

SPECIATION OF COPPER IN MICROPORES

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Abstract. Speciation of copper in the micropores of zeolites and a contaminated soil was studied by extended X-ray absorption fine structural (EXAFS) spectroscopy. The Fourier transformed EXAFS data showed that copper oxide in zeolites ZSM-5 and ZSM-48 possessed a Cu-O bond distance of 1.95 Å with coordination numbers (CNs) of 1–2. Since ZSM-5 and ZSM-48 possessed channel openings of 5–6 Å, the possible sizes of the linear-type copper oxides in these confined pores were 2.93–2.95 Å. However, in the supercages (~13 Å) and channels (7.4 Å) of zeolite Y, a three dimensional structure of CuO was observed. Interestingly, we found that CuO in the Cu-contaminated soil had a similar structure to that in ZSM-5 or ZSM-48. Nevertheless, the EXAFS data indicated that the CNs of Cu-O and Cu-O-Cu were 0.4 and 0.3, respectively, suggesting a highly perturbed copper oxide in the irregular micropores of the contaminated soil.

Keywords: contaminated soil, copper oxide, EXAFS, XANES

1. Introduction

Very recently, we found that soil near a printed-circuit board waste recycling plant (located in Tainan County, Taiwan) was heavily contaminated by copper. The total and TCLP (toxicity characteristic leaching procedure) concentrations of copper in the contaminated soil were 21 000 and 84 mg L⁻¹, respectively. Copper is a carcinogenic element and is suspected in causing breast and brain cancers (Warren and Dudas, 1988; Willemin *et al.*, 1995). However, speciation of copper in the contaminated soil is not well studied. Data for the fate of copper in the micropores of soil are also lacking in the literature.

Zeolites are crystalline aluminosilicates containing an assemblage of SiO₄ and AlO₄ tetrahedra, joined together by oxygen atoms to form a microporous solid, which has a precise pore structure (Ward, 1967). The straight channels of ZSM-5 have an elliptical cross section of 5.7–5.8 by 5.1–5.2 Å (Breck, 1974). These channels are interconnected by zigzag channels with a nearly circular cross section diameter of 5.4 Å and a channel length of 4.5–6.6 Å (Breck, 1974; Lee *et al.*, 1992). ZSM-48 has a uni-dimensional channel structure based on the ferrierite sheet with linear non-interpenetrating 10-membered ring channels (ideal dimensions are 5.3–



5.6 Å running perpendicular to the sheet) (Breck, 1974; Wang *et al.*, 1998). Zeolite Y has a three-dimensional channel structure with cages and pore sizes of 13 and 7.4 Å, respectively (Breck, 1974). Zeolites possessing well-defined channel/pores structures can be used as a model system in studying the chemical structure of copper in the pores of environmental soils, such as a contaminated soil.

Extended X-ray absorption fine structural spectroscopy (EXAFS) is very useful in identification of elements with a different environment, degree of aggregation or location (Grunet *et al.*, 1994; Yamashita *et al.*, 1996; Stern *et al.*, 1995). By EXAFS, we found that nano copper oxides involved in the catalytic decomposition of NO (Huang and Wang, 1999) and oxidation of chlorophenols in supercritical water (Lin and Wang, 2000). These molecular scale data were very useful in revealing structure and possible reaction pathways in the catalysis process. Thus, the main objective of the present work was to study the speciation of copper in the well defined channels/pores of zeolites (ZSM-5, ZSM-48, and Y) by EXAFS spectroscopy. Specifically, chemical structure as well as the location of copper in the very complex contaminated soil were also investigated.

2. Experimental

Zeolites ZSM-5 and ZSM-48 were synthesized from a mixture containing rice husk ash (detailed procedures are described in the references (Rawtani *et al.*, 1989; Huang *et al.*, 1999; Wang *et al.*, 1998)). Zeolite Y was obtained from the Degussa Pacific Ltd. Copper (2000–2400 ppm) on zeolites ZSM-5 (CuO/ZSM-5), ZSM-48 (CuO/ZSM-48) and Y (CuO/Y) were prepared in an 0.02 M Cu(NO₃)₂ solution by the ion exchange method at 25 °C for 24 hr and calcined at 550 °C for 6 hr. The contaminated soil (containing 21 000 ppm copper) was sampled from a Cu-contaminated site nearby a printed circuit board wastes acid leaching plant at Won-Li, Tainan County, Taiwan. These samples were dried at 105 °C for 24 hr and calcined at 550 °C for 6 hr. The specific surface area and average pore diameter of the soil were 34.7 m² g⁻¹ and 16.8 Å, respectively.

