

Structure of natural and NH₄-exchanged Sasbach faujasite: a single-crystal study

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Abstract: The interest for the environmental, industrial and technological applications of Si-rich zeolites is very high. Among the large-pore zeolites, faujasite is one of the most exploited. The aim of this paper is to obtain detailed structural information on natural and NH₄-exchanged faujasite before using this zeolite for dealumination tests, targeting the realization of large single crystals of all-silica faujasite. As one of the most Si-rich natural samples, faujasite from Sasbach (Na_{13.64}K_{0.87}Mg_{10.46}Ca_{8.89}Sr_{0.34}(Al_{51.95}Si_{139.57})O₃₈₄·272.29 H₂O; space group *Fd-3m*; *a* = 24.6906(2) Å) was chosen for study. Single-crystal X-ray diffraction structural refinements of both natural and NH₄-exchanged samples are reported and discussed. In the natural faujasite sample, almost all the extraframework species could be located for the first time. In the NH₄-exchanged sample the ammonium and water molecule sites were located. Ammonium cations occupy two of the sites occupied by the extraframework species in the original mineral.

Key-words: natural faujasite; FAU; NH₄-exchanged form; crystal structure; single-crystal X-ray diffraction; zeolite.

1. Introduction

Zeolites are natural and synthetic microporous materials that, thanks to unique physicochemical properties derived from their structural peculiarities, can be exploited for several purposes, spanning from low-added-value agricultural and ion-exchange applications to high-added-value specialty industrial applications. Beyond their traditional applications as shape-selective catalysts and selective sorbents (Bish & Carey, 2001; Corma, 1997), zeolites can be exploited in several new fields, e.g. gas sensors (Bahtz *et al.*, 2000) and biomedical devices (Lülf *et al.*, 2013). Fine-tuned zeolites with controlled pore architectures and chemistry have improved their performances for technological applications and represent a formidable challenge in material sciences (Calzaferri *et al.*, 2000; Corma, 2003; Davis, 2002; Gigli *et al.*, 2014).

High-silica (HS) zeolites – with high SiO₂/Al₂O₃ ratios – are organophilic materials with strong selectivity towards non-polar organic species (e.g. Damjanovic *et al.*, 2010; Datt *et al.*, 2012; Martucci *et al.*, 2013).

The effectiveness of HS zeolites as selective sorbents for the remediation of wastewater from organic pollutants, such as antibiotics (Braschi *et al.*, 2016; Martucci *et al.*, 2014) and hydrocarbons (Arletti *et al.*, 2012; Martucci *et al.*, 2012), has been recently demonstrated. High-silica zeolites are effective also in other technological applications, such as in energetics. It has been found that, depending on external moderate pressure, non-wetting fluids (e.g. water or water and salt solutions) can intrude into the nanopores of hydrophobic nanoporous materials (Washburn, 1921).

One of the most powerful tools to unravel the nature and the amounts of the intruded/adsorbed species and their interaction with the framework is X-ray diffraction. In both the cited fields (*i.e.* pollutants adsorption and energetics) the experiments are in general performed on powders, firstly because the adsorption and diffusion dynamic is faster when the particle dimensions are small, and secondly because of the larger availability of synthetic HS zeolites in form of micrometric crystal powder. However, X-ray powder diffraction experiments on such

complex systems are very challenging, because of the low amount of the guest molecules and for the need of detecting light elements. Even if the technological applications require the tests to be performed on powdered zeolites, from the structural point of view the availability of large crystals would allow single-crystal diffraction experiments and, as a consequence, an easier location and quantification of the guests.

The direct synthesis of Si-rich zeolites depends on two basic requirements: a low alkalinity of the system (needed to increase the Si incorporation) (Di Renzo, 1998; Zhdanov, 1968) and, in most cases, the presence of organic templates with low charge density, like large tetraalkylammonium cations (Jacobs & Martens, 1987) or, quite seldom, oxygenated templates (Giordano *et al.*, 1994). Most zeolites can be obtained in a quite wide range of Si/Al ratio. However, several zeolitic structures are unstable at high Si/Al ratio. The metastability of zeolites has prompted the elaboration of specific synthesis conditions for each structure.

Among the large-pore zeolites (pores with diameter larger than 0.6 nm defined by rings of 12 tetrahedra), zeolite Y (FAU framework type, Baerlocher *et al.*, 2007) is usually synthesized as micrometric crystals with Si/Al=2.5. The use of organic templates allows the formation of this zeolite with a lower aluminum content (Delprato *et al.*, 1990; He *et al.*, 2016) and only slightly increased crystals size (Berger *et al.*, 2005). On the other hand, natural faujasite occurs as millimeter-sized crystals with the same Si/Al ratio as zeolite Y. Hence, large crystals of Si-rich faujasite can in principle be obtained by dealumination of a natural faujasite, a process that requires the preliminary NH_4 -exchange of the sample.

This work is aimed to obtain detailed structural information on both natural and NH_4 -exchanged faujasite from Sasbach – Kaiserstuhl (Germany), needed to proceed with the subsequent dealumination process. In addition, the understanding of the NH_4 -exchanged faujasite structure is important since cation substitution is the most important method of modifying the physical and chemical properties of zeolites. Proton-exchanged zeolite Y (H–Y) is a largely used zeolite in heterogeneous catalysis, including large-scale applications in the petrochemical industry.

