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Preparation and single-crystal structure of mesitylene sorption complex of fully dehydrated fully Mn^{2+}-exchanged zeolite Y (FAU)

Md. Shamsuzzoha [a], Sung Man Seo [a], Young Hun Kim [b], Woo Taik Lim [a,*]

[a] Department of Applied Chemistry, Andong National University, Andong 760-749, South Korea
[b] Department of Environmental Engineering, Andong National University, Andong 760-749, South Korea

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ABSTRACT

The single-crystal structure of a mesitylene sorption complex of fully dehydrated fully Mn^{2+}-exchanged zeolite Y, $|Mn_{37.5}(C_9H_{12})_{15}|[Si_{117}Al_{75}O_{384}]$-FAU, has been determined by single-crystal synchrotron X-ray diffraction techniques in the space group $Fd\bar{3}m$ at 100(1) K. A fully dehydrated fully Mn^{2+}-exchanged zeolite Y crystal ($|Mn_{37.5}|[Si_{117}Al_{75}O_{384}]$-FAU, Si/Al = 1.56) was treated with zeolitically dried mesitylene at 297(1) K for 3 days. The structure of the resulting dark-brown crystal was refined using all intensities to the final error indices (using the 570 reflections for which $F_o > 4\sigma(F_o)$) of $R_1 = 0.063$ and $wR_2 = 0.151$. In this structure, 37.5 Mn^{2+} ions per unit cell are found at four crystallographic positions: 14.5 are at the centers of the double 6-rings (site I) and three are in the sodalite cavity opposite the double 6-rings (site I′). The remaining 20 are found at two nonequivalent sites II, near 6-rings in the supercage with occupancies of 5 and 15, respectively. Fifteen mesitylene molecules per unit cell lie on threefold axes where these interact facially with the 15 Mn^{2+} ions at the first site II (Mn^{2+}-mesitylene center = *ca.* 2.65 Å). Of the three hydrogen atoms per methyl group, one is calculated to be 2.14 Å from a framework oxygen and another one is 2.48 Å from another framework oxygen atom. Mesitylene appears to be slightly distorted in the same way.

1. Introduction

Zeolites have been extensively used as microporous materials for applications in separation, storage, and heterogeneous catalysis due to their high stability and structural diversity [1,2]. Sorption is an important aspect of zeolite catalysis and plays a leading role in number of reactions.

The sorption of hydrocarbons in zeolites has been investigated by a number of experimental methods such as X-ray diffraction [3], neutron diffraction [4], infrared spectroscopy [5], molecular dynamics calculations [6], and Xenon-129 NMR [7]. Seff and coworker [8] have summarized the single-crystal structures of some hydrocarbon sorption complexes of zeolites. Among of these, particular interest of active research is the sorption of aromatic hydrocarbons in zeolites because of the utility of zeolites as molecular sieves and catalysts, and the foundation of several industrially important reactions such as the processing of BTX (benzene, toluene, and xylene); e.g., toluene disproportionation, adsorptive separation of the xylene isomers, and benzene alkylation [9].

Perdeuterobenzene sorption structure in zeolite H-SAPO-37 was investigated by powder neutron diffraction and ^2H NMR techniques [10]. The diffraction measurements at 5 K revealed that benzene was located both above the 6-ring window and on the plane of the 12-ring window. The influence of the temperature on benzene sorption in K^+, Ca^{2+}, and Sr^{2+}-exchanged faujasite-type zeolites was investigated by high-speed X-ray powder diffraction method [11]; benzene molecules on the cation distribution rapidly increased with the cation–molecule interaction energy. The structure of benzene-sorption complexes of Ca^{2+}-X, Cd^{2+}-X, Sr^{2+}-Y, Mn^{2+}-X, and Mn^{2+}-Y were studied by using single-crystal X-ray diffraction techniques [12–16]. In these structures, benzene molecules were found at two distinct sites within the supercage; one was in the supercage near site II, where they interact facially with cation and another was centered in the plane of the 12-ring window between adjacent supercages, they were stabilized by multiple van der Waals forces and electrostatic interactions.

