Rietveld structure refinement of NH$_4$-exchanged natural chabazite

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Abstract: In this work the results of the X-ray Rietveld structure refinement of a natural and the corresponding NH$_4$-exchanged chabazite from Nova Scotia (Canada) are exposed. Experimental data were collected using a laboratory powder diffractometer equipped with copper tube and graphite crystal monochromator. The outcome of this crystal-structure study is useful for (i) understanding the structure modifications induced by the NH$_4^+$ exchange; (ii) understanding the physical-chemical and technological properties of NH$_4$-chabazite, a zeolite vastly used for industrial applications; (iii) understanding the mechanism of proton conductivity of the NH$_4$-exchanged zeolites, precursors of catalytically active H$^+$ forms. The position and orientation of the NH$_4^+$ ion were initially refined using the rigid body model and later with the aid of soft constraints. The coordination number of the ammonium ion is 9 with two equally possible and mutually exclusive configurations. One coordination environment includes 3 oxygen atoms O3, 3 oxygen atoms O4, and 3 H$_2$O molecules W2a. The other environment includes 3 oxygen atoms O3, 3 oxygen atoms O4, and 3 H$_2$O molecules W3. As already shown for other NH$_4$-zeolites, the N-O distances are larger than the N-H$_2$O distances. The local geometry of the ammonium ion points to a monodentate configuration. A bidentate configuration of the hydrogen bonds for NH$_4^+$ is also possible if the long H2...O3 separation is considered to be at bond distance. For industrial and technological applications, knowledge of the local environment of NH$_4^+$ in the cavities of zeolites is important. Weak hydrogen bonds with framework oxygen atoms implies that the ammonium molecule can be easily exchanged or desorbed. This property is attractive for agronomy, horticulture and soil remediation where zeolite can be added to chemical fertilizers to improve the soil's chemical and physical properties for plant growth, to increase fertilizer efficiency and to reduce the leaching of nutrients, to reduce the dissolution rate of a soluble fertilizer *via* ion exchange or combination of mineral dissolution and ion exchange, and to act as remediation agents in soils.

Key-words: ammonium ion, chabazite, Rietveld refinement, chemical environment, industrial applications.

Introduction

Considerable attention has been paid to the NH$_4$-forms of natural and synthetic zeolites, precursors of catalytically active H$^+$ forms (Moroz *et al.*, 2002). Of great interest is the high proton conductivity of NH$_4$-forms. Unfortunately, the mechanism of such conductivity has not been discovered, mainly because of a lack of data on the localization and mobility of molecules and ions in crystal cavities. To our knowledge, there are only few structural investigations on anhydrous (Stuckenschmidt *et al.*, 1998; Moroz *et al.*, 1998; Mortier, 1983; Pearce *et al.*, 1980) and hydrated (Moroz *et al.*, 2002; Yang & Armbruster, 1998; Meneghiniello *et al.*, 2000; Gualtieri, 2000; Alberti *et al.*, 1999) NH$_4$-exchanged or NH$_4$-synthetic zeolites.

Natural zeolites are vastly used for large-scale applications such as animal nutrition (Pond, 1995; Bergero *et al.*, 1997a; Yannakopoulos *et al.*, 2000), wastewater purification (Kalló, 1995; Passaglia *et al.*, 1999), aquaculture (Piper & Smith, 1984; Bergero *et al.*, 1997b), and agriculture (de' Gennaro *et al.*, 1997; Ming & Allen, 2000). To this aim, zeolite-rich rocks (zeolitites) with high (~ 70 wt %) chabazite content are appre-

ciated. Chabazite, with framework type CHA, space group $R\overline{3}\,m$, and a_H = 13.85 Å, c_H = 14.94 Å in hexagonal setting (Smith *et al.*, 1964), has a tetrahedral framework composed of parallel layers of double 6-membered rings in a ABC sequence. Chabazite has cavities of different size (the wider channel is bonded by 8-membered rings) which may host extraframework cations and H$_2$O molecules. Ca, Na and K are most frequently found as exchangeable cations in natural crystals. Although the topological symmetry of the framework is rhombohedral, the real symmetry is likely lower (triclinic) with partial Si/Al ordering in the tetrahedral sites. Mazzi & Galli (1983) suggested that chabazite may have randomly arranged domains with (Si,Al) ordering. Thus, the overall rhombohedral symmetry should be a consequence of complex twinning. The single-crystal structural data of the cation-exchanged forms of both hydrated and dehydrated chabazite at room temperature available in the literature, allowed to identify four possible sites for the extraframework cations (Alberti *et al.*, 1982). Often extraframework cations and H$_2$O molecules are disordered.

Due to its properties, chabazite can be succesfully utilized for a wide range of industrial and technological appli-

cations. Among others, chabazite has a large capability to host NH_4^+ by cation exchange. Consequently, it is possible to regulate the digestive process in animals, to correct the physical and chemical properties of soils, and to reduce the dispersion of ammonium ion in the environment. The filtration of NH_4-polluted waste waters using zeolite-rich filters yields a NH_4^+ content well below the limit imposed by current regulations. Moreover, the NH_4-containing zeolites can be recycled as active fertilizers with a low rate of NH_4^+ release with a promising use in agricultural and green-house soils in place of synthetic fertilizers. This permits a lower spread of nitrogen compounds at the soil surface (rivers, lakes, sea) and inside the hydrologic system.

