon heating.

As mentioned above, an important point concerns the geometry of the silanol-silanolate $(SiO-H \cdots OSi)^-$ sites: whether this can be considered a true (though particularly strong) H-bond, or rather a shared hydrogen atom in a single-well potential minimum, has been debated. The very short oxygen-oxygen distance (2.3 Å, according to XRPD structure) allows both hypotheses. In the absence of neutron diffraction data showing the actual hydrogen positions, we can resort to theoretical optimisation to get some insights about this point. In the periodic structure optimized with MSINDO the O–O distance is markedly larger, 2.68 Å, but it reduces to 2.46 Å in the ab initio calculation with CRYSTAL06: in both cases the hydrogen is much closer to one of the oxygen atoms, indicating a strong H-bond rather than a shared hydrogen atom. The double-well nature of the H stretching between the two oxygen atoms is not in contrast with the findings of Gies and co-workers, who actually found a delocalized network of hydrogen atoms at higher temperatures, when the hydrogen atom can flip between the two minima, interconverting silanol into silanolate and vice versa. This point is discussed in greater detail below, when different computational models of the silanol group are described.

The 2D model of the partially de-hydrated β-Na-RUB-18 structure, observed by heating at 75 °C, was optimized at the MSINDO level and refined with CRYSTAL06, with the result presented in Fig. 4.

As a consequence of the dehydration, the silicate layers get closer, as expected, and a large movement of the sodium ions is observed, leading the Na^+ almost *inside* the layers, as the cations move towards lattice oxygen atoms, to restore their coordination shell. In the optimized slab, we observe two types of coordination shell for Na^+, shown in Fig. 5 (A) and (B): half of the ions coordinate to the two silanol-silanolate oxygen atoms, to one oxygen of Q^4 sites and to three water molecules, half use four oxygen atoms of Q^4 sites and two water molecules. Also the silanol-silanolate moieties are split into two classes: half of them
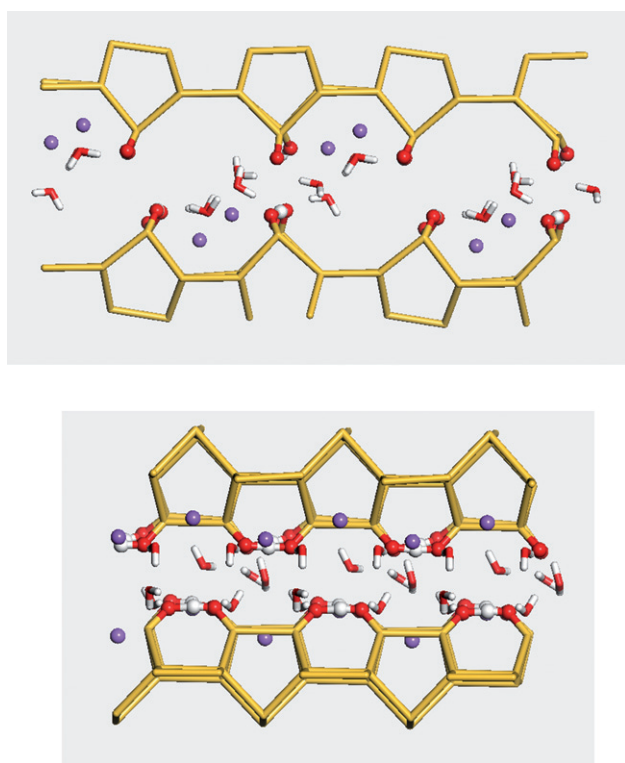
This journal is © The Royal Society of Chemistry 2009