Poissant et al. [17] studied the sorbate–sorbent interactions in xylene–sorption complex of zeolites Y by FT-Raman spectroscopy. They observed the formation of a π-complex between the xylene and cations, and the strong interaction between methyl groups of xylene and the six membered ring of the framework. The structures of Yb,Na-Y zeolites containing sorbed perdeuterated xylenes had been studied for two different xylene coverages at 5 K by powder neutron diffraction technique [18]. The xylene molecules were located in the supercage and had short contacts with the Na^+

* Corresponding author. Tel.: +82 54 820 5454; fax: +82 54 822 5452.
E-mail address: wtlim@andong.ac.kr (W.T. Lim).

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cations at site II′ due to the perpendicular planes of their aromatic rings to the threefold axes.

Local and macroscopic distribution of mesitylene in the cavities of Na-Y had been studied by ^{129}Xe and multiple-quantum NMR [19]. The location of mesitylene sorbed in Na,Tb-Y zeolite was studied by neutron powder diffraction technique at 5 K [20]. Mesitylene molecules were found in the supercage, near site-II Na^+ ions. Two distinct sites II, corresponding to two different orientations of the molecules with respect to the framework were observed. The distances between the ring centers and Na^+ ions were 2.604(2) and 2.582(2) Å for the molecules in these two positions which indicated the formation of π-complexes.

Choi et al. [21] determined the crystal structure of mesitylene sorption complex of fully dehydrated Ca^{2+}-exchanged zeolite X by single-crystal X-ray diffraction techniques. Their crystallographic studies showed that one mesitylene molecule per supercage lay on a threefold axis where it interacted facially with Ca^{2+} ion (Ca^{2+}-mesitylene center = 2.70 Å). Mesitylene appeared to be distorted and to a similar extent as half of the strained molecule [2.2.2](1,3,5)cyclophane-1,9,17-triene.

This work was carried out to investigate the position of the sorbed of mesitylene molecule, the cation shifts upon sorption of mesitylene, and cation-sorbate interactions in fully dehydrated fully Mn^{2+}-exchanged zeolite Y by single-crystal X-ray diffraction technique.

Table 1
Summary of experimental and crystallographic data.

$\|Mn_{37.5}(C_9H_{12})_{15}\|[Si_{117}Al_{75}O_{384}]$-FAU	
Crystal cross-section (mm)	0.29
Ion exchange T (K)	343
Ion exchange for Mn^{2+} (day, mL)	20, 200
Dehydration T (K)	723
Crystal color	Dark brown
Data collection T (K)	100(1)
Space group, Z, X-ray source	$Fd\bar{3}m$, 1, PLS (6B MXI BL)
Wavelength (Å)	0.90000
Unit cell constant, a (Å)	24.605(1)
2θ range in data collection (°)	60.69
No. of unique reflections, m	573
No. of reflections with $F_o > 4\sigma(F_o)$	570
No. of variables, s	55
Data/parameter ratio, m/s	10.42
Weighting parameters, a/b	0.0410/587.9
Final error indices	
R_1/wR_2 ($F_o > 4\sigma(F_o)$)[a]	0.063/0.151
R_1/wR_2 (all intensities)[b]	0.064/0.153
Goodness-of-fit[c]	1.262

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; R_1 and wR_2 are calculated using only the 570 reflections for which $F_o > 4\sigma(F_o)$.
[b] R_1 and wR_2 are calculated using all 573 unique reflections measured.
[c] Goodness-of-fit = $(\Sigma w(F_o^2 - F_c^2)^2/(m\text{-}s))^{1/2}$, where m and s are the number of unique reflections and variables, respectively.

