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Structure of a cyclohexane sorption complex of partially dehydrated, fully Mn^{2+}-exchanged zeolite Y (FAU, Si/Al = 1.56)

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ABSTRACT

The structure of a cyclohexane sorption complex of partially dehydrated, fully Mn^{2+}-exchanged zeolite Y has been determined at 100(1) K by single-crystal synchrotron X-ray diffraction techniques. It was refined using all intensities to the final error indices $R_1 = 0.052$ and $wR_2 = 0.174$. Cyclohexane molecules of symmetry $\bar{3}2/m$ (D_{3d}, chair form) occupy 5.7 of the 16 12-rings per unit cell. Each cyclohexane molecule is held in place by 18 weak hydrogen bonds between its six equatorial hydrogen atoms and all 12 oxygen atoms of its 12-ring: C···O *ca.* 3.85 Å. Mn^{2+} ions are found at four crystallographic sites, I, I′, II′, and II. Each of the 17.7(2) Mn^{2+} ions per unit cell at site II (opposite 6-rings in the supercage) coordinates tetrahedrally to three framework oxygen atoms and a water molecule. The cyclohexane molecules interact neither with the Mn^{2+} ions nor with the water molecules.

1. Introduction

Zeolites are of great interest due to their widespread industrial use as catalysts, ion exchangers, and selective sorbents [1,2]. These functions depend on the structure of zeolite and its interactions with guest molecules. Knowing how these molecules interact with the zeolite provides a structural basis for understanding the chemistry involved [3–5].

The dynamic properties of cyclohexane guest molecules in various solid host structures such as the thiourea [6], $Cd(CN)_2$ [7], $Cd(CH_3NH(CH_2)_3NH_2)Ni(CN)_4$ [8], and zeolite H-ZSM-5 [9] have been investigated by wide-line solid-state ^2H NMR spectroscopy, a particularly sensitive probe of molecular motions with characteristic time scales in the intermediate motion regime.

Poupko et al. used ^2H NMR to study the thiourea-perdeuterocyclohexane inclusion complex from 93 to 333 K [6]. They identified three temperature regions involving the structure of the host thiourea lattice and the behavior of the guest cyclohexane molecules. Below 129 K, the host lattice was monoclinic and the guest molecules undergo thermally activated reorientation about the C_3 axis. Between 129 and 156 K, the monoclinic host lattice gradually transformed into a hexagonal form and three nonequivalent kinds of guest molecules were found. Above 156 K, the host lattice was hexagonal and the guest molecules were highly disordered.

Nishikiori et al. studied the molecular motion of cyclohexane enclathrated in $Cd(CH_3NH(CH_2)_3NH_2)Ni(CN)_4$ using CP/MAS ^{13}C NMR and ^2H NMR [8]. They suggested that the chair form of cyclohexane was undergoing n-fold reorientation about its 3-fold axis. This motion was retained to 397 K accompanied by inversion of the ring above *ca.* 239 K.

Aliev et al. studied the dynamic properties of C_6D_{12} molecules in zeolite H-ZSM-5 using variable temperature wide-line solid state ^2H NMR spectroscopy [9]. They reported that the C_6D_{12} molecules underwent three types of rapid motion between 93 and 233 K: (1) reorientation about its C_3 axis, (2) restricted wobbling (precession) about its C_3 axis, and (3) a four-site jump motion.

The sorption of the hydrocarbons benzene [10–12], xylene [13], toluene [14], mesitylene [15,16], ethylene [17], acetylene [18], and cyclopropane [19] in FAU-type zeolites were investigated by single-crystal X-ray diffraction techniques to learn their sorption sites. From this their interactions with the cations and the zeolite framework could be described. The sorption of these hydrocarbons is governed mainly by their sizes, the identity of the cations, and the Si/Al ratio of the framework.