2. Faujasite

The faujasite framework (Fig. 1) is obtained when cuboctahedral sodalite cages (or sod-cages) are connected to double hexagonal rings (d6r) through four of their eight 6-ring windows. The resulting structure is characterized by a tridimensional 12-membered channel system and by large cavities referred to as “supercages” or “fau cages”, with a diameter of approximately 12 Å, interconnected via 12-membered ring (12mr) windows (7.4 Å free diameter) to four other supercages. The topological symmetry, corresponding to a fully disordered Si/Al distribution, is cubic $Fd\bar{3}m$.

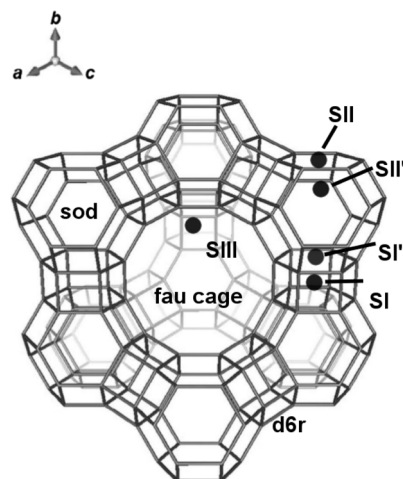


Fig. 1. Framework of faujasite viewed along $[111]$.

A detailed description of the exchangeable cations, which balance the negative charge of the faujasite framework, was given by Frising & Leflaive (2008). The relative sites are labeled with Roman numerals in Fig. 1. The position of the extraframework cation sites depends on the distribution of the surrounding Al atoms and on the distortion of the zeolite framework. Position and site occupancies of the cationic sites change with the Si/Al ratio of the zeolite.

To obtain large crystals of dealuminated faujasite, minimizing the framework destabilization and the consequent structure collapse expected upon Al cations migration (Breck & Skeels, 1985), a sample of natural faujasite from Sasbach – Kaiserstuhl (Germany) with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ (3.22 as determined by Rinaldi *et al.*, 1975) was chosen. The crystal structure of faujasite from Sasbach – known since 1842 as the main faujasite occurrence site – was determined by Bergerhoff *et al.*, (1958) and by Baur (1964), but in both cases it was impossible to determine the positions of all the cations and water molecules. Baur (1964) located only 43 water molecules out of 260 and 17 cations out of approximately 43 per unit-cell. Up to now, a detailed structure of natural faujasite is still lacking.

3. Methods

3.1. Scanning electron microscopy

Both natural and NH_4 -exchanged crystals (FAU and FAU- NH_4 from now on) were studied with an environmental scanning electron microscope (ESEM) Quanta-200 (Fei Company, Oxford Instruments) equipped with energy-dispersive system (EDS) Oxford INCA sited at the “CIGS-Centro Interdipartimentale Grandi Strumenti” of University of Modena and Reggio Emilia. All the images were obtained at 15 kV in low-vacuum operating conditions (≤ 1.5 Torr) to avoid sample metallization.

The FAU and FAU- NH_4 crystals used for the X-ray data collection were analyzed for major and minor elements with a JEOL 8200 Super Probe operating in X-ray

Table 1. Electron-microprobe analyses and formulae of FAU and FAU-NH₄.

Oxides (wt%)	FAU	FAU-NH ₄	Elements (wt.%)	FAU	FAU-NH ₄	Atoms p.u.c.	FAU	FAU-NH ₄
SiO ₂	48.45	55.75	Si	23.26	26.77	Si	139.57	139.97
Al ₂ O ₃	15.30	17.58	Al	4.05	4.65	Al	51.95	52.03
CaO	2.88	0.91	Ca	2.06	0.65	Ca	8.89	2.46
MgO	2.44	0.12	Mg	1.47	0.07	Mg	10.46	0.44
SrO	0.19	0.07	Sr	0.17	0.06	Sr	0.34	0.11
K ₂ O	0.24	0.35	K	0.10	0.15	K	0.87	1.14
Na ₂ O	2.44	0.50	Na	0.91	0.19	Na	13.64	2.43
(NH ₄) ₂ O		6.74	NH ₄	0.00	2.34	NH ₄	0.00	42.44
H ₂ O	28.07	17.97	H	1.56	1.00	O	384.00	384.00
Total	100.00	100.00	O	33.58	35.88	H ₂ O	272.29	152.98

wavelength-dispersive mode (WDS-EMPA) at the Department of Earth Sciences “A. Desio”, University of Milan. The mean analyses, derived from the average of five points, are reported in Table 1. Operating conditions were: accelerating voltage 15 kV, specimen current 5 nA, and beam diameter of 50 µm. Corrections of the raw data were made with the $\varphi\rho Z$ procedure. The following standard and spectral lines were used for calibration: omphacite (NaK α), K-feldspar (KK α), grossular (CaK α , SiK α , AlK α), olivine (MgK α), fayalite (FeK α), sanbornite (BaL α), celestine (SrL α). Nitrogen was not measured on FAU-NH₄, but 13.5 wt% of N₂O (value calculated on the basis of the Al content, assuming that the exchange was complete) was assumed in the calculation of the matrix effects.

