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Single-crystal structures of highly NH_4^+-exchanged, fully deaminated, and fully Tl^+-exchanged zeolite Y (FAU, Si/Al = 1.56), all fully dehydrated

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ABSTRACT

Single crystals of zeolite Y, $|Na_{75}|[Si_{117}Al_{75}O_{384}]$-FAU, with diameters up to 0.30 mm were grown from gels; Si/Al = 1.56. They were ion exchanged and fully dehydrated to generate $|(NH_4)_{67}H_5Na_3|[Si_{117}Al_{75}O_{384}]$-FAU (crystal 1, partially deaminated), $|H_{72}Na_3|[Si_{117}Al_{75}O_{384}]$-FAU (crystal 2, fully deaminated at 473 K) and $|Tl_{75}|[Si_{117}Al_{75}O_{384}]$-FAU (crystal 3). Their structures were determined crystallographically at 294 K using synchrotron X-radiation in the cubic space group $Fd\bar{3}m$. They were refined to the final error indices R_1/wR_2 = 0.037/0.126, 0.055/0.190, and 0.044/0.121 using 884, 723, and 851 reflections with $F_o > 4\sigma(F_o)$ for crystals 1, 2, and 3, respectively. In crystal 1, 67 NH_4^+ and 3 Na^+ ions per unit cell are found at four different crystallographic sites. Six NH_4^+ ions were found at the centers of double 6-rings (site I; N···O = 2.888(3) Å). Filling site I′ are 32 NH_4^+ ions (N···O = 2.774(5) Å); each is recessed 1.59 Å into the sodalite cavity from the plane of the three oxygens to which it bonds. Filling site II in the supercages are 29 NH_4^+ and 3 Na^+ ions, each of which extends 1.69 Å and 1.10 Å, respectively, into the supercage from its 3-oxygen plane (N···O = 2.818(5) Å, Na–O = 2.512(19) Å). The remaining 5 of the 72 NH_4^+ ions originally present per unit cell have apparently been deaminated by vacuum dehydration at 294 K. NH_4^+ ions simultaneously occupy sites I and I′ as K^+ ions did in $|K_{71}|[Si_{121}Al_{71}O_{384}]$-FAU, $|K_{92}|[Si_{100}Al_{92}O_{384}]$-FAU, and $|K_{96}|[Si_{96}Al_{96}O_{384}]$-FAU; the internitrogen distance is 3.36 Å. In crystal 2, three Na^+ ions per unit cell are found at site I′ (Na–O = 2.207(13) Å); no other cations were found so the deamination of NH_4^+ is complete at 473 K. In crystal 3, 30, 30, 9, 4, and 2 Tl^+ ions were found at sites I′, II, and three sites III′ per unit cell, respectively. The total, 75, agrees with the results of EDX analysis to establish the framework composition (the Si/Al ratio) of these crystals.

1. Introduction

Cation substitution (ion exchange) is the most important method of modifying the physical and chemical properties of zeolites [1–3]. More specifically, the catalysis and sorption properties of zeolites depend largely on the extraframework species present, notably the cations [4]. Most recently, Frising and Leflaive compiled and reviewed the cation distributions in faujasite-type zeolites through mid-2007 [4].

Proton-exchanged zeolite Y (H–Y) is the most widely used zeolite in heterogeneously catalyzed reactions, including large-scale applications in the petrochemical industry. These Brønsted acids donate protons to molecules in the zeolite cages [2–5]. The market for H–Y currently exceeds 2 × 10^9 US$ per year [6,7]. H–Y is prepared by NH_4^+ ion exchange and subsequent heating to temperatures at which NH_3 is completely removed and some dehydroxylation (loss of some H^+ ions and framework oxygen atoms as H_2O) takes place.

Because of its importance, numerous scientists have studied H–Y by infrared [8–13], quantum mechanical [14,15], powder diffraction [16–19], and single-crystal X-ray diffraction methods during the past several decades [20,21].

