Single-crystal Structure of Cd\(^{2+}\)-exchanged Zeolite Y (FAU, Si/Al = 1.56), [Cd\(_{27.5}(Cd\(_6\)O\(_4\))_{2.5}[Si\(_{117}Al\(_{75}O_{384}]\)-FAU

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Zeolite framework contains channels and windows and interconnected voids which are occupied by the cations and water molecules. The cations are quite mobile and may usually be exchanged by other cations.\(^{1,2}\) Ion exchange is the most important method for the modification of the physical and chemical properties of zeolites for use as catalysts, sorbents, and molecular sieves. The results of ion exchange into zeolites from aqueous solution are usually not simple. Often only a fraction of the original cations can be replaced, and attempts to overcome this may reveal a relatively sharp upper limit to exchange. When acetate salt of metal cations dissolves in water for exchange solution, metal hydroxide ions occurred. It can be exchanged for Na\(^+\) ions into zeolite framework, leading to over exchange.

The catalytic activity of Cd\(^{2+}\)-exchanged zeolite Y for the formation of acetonitrile was studied for comparison with the formation of acetonitrile from ethane and ammonia. It was found to be essentially inactive for the formation of acetonitrile from ethylamine.

When zeolite Y (Si/Al = 1.69) was ion exchanged in aqueous stream 0.05 M in Cd\(^{2+}\) (0.025 M Cd(NO\(_3\))\(_2\) and 0.025 M Cd(C\(_2\)H\(_4\)O\(_2\))\(_2\) for 5 days and dehydrated at 723 K and 2 \(\times\) 10\(^{-6}\) Torr for 2 days, the resulting composition, [Cd\(_{27.5}(Cd\(_6\)O\(_4\))_{2.5}[Si\(_{117}Al\(_{75}O_{384}]\)-FAU, indicated that eight molecules of Cd(OH)\(_2\) had been imbibed per unit cell.\(^3\) With eight non-framework oxides, two Cd\(_6\)O\(_4\)^{2+} clusters had formed per unit cell. It was stated that the ability of Cd\(^{2+}\) ions to hydrolyze at pH 7 facilitated this process, as did the ability of the sodalite unit to host and stabilize Cd\(_6\)O\(_4\)^{2+} clusters.

This study was done to investigate the behavior of Cd\(^{2+}\) in Cd\(^{2+}\)-exchanged zeolite Y (Si/Al = 1.56) prepared at high ion-exchange temperature (353 K), with the expectation of forming more cadmium oxide cluster, Cd\(_6\)O\(_4\)^{2+}. Synchrotron X-ray diffraction data were collected at 100 (1) K using an ADSC Quantum 210 detector at Beamline 6B MXI at the Pohang Light Source. Crystal evaluation and crystallographic data is presented in Table 1.

Table 1. Summary of experimental and crystallographic data

<table>
<thead>
<tr>
<th>Crystal cross-section (mm)</th>
<th>0.30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion exchange T (K)</td>
<td>353</td>
</tr>
<tr>
<td>Ion exchange for Cd(^{2+}) (mL, days)</td>
<td>20, 3</td>
</tr>
<tr>
<td>Dehydration T (K)</td>
<td>723</td>
</tr>
<tr>
<td>Crystal color</td>
<td>dark yellow</td>
</tr>
<tr>
<td>Data collection T (K)</td>
<td>100(1)</td>
</tr>
<tr>
<td>Space group, Z</td>
<td>F(_d\bar{d}) \bar{m}</td>
</tr>
<tr>
<td>X-ray source</td>
<td>Pohang Light Source (6B MXI BL)</td>
</tr>
<tr>
<td>Wavelength ((\lambda))</td>
<td>0.90000</td>
</tr>
<tr>
<td>Unit cell constant, a((\AA))</td>
<td>24.8600(1)</td>
</tr>
<tr>
<td>20 range in data collection (deg)</td>
<td>70.32</td>
</tr>
<tr>
<td>Total reflections harvested</td>
<td>87,989</td>
</tr>
<tr>
<td>No. of unique reflections, m</td>
<td>852</td>
</tr>
<tr>
<td>No. of reflections with (F_\sigma &gt; 4\sigma(F_\sigma))</td>
<td>849</td>
</tr>
<tr>
<td>No. of variables, s</td>
<td>51</td>
</tr>
<tr>
<td>Data/parameter ratio, m/s</td>
<td>16.7</td>
</tr>
<tr>
<td>Weighting parameters, a/b</td>
<td>0.041/668.1</td>
</tr>
<tr>
<td>Initial error indices</td>
<td>R(_{\text{wp}}) = 0.5416/0.8411</td>
</tr>
<tr>
<td>Final error indices</td>
<td>R(_{\text{wp}}) = 0.0643/0.1747</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Notes

