Microporous and Mesoporous Materials 165 (2013) 265–273

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

# Using InCl vapor to ion exchange indium into zeolite Na–X. II: A single crystal structure containing $(In_8Cl_8)^{16+}$, $In_5{}^{7+}$–$Cl^-$–$In_5{}^{7+}$, and $In^+$

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ARTICLE INFO

*Article history:*
Available online 19 August 2012

*Keywords:*
Vapor phase ion exchange
Zeolite X
Structure
Indium
Chloride

## ABSTRACT

Anhydrous vapor phase ion exchange (VPIE) using InCl(g) had been used to introduce indium ions into zeolite $Na_{92}$–X (FAU, Si/Al = 1.09); the product was $In^+_{14}(In_5^{7+})_4Na^+_{50}$—X. Treatment of $Na_{92}$–X with a lower vapor pressure of InCl(g) at lower temperatures has now yielded $In^+_{6.4}(In_8Cl_8)^{16+}_{1.73}(In_{10}Cl)^{13+}_{1.0}Na^+_{45.6}$—X; $Cl^-$ ions were retained and cationic $In_nCl_m^{p+}$ clusters have formed. Its structure was determined using single-crystal crystallography with synchrotron X-radiation and was refined in the space group $Fd\bar{3}$ ($a$ = 24.890(1) Å) to the final error index $R_1$ = 0.066. $In_8Cl_8^{16+}$ clusters center and extend out of 22% of the sodalite cavities. Each consists of a tetrahedrally distorted $In_4Cl_4$ cube (In–Cl = 2.323(23) Å) with –In–Cl extending radially from each of its $Cl^-$ ions (the Cl–In–Cl distances are 2.302(17) and 2.406(14) Å, respectively). With $Cl^-$ ions and oxygen atoms of the zeolite framework, these indium ions, all $In^{3+}$, have octahedral and trigonal bipyramidal coordination, respectively. $In_5^{7+}$ cationic clusters center another 25% of the sodalite cavities. $In_5^{7+}$ is a centered tetrahedron with In–In = 2.745(8) Å; each terminal atom bonds to three framework oxygen atoms of a double 6-ring with In–O = 2.150(5) Å and O–In–O = 105.1(3)°. One terminal atom of each $In_5^{7+}$ cluster also bonds to a $Cl^-$ ion at site I, which in turn bonds linearly to a terminal atom of another $In_5^{7+}$ cluster. In this way the $In_5^{7+}$ units link together in pairs to give $In_{10}Cl^{13+}$. The remaining indium cations, 6.4 $In^+$ per unit cell, are in the sodalite cavities. Most of the $Na^+$ ions, 25.1 per unit cell, complete the filling of the single 6-rings; the remainder are at 12-ring sites.

## 1. Introduction

### 1.1. Catalysis by indium zeolites

Indium zeolites are important industrial catalysts with high activity and selectivity for several catalytic reactions [1–4]. Intrazeolitic indium species appear to be present at the active sites for the reduction of $NO_X$ with hydrocarbons [5,6], the conversion of light hydrocarbons to heavier ones [7,8], the benzoylation of naphthalene [9], and the isomerization of *m*-xylene [10]. Mavrodinova et al. found that the In-containing zeolites obtained by reductive solid state ion exchange have very different catalytic activity, stability, and selectivity in the *m*-xylene transformation process than those prepared by other methods [11]. This is attributed to the ability of In cations, acting as Lewis acids, to activate *m*-xylene by way of hydride ion abstraction. The incorporation of $In^+$ ions into the zeolites produces well defined Lewis/Brønsted acid site ratios and the Lewis sites so produced can be of well defined nature and oxidation state, according to the IR spectra of adsorbed pyridine [12,13]. Ogura et al. showed that the addition of a noble metal, especially iridium, to In/H–ZSM-5 could remarkably enhance the production of $N_2$ [14].