Structure of samples was determined by X-ray diffraction spectroscopy (XRD) (RIGAKU, Model D/MAX III-V) with a CuK_α radiation. Samples were scanned from 5 to 60° (2θ) at a scan rate of 4° min⁻¹. EXAFS (Extended X-ray absorption fine structural) and XANES (X-ray absorption near edge structural) spectra were recorded at the Taiwan SRRC (Synchrotron Radiation Research Center). The electron storage ring was operated at an energy of 1.5 GeV and current of 120–200 mA. A Si(111) double-crystal monochromator was used for the selection of energy. Energy resolution (ΔE/E) of the beamline was about 1.9 × 10⁻⁴ eV/eV. The transmission mode was used in all EXAFS spectra measured. Photon energy was calibrated by characteristic preedge peaks in the absorption spectrum of a Cu foil (8979 eV). The standard deviation calculated from the averaged spectra was used to estimate the statistic noise and error associated with each structural parameter.

The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 programs (Stern *et al.*, 1995). The isolated EXAFS data was normalized to the edge jump, converted to the wavenumber scale, and Fourier transformed on k^3 -weighted oscillations in the range of 2.8–14 \AA^{-1} . The absorption edge was determined at the half-high (precisely determined by the derivative) of the XANES spectrum after preedge baseline subtraction and normalization to the maximum post edge intensity. Principal component (factor) analysis was used in the data treatment to optimize the quantitative extraction of relative concentrations of copper species. Semi-quantitative analyses of the edge spectra were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the sample. The height and area of the near-edge band in a copper spectrum were quantitatively proportional to the amount of copper species. XANES spectra of standard copper compounds such as CuCl_2 , Cu_2O , $\text{Cu}(\text{OH})_2$, CuO , CuS , CuCO_3 , CuSO_4 , and Cu foil were also measured on the Wiggler beamline. It was found that the XANES fitting percentages almost directly correspond to weight percentages. On average, an uncertainty limit of 5% corresponds to an error of ca. 2.0% in the fitting results was found.

3. Results and Discussion

The XRD patterns of copper in the contaminated soil and zeolites are shown in Figure 1. The peaks at 5–10° (see Figures 1a–c) are suggestive of well-defined microporous systems in the zeolites. However, simply due to the complex structure of the soil, the XRD pattern in Figure 1d provides little pore structure information. Note that main copper species in zeolites was CuO while copper (~2100 ppm) in the contaminated soil was not clearly observed.

For a better understanding of the copper speciation in the contaminated soil and zeolites, EXAFS and XANES measurements were conducted at the Taiwan SRRC. XANES spectra of copper model compounds and copper species in zeolites ZSM-5, ZSM-48 and Y and the contaminated soil are shown in Figure 2. The preedge XANES spectra of copper in zeolites exhibited a shoulder at 8980–8984 eV and an intense band at about 8989–8996 eV (attributed to the 1s-to-4p transition) that indicates the existence of Cu(II) species in the channels of zeolites. Mainly CuO was found in the zeolites. The component fits of XANES spectra showed that 95% CuO and 5% metallic Cu were in the contaminated soil.

The EXAFS spectra were also recorded and analyzed in the k range of 2.5–11 \AA^{-1} . The bond distances of Cu-O and Cu-(O)-Cu in zeolites were 1.93–1.95 and 2.93–2.97 \AA , respectively (see Table I). Since about one or two oxygen atoms were bound to the central copper atoms in the first shells of copper, a linear structure of CuO might exist in the confined channels of ZSM-5 and ZSM-48 (see Figures 3a and b). However, in zeolite Y, the bond distance of CuO was 1.93 \AA (which was less than that in ZSM-5 or ZSM-48) with CNs of 3–4, suggesting that CuO might have

