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Using CuCl vapor to ion exchange copper into zeolite Na–Y. Single crystal structure of $|Cu_{30}Na_{30}Cl_9|[Si_{121}Al_{71}O_{384}]$–FAU containing $Cu_{16}Cl_7^{21+}$, Cu_4Cl^{7+}, Cu_3Cl^{2+}, and Cu^{2+}

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ABSTRACT

A single crystal of zeolite Na–Y (FAU, Si/Al = 1.69) was treated with 1.6 Pa of anhydrous CuCl vapor at 623 K to yield $Cu_{30}Na_{30}Cl_9$–Y, in more detail $|Na^+{}_{30}Cu^{2+}{}_2(Cu_{16}Cl_7^{21+})_{0.44}(Cu_4Cl^{7+})_{3.2}(Cu_3Cl^{2+})_{2.8}|[Si_{121}Al_{71}O_{384}]$–FAU. Its structure was determined crystallographically with synchrotron X-radiation and was refined in the space group $Fd\bar{3}m$ ($a = 24.644(1)$ Å) with all 1159 unique data; the final error index, $R_1 = 0.064$, was calculated using only the 1028 reflections with $F_o > 4\sigma(F_o)$. About 58% of the Na^+ ions in the zeolite were replaced by Cu^{2+}, Cu_3Cl^{2+}, Cu_4Cl^{7+}, and $Cu_{16}Cl_7^{21+}$. Cu_4Cl^{7+} clusters center 41% of the sodalite cavities. Each is a centered tetrahedron with Cu–Cl = 2.931(3) Å; each terminal Cu^{2+} ion bonds to three framework oxygen atoms of one ring of a double 6-ring with Cu–O = 2.222(4) Å and O–Cu–O = 110.8(5)°. $Cu_{16}Cl_7^{21+}$ clusters center 5.5% of the supercages. Four Cu^+ ions coordinate tetrahedrally to the chloride ion at its center (Cu–Cl = 2.66(11) Å). Each pair of these Cu^+ ions is bridged by a Cl^- ion (Cu–Cl = 3.03(7) Å) along each tetrahedral edge. Each of these Cl^- ions then coordinates to two Cu^{2+} ions (Cu–Cl = 2.58(7) Å), each of which bonds to two 12-ring oxygen atoms (Cu–O = 2.35(3) and 2.41(4) Å with O–Cu–O = 67.8(8)°). About 17.5% of the 12-rings are centered by near trigonal planar Cu_3Cl^{2+} clusters (Cl^- at the center, Cu–Cl–Cu = 117.2(3)°, and Cu–O = 2.52(4) Å). The single 6-rings are fully occupied by the remaining 2.0(5) Cu^{2+} ions (Cu–O = 2.158(7) Å) and the 30.0(5) Na^+ ions (Na–O = 2.297(4) Å) per unit cell. Most of the Cu^+ and Cu^{2+} ions in this material are accessible to guest molecules via the 12-ring channel system.

1. Introduction

1.1. Catalysis by copper zeolites

The decomposition of NO to the elements is a thermodynamically favored reaction; it is the most attractive and yet the most challenging approach to NO_x abatement [1]. Copper exchanged zeolites show catalytic activity for this, and they are useful models for understanding the interactions and transformation of NO on surfaces [1]. The decomposition of NO over the Cu-exchanged zeolites FAU and MFI were first studied by Iwamoto and his coworkers [2,3]. Kuroda et al. reported that zeolites with an appropriate Si:Al ratio, one that allows copper ions to exist as dimer species, may provide the key to the catalytic redox cycle of copper in NO decomposition [4]. This conclusion coincides with the results of a theoretical calculation [5] in which bent Cu–O–Cu structures were found in Cu-MFI; these are suggested to be part of the catalytic cycle [1]. Copper zeolites can also be used in the selective reduction of NO by hydrocarbons in an oxidizing atmosphere [1,6]. Three reaction schemes have been proposed for this [1]: (a) NO decomposes to the elements and the active sites are regenerated by the hydrocarbons, (b) some reaction intermediates, formed in the partial oxidation of the hydrocarbons, selectively reduce NO, and (c) NO and O_2 react to form the strong oxidizing agent NO_2 which reacts with the hydrocarbons. It is believed that a combination of mechanisms (b) and (c) operate in Cu zeolites [1,7].