J. Mater. Chem., 2009, **19**, 2610–2617 | 2613

Fig. 4 Optimized structure for the 2D model of the partially de-hydrated β-Na-RUB-18 ($Na_4Si_{32}O_{72} \cdot 8H_2O$), viewed from the two periodic directions; the oxygen atoms in the silicate structure are not indicated for clarity, as well as the silanol groups saturating the top and bottom external surfaces.
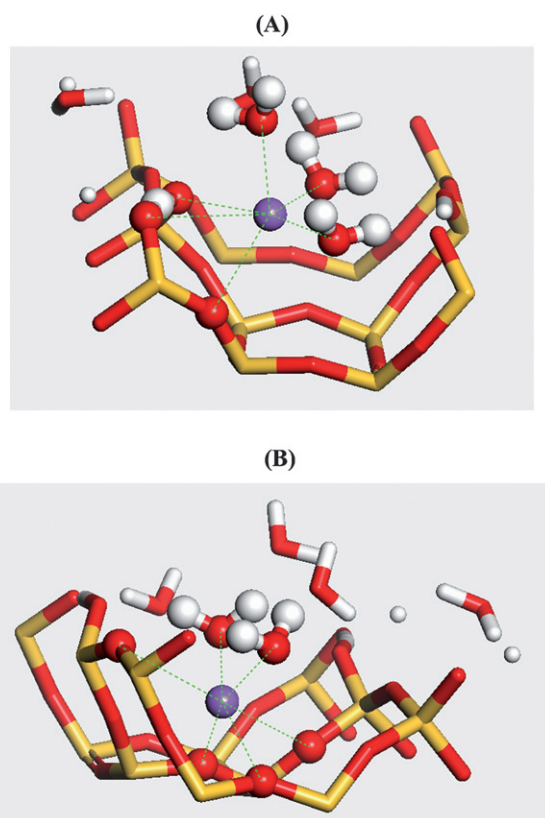

Fig. 5 Detail of the two ion coordination shells in the partially de-hydrated structure. (A) Na^+ is coordinated by the silanol-silanolate group, by three water molecules and one Q^4 (silicate) oxygen. (B) Na^+ is coordinated by two H_2O and four silicate oxygen atoms.

Table 2 Measured and computed stacking distance (Å) of Na-RUB-18. Hydrated and de-hydrated states of Na-RUB-18 refer respectively to the as-synthesised and heated at 75 °C samples

Experimental (XRD)		Calculated (CRYSTAL06)	
hydrated Na-RUB-18[a]	11.25	(4 H_2O/Na^+)	11.43
β-Na-RUB-18[b]	9.48	(2 H_2O/Na^+)	10.19

[a] $Na_8Si_{32}O_{64}(OH)_8 \cdot 32H_2O$. [b] $Na_8Si_{32}O_{64}(OH)_8 \cdot 16H_2O$.

coordinate a sodium ion, while the rest are H-bonded to water molecules.

This is likely to be one of the possible minima of the potential energy surface, and probably other arrangements could be found that saturate the ion coordination shell: anyway, the optimization was performed without symmetry constraints, and the interlayer distance in the present structure is compatible with the XRPD profile. A general conclusion is that the interlayer distance reduces, as determined by XRPD (*vide supra*), to allow silicate oxygen atoms to saturate the Na^+ coordination shell. Similar behaviour was already observed for zeolites, where cation migration through the zeolite structure occurs in relation to the hydration degree of the solid.[15,16]

The computed and measured stacking distances of Na-RUB-18 are summarised in Table 2.

More insights can be obtained from the analysis of the vibrational spectra at increasing temperature, corresponding to different degrees of hydration, reported in Fig. 6.

The spectrum collected maintaining the sample under nitrogen flow at rt for 30 minutes (Fig. 6a) shows a broad absorption in the 3800–3000 cm^{-1} range, where different overlapped bands emerge with maxima located at 3655, 3625, 3460 and 3225 cm^{-1}. The latter two bands show a shoulder at *ca.* 3345 cm^{-1} and a large tail at *ca.* 3035 cm^{-1}, respectively, which are more evident upon heating at temperatures $\geqq$ 50 °C (Fig. 6b and c). Broad absorptions in the 2800–1800 cm^{-1} range, with three maxima located at *ca.* 2650, 2330 and 1815 cm^{-1}, are also observed. In

addition, narrow and intense peaks at 1670 and 1630 cm^{-1}, superimposed to a broad band in the 2000–1300 cm^{-1} range, are also present.