The rarity of Sasbach faujasite and the small number of exchanged crystals hindered performing thermal analyses, hence the water content was assumed as difference to 100 wt% of the EMPA analyses.

3.2. NH₄-exchange procedure

The dealumination procedure proposed by the Skeels (1991) patent improved previous methods based on the hydrothermal steam treatment (Kerr, 1969) and on the use of fluorosilicate reagents (Breck & Skeels, 1985), generating a high amount of lattice interruptions and leadings to partial amorphization of the solid (Engelhardt *et al.*, 1982). The treatment proposed by Skeels (1991) introduces a stepwise procedure aimed to obtain more homogeneous HS organophilic zeolites in powders. The substitution of Si for Al involves the formation of Al salts – usually called extraframework aluminum species (EFAL) – and it is necessary that these salts be water-soluble to facilitate their removal from the product. Since ammonium cations form the most soluble salts, a preliminary NH₄-exchange of the faujasite crystals is necessary. For this reason we decided to perform the structural characterization of both the natural and the exchanged faujasite.

The cation exchange was performed at high temperature in batch condition using the “static” run mode. Ten faujasite crystals were placed in a Pt crucible along with a 2M NH₄Cl solution prepared with extra-pure distilled

Table 2. Crystallographic and refinement data for FAU and FAU-NH₄.

	FAU	FAU-NH ₄
Unit-cell parameter (Å)	24.6906(2)	24.7567(2)
Space group	<i>Fd-3m</i>	<i>Fd-3m</i>
<i>h</i> min/max	–35/32	–31/32
<i>k</i> min/max	–38/20	–40/40
<i>l</i> min/max	–38/13	–41/40
Unique reflections	1504	1727
Observed reflections <i>I</i> > 4 σ (<i>I</i>)	1213	1065
<i>R</i> _{int} (obs)	0.020(9)	0.0893
Number of l.s. parameters	72	62
<i>R</i> ₁ (obs)	0.0698	0.0584
<i>R</i> ₁ (all)	0.0877	0.1141
<i>wR</i> ²	0.2691	0.1871
GooF	1.970	1.040
Residuals (e [–] /Å ³)	+1.25	+0.82
	–2.01	–0.53

water. The Pt crucible was placed in a Teflon autoclave and kept at 80 °C for 15 days, the solution was renewed every 3 days. At the end of the exchange procedure the crystals were cleaned with extra-pure distilled water and then dried at room temperature.

3.3. Single-crystal X-ray diffraction of natural faujasite

The single-crystal X-ray data collection of FAU was performed on a crystal of 0.5 × 0.2 × 0.2 mm³ on a Bruker-Nonius X8APEX diffractometer equipped with MoK α generator and area detector sited at the “CIGS-Centro Interdipartimentale Grandi Strumenti” of University of Modena and Reggio Emilia. Data collection and reduction were carried out using APEX2 and SAINT (Bruker AXS, 2008) software, respectively, while absorption correction was applied with SADABS (Bruker AXS, 2008). The structure was refined on *F*_o² by standard methods, using SHELXL-2014/7 (Sheldrick, 2015) program implemented in the WINGX v2014.1 suite (Farrugia, 2012).

Least-squares refinement of the peak positions leads to the following cell parameters: *a* = 24.6906(2) Å, and *V* = 15052.03(2) Å³. The *hkl* reflections were always found

Table 3. Atomic fractional coordinates and displacement parameters of FAU and FAU-NH₄ (in *italic*).