Despite the importance of this natural zeolite species, especially in the natural and NH_4-exchanged form, to our knowledge there is actually only one paper found in the literature that describes the structure of NH_4-chabazite (Moroz *et al.*, 2002) and few more about cation-exchanged forms of chabazite (Smith *et al.*, 1964; Butikova *et al.*, 1993; Butikova *et al.*, 1994).

The single-crystal study of NH_4-chabazite described by Moroz *et al.* (2002) does not report atomic coordinates and site populations/adp's. On page 596, the authors state that "*Full data on the structure will be reported in a separate publication*" which has never been published. Thus, the current study fills this gap of knowledge.

Because a thorough understanding of cation exchange and the physical-chemical and technological properties of NH_4-chabazite is of vast importance not only for basic science but also for the proper and profitable use of chabazite for different industrial needs, this work is an attempt to provide structural details of natural and the NH_4-exchanged chabazite samples using the Rietveld method.

Experimental

The chabazite crystals selected as starting material were white, transparent rhombohedra occurring in fractures of a basaltic rock from Wasson's Bluff, Two Islands (Nova Scotia, Canada). The chemical composition was obtained by the average of several microprobe point-analyses performed on the rim and core of five crystals. Electron probe micro-analysis (EPMA) was performed using an ARL-SEMQ instrument operating in wavelength-dispersive mode with 15 kV and 20 nA beam current and a defocused beam of 30 μm in diameter. Natural and synthetic silicates were used as standards, and on-line data processing was done using the PROBE program (Donovan, 1995). Microprobe data were normalized to 100 wt% using the weight loss of the thermogravimetric (TG) analyses.

Cation exchange was carried out in batch using the "static" run mode. A pyrex tube containing 50 mg of chabazite and 50 cc of 1N NH_4^+ solution (zeolite/solution 1:1000) was sealed, placed in an oven at 70 ± 5 °C and slowly oscillated for 2 weeks with one renewal of the exchanging solution after the first week. The exchanging solution was prepared with Baker "suprapur" NH_4Cl and deionised water. The exchangeable cation contents of the chabazite before (natural) and after the exchange process were determined by atomic absorption spectrophotometry (AAS) using a Perkin Elmer (Analyst 100) instrument.

For IR spectroscopy, the chabazite samples were equilibrated at 30 °C and relative humidity of *ca.* 35%. Pellets were prepared using the KBr wafer technique (3 mg of sample powder and 97 mg of KBr) and data were collected at room temperature between 600 and 3800 cm^{-1} using a Bruker spectrometer mod. IFS 113 V with a resolution of 1 cm^{-1}.

The crystal structures of both the natural and the NH_4-exchanged chabazite were refined with the powder Rietveld method. In principle, it could have been possible to refine the structures using the single-crystal method, which in general yields more accurate structural results. However, the single-crystal method was not used because: (i) we noticed that the degree of exchange was not uniform from crystal to crystal. Consequently, only refinement of a number of crystals would have given a statistically sound picture for the crystal structure of NH_4-chabazite; (ii) After the intense cation-exchange, most of the crystals were damaged and were not suitable for a single-crystal study.

For the Rietveld refinements of both the natural and NH_4-exchanged forms, the powder (with average particle size lower than 5 μm) was side loaded to minimize preferred orientation on a 2 mm thick flat Al holder. Due to the small amount of sample powder, the holder was not totally filled. This is likely the reason because aluminum holder peaks are observed in the patterns. Prior to the measurements the powder samples were equilibrated at 30 °C and relative humidity of *ca.* 35%. Data collection was performed at *ca.* 25 °C with relative humidity of *ca.* 40%. Data collection for the natural sample was performed using a Philips PW 1710 instrument with a conventional Bragg-Brentano (BB) parafocusing geometry equipped with Cu tube and secondary beam pyrolitic graphite crystal monochromator. Data were collected in two angular regions: (i) 7–17 °2θ with steps of 0.02° and 20 s/step, a divergence slit of 1/4° and a receiving slit of 0.1 mm; (ii) 17–100 °2θ with steps of 0.02° and 10 s/step, a divergence slit of 1° and a receiving slit of 0.2 mm.

Data collection for the NH_4-exchanged sample was performed using an X'Pert Pro Panalytical θ-θ BB diffractometer (Cu radiation), equipped with an RTMS detector. Data were collected in two angular regions: (i) 7–17 °2θ with a detector aperture of 2.12° and virtual 200 s per step of 0.0167273°, a divergence slit of 1/8° and a receiving slit of 0.1 mm; (ii) 17–100 °2θ with a detector aperture of 2.12° and virtual 100 s per step of 0.0167273°, a divergence slit of 1/2° and a receiving slit of 0.1 mm.

The refinements were performed using the GSAS package (Larson & Von Dreele, 1999) and the EXPGUI graphical interface (Toby, 2001). For each structure refinement, the two data sets were treated independently in GSAS. The treatment of multiple data sets is a common procedure in GSAS which permits to independently refine scale factors, background parameters, zero shifts, and profile function coefficients for each data set and to refine the structural parameters using each data set as dependent observation.