The broad band in the 3800–3000 cm^{-1} range suggests the presence of water molecules interacting differently with the sodium ions: in this spectrum and in those recorded at higher temperature, we can distinguish three kinds of water, forming weak, medium and strong H-bonds with the layer oxygen atoms (with vibrational frequencies broadly resembling those of vapour, liquid and ice water, respectively).[17] In particular, the absorptions at 3655 and 3625 cm^{-1} can be associated to the asymmetric (ν_1) and symmetric (ν_2) stretching modes, respectively, of water molecules weakly bound to sodium ions and almost non-interacting with (or very weakly H-bonded to) the lattice oxygen atoms: the corresponding bending mode falls at 1630 cm^{-1}. In addition, water molecules forming medium
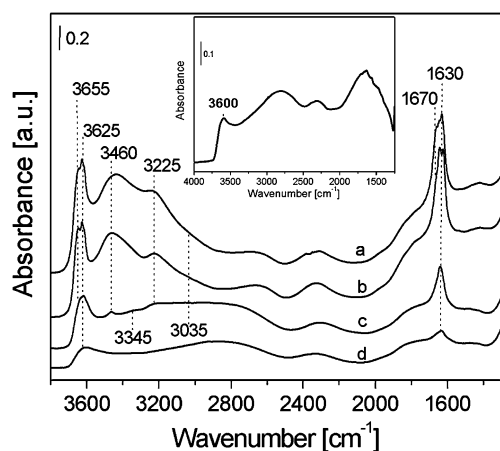
Fig. 6 Variable temperature FTIR spectra collected under N_2 flow (100 mL/min) of Na-RUB-18 samples. Spectra were recorded at rt (a) and after heating at 50 °C (b), 75 °C (c) and 100 °C (d). The inset shows a curve resulting from subtracting the spectrum collected after heating the Na-RUB-18 sample at 200 °C from that of the same sample treated at 500 °C (direct spectra not shown for the sake of brevity).

strength H-bonds are also present, as indicated by the bands at 3460 and 3225 cm^{-1}, associated with their asymmetric and symmetric stretching vibrations, respectively, and by the bending mode located at *ca.* 1670 cm^{-1}.[18,19] Considering the structural model presented above, weakly and medium H-bonded molecules can be clearly assigned to apical and equatorial water, respectively, confirming their different levels of interaction with the sodium ions and the silicate network.

Upon heating at 50 °C, the IR spectrum of Na-RUB-18 (Fig. 6b), undergoes very limited changes, suggesting that at this stage almost all water molecules remain bound to sodium ions, in agreement with TGA and XRD results.

The further temperature increase to 75 °C (Fig. 6c) is accompanied by a significant modification of the IR spectrum, where a noteworthy depletion of both couple of bands at 3655–3625 cm^{-1} and 3460–3225 cm^{-1}, together with the narrow bands in the 1700–1550 cm^{-1} range is observed. After this process, the IR spectrum appears dominated by a broad absorption in the 3500–2500 cm^{-1} range. Weak bands associated with the stretching modes of remaining water molecules with medium strength H-bonds are still detected, and now the components at 3345 and 3035 cm^{-1}, which were also present in the hydrated sample (Fig. 6a), are more easily observed. These vibrations can be assigned to water molecules engaged in a stronger network of H-bonds, in agreement with the structure proposed above for the partially dehydrated Na-RUB-18 (Fig. 5), where the water molecules are strongly bound to the sodium ions and to the silanol-silanolate groups, giving rise to a more compact and interrelated network.

Upon heating at 100 °C, an almost complete removal of the bands related to adsorbed water molecules occurs, and a broad band at *ca.* 3600 cm^{-1}, assigned to the presence of silanols in defect positions of the Na-RUB-18 crystal structure,[20] is found along with a complex absorption in the 3200–1300 cm^{-1} range. The origin of these latter bands will be discussed in the following text.

According to Gies and co-workers,[7] and to our computational model described above, the hydrated silicate structure at rt

contains (SiOH···OSi)$^{-1}$ bridged moieties, strongly interacting *via* H-bonding. The spectroscopic features of such moieties can be deduced more clearly by examining the IR spectrum of the fully de-hydrated Na-RUB-18 (inset of Fig. 6), where all the absorptions can be attributed to silanols. Besides the band at *ca.* 3600 cm^{-1}, due to the stretching mode of defective silanols, the spectrum is characterized by the presence of three main and broad bands at *ca.* 2650, 2330 and 1815 cm^{-1}. These absorptions can be related to a strong hydrogen bond of the (SiOH···OSi)$^{-1}$ moiety, showing Fermi resonance phenomena between the OH stretching mode and the overtones (and/or combinations) of the bending modes of the same group: these effects produce three sub-bands (2650, 2330 and 1815 cm^{-1}) and two Evans windows[21,22] (at *ca.* 2490 and 2100 cm^{-1}).