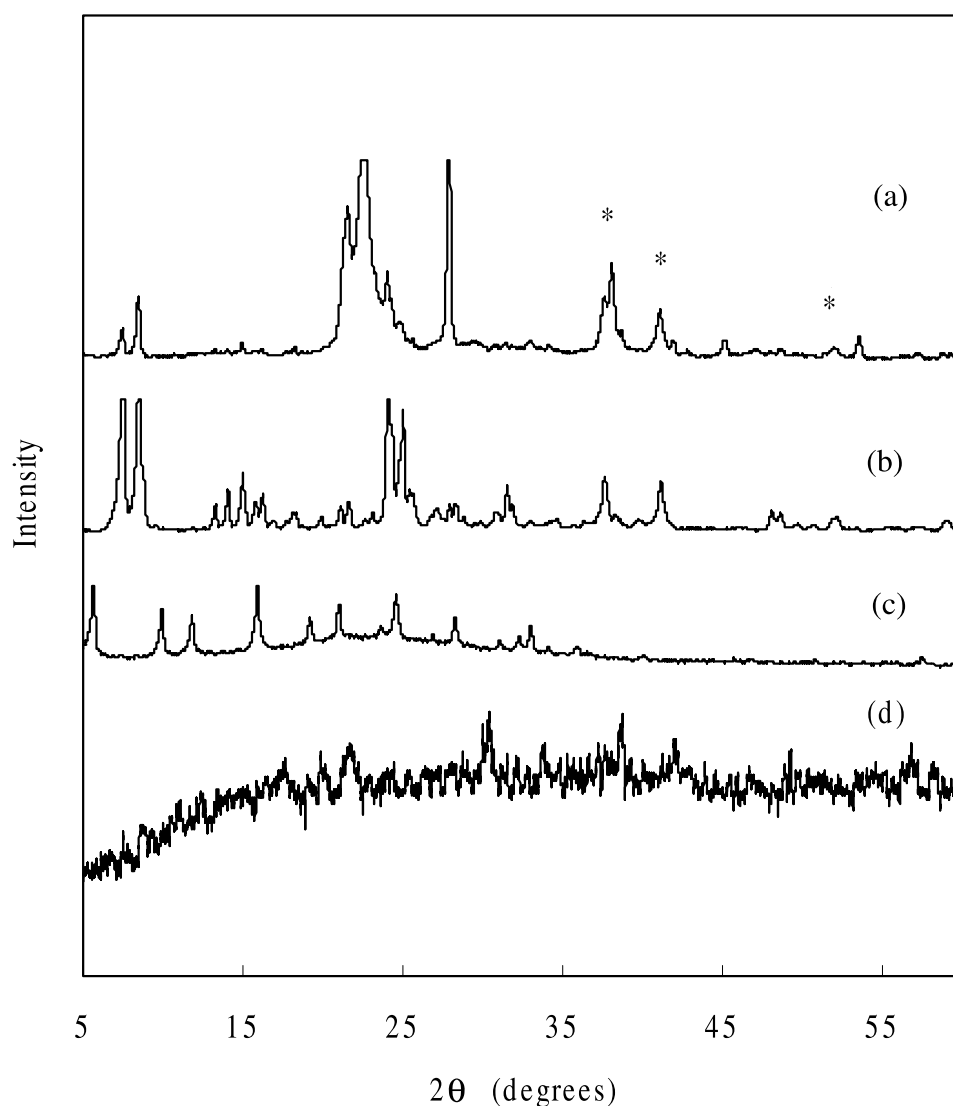


Figure 1. XRD spectra of copper in (a) ZSM-48, (b) ZSM-5, (c) Y, and (d) the contaminated soil (* denotes the characteristic peaks of CuO).

a three-dimensional structure in the supercages or channels of zeolite Y. Figure 3c also shows that about 113 units of CuO can tight fit in the supercages of zeolite Y. The diameter of the copper oxide in the channels of zeolite Y might be about 5.9 Å.

In the pores of the contaminated soil, the bond distance of Cu-O was 1.83 Å, which was smaller than that in the well defined channels (5–6 Å) of zeolite ZSM-5 or ZSM-48 by 0.10–0.12 Å. The highly perturbed CuO in the contaminated soil also possessed a low CN of about 0.4. By comparison with the observation in