Starting atomic coordinates for the structural models were taken from Alberti *et al.* (1982) and refined in space group $R\overline{3}m$. The background profile was fitted with a Chebyshev polynomial function with a different number of coefficients

depending on the angular range (9 for the 7–17 °2θ region and 3 for the 17–100 °2θ region, respectively). The profile of the diffraction peaks was modelled using a pseudo-Voigt function with one Gaussian and two Lorentzian coefficients. The refinement of atomic coordinates, site occupancies for extra-framework positions, and isotropic atomic displacement parameters (adp's) has been performed with soft constraints (with an initial weight of 2500) on the tetrahedral bond lengths which were used as additional observations in the earlier stages of the refinement and the weights were progressively reduced to zero. The distinction of NH_4^+ and H_2O by X-ray diffraction is troublesome due to the similar scattering factors, large adp's, and large distances to framework oxygen atoms (*ca.* 2.8 Å). A reliable discrimination was possible by comparison with the structure refinement of the same sample in its natural form. This strategy was successfully adopted by Yang & Armbruster (1998) for NH_4-exchanged heulandite. In addition, in the first cycles of the refinement, rigid body units were used to model NH_4^+ ions. The use of rigid bodies has a number of advantages. First of all, it permits to include hydrogen atoms in the refinement whose contribution to the profile is clearly measurable (Lightfoot *et al.*, 1993); it drastically reduces the number of refined parameters, and allows their refinement with much higher accuracy (Schreinger, 1963). Shift and rotational degree of freedom of the NH_4^+ group, the N-H, and H-H distances were constrained using weights. An overall adp was refined for each rigid body unit according to the strategy reported by Dinnebier (1999). In the last cycles of refinement, the rigid body model was substituted by corresponding atomic coordinates (N, H1 and H2) and soft constraints on the N-H and H-H bond distances. The initial weight for soft constraints (1000) was progressively decreased to 1 in the last series of refinement cycles. With this combined strategy, esd's on the bond distances between the atoms of the ammonium ion tetrahedron may also be calculated.

Results

The chemical formula of the natural chabazite has been derived from the EPMA and TG analyses. The H_2O content corresponds to the weight loss of the sample at 800 °C,

$$(Ca_{1.32}Sr_{0.10}Na_{0.13}K_{0.45})[Si_{8.55}Al_{3.45}O_{24}] \; 11.30 \cdot H_2O$$

The reliability of the chemical formula is supported by the very low (0.9%) charge balance error. The concentrations (%) of the exchangeable cations determined by AAS are very similar to those from EPMA (in parenthesis): Ca 5.30 (5.24), Sr 0.70 (0.84), Na 0.40 (0.30), K 1.60 (1.74). Following the exchange with NH_4^+, chabazite crystals analysed by AAS showed 0.21% of Ca, 0.16% of K and traces of Sr and Na. The chemical results indicate nearly complete exchange of the original extraframework cations by NH_4^+. Consequently, in order to balance the anionic charge of the framework, the chemical formula of the NH_4-exchanged chabazite should likely be:

$$((NH_4)_{3.30}Ca_{0.05}K_{0.05})[Si_{8.55}Al_{3.45}O_{24}] \; 9.2 \cdot H_2O$$

The H_2O content corresponds to a total weight loss of 15.2 wt% of the sample kept at 250 °C for 1 h. The TG analysis
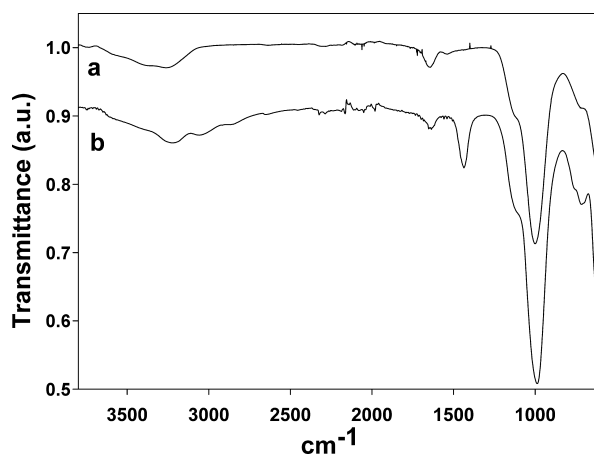

Fig. 1. The FTIR patterns of the natural (a) and NH₄-chabazite (b) samples in the range 600–3800 cm⁻¹.

Table 1. The agreement indices for the final least squares cycles of the refinements, the cell constants and volume.

	Natural chabazite	NH₄-chabazite
Merged* total number of data points	4360	4483
Number of reflections first pattern˟	6	6
Number of reflections second pattern˟	790	652
R(F²) first pattern	0.0671	0.0877
R(F²) second pattern	0.1539	0.1384
Merged χ² for 25 refined variables	1.54	3.91
Merged R$_{wp}$	0.1688	0.1713
Merged R$_p$	0.1265	0.1406
Merged R$_{wp}$ (background subtracted)	0.1776	0.1813
Merged R$_p$ (background subtracted)	0.1344	0.1493
Merged Durbin Watson Statistics	0.966	0.975
a_R (Å)	9.38749(8)	9.41709(11)
α(°)	94.379(1)	94.678(1)
a_H (Å)	13.7734(1)	13.8502(1)
c_H (Å)	14.9841(1)	15.0313(1)
V(Å³)	819.635(21)	826.288(27)

*Merge of the first and second pattern
˟first pattern = 7–17 °2θ region; second pattern = 17–100 °2θ region

shows that above 250 °C, the weight loss, attributed to the loss of ammonia, is observed up to 800 °C. The observed weight loss of about 6 wt% is in agreement with the expected NH_4^+ content.

