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Single crystal structure of fully dehydrated partially Co^{2+}-exchanged zeolite X: Comparison with partially dehydrated partially Co^{2+}-exchanged zeolites X

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Abstract

The crystal structure of the fully dehydrated Co, Na–X zeolite ($Na_{16}Co_{38}Al_{92}Si_{100}O_{384}$) is investigated and compared to that of three partially hydrated zeolites. In the fully dehydrated crystal, cobalt ions almost entirely occupy Site I, and partially Site II while the residual sodium cations partly occupy Site II and Site III. The dehydration induces a migration of Co^{2+} cations from Site I′ to Site I and severely affects the structure, the structural strain being released by changes of framework valence angles or, to a less extent, by distortions of TO_4 tetrahedra. Comparison with dehydrated M–X zeolite structures (M = Ba, Na, Ca, Tl, Li) confirms the relation between the size of the charge compensating cation and the stresses on the skeleton that are mainly explained by cation–oxygen electrostatic interactions.

Keywords: Zeolite X; Cobalt^{2+}; Dehydration; X-ray diffraction

1. Introduction

The numerous applications of natural/synthetic zeolites as catalysts, ion exchangers or for gas separation rely on their porous crystal structure (sieving effect) together with their electrostatic properties (cations/acid sites distribution). Among them, the FAU zeotype offers a widely open (7.4×7.4 Å^2) three-dimensional framework available over large compositional range, in peculiar in its aluminosilicate form [1]. According to the composition of the skeleton, which is built on sodalite units formed by condensation of TO_4 ($T = Si^{4+}$ or Al^{3+}) tetrahedra, one usually distinguishes LSX (Si/Al = 1), X (1.0 < Si/Al < 1.5), Y (Si/Al > 1.5), and US-Y (ultrastable dealuminated Y-zeolite) denominations for the FAU zeotype.

Y-type zeolites, which have almost neutral framework but can accommodate a large amount of silanol groups, are mainly used as catalysts. LSX and X types, which exhibit the more negatively charged framework, also host the larger number of charge compensating cations that are responsible for the high and anisotropic electric field in the cavities. LSX and X type zeolites are generally synthesized in the presence of Na^+ [2] or, more seldom, K^+ [3] alkali cations. As these cations are readily exchangeable, the electrically-driven selective sorption properties of FAU zeolite can be finely tuned for the applications in gas-separation processes, like Ca–X, Ba–X… zeolites [4–6]. In another hand, the zeolites exchanged with transition-metal cations possess interesting catalytic activity and are used, for example, in oxidation reactions of organic compounds [7,8]. Potential applications as constructive element in electronic devices made by insertion of pyridine-based molecules in transition-metal complexes FAU zeolite have also been evoked in early 1980s [9,10]. However,

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despite all applications of zeolites rely on the interactions of sorbed molecules with the framework and more specifically with the cations, the crystal structures of these compounds are still uncertain.

This study was performed in order to determine the preferred sites for cobalt ions in completely dehydrated and exchanged low-silica zeolite X by single crystal X-ray diffraction. Although, the single crystal obtained is only partially exchanged, an accurate description of the Co^{2+} sites is obtained and the influence of the dehydration rate is studied and compared to previously known M^{n+}–X crystal structures ($M^{n+} = Li^{+}$ [11], Tl^{+} [12], Co^{2+} [13], Ca^{2+} [11], Ba^{2+} [14]).

2. Experimental part

2.1. Sample preparation

Large crystals (mean diameter ~0.18 mm) of Na–X zeolite along with Na–A and P zeolites were obtained by a modified Charnell's method [15] without seeding. Their Si/Al ratio (Si/Al ~1.07) and Na content were determined by microprobe analysis ($Na_{93}Al_{93}Si_{99}O_{384}$). The cobalt form was obtained by cation exchange using an aqueous $Co(NO_3)_2$ solution (0.02 mol/l) heated at 60 °C. The ion-exchange was performed in slightly acid solution (pH 5.8–6.5) in order to avoid the precipitation of cobalt hydroxides (resulting from hydrolysis of water by cobalt ion) and to reduce the possibility of proton exchange (accompanying excess of protons in the solution).