Atom	Wyckoff letter	<i>x</i>	<i>y</i>	<i>z</i>	s.o.f.*	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²	<i>U</i> _{eq}
Si1	<i>i</i>	0.12524(2)	0.94649(2)	0.03618(2)	0.73	0.0130(3)	0.0143(3)	0.0117(3)	0.0007(2)	−0.0023(1)	−0.0019(2)	0.0130(3)
Al1	<i>i</i>	0.12524(2)	0.94649(2)	0.03618(2)	0.27	0.0130(3)	0.0143(3)	0.0117(3)	0.0007(2)	−0.0023(1)	−0.0019(2)	0.0130(3)
<i>Si1</i>	<i>i</i>	<i>0.12574(3)</i>	<i>0.94560(3)</i>	<i>0.03597(2)</i>	<i>0.73</i>	<i>0.0168(3)</i>	<i>0.0191(3)</i>	<i>0.0152(3)</i>	<i>0.0005(2)</i>	<i>−0.0021(2)</i>	<i>−0.0018(2)</i>	<i>0.0170(2)</i>
<i>Al1</i>	<i>i</i>	<i>0.12574(3)</i>	<i>0.94560(3)</i>	<i>0.03597(2)</i>	<i>0.27</i>	<i>0.0168(3)</i>	<i>0.0191(3)</i>	<i>0.0152(3)</i>	<i>0.0005(2)</i>	<i>−0.0021(2)</i>	<i>−0.0018(2)</i>	<i>0.0170(2)</i>
O1	<i>g</i>	0.17406(7)	0.17406(7)	0.9680(1)	0.5	0.0221(7)	0.0221(7)	0.035(1)	−0.0014(6)	−0.0014(6)	0.0042(8)	0.0265(5)
<i>O1</i>	<i>g</i>	<i>0.17275(8)</i>	<i>0.17275(8)</i>	<i>0.9644(1)</i>	<i>0.5</i>	<i>0.0251(8)</i>	<i>0.0251(8)</i>	<i>0.039(2)</i>	<i>−0.0009(8)</i>	<i>−0.0009(8)</i>	<i>0.004(1)</i>	<i>0.0298(6)</i>
O2	<i>g</i>	0.17823(7)	0.17823(7)	0.3233(1)	0.5	0.0236(7)	0.0236(7)	0.026(1)	−0.0024(6)	−0.0024(6)	0.0078(8)	0.0244(5)
<i>O2</i>	<i>g</i>	<i>0.18014(8)</i>	<i>0.18014(8)</i>	<i>0.3223(1)</i>	<i>0.5</i>	<i>0.0254(8)</i>	<i>0.0254(8)</i>	<i>0.029(1)</i>	<i>−0.0019(8)</i>	<i>−0.0019(8)</i>	<i>0.007(1)</i>	<i>0.0269(6)</i>
O3	<i>g</i>	0.25272(8)	0.25272(8)	0.1436(1)	0.5	0.0308(8)	0.0308(8)	0.027(1)	0.0050(7)	0.0050(7)	0.013(1)	0.0294(6)
<i>O3</i>	<i>g</i>	<i>0.2523(9)</i>	<i>0.25323(9)</i>	<i>0.1413(1)</i>	<i>0.5</i>	<i>0.0303(9)</i>	<i>0.0303(9)</i>	<i>0.031(1)</i>	<i>0.0051(8)</i>	<i>0.0051(8)</i>	<i>0.009(1)</i>	<i>0.0305(6)</i>
O4	<i>h</i>	0.10608(8)	0.89392(8)	0	0.5	0.0269(8)	0.0269(8)	0.034(1)	−0.0103(6)	−0.0103(6)	−0.0017(9)	0.0291(6)
<i>O4</i>	<i>h</i>	<i>0.10711(9)</i>	<i>0.89289(9)</i>	<i>0</i>	<i>0.5</i>	<i>0.0298(9)</i>	<i>0.0298(9)</i>	<i>0.031(1)</i>	<i>−0.0069(8)</i>	<i>−0.0069(8)</i>	<i>−0.006(1)</i>	<i>0.0302(6)</i>
Ca	<i>e</i>	0.0699(1)	0.0699(1)	0.0699(1)	0.0674(9)	0.0414(8)	0.0414(8)	0.0414(8)	0.0018(9)	0.0018(9)	0.0018(9)	0.0414(8)
<i>Ca</i>	<i>e</i>	<i>0.0828(2)</i>	<i>0.0828(2)</i>	<i>0.0828(2)</i>	<i>0.054(1)</i>	<i>0.077(2)</i>	<i>0.077(2)</i>	<i>0.077(2)</i>	<i>−0.002(3)</i>	<i>−0.002(3)</i>	<i>−0.002(3)</i>	<i>0.077(2)</i>
Mg	<i>g</i>	0.2334(6)	0.2334(6)	0.4707(8)	0.059(2)	0.06						
K	<i>e</i>	0.2667(6)	0.2667(6)	0.2667(6)	0.035(2)	0.09						
<i>N2</i>	<i>e</i>	<i>0.2657(3)</i>	<i>0.2657(3)</i>	<i>0.2657(3)</i>	<i>0.16667</i>	<i>0.069(3)</i>	<i>0.069(3)</i>	<i>0.069(3)</i>	<i>−0.002(3)</i>	<i>−0.002(3)</i>	<i>−0.002(3)</i>	<i>0.069(3)</i>
Na	<i>d</i>	0.25	0.25	0.0	0.007(2)	0.09						
W1	<i>e</i>	0.1038(5)	0.1038(5)	0.1038(5)	0.096(3)	0.11						
W2	<i>g</i>	0.0821(1)	0.1679(1)	0.0821(1)	0.183(3)	0.043(1)	0.043(1)	0.043(1)	0.001(1)	−0.001(1)	0.001(1)	0.043(1)
W4	<i>g</i>	0.248(1)	0.2856(9)	0.2856(9)	0.134(7)	0.11						
W5	<i>g</i>	0.831(1)	0.831(1)	0.201(2)	0.093(8)	0.11						
<i>W5/N1</i>	<i>g</i>	<i>0.840(1)</i>	<i>0.840(1)</i>	<i>0.204(1)</i>	<i>0.121(7)</i>	<i>0.129(6)</i>						
W7	<i>g</i>	0.2045(8)	0.2045(8)	0.444(1)	0.141(7)	0.11						
<i>W7</i>	<i>g</i>	<i>0.181(1)</i>	<i>0.181(1)</i>	<i>0.442(2)</i>	<i>0.100(8)</i>	<i>0.129(6)</i>						
W8	<i>g</i>	0.2573(7)	0.2573(7)	0.347(1)	0.131(7)	0.11						
<i>W8</i>	<i>g</i>	<i>0.248(2)</i>	<i>0.248(2)</i>	<i>0.388(2)</i>	<i>0.079(6)</i>	<i>0.129(6)</i>						
W9	<i>i</i>	0.8436(9)	0.9295(9)	0.1929(8)	0.24(1)	0.11						
<i>W9</i>	<i>i</i>	<i>0.875(1)</i>	<i>0.946(1)</i>	<i>0.210(1)</i>	<i>0.18(1)</i>	<i>0.129(6)</i>						
W10	<i>g</i>	0.2391(8)	0.2391(8)	0.404(1)	0.121(7)	0.11						
<i>W10</i>	<i>g</i>	<i>0.215(2)</i>	<i>0.215(2)</i>	<i>0.429(3)</i>	<i>0.067(8)</i>	<i>0.129(6)</i>						
W11	<i>i</i>	0.783(1)	0.894(1)	0.216(1)	0.19(1)	0.11						
<i>W11</i>	<i>i</i>	<i>0.774(2)</i>	<i>0.925(2)</i>	<i>0.197(2)</i>	<i>0.130(1)</i>	<i>0.129(6)</i>						