\(^{1}\) Goodness-of-fit = \[\sum \frac{|F_\sigma| - \sqrt{\sum w(|F_\sigma|)^2}}{\Sigma w(F_\sigma)^2}(m-o)^2\] \(R_1\) and \(R_2\) are calculated using only the reflections for which \(F_\sigma > 4\sigma(F_\sigma)\). \(R_1\) and \(R_2\) are calculated using all unique reflections measured. \(w = n/m\) is the number of unique reflections and \(s\) is the number of variables, respectively.

The reflections were successfully indexed by the automated indexing routine of the DENZO program.\(^6\) The 87,989 reflections were harvested by collecting 144 sets of frames with 5\(^{o}\) scans and an exposure time of 1 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects, and (negligible) corrections for crystal decay were also applied. The cubic space group \(F\(_d\bar{d}\)\bar{m}\) was determined by the program XPREP.\(^7\) The summary of the experimental and crystallographic data is presented in Table 1.

Full-matrix least-squares refinement (SHELXL97)\(^8\) was done on \(F_\sigma^2\) using all data. Refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), (O(1), O(2), O(3), and O(4))] in dehydrated [Tl\(_{12}\)[Si\(_{117}Al\(_{75}O_{384}]\)-FAU.\(^9\) Initial refinement used anisotropic thermal parameters and...
converged to the high error indices (given in Table 1). All shifts in the final cycles of refinement were less than 0.1% of their corresponding estimated standard deviations. The final error indices are given in Table 1. Structural parameters are given in Table 2, and selected interatomic distances and angles are given in Table 3.

The framework structure of zeolite Y (FAU) is characterized by the double 6-ring (D6R, hexagonal prism), the sodalite cavity (a cuboctahedron), and the supercage (see Fig. 1). Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs (32 S6Rs), 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 Figure 1. The maximum occupancies at the cation sites I, I', II, II', and III in zeolite Y are 16, 32, 32, 32, and 48, respectively. Site III'
The 13 Cd\textsuperscript{2+} ions per unit cell at Cd(Ia) are found at six equipoints within the unit cell in this structure: site I, two different sites I', and three dissimilar sites II.

As the structure of crystal in this study, Cd\textsuperscript{2+}-exchanged zeolite Y (Si/Al = 1.69) prepared by nearly same experiments with our recipe, just different dehydration temperature, had seemingly imbibed eight Cd(OH)\textsuperscript{x} ions per unit cell. The ion-exchange reaction may be written as

\[
\text{Na}_8\text{Y} + 47.5 \text{Cd}^{2+} + (20 + x)\text{H}_2\text{O} \rightarrow (1)
\]

\[
(C\text{d}^{2+})_{17.5-(20 + x)}(\text{CdOH}^-)_{20}(\text{CdOH}_2)^{x^-}\text{Y} + 75\text{Na}^+ + 20\text{H}^+
\]

By comparison with the structures of fully dehydrated Cd\textsuperscript{2+}-exchanged zeolite Y (Si/Al = 1.69), [Cd\textsubscript{27.5}(Cd\textsubscript{2}O\textsubscript{5})\textsubscript{3}[Si\textsubscript{117}Al\textsubscript{15}O\textsubscript{384}]-FAU, it could be seen and confirmed that suggested five [Cd\textsubscript{4}(OH)\textsubscript{3}]\textsuperscript{27.5} groups per unit cell within sodalite units during Cd\textsuperscript{2+} exchange at 353 K.

\[
(C\text{d}^{2+})_{17.5-(20 + x)}(\text{CdOH}^-)_{20}(\text{CdOH}_2)^{x^-}\text{Y} \rightarrow (2)
\]

\[
(C\text{d}^{2+})_{17.5-(20 + x)}(\text{Cd}_4(\text{OH})_3)^{x^-}(\text{CdOH}_2)^{z^-}\text{Y}
\]