The FTIR spectra of the natural (a) and NH_4-exchanged (b) chabazites are reported in Fig. 1. The characteristic absorption bands of NH_4^+ are: ν3(*f*2) at 3130–3140 cm⁻¹, ν2(*e*) at 1640–1645 cm⁻¹, and a split ν4(*f*2) at 1465 and 1406–1407 cm⁻¹ (Gualtieri, 2000). ν3(*f*2) and ν2(*e*) vibrations are partly overlapped with vibrations typical of chabazite as they are present even in the natural form. Clearly ν4(*f*2) vibration typical of the ammonium ion is observed only in the exchanged sample.

The agreement indices for the final least squares cycles of the refinements are reported in Table 1 together with the unit-cell parameters. In Fig. 2 the observed (crosses) and calculated (continuous line) patterns, and difference curve (bottom line) of the refinements of natural and NH₄-chaba-
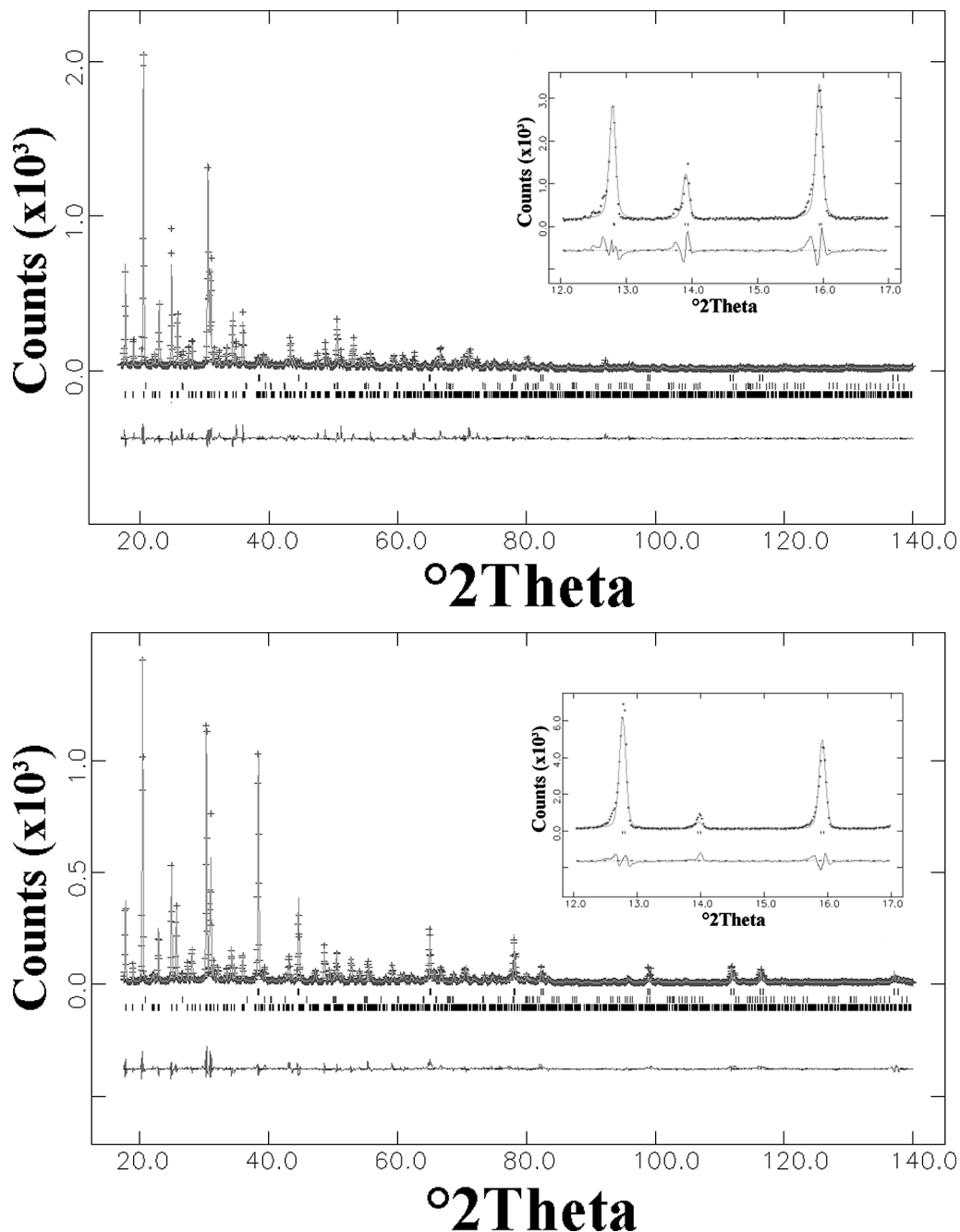
Fig. 2. Observed (crosses) and calculated (continuous line) patterns with the relative difference curve (bottom line) of the refinements of the natural (a) and NH_4-chabazite (b). The plot relative to the refinement in the low-angle region (12–17 °2θ) is depicted in the box. In the natural sample, the additional markers belong to the aluminum holder refined as additional phase. NH_4-chabazite sample, only the two major peaks of the aluminum holder were visible and the relative region was excluded from the calculation.

zite samples are exposed. Table 2 reports the refined structural data of the framework and extraframework content of the natural and NH_4-exchanged chabazite samples. Table 3 reports the tetrahedral bond distances, tetrahedral angles, and interactions of the NH_4^+ with the framework oxygen atoms and water molecules for the NH_4-exchanged chabazite.