Vitale et al. used powder neutron diffraction and energy minimization calculations to learn the locations of sorbed cyclohexane in the acid form of zeolite Y (FAU, Si/Al = 2.43) [20]. From their neutron diffraction work, they found cyclohexane in its chair conformation in 12-rings. They calculated, however, that other positions of lower

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symmetry had similar sorption energies.

Of the organic molecules that can be sorbed into zeolites, polar molecules are most strongly held, unsaturated hydrocarbons are weakly held unless the zeolite contains cations to which they can π-bond, and saturated hydrocarbons are most weakly held. However, saturated hydrocarbons can be effectively sorbed if they fit features of the zeolite structure, so that they can have multiple weak interactions with a relatively small decrease in entropy. Cyclohexane in a round 12-ring is an example of this [20]. This report provides a detailed look at the geometry and thermal motion of that interaction.

2. Experimental section

2.1. Crystal preparation

Large colorless octahedral single crystals of $|Na_{75}|[Si_{117}Al_{75}O_{384}]$-FAU ($Na_{75}$-Y) with diameters up to 0.19 mm were prepared by Lim et al. [21]. Mn^{2+} exchange was done using aqueous 0.1 M Mn$(NO_3)_2{\cdot}xH_2O$ (Aldrich, 99.99%, Co 17.3 ppm, Fe 9.23 ppm, K 5.56 ppm, Cr 5.1 ppm, Na 2.87 ppm, Ce 2.49 ppm). Hydrated Na_{75}-Y (10 mg) was mixed with 10 ml of 0.1 M $Mn(NO_3)_2$, a 20 fold-excess, in a 15 ml conical tube and the mixture was stirred on a shaking incubator at 343 K for 24 h. This procedure was repeated 20 times with fresh Mn$(NO_3)_2$ solution. Finally, the product was washed with distilled water (300 ml), filtered, and oven dried at 323 K for 1 d. The structures of complexes of crystals from this batch have been reported before, and the exchangeable cation and framework composition, $|Mn_{37.5}|[Si_{117}Al_{75}O_{384}]$-FAU ($Mn_{37.5}$-Y) has been established by crystallographic and SEM-EDX methods [12–15,22].

One of these crystals, a clear light brown octahedron about 0.19 mm in cross section, was lodged in a fine Pyrex capillary. This was attached to a vacuum system, and the crystal was cautiously dehydrated under dynamic vacuum by gradually increasing its temperature (*ca.* 25 K/h) to 723 K. The crystal was then maintained at this temperature for 2 d at $P = 1 \times 10^{-4}$ Pa. Still under vacuum in its capillary, the crystal was then allowed to cool at room temperature; it remained light brown.

To prepare the cyclohexane sorption complex of Mn-Y, the crystal was exposed to 1.1×10^4 Pa of zeolitically dried cyclohexane (Aldrich, 99.97%, residue on evaporation 0.0005%) vapor for 5 d at 294(1) K. This vapor was dried by allowing it to pass through a 30 cm tube filled with activated beads of zeolite 5A. The excess vapor was then evacuated from the capillary for 600 s. Finally, the crystal in its capillary was sealed off under vacuum from the line. It had become dark brown.

2.2. X-ray diffraction

X-ray diffraction data for the resulting single crystal were collected at 100(1) K at the Pohang Light Source, Pohang, Korea. Preliminary cell constants and an orientation matrix for the crystal were determined from 36 sets of frames collected at scan intervals of 5° with an exposure time of 1 s per frame. The basic data file was prepared using the HKL2000 program [23]. The reflections were successfully indexed by the automated indexing routine of the DENZO program [23]. About 103,120 reflections were harvested for the crystal by collecting 72 sets of frames with a 5° scan and an exposure time of 1 s per frame. These highly redundant data sets were corrected for Lorentz and polarization effects; negligible corrections for crystal decay were also applied. The space group $Fd\bar{3}m$, standard for zeolite Y, was determined by the program XPREP [24]. A summary of the experimental and crystallographic data is presented in Table 1.