2. Experimental section

2.1. Single-crystal preparation

Large colorless single crystals of sodium zeolite Y, stoichiometry $Na_{75}Si_{117}Al_{75}O_{384}$ per unit cell, with diameters up to 0.32 mm were prepared in the Nano Material Structure Research Laboratory, Andong National University, South Korea [22]. Crystals of hydrated $Mn_{37.5}$-Y, stoichiometry $Mn_{37.5}Si_{117}Al_{75}O_{384}$, were prepared by ion-exchange of Na_{75}-Y with aqueous 0.1 M $Mn(NO_3)_2{\cdot}xH_2O$ (Aldrich, 99.99%). Hydrated sodium zeolite Y (0.01 g) was added to 10 mL 0.1 M $Mn(NO_3)_2$, a 20-fold excess in a 15-ml conical tube and the mixture was placed on a shaking incubator at 343 K for 24 h. This was repeated 20 times with fresh $Mn(NO_3)_2$ solution. The product was washed each time with distilled water (300 mL), filtered and oven-dried at 323 K for 1 day.

One of these crystals, a clear brown octahedron about 0.29 mm in cross section, was lodged in a fine Pyrex capillary. This was attached to a vacuum system and was cautiously dehydrated by gradually increasing its temperature (*ca.* 25 K/h) under dynamic vacuum to 723 K followed by 2 days at this temperature and pressure of 1.3×10^{-4} Pa. While these conditions were maintained, the hot contiguous downstream lengths of the vacuum system, including two sequential U-tubes of zeolite 5A beads fully activated in situ, were cooled to an ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to the crystals. Still under vacuum in the capillary, the crystal was then allowed to cool to room temperature; the resulting crystal was pale brown.

To prepare the mesitylene sorption complex, the crystal was treated with zeolitically dried mesitylene (Sigma–Aldrich, 98%) for 3 days at 298(1) K, and then evacuated for 1 h at this temperature. It was then sealed in its capillary by torch and removed from the vacuum line. Microscopic examination showed that the crystal had become dark brown.

Table 2
Steps of structure determination as atom positions are found.

	Occupancy[a]								
Step	Mn(1)	Mn(1′)	Mn(2a)	Mn(2b)	C(1)	C(2)	C(3)	R_1	wR_2
1[b]								0.4390	0.7843
2[c]	8.9(8)							0.3016	0.7298
3[c]	14.6(4)			16.0(5)				0.1051	0.2781
4[c]	14.6(3)		3.5(6)	13.8(6)				0.0905	0.2527
5[c]	14.4(3)	5.8(8)	3.2(6)	14.6(6)				0.0822	0.2278
6[c]	14.4(3)	3.1(4)	4.6(6)	15.7(5)	82(7)			0.0713	0.1790
7[c]	14.5(2)	3.6(4)	4.5(5)	15.7(5)	65(9)		42(9)	0.0676	0.1638
8[c]	14.6(2)	3.4(4)	4.2(5)	15.6(5)	56(10)	37(10)	26(7)	0.0662	0.1574
9[c,d]	14.7(2)	3.5(4)	4.2(5)	15.4(5)	46(1)	46(1)	46(1)	0.0661	0.1569
10[e]	14.7(2)	3.5(4)	4.7(10)	15.0(9)	45(3)	45(3)	45(3)	0.0639	0.1527
11[f]	14.5	3	5	15	45	45	45	0.0642	0.1530
12[g]	14.5	3	5	15	45	45	45	0.0634	0.1512

[a] The occupancy is given as the number of Mn^{2+} ions and C atoms per unit cell.
[b] Only the atoms of zeolite framework were included in the initial structure model. Framework atoms were allowed to refine anisotropically.
[c] Isotropic temperature factors were used for all Mn^{2+} and carbon positions.
[d] Constraint work was done between Mn(2b) and C atoms.
[e] All Mn^{2+} ions were refined anisotropically.
[f] Mn^{2+} ions and carbon atoms were fixed.
[g] Hydrogen atoms of Mesitylene were simulated.