In the natural sample, the agreement of the refined Ca content (*ca.* 1.21 a.f.u., atoms per formula unit) with the measured Ca content (1.32 a.f.u.) is excellent whereas the refined K content (*ca.* 0.79 a.f.u., atoms per formula unit) is overestimated with respect to the measured K content (0.45 a.f.u.). This is probably due to Sr and Na which possibly occupy the same crystallographic site, C2, and were not refined using mixed scattering curves. A slight underestima-

tion of the refined number of H_2O molecules (10.38 a.f.u. *vs.* 11.30 a.f.u. from the TG analysis) was observed. According to Bish & Carey, 2000), the systematic difference between the XRD- and TGA-derived water contents likely result from the difficulty in locating all H_2O molecules due to positional disorder and large adp's for H_2O.

In the NH_4-exchanged chabazite, N was refined in site C2a (2 a.f.u.). C2a shifted along the 3-fold axis with respect to site C2 described in Alberti *et al.* (1982). Thus, there is an underestimation with respect to the N content (*ca.* 2.59 a.f.u. if we consider a theoretical NH_4^+ content of 3.30 a.f.u.) calculated from the chemical formula. Additional density attributed to N was refined for site C1 (population of 29.5 %) is not sufficient to fill the gap between the N content deter-

Table 2. The refined structural data of the framework and extraframework content of the natural and NH$_4$-exchanged chabazite samples.

Site	x	y	z	Site symmetry[δ]	Site population	U$_{iso}$
Natural chabazite						
T(Si/Al[ˣ])	0.1038(4)	0.3315(5)	0.8758(6)	1	1[ℑ]	0.014(5)
O1	0.2620(4)	–0.2620(4)	0	2(±0)	1[ℑ]	0.036(4)
O2	0.1527(3)	–0.1527(3)	0.5	2(±0)	1[ℑ]	0.021(4)
O3	0.2515(2)	0.2515(2)	0.8954(7)	M(±0)	1[ℑ]	0.011(3)
O4	0.0179(5)	0.0179(5)	0.3096(5)	M(±0)	1[ℑ]	0.041(5)
C2(K)	0.2205(7)	0.2205(7)	0.2205(7)	3M(111)	0.39(5)	0.054(5)
C3(Ca)	0.4224(8)	0.4224(8)	0.4224(8)	3M(111)	0.21(3)	0.042(8)
C4(Ca)	0.5787(5)	0.5787(5)	0.2441(5)	M(±0)	0.13(4)	0.041(8)
W1(O)	0.5	0.5	0	2/M(±0)	0.88(4)	0.089(7)
W2(O)	0.2415(7)	0.2415(7)	0.5987(6)	M(±0)	0.20(3)	0.039(6)
W3(O)	0.2008(8)	0.3410(5)	0.4941(6)	1	0.33(5)	0.038(7)
W4(O)	0.3601(9)	–0.3601(9)	0.5	2(±0)	0.24(4)	0.029(7)
W5(O)	0.5900(5)	0.5900(5)	0.3160(6)	M(±0)	0.17(4)	0.027(6)
W6a(O)	0.3063(7)	0.3063(7)	0.3063(7)	3M(111)	0.45(6)	0.057(5)
NH$_4$-chabazite						
T(Si/Al[ˣ])	0.1026(5)	0.3299(5)	0.8792(4)	1	1[ℑ]	0.019(5)
O1	0.2625(4)	–0.2625(4)	0	2(±0)	1[ℑ]	0.027(4)
O2	0.1477(5)	–0.1477(5)	0.5	2(±0)	1[ℑ]	0.015(5)
O3	0.2533(3)	0.2533(3)	0.8956(4)	M(±0)	1[ℑ]	0.012(5)
O4	0.0276(4)	0.0276(4)	0.3128(5)	M(±0)	1[ℑ]	0.025(7)
C1	0	0	0	–3M(111)	0.29(3)	0.070(7)**
C2a(N)*	0.2497(7)	0.2497(7)	0.2497(7)	3M(111)	1[ℑ]	0.070(7)
H1*	0.184(2)	0.184(2)	0.184(2)	3M(111)	1[ℑ]	0.088(9)
H2*	0.305(3)	0.305(3)	0.192(2)	M(±0)	1[ℑ]	0.088(9)
W1(O)	0.5	0.5	0	2/M(±0)	0.48(2)	0.047(8)
W2a(O)	0.2764(9)	0.2764(9)	0.5305(8)	M(±0)	0.32(3)	0.053(8)
W3(O)	0.2017(7)	0.3452(5)	0.5146(6)	1	0.27(5)	0.042(7)
W4(O)	0.3636(7)	–0.3636(7)	0.5	2(±0)	0.18(4)	0.094(9)
W5a(O)	0.5376(6)	0.5376(6)	0.2789(6)	M(±0)	0.33(5)	0.050(9)

[δ]as defined in GSAS [26]

[ˣ]only the scattering curve of Si was used in the refinement of the T site

*refined with a rigid body model

[ℑ]site populations which refined very close (within the standard deviation) to unity were kept fixed.