Gallezot et al. investigated the crystal structures of Na,H–Y (Si/Al = 2.5) and 53% dealuminated zeolite Y (Si/Al = 5.7) to learn how dealumination affects the zeolite framework [16]. They reported that silica migration had allowed the zeolite framework to maintain its crystallinity. Their dealuminated powder sample, prepared by chemical extraction using an aqueous solution of ethylenediaminetetraacetic acid (EDTA), had a diminished in unit cell constant. Olson et al. attempted to determine the proton positions in H–Y ($|H_{59}|[Si_{133}Al_{59}O_{384}]$-FAU, calcined NH_4^+-exchanged natural

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faujasite) by single-crystal X-ray crystallographically [20]. They deduced the hydrogen atom positions from the four independent Si(Al)–O distances. They found that the Si(Al)–O(1) and Si(Al)–O(3) bonds were 0.08 Å longer than the others; these were judged to be Si(Al)–OH bonds, leading to the conclusion that the protons bonded to O(1) and O(3). Jirak et al. studied a series of Y zeolites ($|Na_{53}Ca|[Si_{137}Al_{55}O_{384}]$-FAU, Si/Al = 2.49) with various Na^+ and D^+ contents using neutron powder diffraction and found that the deuterons formed structural OD groups with framework oxygen atoms [17]. Czjzek et al. directly located the deuterons and protons in D^+- and H^+-exchanged zeolites Y ($|Na_{56}|[Si_{136}Al_{56}O_{384}]$-FAU, Si/Al = 2.43) by high-resolution neutron powder diffraction [18]. They reported that the preferred proton positions were near the framework oxygens O(1) and O(3) and that the sites were occupied in the order O(1) > O(3) > O(2). Vitale et al. prepared D–Y (Si/Al = 2.43) and its benzene complex by calcining NH_4^+-exchanged zeolite Y and allowing it to sorb benzene; the resulting structures were determined by neutron diffraction [19]. They reported that the deuterons retained their original positions upon benzene sorption; the benzene molecules were located above 6-rings in the supercage and in the 12-ring planes. Most recently, Lim et al. observed crystallographically the dehydration, deamination, and dealumination processes in NH_4^+-exchanged zeolite Y (Si/Al = 1.70) without steaming as a function of evacuation temperature [21]. The positions of the NH_4^+ and nonframework Al^{3+} ions were reported.

This work was done to determine crystallographically the NH_4^+ ion positions in the crystal structure of fully dehydrated NH_4^+-exchanged zeolite Y (Si/Al = 1.57(3)) and, to the extent possible, the H^+ positions after complete deamination. Future work to determine the positions of sorbate molecules in dehydrated (activated) H–Y might reveal the structures of reaction intermediates. Tl^+–Y was studied primarily to establish the Si/Al ratio.

2. Experimental section

2.1. Synthesis of large single crystals of zeolite Y (FAU)

Colorless single crystals of sodium zeolite Y, stoichiometry $Na_{75}Si_{117}Al_{75}O_{384}$ (vide infra), with diameters up to 0.30 mm were synthesized from a gel prepared from fumed silica (99.8%, Sigma), sodium aluminate (technical, Wako), sodium hydroxide (96%, Wako), triethanolamine (TEA, 99 + %, Acros), bis(2-hydroxyethyl)dimethylammonium chloride (TCl, 99%, Acros), and distilled water (resistivity > 18.4 MΩ cm). Its composition was $3.58SiO_2$:$2.08NaAlO_2$:7.59NaOH:$455H_2O$:5.06TEA:2.23TCl. Further description is available [21]. Microscopic examination showed that the single crystals were transparent, colorless, and octahedral faujasite-type single crystals with diameters up to 0.30 mm; see Fig. 1. Crystals larger than 0.25 mm were common.

2.2. Ion exchange, dehydration, and deamination

2.2.1. Crystal 1

Because the complete NH_4^+-exchange of Na–Y is difficult to achieve, complete K^+-exchange was done first, to be followed by NH_4^+-exchange of K–Y. Crystals of hydrated $|K_{75}|[Si_{117}Al_{75}O_{384}]$-FAU ($K_{75}$–Y) were prepared by static ion exchange of $|Na_{75}|[Si_{117}Al_{75}O_{384}]$-FAU ($Na_{75}$–Y) with aqueous 0.1 M KNO_3 (Aldrich, 99.999%, 10.2 ppm Na, 0.6 ppm B, 0.2 ppm Ca), pH 5.9 [21,22]. This was done by mixing 20 mg of hydrated Na–Y containing many large crystals with 15 ml of 0.1 M KNO_3, a 12-fold excess. The mixture was then stirred on an oil bath for 24 h at 353 K. This was repeated 30 times with fresh KNO_3 solution. The product was then filtered and washed with distilled water 10 times.