### 1.2. Vapor phase ion exchange (VPIE)

Conventional aqueous ion exchange using $In(NO_3)_3$ has been used to introduce the $In^{3+}$ into the ammonium forms of ZSM-5 [15,16] and mordenite [17]. This could not be extended to zeolites with higher Al contents because of the loss of crystallinity that occurs at the low pH values required to keep $In^{3+}$ in solution [18,19]. This difficulty and others that are intrinsic to aqueous methods of ion exchange may be overcome by solid state ion exchange (SSIE) or vapor phase ion exchange (VPIE). Work involving indium exchange by SSIE was discussed in a previous report [20].

In VPIE a zeolite is exposed to a volatile compound of the incoming cation, either a volatile salt or a covalent molecular compound [21]. VPIE was first used to prepare Hg–X by exposing anhydrous Na–X to $HgCl_2(g)$ [22]. Exposing anhydrous $NH_4^+$-exchanged zeolite X to $HgCl_2(g)$ led to incomplete ion exchange and some loss of crystallinity [23]. $Cu^+$ has been introduced into zeolites (Z) by

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http://dx.doi.org/10.1016/j.micromeso.2012.08.012

reacting H–Z with CuCl [24–31] vapor. As discussed before [20], VPIE could actually be the main mode of transport in many SSIE reactions. VPIE is a promising method for the preparation of nanosized indium-containing clusters with novel optical or electronic properties within zeolites by VPIE methods [32–36].

### 1.3. Objectives of this work

This work was done to explore the effect of the temperature and vapor pressure of InCl(g) on the composition of the product of its reaction with $Na_{92}$–X. In previous work a crystal of zeolite $Na_{92}$–X had been exposed to 1700 Pa (13 Torr) of InCl(g) at 673 K [37]; about 46% of the $Na^+$ ions reacted to give $In^+_{14}(In_5^{7+})_4Na^+_{50}$–X (approximate formula). It was hoped that the VPIE reaction of Na–X with InCl(g) at milder conditions (a lower vapor pressure of InCl at a lower temperature) would discourage the disproportionation of $In^+$ (to $In^0$ and $In_5^{7+}$) to yield a product with more $In^+$, which might be more active for sorption and catalysis.

As before, the extraframework indium species that formed would be identified, including their relative abundances and positioning within the zeolite, their geometry and coordination environments, and their oxidation states. Some of these chemically and thermally stable species could be of catalytic importance.

## 2. Experimental

### 2.1. Synthesis

Single crystals of sodium zeolite X ($|Na_{92}(H_2O)_n|[Si_{100}Al_{92}O_{384}]$–FAU, $Na_{92}$–X·n$H_2O$, $Na_{92}$–X, or Na–X; Si/Al = 1.09) were prepared in Leningrad, now St. Petersburg, Russia [38]. A single crystal, a colorless octahedron about 0.15 mm in cross-section, was selected and lodged in a fine Pyrex capillary near a larger excess of InCl (Sigma–Aldrich, 99.999% purity). The crystal was then fully dehydrated under vacuum as described in Table 1. The temperatures of the InCl and the crystal were then increased together under vacuum at the rate 70 K/h until all of the InCl had either reacted with the crystal or distilled away and 623 K was reached; this temperature was maintained for another 24 h. The process was the same as that reported earlier for In,Na,Cl–Y [20]. While still under vacuum, the resulting gray opaque crystal was allowed to cool and was sealed in its capillary by torch.

**Table 1**
Experimental and crystallographic data.

| | |
|---|---|
| Crystal cross-section (mm) | 0.15 |
| Dehydration of Na–X (T (K), t (h), P (Pa)) | 623, 48, $1.1 \times 10^{-4}$ |
| Reaction of Na–X with InCl (T (K), t (h), P (Pa)) | $\leqslant$623, 3, $\leqslant$0.1 |
| Evacuation after reaction (T (K), t (h), P (Pa)) | 623, 24, $1.1 \times 10^{-4}$ |
| Temperature for data collection (K) | 294(1) |
| X-ray source | 6B1 MXI[a] |
| Detector to crystal distance (mm) | 60 |
| Wavelength (Å) | 0.90000 |
| Space group, No. | $Fd\bar{3}$, 203 |
| Unit cell constant, *a* (Å) | 24.890(1) |
| Maximum 2$\theta$ for data collection (deg) | 80.76 |
| No. of unique reflections measured, *m* | 2029 |
| No. of unique reflections with $F_o > 4\sigma(F_o)$ | 1868 |
| No. of variables, *s* | 91 |
| Data/parameter ratio, *m/s* | 22.3 |
| Weighting parameters: a/b | 0.0513/404.29 |
| Final error indices: $R_1$[b]/$R_2$[c] | 0.066/0.186 |
| Goodness of fit[d] | 1.27 |

[a] Beamline 6B1 MXI at the Pohang Light Source, Korea.