**fixed to the refined value of the other N atom species in site C2a.
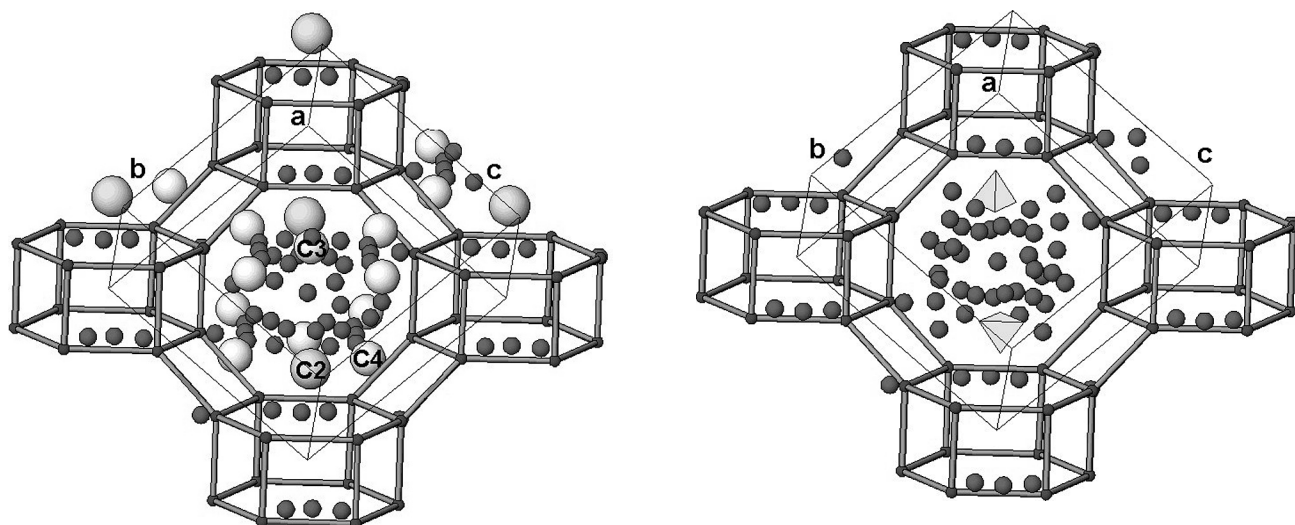

Fig. 3. Plots of the refined structure of the natural (a) and NH$_4$-chabazite (b) samples. Legend: dark small spheres = water molecules; large empty spheres = extraframework cations in the natural form; tetrahedra = ammonium ions in the NH$_4$-exchanged form.

Table 3. The tetrahedral bond distances and interactions of the NH_4^+ with the framework oxygen atoms and water molecules for the NH_4-exchanged chabazite.

	Natural chabazite	NH_4-chabazite
T-O1	1.622(3)	1.633(4)
T-O2	1.660(4)	1.668(2)
T-O3	1.631(2)	1.645(2)
T-O4	1.628(3)	1.630(2)
T-O mean	1.6352	1.6440
O1-T1-O2	107.7(4)	106.1(5)
O1-T1-O3	112.3(5)	112.0(6)
O1-T1-O4	107.6(4)	113.0(7)
O2-T1-O3	106.2(5)	106.2(5)
O2-T1-O4	115.7(7)	113.0(4)
O3-T1-O4	107.4(4)	106.5(5)
mean	109.5	109.5
T1-O1-T1	146.2(3)	143.3(2)
T1-O2-T1	142.5(3)	145.3(3)
T1-O3-T1	147.9(2)	146.1(4)
T1-O4-T1	149.2(4)	143.3(4)
mean	146.4	144.5
C2-O3	3.12(3) x3	
C2-O4	2.80(2) x3	
C2-W2	3.53(3) x3	
C2-W3	2.75(2) x6	
C2-W6a	1.28(3)	
C2a-O3		3.34(4) x3
C2a-O4		2.97(3) x3
C2a-W2a		2.63(4) x3
C2a-W3		2.67(3) x6
C3-W2	2.98(2) x3	
C3-W3	2.32(2) x6	
C3-W4	2.24(2) x6	
C3-W5	2.45(2) x3	
C3-W5	2.47(2) x3	
C3-W6a	1.73(3)	
C4-O2	2.85(3) x2	
C4-O3	2.65(2)	
C4-W1	2.39(3)	
C4-W2	3.18(3) x3	
C4-W3	2.30(3) x2	
C4-W3	3.09(5) x2	
C4-W4	1.46(1) x2	
C4-W5	0.67(1)	
C4-W5	2.50(2) x2	
W2-W3	1.45(1) x2	
W2a-W3		1.00(1) x2
W2a-W4		2.16(4) x2
W3-W3	1.93(2)	1.99(3)
W3-W3	2.10(2)	
W3-W5a		1.88(3)
W3-W6a	2.10(2)	
W4-W4	1.92(2) x2	1.89(2) x2
W4-W5	1.09(1) x2	
W4-W5a		1.27(1) x2
W5-W5	2.17(2)	

mined by the structure refinement and that expected from the chemical analysis. Hence, it is likely that additional ammonium ions are randomly dispersed in the zeolite cavities with low population preventing their determination in the difference Fourier maps. N refined at the origin is questionable as it is well known that density refined in such high symmetry sites could be an artefact of the Rietveld refinement. In this frame, the details relative to such a position will not be further discussed in the section which describes the structural features.