* s.o.f. – site occupancy factor.

to be absent for $h + k, h + l, k + l = 2n + 1$, confirming the *F* centered lattice and therefore the space group *Fd-3m* found by Baur (1964). Least-squares refinement was carried out in this space group starting from the framework atomic coordinates reported by Baur (1964). The inspection of the Difference Fourier map allowed the location of four extraframework cation and nine water molecule sites, all partially occupied. Neutral atoms scattering curves were used for all atoms. For Si site a mixed scattering curve with the Si/Al ratio found from the chemical analysis was used. The crystal structure was

refined using anisotropic displacement parameters for framework atoms, Ca and W2 sites. Because of the high number and closeness of partially occupied sites, the displacement parameters of Mg, K, Na, W1, W4–W11 sites were initially refined – in different refinement cycles with respect to the site occupancy factor (s.o.f.) – and successively fixed to 0.06 for Mg, to 0.09 for K and Na and to 0.11 for the water sites.

Details on the structure refinements are reported in Table 2. Atomic coordinates and displacement parameters are in Table 3 and framework and extraframework

Table 4. Framework bond distances and angles and extraframework coordination polyhedra of FAU and FAU-NH₄. Too short cation–water and water–water distances are not reported for the sake of clarity.

FAU			FAU-NH ₄			FAU			FAU-NH ₄		
Si1–	O1	1.652(1)	Si1–	O1	1.644(1)	W5–	O3	3.07(4)	W5/N1–	O4	3.30(3) × 2
	O2	1.6499(9)		O2	1.648(1)		O4	3.14(3) × 2		W8	2.79(3) × 2
	O3	1.6433(9)		O3	1.642(1)		W4	3.13(5) × 2		W9	2.77(4) × 2
	O4	1.645(1)		O4	1.646(1)		W5	3.08(9)		W11	2.67(4) × 2
Mean		1.648			1.645		W7	3.18(3) × 2			
							W10	3.05(3) × 2			
Si–O1–Si		140.6(2)	Si–O1–Si		145.8(2)	W7–	O2	3.11(3)	W7–	O2	2.96(5)
Si–O2–Si		139.2(2)	Si–O2–Si		139.5(2)		W5	3.18(3) × 2		O4	3.27(3) × 2
Si–O3–Si		144.7(2)	Si–O3–Si		149.0(2)		W8	3.01(4)		W8	2.70(7)
Si–O4–Si		138.5(2)	Si–O4–Si		137.5(2)		W9	3.02(3) × 2			
Mean		140.8	Mean		143.0						
Ca–	O1	2.525(3) × 3	Ca–	O1	2.938(7) × 3	W8–	O2	2.82(3)	W8–	O2	2.89(5)
	O3	3.121(3) × 3		O3	3.343(6) × 3		W4	2.63(4)		W5/N1	2.79(3) × 2
	W1	2.79(1) × 3		Ca	2.95(2) × 3		W7	3.01(4)		W7	2.70(7)
	W2	2.458(4) × 3					W8	3.14(5) × 2		W10	2.72(7) × 2
							W9	2.67(3) × 2		W11	3.17(6) × 2
Mg–	W7	2.68(3) × 2				W9–	O2	3.01(2)	W9–	O4	2.91(3)
	W7	3.03(4)					O4	3.03(2)		W5/N1	2.77(4)
	W8	3.16(3)					W7	3.03(3)		W11	2.76(6)
	W9	2.42(3) × 2					W8	2.67(3)			
	W9	2.85(3) × 2					W9	3.00(4)			
	W9	3.07(3) × 2					W9	3.11(4)			
	W10	2.12(3) × 2					W10	2.69(3)			
	W10	2.95(3) × 2					W10	2.89(3)			
	W11	2.24(4) × 2					W11	3.18(4)			
	W11	2.29(4) × 2				W10–	O2	2.92(3)	W10–	O2	2.91(7)
	W11	2.96(4) × 2					W4	3.16(3) × 2		W8	2.72(7) × 2
	W11	3.05(3) × 2					W5	3.05(3) × 2		W11	3.01(7) × 2
K–	O3	3.08(2) × 3	N2–	O2	3.308(6) × 3		W9	2.69(3) × 2			
	W5	2.77(5) × 3		O3	3.112(8) × 3		W9	2.89(3) × 2			
				W5/N1	3.01(4) × 3		W10	3.01(5) × 2			
				W8	3.09(5) × 3		W11	2.85(4) × 2			
				W9	3.18(4) × 6						
Na–	O1	2.767(3) × 6				W11–	O4	2.99(3)	W11–	O4	2.83(5)
W1–	W2	2.74(2)					W4	2.80(4)		W5/N1	2.67(5)
							W9	3.18(4)		W8	3.17(6)
W2–	O3	3.022(5) × 3					W10	2.85(4)		W9	2.76(6)
	W1	2.74(2)					W11	2.99(5)		W10	3.01(7)
	W2	2.997(9) × 3								W11	2.69(9)
										W11	2.62(6) × 2
W4–	O3	2.83(3)									
	W5	3.13(5) × 2									
	W8	2.63(4)									
	W10	3.16(3) × 2									
	W11	2.80(4) × 2									