3. Structure determination

Least squares refinement using SHELXL-97 [25] was done on F_o^2 using all 1612 unique reflections. Anisotropic refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O1, O2, O3, and O4] in dehydrated $|Tl_{75}|[Si_{117}Al_{75}O_{384}]$-FAU [26]. It converged to the error indexes (agreement parameters), defined in a footnote to Table 1, $R_1 = 0.40$ and $wR_2 = 0.83$. The progress of structure determination as subsequent peaks were found on difference Fourier functions and identified as nonframework atoms, and hydrogen atoms were added at calculated positions, are given in Table 2.

A small decrease in the error indexes was observed when the hydrogen atoms were added at calculated positions, and another small decrease was seen when the thermal parameters at C were assigned to H1 and H2 (Table 2). These decreases were too small to allow further definition to be added to the anisotropic thermal parameters assigned to the hydrogen atoms.

Fixed weights were used initially. The final weights were assigned using the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, with a and b as refined parameters (Table 1). Neutral atomic scattering factors within SHELX-97 were used, and all were modified to account for anomalous dispersion [27,28]. The final structural parameters and selected interatomic distances and angles are presented in Tables 3 and 4.

4. Description of the structure

4.1. Brief description of zeolite Y

The framework structure of zeolite Y (FAU) is characterized by the double 6-ring (D6R, hexagonal prism), the sodalite cavity (a cubooctahedron), and the supercage (Fig. 1) [29]. Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 single 6-rings (S6Rs).

The exchangeable cations, which balance the negative charge of the zeolite Y framework, usually occupy some or all of the sites shown with Roman numerals in Fig. 1. The orders (maximum occupancies, ions per unit cell) of the cation sites I, I′, II′, II, and III are 16, 32, 32, 32, and 48, respectively. Further description is available [30,31].

4.2. Cyclohexane in zeolite Y

Per unit cell, 5.7 cyclohexane molecules are found. Each centers a 12-ring, the best plane of each coinciding with the plane of its 12-ring (Fig. 2). Just 5.7 of the 16 12-rings per unit cell host a cyclohexane molecule. This is the amount of cyclohexane remaining in the crystal when its capillary was sealed off under vacuum at room temperature from the vacuum line.

The sorbed cyclohexane molecules form weak hydrogen bonds to oxygen atoms of the zeolite framework (Table 4 and Fig. 2). They do not interact at all with the Mn^{2+} ions. Their symmetry is $\bar{3}2/m$ (D_{3d}, chair form). Each equatorial hydrogen atom H1 interacts with one O4 and two O1 framework oxygen atoms to give a total of $6 \times 3 = 18$ interactions per molecule. The H1 hydrogen atoms are directed toward lone-pair orbitals of the framework oxygens at distances of 3.02 and 3.16 Å, respectively. The axial H2 hydrogen atoms do not participate in any interactions beyond their bonds to the C atom.

4.3. Mn^{2+} ions

Mn^{2+} ions occupy four different crystallographic sites: I, I′, II′, and II. Of the 40.1(4) Mn^{2+} ions per unit cell, 12.7(1) are found at site I (Mn1). They center D6Rs (Fig. 3(a)). The octahedral Mn1–O3a distance, 2.270(4) Å, is substantially longer than the sum of the conventional ionic radii of Mn^{2+} and O^{2-}, 0.80 + 1.32 = 2.12 Å [32]. This indicates that Mn^{2+} is a little too small for the D6R and that each has pulled the six O3a atoms to which each bonds closer. The O3a-Mn1-O3a angles, 88.81(12)° and 91.19(12)° (Table 4), are nearly octahedral.

The 6.7(2) Mn^{2+} ions per unit cell at Mn1′ occupy site I′. Because the neighboring positions I and I′ are too close to be occupied simultaneously because of the strong interacationic repulsion that would result, pairs of ions