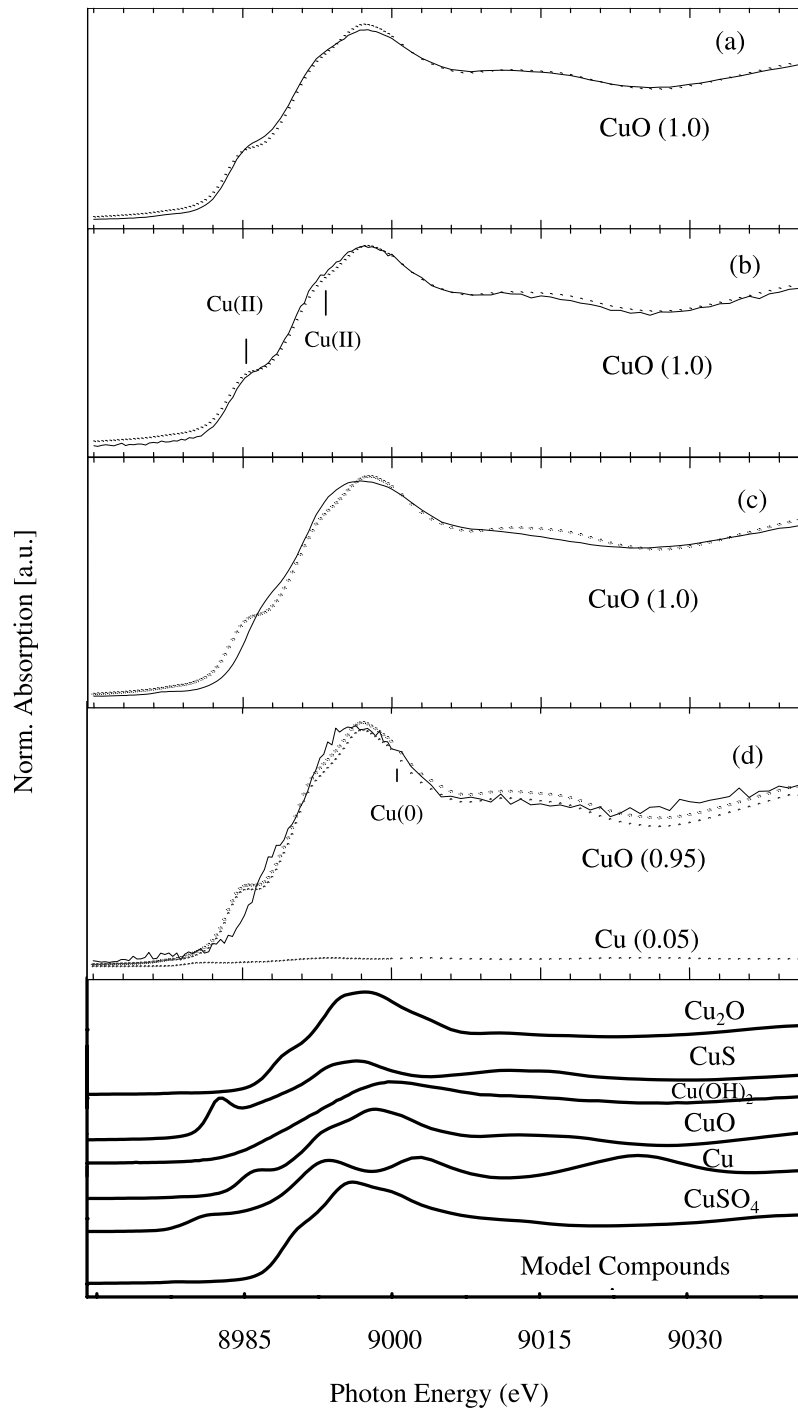


Figure 2. XANES spectra of copper model compounds and copper species in (a) ZSM-48, (b) ZSM-5, (c) Y, and (d) the contaminated soil (dotted lines denote fractional contributions of the principal components making up the fitted spectra).