The refined number of H_2O molecules is about 9.65 a.f.u. and nicely matches the calculated value of 9.2 a.f.u. Ion exchange yielded a complete removal of Ca from sites C3 and C4 which are empty in NH_4-chabazite.

Figure 3 displays a sketch of the refined structure of the natural and NH_4-chabazite samples. For both the natural and NH_4-chabazites, unusually short bond distances observed in Table 3 indicate that the two involved crystallographic sites cannot be simultaneously occupied by the two atomic or molecular species. This is plausible because the occupancy of each of the involved site is partial and invariably lower than 0.5 (see Table 2).

Concerning the hydrogen bonding between the protons of NH_4^+ and the O atoms of the framework and H_2O, Table 4 reports selected hydrogen bond distances involving the ammonium ion in site C2a.

Discussion

Ammonium exchange induced an increase of the unit-cell volume (Table 1) in agreement with NH_4-exchanged phillipsite (Gualtieri, 2000), stilbite (Alberti *et al.*, 1999), and barrerite (Martucci *et al.*, 2000). Ion exchange did not produce strong framework distortions. In fact, the average T-O distance is nearly unchanged in the ion-exchanged form (1.635 Å and 1.644 Å in the natural and NH_4-exchanged chabazite, respectively) and the mean T-O-T angles are only slightly different (Table 3).

Although the interaction of NH_4^+ in C2a with oxygen atoms seems to generate only minor distortions of the framework, a lengthening of the T-O3 distance in the NH_4-exchanged form compared to the natural one was observed (Table 3). This is likely due to the increase of the population of site C2a (site occupancy 100% *vs.* a site occupancy of 39% in the natural form). Thus, the charge over-saturation on O3 is partly reduced by increasing the corresponding T-O distance. In addition, also the C2a-O3 distance increases in the NH_4-exchanged form in agreement with the conclusions reported in Moroz *et al.* (2002).

Figure 4 illustrates the position and orientation of the NH_4^+ ion in the chabazite cage in two different orientations. The rigid body model allowed to locate two distinct positions for the protons of the ammonium ion, H1 and H2. H1 on the 3-fold axis forms one of the tetrahedral corners. The three remaining corners are formed by the three equivalent H2 positions placed on the mirror plane perpendicular to the 3-fold axis. N is at bond distance with 6 framework oxygen atoms (O3 and O4) and 9 H_2O molecules (W2a, shifted with respect to the W2 position reported by Alberti *et al.* (1983),

and W3). Although not clearly stated in the paper, it appears that Moroz *et al.* (2002) refined the ammonium ion in C2 with a population of 49 % with weak bonds to the framework O atoms in agreement with our results. Moroz *et al.* (2002) also report a N(C2)-W3 distance of 2.77 Å which is in very good agreement with the value calculated here (2.67(3) Å in Table 3). The coordination number of the ammonium ion is 9. There are two possible and mutually exclusive configurations because of the site symmetry (see the short distance W2a-W3 of 1.00(1) Å). One coordination environment includes 3 oxygen atoms O3, 3 oxygen atoms O4, and 3 H$_2$O molecules W2a. The other one includes oxygen atoms O3, 3 oxygen atoms O4, and 3 H$_2$O molecules W3. For the latter, the site multiplicity would be six but short separations W3-W3 of 1.99(3) Å prevent simultaneous occupation of all six sites. Consequently, the H$_2$O molecules (site population of 27 %) are distributed over 3 out of the 6 W3 sites and the coordination of the ammonium ion is consequently 9. Thus, the coordination number is comparable to those reported for heulandite (Yang & Armbruster, 1998) for which 8-fold to 10-fold coordination is reported for three distinct NH$_4^+$ sites.

We have confirmed the observation made for other NH$_4$-zeolites: the N-O distances are larger than the N-H$_2$O distances because H$_2$O molecules have more freedom to approach the ammonium ions and minimise the electrostatic energies of the whole geometrical configuration with respect to the ammonium ions (and extraframework cations) that must be located in the equilibrium centre of negative charges of the framework as inferred by Yang & Armbruster (1998). In agreement with the results reported for phillipsite (Gualtieri, 2000), the average bond lengths involving hydrogen atoms of NH$_4^+$ reported in Table 3 seem to indicate that hydrogen bonds formed by acceptor H$_2$O oxygen atoms are stronger than those formed by acceptor framework oxygen atoms as already postulated by Yang & Armbruster (1998).

The geometry of the local chemical environment of the ammonium ion, for which mono-, bi-, tri-dentate or even more complex combinations might be formed (Zecchina *et*

Table 4. Selected hydrogen bond distances involving the ammonium ion in site C2a for NH$_4$-exchanged chabazite.