The "unperturbed frequency" of the OH stretching vibration is likely to be near 2000 ± 100 cm^{-1} in the spectrum of Na-RUB-18 where the water molecules are almost completely removed (inset of Fig. 6). Interestingly, the centre of gravity of such bands is found below 2000 cm^{-1} in the spectrum of the hydrated (as-synthesised) Na-RUB-18 (Fig. 6a), the component at the lowest wavenumber being much more intense than the one at the highest wavenumber. The centre of gravity remains almost unaltered during the heating process of the Na-RUB-18 sample to 50 °C, while it appears shifted to higher wavenumbers upon heating at higher temperature, where a more intense component at 3200–2500 cm^{-1} is found in the IR spectra (Fig. 6c and d). This behaviour suggests that the de-hydration process reduces the strength of the H-bond in the silanol-silanolate bridge.

Note that very similar IR features (*i.e.* shape and intensity of the sub-bands) have been observed for the OH stretching absorption in KH(CH$_3$COO)$_2$ crystals at 90 K, where a strong hydrogen bond is responsible for the appearance of a broad component observed in the 3100–500 cm^{-1} range, with an estimated half-width of 1000 cm^{-1}. In this compound the O···O distance is 2.48 Å,[23] a very similar value to that found for Na-RUB-18.

The above interpretation of the IR spectra can be effectively supported by the theoretical models. As already mentioned, the calculations show that the interlayer water molecules form stronger H-bonds with the layer oxygen atoms in the de-hydrated than in the hydrated structure, qualitatively confirming the observed shift in the vibrational frequencies.

The analysis of the more complex pattern associated with the silanol-silanolate bridge can be compared with the harmonic frequencies computed at the ab initio level. Due to the huge computational demand of the frequency calculations with such a large unit cell (comprising 168 atoms in the hydrated and 144 atoms in the de-hydrated form), the frequencies for the silanol OH stretching were computed with CRYSTAL06 with the procedure FRAGMENT (in which the geometry optimization is performed as usual, allowing all the atoms to move, but the vibrational frequencies are computed by finite difference of gradients involving only a selection of atoms: thus the normal modes are limited to the chosen fragment, including in our case the two silicon atoms, the two oxygen atoms and the hydrogen atom of the bridge).

The OH stretching frequency for the hydrated form is found at 2087 cm^{-1}, in fair agreement with the experimental analysis,

while in the de-hydrated form the frequencies found for the two different silanol bridges (see above) are 1797 and 1418 cm^{-1}. The latter values are clearly too low, seemingly indicating a too strong H-bond in this computed structure. The O···O distances are 2.46 Å in the hydrated form (in reasonable agreement with the experimental value of 2.3 Å), and 2.41 and 2.40 Å, respectively, in the dehydrated structure.

Since the silanol-silanolate vibrational frequencies appear extremely sensitive to the bridge geometry, and to the distribution of charges nearby, which both influence the strength of the H-bond, this point was further analyzed by repeating the calculation on some smaller finite clusters, cut out of the periodic structures and re-optimized with Gaussian03. We considered the $Na_2Si_8O_{16}H_7(OH)\cdot 8H_2O$ cluster for the hydrated and $Na_3Si_{30}O_{41}H_4(OH)_3\cdot 6H_2O$ for the de-hydrated form: the structures are shown in Fig. 7. In all the cases, the vibrational modes were computed for the "central" silanol-silanolate bridge, whose chemical environment resembles that of the corresponding periodic structures; the de-hydrated cluster is larger due to the more disordered structure, which required a larger fragment to obtain a well embedded bridge. The computed frequencies are listed in Table 3, and they support the above interpretation of the experimental spectra: the OH stretches are computed in the expected range (2000 ± 100 cm^{-1} for the hydrated form, somehow higher wavenumber for the de-hydrated), and the deformations fall at frequencies compatible with the observed resonance effects.