After dehydration at 723 K, 20 Cd\textsuperscript{2+} ions are decomposed to give 2.5[Cd\textsubscript{2}O\textsubscript{5}]\textsuperscript{11+} clusters with complete dehydration. It appears that the following reaction occurred upon dehydration

\[
(C\text{d}^{2+})_{17.5-(20 + x)}(\text{Cd}_4(\text{OH})_3)^{x^-}(\text{CdOH}_2)^{z^-}\text{Y} \rightarrow (3)
\]

\[
(C\text{d}^{2+})_{27.5}(\text{Cd}_4\text{O}_2)^{x^-}\text{Y} + (10 + x)\text{H}_2\text{O}
\]

As the structure of crystal in this study, Cd\textsuperscript{2+}-exchanged zeolite Y (Si/Al = 1.69) prepared by nearly same experiments with our recipe, just different dehydration temperature, had seemingly imbibed eight Cd(OH)\textsubscript{2} molecules per unit cell. These decomposed upon vacuum dehydration at 623 K to give two Cd\textsubscript{2}O\textsubscript{5}\textsuperscript{11+} clusters. When the fully dehydrated structures of [Cd\textsubscript{27.5}(Cd\textsubscript{2}O\textsubscript{5})\textsubscript{3}[Si\textsubscript{117}Al\textsubscript{15}O\textsubscript{384}]-FAU (in this study) and [Cd\textsubscript{27.5}(Cd\textsubscript{2}O\textsubscript{5})\textsubscript{3}[Si\textsubscript{121}Al\textsubscript{17}O\textsubscript{384}]-FAU are
compared, it can be seen that two structures are nearly similar appearance of [CdO$_8$]$^{8+}$ cluster. The distances of Cd-O formed distorted cube and another Cd-O formed cubane in |Cd$_{27.5}$- (Cd$_8$O$_4$)$_{2.5}$|[Si$_{117}$Al$_{75}$O$_{384}$]-FAU (in this study) and |Cd$_{27.5}$- (Cd$_8$O$_4$)$_{2.5}$|[Si$_{121}$Al$_{71}$O$_{384}$]-FAU are 2.096(15) and 2.23(5) Å and 2.12(8) and 2.324(9) Å, respectively, which are considerably different due to their Si-Al ordering in tetrahedral site by Si/Al ratio of zeolite Y leading to the diverse kinds of 6-rings (3Si3Al, 4Si2Al, and 5Si1Al).

**Experimental Section**

Large, clear, colorless, octahedral single crystals of sodium zeolite Y, |Na$_{75}$|[Si$_{117}$Al$_{75}$O$_{384}$]-FAU (Si/Al = 1.56), with diameters up to 0.32 mm were prepared by Lim et al. One of these was lodged in its own Pyrex capillary. It was Cd$^{2+}$-exchanged by the flow method using aqueous exchange solution of Cd(NO$_3$)$_2$ (Aldrich, 99.999%, K 0.9 ppm, Na 0.8 ppm, Zn 0.3 ppm, Ag 0.1 ppm, Cr 0.1 ppm) and Cd(C$_2$H$_3$O$_2$)$_2$ (Aldrich, 99.99+%, Hg 4.2 ppm, Pb 3.0 ppm, Na 0.9 ppm, Ti 0.8 ppm, Ag 0.7 ppm, Zr 0.6 ppm, Zn 0.5 ppm, Mg 0.4 ppm, Ca 0.3 ppm, Fe 0.1 ppm, Mn 0.1 ppm, Co 0.1 ppm) in the molar ratio 1:1 with a total Cd$^{2+}$ concentration of 0.05 M for 3 days at 353 K. The pH of this solution was 6.0 at 294 K. The resulting clear colorless crystal was dehydrated at 723 K and a dynamic vacuum of 1 × 10$^{-6}$ Torr for 2 days. After dehydration, microscopic examination showed that crystal had become dark yellow.

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**Supporting Information Available.** Tables of calculated and observed structure factors (9 pages). The supporting materials are available via the Internet http://www.kcsnet.or.kr/bkcs.

**References**