[b] $R_1 = \sum |F_o - |F_c|| / \sum F_o$; $R_1$ is calculated using only those reflections for which $F_o > \sigma(F_o)$.

[c] $R_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $R_2$ is calculated using all unique reflections measured.

[d] $\text{Goodness}-\text{of}-\text{fit} = (\sum w(F_o^2 - F_c^2)^2/(m-s))^{1/2}$.

### 2.2. Diffraction

X-ray diffraction data were gathered at 294(1) K on an ADSC Quantum210 detector at Beamline 6B1 MXI at the Pohang Light Source. Preliminary cell constants and an orientation matrix 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 program HKL2000 [39]. The reflections were successfully indexed by the automated indexing routine of the DENZO program [39]. About 90,000 reflections were harvested 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; very small corrections for crystal decay were also applied. An empirical absorption correction ($\mu_l = 3.69\ mm^{-1}$) was made. The space group $Fd\bar{3}$, standard for zeolite X, was determined by the program XPREP [40]. A summary of the experimental and crystallographic data is presented in Table 1.

## 3. Structure determination

Full-matrix least-squares refinements using SHELXL97 [41] were done on $F^2$ using all unique reflections measured. They were initiated with the atomic parameters of the framework atoms (Si, Al, O1, O2, O3, and O4) from Olson's structures of dehydrated Na–X [42].

The initial refinements with isotropic thermal parameters for all framework atoms converged to the high error indices $R_1 = 0.53$ and $R_2 = 0.90$ (see Table 2). Fixed weights were used initially. The detailed progress of structure determination as subsequent peaks were found on difference Fourier functions and identified as extraframework atoms are given in Table 2. The final weights were assigned using the formula $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = [\text{Max}(F_0^2, 0) + 2F_c^2]/3$, and a and b are refined parameters (Table 1).

Because of the silicon and aluminum disorder in the zeolite framework, which extends to all framework oxygen positions and is substantially compounded by the local distortions induced by the partially occupied non-framework cation positions, careful consideration was given to the acceptability of the structural parameters, especially the thermal and occupancy parameters, that emerged at each stage of structure determination and least-squares refinement. Because of this, the results reported here are less reliable than those reported for ordered crystals where each position is fully occupied as is usually the case in crystallography. Constraints were applied to direct the refinement to a crystallographically and chemically acceptable conclusion (see Table 2, especially its footnotes). For the most part, the effects of disorder have been absorbed into thermal parameters, which are therefore inflated.

A suitable InU–In11 bond length and an occupancy ratio at the In11 and InU positions, In11/InU = 8.67(15)/2.01(6) = 4.31(20), where 4 is the maximum value by symmetry, indicated the presence of $(In11)_4(InU)$ clusters in some sodalite cavities. Such a ratio had been seen several times before with values ranging from 3.2 to 4.3 in In–A [19,43,44], In–X [36,45], and In–Y [46]. Similarly, the ratio of the occupancies at Cl and InU is 2.0(5)/2.01(6) = 1.0(3), which may be more than that observed in In,Na,Cl–Y [20] (0.63(15)), indicating some presence at Cl. However, the $U_{iso}$ value at Cl, 0.14(5) $Å^2$, was unacceptably high, indicating that the frequently observed high correlation in least squares between occupancy and thermal parameters for weakly scattering positions (low occupancy × small scattering factor) was present. When these ratios were constrained to be 4.0 and 0.5, respectively, in subsequent least-squares refinements, $U_{iso}$ at Cl decreased to