Copper exchanged zeolite Y also catalyzes the oxidation, dehydrogenation, cracking, and isomerization reactions of various organic compounds [8] and it acts as a good sorbent in the desulphurization of diesel fuels [9,10]. It has been found that the position, coordination, and oxidation state of the copper in the zeolite are key factors governing these functions [8,11]. A recent review article on copper in zeolites is available [12].

1.2. Copper exchange into zeolites

Copper has been introduced into Na–Z by conventional aqueous ion exchange using $Cu(NO_3)_2$ or $CuCl_2$ [13–15]. In no case was complete ion exchange without crystal damage easily achieved [9]. Quite generally, if the cation hydrolyzes in aqueous solution, the

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H_3O^+ concentrations may increase by orders of magnitude, encouraging H_3O^+ exchange which, for zeolites with higher Al content, can lead to crystal destruction or dissolution. To prevent crystal damage from this acidity, Lee and Seff prepared four differently desolvated Cu^{2+}-exchanged zeolite A crystals in a closed vessel at 373 K from ammoniacal aqueous $Cu(NO_3)_2$ solution and determined their structures [16]. Iwamoto et al. reported that high-silica ZSM-5 (Si/Al = 23.3) zeolites with an excess loading of copper ions are readily prepared in a single step through the addition of basic compounds such as NH_4OH or $Mg(OH)_2$ to the $Cu(NO_3)_2$ exchange solution, and that ion exchange occurred between Na^+ and $Cu_2(OH)^{3+}$ or $Cu(OH)^+$ at specific pH values. This preparative procedure was believed to promote the formation of [Cu(II)–O–Cu(II)] pairs, where the oxygen is either from the zeolite framework or from hydroxide groups [17,18].

Solid state ion exchange (SSIE) has been used to incorporate Cu^{2+} ions into zeolites with the hope that it could overcome the difficulties associated with aqueous ion exchange. Clearfield et al. [19] heated mixtures of $CuCl_2$ and zeolite to introduce Cu^{2+} ions into Na,H–Y and found that 15% of the Na^+ cations could be replaced by Cu^{2+}. Similarly, Seff et al. treated vacuum dehydrated Na_{55}–Y with $CuCl_2(s)$ and found 60% exchange [20]. Schay et al. reported 100% exchange when H-ZSM-5 and $CuCl_2$ were heated at 873 K for 3 h under dry N_2 [21].

1.3. Vapor phase ion exchange (VPIE)

The difficulties associated with Cu-exchange into zeolites with high framework Al contents might be overcome by vapor phase ion exchange (VPIE). In VPIE, a zeolite is exposed to a volatile compound of the incoming cation, either a salt or a covalent molecular compound [22]. VPIE was first used to prepare Hg–X by exposing anhydrous Na–X to $HgCl_2(g)$ [23]. Exposing anhydrous NH_4^+-exchanged zeolite X to $HgCl_2(g)$ led to incomplete ion exchange and some loss of crystallinity [24]. VPIE with InCl has been used to introduce indium into anhydrous Na–Y (Si/Al = 1.69) [25] and Na–X (Si/Al = 1.09) [26] at moderate temperatures [22]. Fully Cu^+-exchanged zeolites have very nicely been prepared by reacting $CuCl(g)$ with H–Y at 923 K [27] and H–ZSM-5 at 973 K [28].