In the first attempts, the crystals were prepared by the "continuous flow" exchange method in column (~20 ml/h flow, 11 days exchange); but they got fully amorphous, although their octahedral morphology was retained. The leaching of silicon out of the framework was attested by microprobe images (Fig. 1), showing the Si/Al ratio gradually decreasing from 1.01 (center of the crystals) to 0.92 (border); it was caused by framework hydrolysis in acidic solution. In next attempts, the exchange was performed by a batch method (13 days, 5 batches) and the sample retained its crystallinity, but microprobe analysis revealed that 14% of sodium ions were not exchanged albeit different cobalt ion concentrations, temperature and time of exchange were tested. Such a trend was also observed for zeolite X [13], A [16] and Y [17]. The chemical composition, ($Na_{13(2)}Co_{32.1(7)}Al_{93(2)}Si_{99(7)}O_{384}$), from microprobe analysis is only indicative since about 17% of cations are missing because of their migration under electron beam and of the collapse of the framework with the sudden departure of water molecules. As a consequence, partial $Na^{+} \rightarrow H^{+}$ ion-exchange is not totally excluded. The crystal color changed from colorless to purple over ion-exchange. Finally, in order to test the dehydration protocols, three large purple crystals (diameter ~0.18 mm (crystal 1), diameter ~0.17 mm (crystal 2) and diameter ~0.18 mm (crystal 3)) suitable for diffraction experiments were put in Pyrex capillaries, and exposed to different thermal treatments. Crystal 1 was progressively heated up to 400 °C for 7 days under 5×10^{-4} Pa before being sealed at room temperature under vacuum and became dark-blue. Crystal 2 and 3 were dehydrated for six days at room temperature and at pressure of 5×10^{-4} Pa. Crystal 3 was, then, sealed at room temperature and under vacuum while crystal 2 was gradually heated to 150 °C for 2 days before being sealed under vacuum at room temperature in its capillary. Both became blue. Besides the dehydrated crystals, a fully hydrated crystal (Crystal 4) was also prepared for XRD experiment.

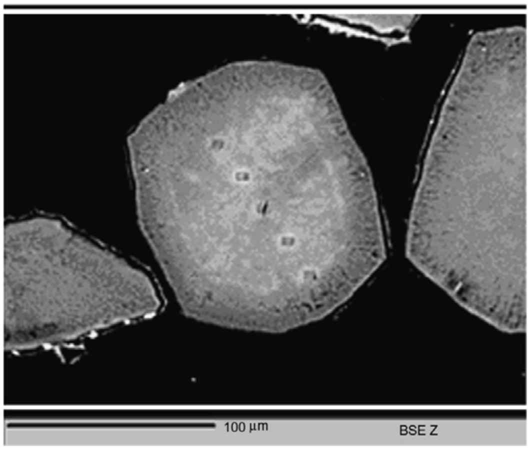

Fig. 1. Scanning electron microscopy image showing the inhomogeneous chemical contrast in Co, Na–X zeolite crystal ion-exchanged by flow method.

2.2. X-ray data collections of the Co, Na–X crystals

The X-ray diffraction experiments were carried out at room temperature using an Oxford Xcalibur diffractometer equipped with a CCD detector on all four CoX crystals differing by their water content, from totally dehydrated (crystal 1) to fully hydrated (crystal 4). The same data collection strategy was used, half of the Ewald sphere, up to $\sin\theta/\lambda \sim 0.7$ Å^{-1} was recorded with Mo(Kα) radiation. The Fd-3 space-group was checked on the basis of systematic extinctions (F-centering, diamond *d* mirror) and Bragg intensities distribution (absence of $^{[110]}$m). Data reduction was performed with CrysAlisPro (version 1.171.29.2) [18] and SORTAV [19] softwares, structure solution with SHELX97 [20] and least-squares refinements with Jana2000 [21]. The initial model was derived from the framework of the parent dehydrated Na–X zeolite [2]. Experimental details for the four studied crystals are summarized in Table 1.

2.3. Structure refinement for fully dehydrated Co, Na–X zeolite (crystal 1)

The more satisfying structural refinement is obtained with the totally dehydrated crystal 1 whose refinement strategy is described below. The Co^{2+} ions in Sites I (Co1) and II (Co2) are located on the first difference