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Using InCl Vapor to Ion Exchange Indium into Zeolite Na-X. Single Crystal Structure of $|In_{34}Na_{50}|[Si_{100}Al_{92}O_{384}]$-FAU Containing In^+ and In_5^{7+}

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Introduction

Indium zeolites are important industrial catalysts with high activity and selectivity for several catalytic reactions [1,2]. Some of the difficulties intrinsic to aqueous methods of ion exchange can be overcome by vapor phase ion exchange (VPIE). Because the vapor pressure of InCl is appreciable, 13 Torr, at a moderate temperature, 673 K, it was hoped that In^+ could be introduced into zeolites in their dehydrated as-synthesized Na^+ forms by VPIE. This work was done with one step reaction in mind,

$$Na–Z + InCl(g) \rightarrow NaCl(s) + In–Z. \quad (1)$$

Experiment

A single crystal, of sodium zeolite X ($|Na_{92}(H_2O)_x|[Si_{100}Al_{92}O_{384}]$-FAU**,** Na_{92}–X·xH_2O [3] a colorless octahedron about 0.15 mm in cross-section, was selected and loaded into a fine Pyrex capillary near 0.04 g InCl (Sigma-Aldrich, 99.999%). The crystal was then dehydrated at 673 K at 1 x 10^{-6} Torr for two days. After complete dehydration, the reaction vessel containing the remaining dry InCl not in physical contact with the crystal in its capillary was sealed off under vacuum and baked at 673 K for two days, exposing the crystal to 13 Torr of InCl(*g*). The crystal, now gray and opaque, was sealed off under vacuum in its capillary by torch. Finally, X-ray diffraction data for the resulting crystal were collected at 294(1) K at the BL-17A beam line of the Photon Factory, KEK, Japan.

Results and Discussion

$In_{14}^{+}(In_5^{7+})_4Na_{50}^{+}$–X (approximate formula, see Table 1) was prepared by the reaction of fully dehydrated Na_{92}^{+}–X with 13 Torr of InCl(*g*) at T = 673 K. Its structure was determined using single-crystal crystallography with synchrotron X-radiation and was refined in the space group $Fd\bar{3}$ (a = 24.996(1) Å) with all 1566 unique data; the final error index R_1 is 0.076. Thus, InCl(*g*) reacted with about 46% of the Na^+ ions in the zeolite, to give In_5^{7+} (centered tetrahedral, In–In = 2.684(7) Å) and In^+ cations. In_5^{7+} centers exactly half of the sodalite cavities, strongly suggesting alternating occupancy; each terminal atom (at site I') bonds to three framework oxygen atoms of a double 6-ring (In–O = 2.248(6) Å and O–In–O = 102.2(2)°). The In^+ ions occupy four crystallographically distinct cationic sites: 5.8(3) per unit cell are in the sodalite cavities (site I'), 2.7(7) are near single 6-rings in the supercage (site II), 2.6(4) are near triple 4-rings in the supercage (site III'), and 3.1(5) are at second III' site. About half of the Na^+ ions complete the filling of the single 6-rings; the remainders are at 12-ring sites. Most of In^{n+} ions are easily approachable by guest molecules through th e zeolite's 12- ring channel system.

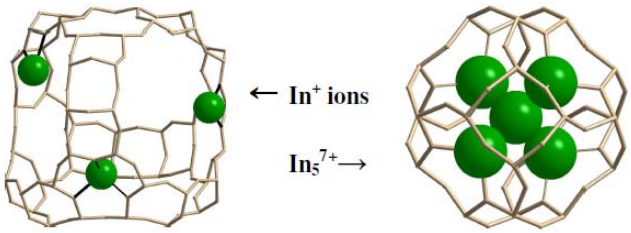

Figure 1. Distribution of In^{n+} ions in the supercage and sodalite cavity.

Table 1. Assignment of Oxidation States and Charge Budget

Sites	Atoms	Occ.[a]	r,[b] Å	NC[c]	Charge	ΣCharges
I′	In11	16.0(3)	0.93	4	+2[d]	32.0
	In12	5.8(3)	1.12	3	+1	5.8
II	In2	2.7(7)	1.16	3	+1	2.7
	Na2	22(3)	0.99	3	+1	22
III′	In31	2.6(4)	1.14	2	+1	2.6
	In32	3.1(5)	1.25	2	+1	3.1
	Na31	16(2)	1.2	2	+1	16
	Na32	7.6(17)	1.14	2	+1	7.6
U	InU	4.00(7)		4	–1[f]	–4.0
	Σ In	34.2[e]				87.8(42)[f]
	Σ Na	45.6[e]				

[a]Occupancy given as the number of ions per unit cell. [b]Radii of In and Na species obtained by subtracting 1.32 Å from the shortest In–O and Na–O bond lengths. [c]Coordination numbers. [d]Formal charges of the component atoms of In_5^{7+}. [e]Number per unit cell. [f]This value, 87.8(42)+, differs from the negative charge of the zeolite framework per unit cell, 92– (known only to the nearest integer), by one esd. To achieve charge balance with ∑Na = 50, the occupancies at Na2 and Na3 have each been increased by ca. 0.8 σ.

References

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