1.4. Structures of Cu-exchanged zeolites

The structures of copper exchanged zeolites were first studied by Gallezot et al. [29]. From their X-ray diffraction study of powder samples of fully dehydrated $Cu_{16}Na_{24}$–Y and $Cu_{12}Na_5H_{27}$–Y, they learned that Cu^{2+} ions occupy sites I and I′ with Na^+ at site II. Some of these Cu^{2+} ions were seen to move into the supercages upon the introduction of organic guest molecules. They also noted proton transfer from organometallic complexes to framework oxygen atoms. The structure of fully Cu^{2+}-exchanged zeolite A, prepared by a static method using 0.1 M $Cu(NH_3)_4^{2+}$ and desolvated at 773 K for 120 h, was determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$ [16]. All Cu^{2+} ions were found on 3-fold axes in 6-rings. Each Cu^{2+} ion coordinated to three oxygen atoms at a distance of 2.14(4) Å and extended slightly into the large cavity; the O–Cu^{2+}–O angle was 119°. Recently, Seo et al. prepared Cu^{2+}-exchanged zeolite Y by the exchange of Na_{75}–Y (Si/Al = 1.56) with an aqueous stream 0.05 M in $Cu(NO_3)_2$, pH 4.2 [30]. This low pH value was chosen to minimize Cu^{2+} hydrolysis and the uptake of OH^-. Using single-crystal crystallography with synchrotron X-radiation, all of the copper ions (all Cu^{2+}) in these structures were found, at 100 K, to coordinate to four of the oxygen atoms of their 6-rings with severely distorted square planar geometry. This result is in good agreement with DFT (density functional theory) calculations [31,32].

1.5. Objectives of this work

Because the vapor pressure of CuCl is appreciable, 1.6 Pa [33], at a moderate temperature, 623 K, it was hoped that Cu^+ could be introduced into zeolites (Z) in their dehydrated as-synthesized Na^+ forms by VPIE. Accordingly, this work was done with this one-step reaction in mind,

$$\mathrm{Na{-}Z} + \mathrm{CuCl}(g) \rightarrow \mathrm{Cu{-}Z} + \mathrm{NaCl}(s) \quad (1)$$

As in our previous work [25,34], it was hoped that the sodium chloride product would have sufficient mobility at 673 K or similar temperatures to exit the zeolite, leaving only Cu–Z free of Na^+ and Cl^-. Zeolite Y was selected for this study because its transition-metal exchanged forms show considerable chemical and thermal stability [35,36]. The framework Al content of the single crystal that would be used is about 30% higher than that of commercial zeolite Y, thus requiring more extraframework cations for charge balance and facilitating the crystallographic determination of their positions.

The extraframework copper species that formed would be identified crystallographically, 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. If a simple stoichiometry emerged, sorption complexes of Cu–Y could be prepared and their structures determined.

2. Experimental section

2.1. Synthesis

Single crystals of sodium zeolite Y ($|Na_{71}(H_2O)_x|[Si_{121}Al_{71}O_{384}]$–FAU, Na_{71}–Y·$x$$H_2O$, Na_{71}–Y, or Na–Y; Si/Al = 1.69) were prepared by Lim et al. [35,36] using the synthetic method of Vaughan et al. [37]. A single crystal, a colorless octahedron about 0.15 mm in cross-section, was selected and loaded into a fine capillary extending from the Pyrex reaction vessel. Anhydrous CuCl (Sigma Aldrich, 99.99%, ampule) was transferred under nitrogen to a vessel with a break-off seal; it was temporarily sealed with vacuum grease and then sealed properly by torch. It was transferred again under vacuum (1×10^{-4} Pa) to another small Pyrex vessel fragile at one end. This was sealed, placed in the reaction vessel with the crystal and a hammer (an iron rod sealed in Pyrex), and the reaction vessel was evacuated (1×10^{-4} Pa). The fragile CuCl-containing vessel was then broken by the hammer using a magnet. The crystal was then dehydrated at 673 K at 1×10^{-4} Pa for 2 days. With the intention of further drying the CuCl, its temperature was slowly increased to 673 K under dynamic vacuum; it distilled to another position in the reaction vessel (outside the heater). The pure white color of the CuCl remained unchanged after this distillation. The Pyrex reaction vessel containing both the dehydrated crystal and the dry CuCl was then sealed off under the vacuum and maintained at 623 K for 2 days; P_{CuCl} = 1.6 Pa. The crystal end of the reaction vessel was then heated for an additional 24 h at 623 K in an attempt to distill away any excess CuCl that might have been retained by the crystal. After cooling to room temperature, the Pyrex capillary containing the crystal, now flat black in color, was sealed off for diffraction experiments.

2.2. Diffraction

X-ray diffraction data for this crystal were collected at 294(1) K. 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 7 s per frame. The basic data file was prepared