coordination distances in Table 4. The CIF file is provided as Supplementary Material linked to this article at <https://pubs.geoscienceworld.org/eurjmin/>.

3.4. Single-crystal X-ray diffraction of NH₄-exchanged sample

Single-crystal X-ray studies on FAU-NH₄ were carried out on a crystal of $0.42 \times 0.32 \times 0.28 \text{ mm}^3$ using an Oxford Xcalibur Sapphire2 diffractometer equipped with a CCD area

detector at the Dipartimento di Scienze della Terra “A. Desio” (University of Milan, Italy) with graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The sample-to-detector distance was 8.1 cm. A total of 2322 exposures (step = 1° , time/step = 30 s), covering a full reciprocal sphere with a redundancy of about 15 were used. Data were integrated and corrected for Lorentz and polarization background effects, using the package CrysAlisPro, Agilent Technologies, Version 1.171.37.31 (release 15-10-2015 CrysAlis171.38.41). Refinement of the unit-cell parameters was



Fig. 2. Macro-photograph of Sasbach faujasite crystals.

based on 13692 measured reflections, and gave the following lattice parameters: $a = 24.7567(2) \text{ \AA}$, $V = 15173.2(2) \text{ \AA}^3$. The data were corrected for absorption using the multi-scan method (SCALE3 ABSPACK) with a $d_{\min}$ of $0.60 \text{ \AA}$.

The structure was refined with SHELXL-2014/7 (Sheldrick, 2015) program implemented in the WINGX v2014.1 suite (Farrugia, 2012) in the cubic space group $Fd-3m$, starting from the framework atom coordinates of FAU sample (this work). Neutral atoms scattering curves were used for all atoms. For the Si site a mixed scattering curve with the Si/Al ratio found from the chemical analysis was used. Framework, Ca and N2 nitrogen atoms sites were refined with anisotropic displacement parameters, while the displacement parameters of the water molecules sites were refined with the same value. The residual not exchanged cations, NH_4^+ cations and water molecules were located by the Fourier difference maps.

Details on the structure refinements are reported in Table 2, atomic coordinates and displacement parameters in Table 3 and framework and extraframework distances in Table 4. The CIF file is provided as supplementary material linked to this article.

4. Results and discussion

4.1. Morphology and chemical composition of FAU

Faujasite crystals employed for this work appear as well-shaped octahedra (Fig. 2), some of which are twinned on (111). The EMP analysis of FAU (Table 1) gave the following formula: $(\text{Na}_{13.64}\text{K}_{0.87}\text{Mg}_{10.46}\text{Ca}_{8.89}\text{Sr}_{0.34})_{\Sigma 34.2}(\text{Al}_{51.95}\text{Si}_{139.57})_{\Sigma 191.52}\text{O}_{384} \cdot 272.29 \text{ H}_2\text{O}$. This composition is very similar to that reported by Rinaldi (1975), with a slightly higher amount of Mg and Na and a lower one of Ca and K.

4.2. Structure of the natural sample FAU

In faujasite structure about 32 extraframework cations and about 255 water molecules were located, in good agreement with the values found from the chemical analysis (34.20 and 272.29, respectively) (Table 1 and Table 3).

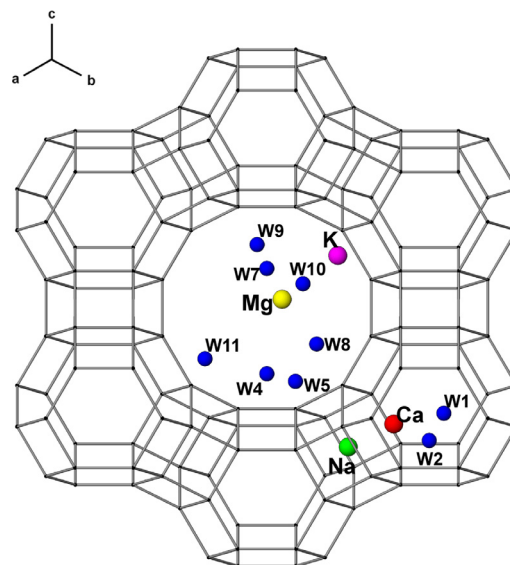


Fig. 3. Structure of FAU viewed along $[111]$. Only one of each extraframework cation and water molecule site is shown for the sake of clarity.