Two main conclusions can be drawn from these calculations: i) the broad band observed in IR spectra around 2000 cm^{-1}, and

Table 3 Harmonic frequencies (cm^{-1}) computed at the ab initio level for the (SiOH···OSi)$^{-1}$ moiety in the clusters shown in Fig. 7

	Si$_8$	Si$_{30}$
OH stretching	2056	2151
in-plane deformation	1422	1420
out-of-plane deformation	1198	1340

attributed to the stretching of the silanol-silanolate bridge, appears much more compatible with a localized H-bond, though very strong, rather than a shared hydrogen in a single-well potential; ii) the O···O distance is not the only relevant parameter affecting the H-bond strength (as shown by the very different computed frequencies on Si$_8$ and Si$_{32}$ clusters), but also the local distribution of counterions and solvating water can modify substantially the potential energy shape and the vibrational pattern.

Conclusions

The partial loss of the interlayer water molecules upon heating at around 75 °C causes major structural changes in the layer silicate Na-RUB-18: in this paper the structure of the partially de-hydrated β-Na-RUB-18 is described for the first time, on the basis of TGA, temperature dependent XRPD, IR spectra, and ab initio calculations. Moreover, the local structure of the silanol-silanolate moieties observed in both the hydrated and the de-hydrated forms is described in detail.

Besides the novelty of the proposed structures, the method adopted can be of more general interest and utility: we show that a sound combination of crystallographic, spectroscopic and computational techniques can be very efficient and reliable to refine structures which are not fully accessible to standard X-ray analysis. Powder XRPD spectra recorded at various temperatures indicate that the Na-RUB-18 structure undergoes a deep yet reversible phase transformation upon heating at around 75 °C, while an irreversible collapse of the structure is observed above 100 °C. The XRPD of the as-synthesized silicate corresponds to that obtained by Gies and co-workers, while at 75 °C the layers get markedly closer and the crystallinity is preserved, even if the quality of the data does not allow a full resolution of the new phase. On the other hand, TGA analysis shows that two water molecules per Na$^+$ ion are lost when the silicate is heated at 75 °C, followed by a complete de-hydration at around 120 °C.

A theoretical model of the hydrated, as-synthesized Na-RUB-18, optimized by DFT with periodic boundary conditions and in fair agreement with the structure recently published, shows that two water molecules in each solvation shell (in apical position) are less strongly bound, and they are likely to be lost in the first de-hydration. Another structure has been optimized in the same conditions, modeling the de-hydrated β-Na-RUB-18 system: as expected, the interlayer distances are reduced (in very good agreement with the XRD findings) and the Na$^+$ ions are found to move closer to the silicate layers in order to restore their coordination shell.

More insights about the changes induced by the de-hydration are obtained from variable temperature IR experiments: in the hydrated form the spectra reveal water molecules engaged in
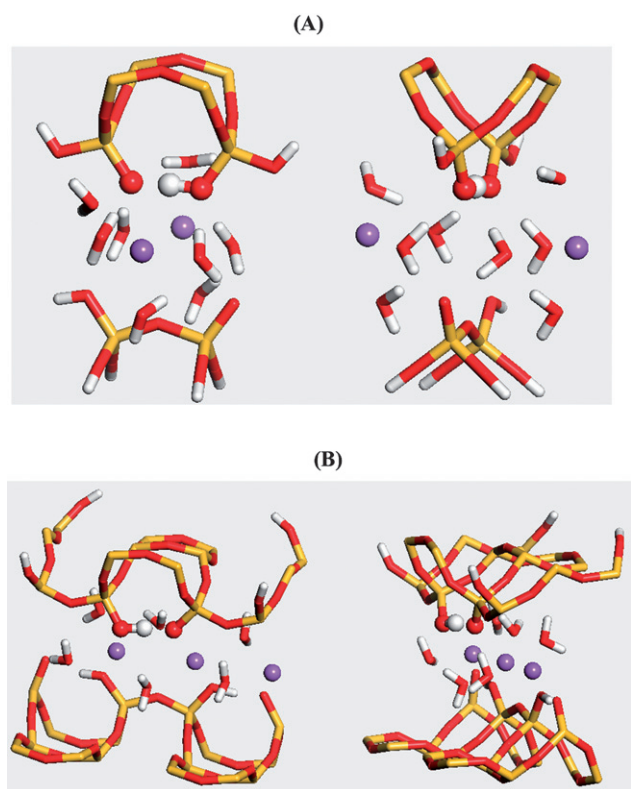

Fig. 7 (A) $Na_2Si_8O_{16}H_7(OH)\cdot 8H_2O$ cluster used to model the silanol bridge in the hydrated structure. (B) $Na_3Si_{30}O_{41}H_4(OH)_3\cdot 6H_2O$ cluster used to model the silanol bridge in the de-hydrated structure.

