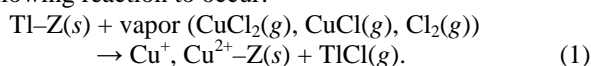# Introducing Copper Ions into Zeolite Y by the Thallous Ion Exchange Method: Single Crystal Structure of |Cu$_{21.6}$Tl$_{39.2}$|[Si$_{121}$Al$_{71}$O$_{384}$]–FAU

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1. Introduction

Copper containing zeolites are effective catalysts for the decomposition [1] and reduction [2] of NOx, and are good sorbents in the desulfurization of diesel fuels [3]. The thallous ion exchange (TIE) method might allow the difficulties seen in conventional aqueous ion exchange to be avoided. The fully Tl-exchanged zeolite Y (Tl–Y) was treated with the vapors over CuCl$_2$(s) at 673 K under anhydrous conditions. The vapor pressures of both CuCl$_2$ and its decomposition product CuCl are adequate for the following reaction to occur:

$$\text{Tl–Z}(s) + \text{vapor } (\text{CuCl}_2(g), \text{CuCl}(g), \text{Cl}_2(g))$$
$$\rightarrow \text{Cu}^+, \text{Cu}^{2+}\text{–Z}(s) + \text{TlCl}(g). \quad (1)$$

2. Experiment

A single crystal of Fully Tl$^+$-exchanged zeolite Y (|Tl$_{71}$(H$_2$O)|y[Si$_{121}$Al$_{71}$O$_{384}$]–FAU, Tl$_{71}$–Y, or Tl–Y) [4], a colorless octahedron about 0.15 mm in cross-section, was selected and loaded into a fine Pyrex capillary. Then 0.03 g of anhydrous CuCl$_2$ (brown, Sigma-Aldrich, 99.99%) was put into the same capillary just above the crystal. The crystal and the CuCl$_2$ were then dehydrated at 673 K at 1 x 10^{-6} Torr for two days. During this process, the CuCl$_2$ vaporized and decomposed (most of the condensed solid was CuCl$_2$ (brown) but a small amount was CuCl (white)). The dehydrated crystal was black. The Pyrex reaction vessel containing both the crystal and the dry CuCl and CuCl$_2$ was then sealed off under the vacuum and heated for 2 days at 673 K. After cooling to room temperature, the capillary containing the crystal, now opaque white, was sealed off. 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.

3. Results and Discussion

|Cu$^+_{10.9}$Cu$^{2+}_{10.7}$Tl$^+_{39.2}$|[Si$_{121}$Al$_{71}$O$_{384}$]–Y (approximate formula, see Table 1) was prepared by reacting fully dehydrated and fully Tl$^+$-exchanged zeolite Y with CuCl$_2$(g) and its decomposition products CuCl(g) and Cl$_2$(g) at 673 K under anhydrous conditions. Its structure was determined using single-crystal crystallography with synchrotron X-radiation and was refined in the space group $Fd\bar{3}m$ (a = 24.769(1) Å) with all 903 unique data; the final error index, $R_1 = 0.075$, was calculated using only the 858 reflections with $F_o > 4\sigma(F_o)$. About 45 % of the Tl$^+$ ions were replaced by 21.6 copper ions per unit cell at the following sites (distances to nearest framework oxygen atoms are given, see Figure 1): 10.7 Cu^{2+} at site I' in the sodalite cavity opposite double 6-rings (Cu^{2+}–O =

2.093(9) Å), 3.5 Cu$^+$ at site II opposite single 6-rings in the supercage (Cu$^+$–O = 2.24(3) Å), and 7.4 Cu$^+$ at site III near 12-rings in the supercage (Cu$^+$–O = 2.45(7) Å). All Cu$^+$ ions are in supercages where they are easily accessible to guest molecules. The remaining ca. 39Tl$^+$ ions per unit cell occupy three distinct positions: 12 are at a second site I' (Tl$^+$–O = 2.571(9) Å), 23 are at a second site II (Tl$^+$–O = 2.732(10) Å), and 4 are at site III' (Tl$^+$–O = 2.871(16) Å) near triple 4-rings in the supercages.
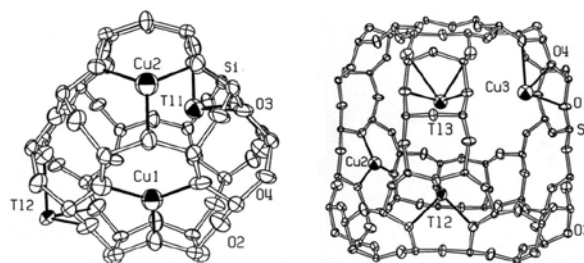
Figure 1. Distribution of Cu$^+$, Cu^{2+}, and Tl$^+$ ions in the sodalite cavity and supercage.

Table 1. Assignment of Oxidation States and Charge Budget

Sites	Atoms	Occ.^{a}	r,^{b}Å	NC^c	Charge	ΣCharges
I'	Cu1	10.7(5)	0.77	3	+2	21.4
	Tl1	12.00(17)	1.25	3	+1	12.0
II	Cu2	3.5(9)	0.92	3	+1	3.5
	Tl2	23.1(3)	1.41	3	+1	23.1
III	Cu3	7.4(12)	1.13	3	+1	7.4
III'	Tl3	4.1(3)	1.55	4	+1	4.1
	Σ Cu	21.6^d				71.5^f
	Σ Tl	39.2^d				

^{a}Occupancy given as the number of ions per unit cell. ^{b}Radii of Cu and Tl species obtained by subtracting 1.32 Å from the shortest Cu–O and Tl–O bond lengths. ^{c}Coordination numbers. ^{d}Number per unit cell. ^{e}These 71.5 positive charges closely balance the 71– charge of the zeolite framework per unit cell.

4. References

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