The four partially occupied extraframework sites are labeled Ca, Mg, K and Na in Table 3. The water molecules are labeled from W1 to W10 according to Olson (1970), while W11 is a new site. The attribution of the cation sites to the four more abundant extraframework atomic species present in the natural phase was based on the distances from the framework oxygen atoms and the water molecules (Table 4), the site occupancy factors (Table 3) and the agreement with the chemical analysis.

The Na site is at the center of the double six-membered rings (Fig. 3), corresponding to site I in the classical nomenclature (Frising & Leflaive, 2008) and coordinates six O1 framework oxygen atoms (Table 4). The Ca site is located on the threefold axis in the sodalite cage, near the six-membered ring between sodalite cage and d6r, corresponding to site I'. It coordinates three O1, three O3 framework oxygen atoms and is at bond distance from the partially occupied sites W1 and W2 (Table 4). The K site, corresponding to site II, is in the supercage near the six-membered ring of the sodalite cage. K coordinates three O3 oxygen atoms and three partially occupied W5 sites (Table 4). The Mg site is in the fau supercage near the water site W6 of Olson (1970) and is at coordination distance from the partially occupied sites W7, W8, W9, W10, and W11.

The number of cations found in the refinement correspond to 32.33 in very good agreement with the chemical analysis (34.20). A reasonable cation distribution (also confirmed by the NH_4^+ exchange results) could be the following: i) in Na site, only Na cations (1.34); ii) in Ca site, all the Ca cations (8.89) and 7.37 Na cations; iii) in K site, the large cations K (0.87) and Sr (0.34), Na (3.98) and water molecules (6.80); iv) in Mg site, all Mg (10.46) and 0.95 Na cations.

Water molecules W1 and W2—each other coordinated—are in the sodalite cage (Fig. 3) and coordinate Ca and

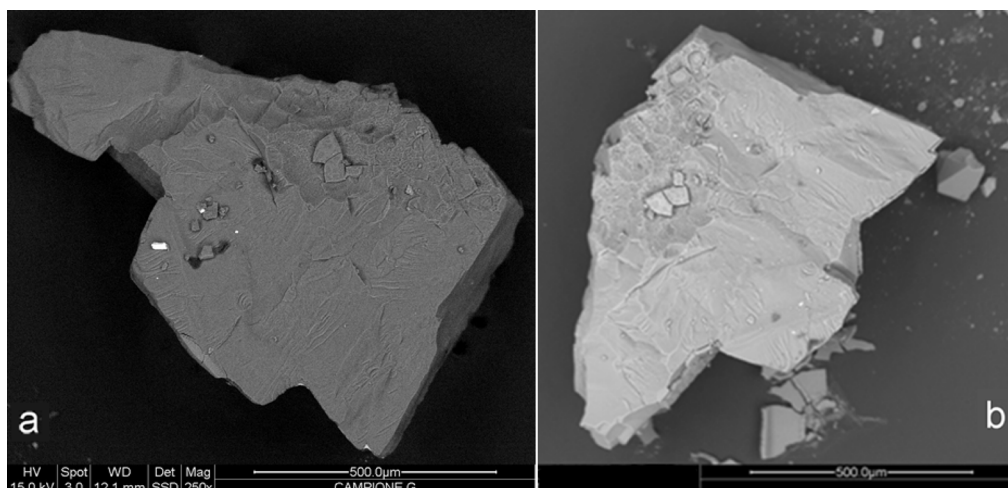


Fig. 4. Scanning electron microscope images of natural (a) and NH₄-exchanged (b) faujasite crystals.

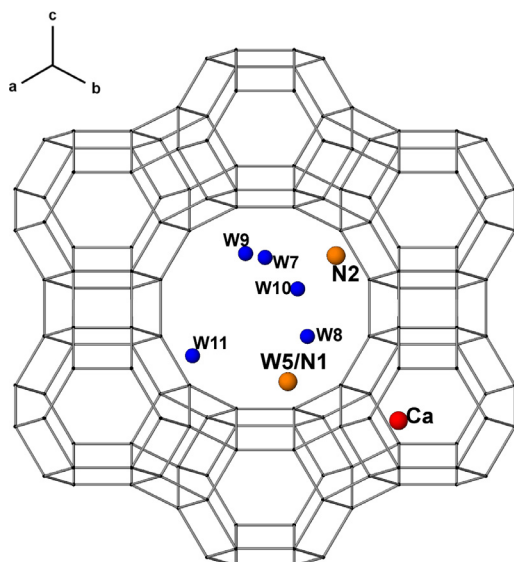


Fig. 5. Structure of FAU-NH₄ viewed along [111]. Only one of each extraframework cation and water molecule site is shown for the sake of clarity.

framework oxygen atoms, as well. All the other water molecules are located in the fau supercage and coordinate both framework oxygen atoms and water molecules (Table 4). On the basis of the site occupancy factors of the water sites and of the presence of 6.80 water molecules in the K site, a total of 261.97 water molecules is obtained in very good agreement with the calculated chemical data (272.29 water molecules).