N-H⋯B*	d_{N-H}	$d_{H⋯B}$	$d_{N⋯B}$
C2a-H2⋯O3	0.94(3)	2.79(2)	3.34(4) x3
C2a-H1⋯O4	0.97(1)	2.46(1)	2.97(3) x3
C2a-H2⋯W2a x2	0.94(3)	2.25(2)	2.63(4) x3
C2a-H2⋯W3	0.94(3)	1.97(2)	2.67(3) x6
C2a-H2⋯W3	0.94(3)	2.64(2)	2.67(3) x6

*oxygen atom of the framework or of a water molecule

al., 1997), indicates that stable adducts are apparently formed between NH$_4^+$ and the Brönsted sites. A monodentate configuration has one hydrogen atom out of four that interacts with one framework oxygen, bidentate has two out of four hydrogen atoms interacting with two different framework oxygen atoms, and so on. Table 4 shows that the ammonium ion is linked to the framework *via* the hydrogen bonding H1...O4 (2.461 Å) and H2...O3 (2.793 Å). Hence, if only the short H1...O4 bond is considered (Fig. 4a), a monodentate configuration for NH$_4^+$ is obtained. A bidentate configuration for NH$_4^+$ is also possible if the long H2...O3 bond is considered. Moroz *et al.* (2002) seem to support the bidentate configuration as they postulate two weak H-bonds with the framework oxygen atoms for site N2.

Although the resolution is poor, the FTIR pattern of the NH$_4$-exchanged chabazite in Fig. 1 seems to point to a monodentate structure of the ammonium ion. In fact, all the absorption bands attributed to vibrations of the NH$_4^+$ molecule observed for a monodentate structure (see the calculated pattern for a monodentate structure (b) in Fig. 1 after Zecchina *et al.*, 1997) and the measured pattern of NH$_4$-heulandite with a monodentate structure (see Fig. 3 after Yang & Armbruster, 1998) are also observed in this spectrum.

For industrial and technological applications, the knowledge of the local environment of NH$_4^+$ in the cavities of a zeolite is crucial. Weak hydrogen bonds with the framework oxygen atoms (such as in monodentate or bidentate structures) implies that the ammonium molecule has a weak interaction with the framework and can be consequently easi-
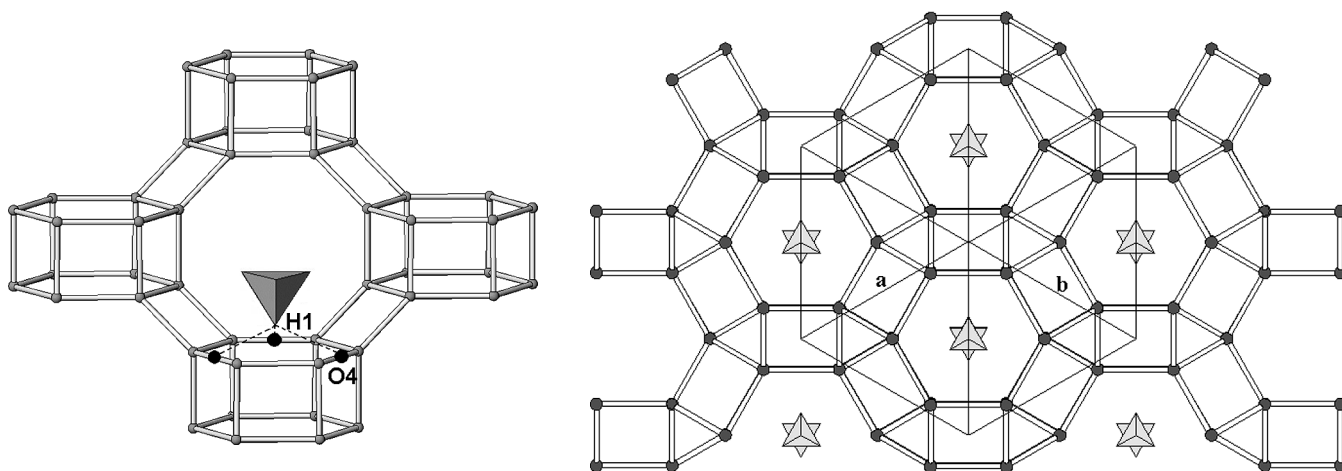

Fig. 4. (a) Plot of the position and orientation of NH$_4^+$ ion in the chabazite cage of NH$_4$-chabazite and connections of the hydrogen atom H1 with the closest framework oxygen atom O4. (b) Plot taken down to the c axis showing the position and orientation of NH$_4^+$.

ly exchanged. This property is useful in agriculture where the zeolite is used in addition to chemical fertilizers. On the other hand, stronger hydrogen bonds with the framework oxygen atoms (such as in tridentate or tetradentate structures) mean that the ammonium molecule has a stronger interaction with the framework and is more difficult to be exchanged. In this scenario, in chabazite and clinoptilolite, the ammonium ion with a monodentate local structural environment may be easily released or desorbed. In agreement, Moroz *et al.* (2002) report low energy barriers for NH_4^+ migration. The structure refinement of NH_4-phillipsite (Gualtieri, 2000) shows instead that the ammonium ion is in a tetradentate local environment and it is consequently more difficult to be released or desorbed in solution. As a matter of fact, incomplete NH_4-exchange and low degree of release is actually reported for phillipsite (Bazzocchi *et al.*, 1996). On the same line, mordenite which shows heterogeneous local environments (from monodentate to tetradentate) for the ammonium ion (Bučko *et al.*, 2004), is well known to generally exhibit incomplete NH_4-exchange curves (Pabalan & Bertetti, 2004).

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