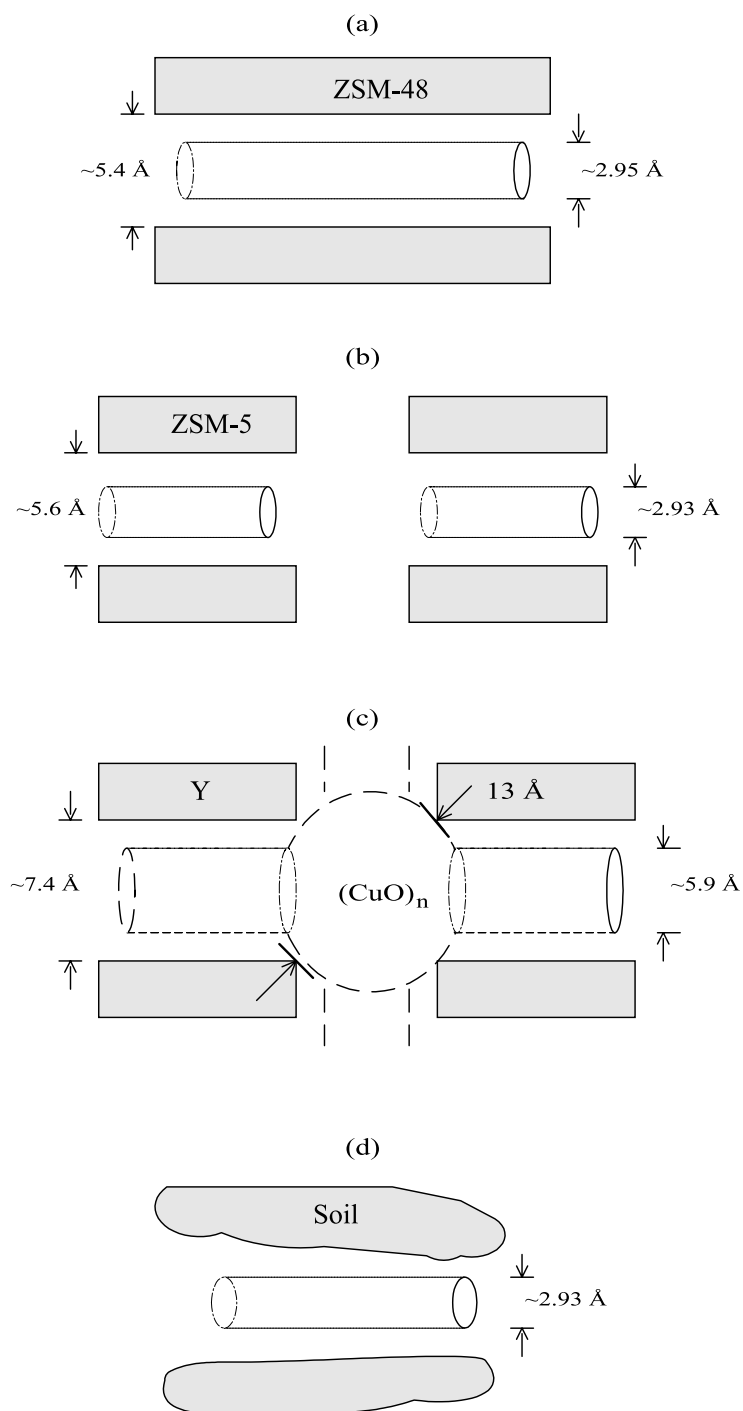


Figure 3. The possible structure of copper oxide in the micropores of (a) ZSM-48, (b) ZSM-5, (c) Y, and (d) the contaminated soil.

TABLE I

Speciation parameters of copper in the contaminated soil and zeolites

	Shells	Bond distance (Å)	CN	σ^2 (Å ²)
CuO/ZSM-5	Cu-O	1.95	1.2	0.005
	Cu-(O)-Cu	2.95	3.7	0.028
CuO/ZSM-48	Cu-O	1.95	2.0	0.004
	Cu-(O)-Cu	2.93	4.6	0.020
CuO/Y	Cu-O	1.93	3.5	0.005
	Cu-(O)-Cu	2.97	3.4	0.014
CuO/Soil	Cu-O	1.83	0.4	0.017
	Cu-Cu	2.54	0.5	0.037
	Cu-(O)-Cu	2.93	0.3	0.124

CN: Coordination number.

σ^2 : Debye-Waller factor.

zeolites, it seems that copper in the soil might be located in the highly confined pore systems (<5–6 Å). It should be noted that the EXAFS data also indicated little chemical interaction of copper with surfaces of the soil. A tight-fit copper oxide in the micropores of the contaminated soil might, therefore, exist. Note that the low CN for copper in the soil was also suggestive of a possible linear type CuO in the micropores of the soil (shown in Figure 3d).

4. Conclusions

The fourier-transformed EXAFS spectra of copper showed that the bond distance of Cu-O in zeolites ZSM-5 and ZSM-48 was 1.95 Å with a coordination number (CN) of 1.2–2.0 in the first shells of copper. A linear-type copper oxide atoms might be formed in the confined channels (5–6 Å) of ZSM-5 or ZSM-48. However, in the supercages and channels of zeolite Y, the CN of Cu-O was approximately 3.5, suggesting an existence of a three dimensional CuO structure in zeolite Y. Interestingly, the speciation of CuO in the pores of the Cu-contaminated soil was similar to that in ZSM-5 or ZSM-48. However, the highly perturbed copper oxide in the pores of the soil possessed a low CN of about 0.4, which was suggestive of a possible linear-type CuO in the soil. This work also exemplifies the utilization of XANES and EXAFS for revealing the speciation of copper in the micropores of zeolites as well as in the contaminated soils.

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