H-bonds of different strengths (thus confirming the difference between apical and equatorial positions), while in the partially de-hydrated form the H-bonds appear stronger, in agreement with the structure optimized theoretically.

An important point concerns the nature of the H-bond between silanol and silanolate groups on the layer surface, which has been debated in the literature. The IR spectra analysis shows that the stretching of this H-bond is associated with a large feature in the 3200–1300 cm^{-1} range, showing Fermi resonance phenomena with the overtones (and/or combinations) of the bending modes of the same group: these effects produce three sub-bands and two Evans windows. The centre of gravity of such bands falls at 2000 ± 100 cm^{-1} in the hydrated form, and is slightly shifted towards higher frequencies in the de-hydrated form, thus suggesting that the silanol-silanolate H-bond weakens in the latter structure. These frequencies are reproduced by ab initio calculations performed on small clusters cut out of the periodic structures in order to reproduce the chemical environments of the silanol-silanolate bridge in the hydrated and de-hydrated forms. Experimental and theoretical findings agree in indicating a strong H-bond in the silanol-silanolate bridge, rather than a shared hydrogen in a single-well potential.

Acknowledgements

References

1 K. Kosuge and A. Tsunashima, *J. Chem. Soc., Chem. Commun.*, 1995, 2427.

2 W. Schwieger, G. Lagaly, *Handbook of layered materials*, edited by S. M. Auerbach, K. A. Carrado, and P. K. Dutta, Marcel Dekker, Inc., New York, 2004.

3 K. Kosuge and P. S. Singh, *Chem. Mater.*, 2000, **12**, 421.

4 K. H. Bergk, W. Schwieger and M. Porsch, *Chem. Technol.*, 1987, **11**, 459.

5 M. Borowski, O. Kovalev and H. Gies, *Microp. Mesop. Mater.*, 2008, **107**, 71.

6 S. Vortmann, J. Rius, S. Siegmann and H. Gies, *J. Phys. Chem. B*, 1997, **101**, 1292.

7 M. Borowski, I. Wolf and H. Gies, *Chem. Mater.*, 2002, **14**, 38.

8 U. Brenn, H. Ernst, D. Freude, R. Herrmann, R. Jähnig, H. G. Karge, J. Kärger, T. König, B. Mädler, U.-T. Pingel, D. Prochnow and W. Schwieger, *Microp. Mesop. Mater.*, 2000, **40**, 43.

9 http://www.rigaku.com.

10 T. Bredow, G. Geudtner and K. Jug, *J. Comput. Chem.*, 2001, **22**, 861.

11 R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, Ph. D'Arco, M. Llunell *CRYSTAL06*, 2006, University of Torino.

12 A. D. Becke, *Phys. Rev. B*, 1988, **38**, 3098.

13 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299; W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.

14 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

15 E. Borissenko, F. Porcher, A. Bouche, C. Lecomte and M. Souhassou, *Microp. Mesop. Mater.*, 2008, **114**(1–3), 155.

16 G. Martra, N. Damilano, S. Coluccia, H. Tsuji and H. Hattori, *J. Chem. Soc., Faraday Trans.*, 1995, **91**(17), 2961.

17 P. F. Bernath, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1501.

18 D. Eisenberg and W. Kauzmann, *The structure and properties of water*, Oxford University Press, London, 1969.

19 A. Millo, Y. Raichlin and A. Katzir, *Appl. Spectroscopy*, 2005, **59**, 460.

20 G. B. Superti, E. C. Oliveira, H. O. Pastore, A. Bordo, C. Bisio and L. Marchese, *Chem. Mater.*, 2007, **19**, 4300.

21 D. A. Othen, O. Knop and M. Falk, *Can. J. Chem.*, 1975, **53**, 3837.

22 J. C. Evans, *Spectrochim. Acta*, 1960, **16**, 994.

23 A. Novak, *Hydrogen Bonding in Solids. Correlation of Spectroscopic and Crystallographic data, from Structure and Bonding*, Vol 18, Springer-Verlag, Berlin-Heidelberg-New York, 1974.