To prepare NH_4–Y, these crystals were treated with 15 ml of 0.1 M $NH_4C_2H_3O_2$ (Aldrich, 99.999% $NH_4C_2H_3O_2$, 4.4 ppm Na, 0.7 ppm Li, 0.2 ppm Zn, 0.1 ppm Mg), a 15-fold excess, pH 6.9 [21] and the mixture was stirred as before. This procedure was repeated 20 times with fresh $NH_4C_2H_3O_2$ solution. The product was oven-dried at 323 K for 1 day. The crystals remained colorless and transparent throughout.

One large single crystal of NH_4–Y, a colorless octahedron about 0.27 mm in cross-section, was lodged in a fine Pyrex capillary and dehydrated under dynamic vacuum at 294 K. The system was maintained at this temperature and 1×10^{-3} Pa for 48 h. Thereafter the hot contiguous downstream lengths of the vacuum system, including a sequential 17-cm U-tube of zeolite 5A beads fully activated in situ, were allowed to cool to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to the crystal. Still under vacuum in its capillary, the still colorless crystal was sealed in its capillary and removed from the vacuum line by torch.

2.2.2. Crystal 2

Another large single crystal of NH_4–Y, a colorless octahedron about 0.25 mm in cross-section, was lodged in a fine Pyrex capillary that was then attached to a vacuum system. It was cautiously dehydrated by gradually increasing its temperature (*ca.* 25 K/h) under dynamic vacuum to 473 K. Finally, the system was maintained at 473 K and 1×10^{-3} Pa for 50 h. Still under vacuum in its capillary and with the precautions against partial rehydration described above, the still colorless crystal was sealed in its capillary and removed from the vacuum line by torch.

2.2.3. Crystal 3

A large single crystal of Na_{75}–Y, a colorless octahedron about 0.27 mm in cross-section, was lodged in a fine Pyrex capillary. An aqueous 0.05 M $TlC_2H_3O_2$ (Alfa Aesar, 99.995%) solution (pH 6.4) was allowed to flow past the crystal for 7 days at 294 K. The capillary containing the still colorless crystal was attached to a vacuum system, and the crystal was cautiously dehydrated by gradually increasing its temperature as above to 673 K. Finally, the system was maintained at 673 K and 1×10^{-3} Pa for 48 h. Still under vacuum in its capillary and with the precautions described above, the crystal was allowed to cool and was sealed in its capillary and removed from the vacuum line by torch. The resulting crystal was black. This procedure was repeated for four additional crystals.

2.3. Instrumental measurements

2.3.1. SEM–EDX

The product as first synthesized was characterized by optical and scanning electron microscopy (SEM). SEM showed that the octahedral products were large faujasite-type single crystals with diameters up to 0.3 mm and that the polycrystalline spherical impurities were gismondine (see Fig. 1(a) and (b)). Microscopic examination showed that the single crystals were transparent and colorless. The five Tl^+-exchanged single-crystals were intentionally broken to expose fresh surface (Fig. 1(c)) and were attached to carbon-attach tape for energy dispersive X-ray (EDX) analysis. Images were taken using a JSM-6300 SEM instrument, and atomic concentrations were measured with EDX, both at 294 K and 1×10^{-4} Pa (see Fig. 1(d)). Each crystal was analyzed five times; the resulting Si/Al ratio was 1.56(5).

2.3.2. X-ray diffraction

X-ray diffraction data for all single crystals were collected at 294(1) K using an ADSC Quantum210 detector at Beamline 4A MXW at The Pohang Light Source. Crystal evaluation and data collection were done using $\lambda = 0.76999$ Å radiation with a detector-to-