4.3. Cation exchange and FAU-NH₄ chemical composition

The SEM images reported in Fig. 4 a,b show that the morphology of the crystals is preserved after the cation exchange. To test the exchange homogeneity in these large crystals, one of the specimen was cut into three fragments which were analyzed by EDS in different points, both in the

central part and near the crystal surface. The results indicate that the exchange can be assumed as homogeneous.

The EMP analysis performed after the exchange procedure on the same crystal used for the X-ray data collection leads to a cation exchange rate of 82% (Table 1). In particular, Mg is almost completely substituted by NH₄, while some residual Ca and Na were found, and the low amount of K present in the original faujasite did not exchange at all.

4.4. Structure of FAU-NH₄

The structural refinement of FAU-NH₄ gave a unit-cell volume of 15173.2 Å³, versus 15052.03 Å³ determined for the natural FAU. The slight volume increase (0.76%) is compatible with that observed in other NH₄-exchanged natural zeolites, like chabazite (Gualtieri & Passaglia, 2006), phillipsite (Gualtieri, 2000), stilbite (Alberti *et al.*, 1999), barrerite (Martucci *et al.*, 2000). This increase can be due to a very slight framework distortion due to the tetrahedra rotation and the increase of the T-O-T angles (Table 4).

The N atoms were found in the K site (now labeled N2 in Fig. 5 and Tables 3 and 4) and in the W5 site of the original FAU, which, in the exchanged phase, show higher occupancy factors. The Mg and Na sites are empty in the exchanged sample. Regarding the NH₄ distribution, we assumed that the N2 site is occupied by the residual K (1.14) and by ammonium ions (28.91 NH₄), while W5/N1 hosts the remaining ammonium (13.57 NH₄) and 12.13 water molecules. The residual Ca and Na cations are hosted in the Ca site together with 15.25 water molecules.

Of the nine water sites present in FAU, W1, W2 and W4 are now empty and the others, except W5, show a lower occupancy factor. As a whole, 134.13 water molecules were located, in good agreement with that calculated out of the chemical analysis (Table 1), but this value is significantly lower than that found in FAU refinement (261.97). However, as also observed in other NH₄-exchanged zeolites (Alberti *et al.*, 1999; Gualtieri, 2000; Gualtieri & Passaglia, 2006; Martucci *et al.*, 2000; Yang & Armbruster, 1998), this result

is reasonable because the exchange process reduces the space available for the water molecules.

Site N2 is coordinated to three O2 and three O3 framework oxygen atoms and to the partially occupied W5/N1, W8 and W9 sites (Table 4). Site W5/N1 coordinates two O4 and the water molecules in the partially occupied sites W8, W9 and W11 (Table 4). The Ca site is coordinated to three O1 and three O3 framework oxygen atoms. From the distances reported in Table 4 it can be assumed that hydrogen bonds are formed between nitrogen and both framework and water oxygen atoms. All the water molecules are at bond distance from at least one framework oxygen atom and form clusters with other water molecules. Figure 5 shows the distribution of cations and water sites in the NH₄ exchanged sample.

The presence of NH₄ cations in site N2 was already reported by Mortier *et al.* (1973) and Lim *et al.* (2007, 2010) in NH₄-Y and by Zhen & Seff (1999) for NH₄-X. In addition, NH₄ was located in sites I and I' (classical nomenclature) in NH₄-Y and in *x*, *y*, *z*=0.42 in NH₄-X. The position refined for I' (*x*, *y*, *z*=0.07) by Lim *et al.* (2007, 2010) and Mortier *et al.* (1973) is half-way between that of Ca in FAU and in NH₄-FAU of our study. Kaduk & Faber (1995) discuss the crystal structure of zeolite Y, with different Si/Al ratio, exchanged with various cations. These authors report that ammonium ions are observed only at sites I' and II. However, even when the I' site is largely occupied, the distance of each ammonium ion with the other three equivalent ones is too short.

5. Conclusions

This work was aimed to obtain detailed structural information on natural and NH₄-exchanged faujasite, before using this zeolite for dealumination tests, targeting the realization of large single crystals of all-Si FAU. A single-crystal X-ray diffraction study of Sasbach faujasite was performed since detailed siting of the extraframework cations and water molecules had not been reported yet. The structure refinement identified four cation sites partially occupied by Na, Ca, K and Mg. Sodium is hosted in the double six-membered ring, Ca in the sodalite cage and Mg and K in the supercage; Mg is completely solvated, while Na is coordinated to only framework oxygen atoms and Ca and K are coordinated to both framework oxygen atoms and water molecules.

The adopted NH₄-exchange procedure demonstrated to be effective since the homogeneous exchange was verified in crystals of up to 0.06 mm³, although the exchange was not completed, resulting in 82%. Specifically, while the hydrated Mg cation is completely exchanged, some residual Ca and Na were found, probably as a consequence of their strong bonds with the framework oxygen atoms. Also the low amount of K present in the original faujasite did not exchange. The lower water amount determined in the exchanged sample with respect to the natural phase is due to the reduced space left for the water molecules after the NH₄-exchange.

A preliminary dealumination test was then performed and some FAU-NH₄ crystals were submitted to the procedure proposed by Skeels (1991). The results indicate that, when large crystals are treated, milder conditions are needed since, even if the dealumination proved complete, the crystals amorphized.

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