The chemical transformation of copper in aluminium oxide during heating

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Abstract
Thermal treatment has recently been emerging as a promising environmental technology to stabilize heavy metal-containing industrial sludge. This study used x-ray absorption spectroscopy (XAS) to identify the species of copper contaminant contained in aluminium oxide that is one of the main compositions of sludge and soil. Results indicate that the originally loaded copper nitrate was transformed into $Cu(OH)_2$ after its dissolution in the aluminium oxide slurry. Extended x-ray absorption fine structure (EXAFS) fitting indicates that the main copper species in the 105 °C dried $Cu(NO_3)_2$-loaded aluminium oxide is $Cu(OH)_2$ which accounts for ca. 75% of the loaded copper. After thermal treatment at 500 °C for 1 h, both x-ray absorption near-edge structure (XANES) and EXAFS fitting results show that CuO became the prevailing copper species (about 85%); the rest of the copper consisted of ∼15% $Cu(OH)_2$ and a negligible amount of $Cu(NO_3)_2$. It was found that most $Cu(OH)_2$ and $Cu(NO_3)_2$ decomposed into CuO at 500 °C. Further increase of the heating temperature from 500 to 900 °C resulted in more decomposition of $Cu(OH)_2$ and $Cu(NO_3)_2$; therefore CuO remained as the main copper species. However, it was suggested that about 15% of the loaded copper formed $CuAl_2O_4$ through the chemical reaction between CuO and Al_2O_3 at 900 °C.

1. Introduction

Copper compounds in the environment usually exist in two common oxidation states: Cu^+ and Cu^{2+}. If not properly treated before discharge, Cu-containing wastewater has a great potential to contaminate the soil and water systems, and eventually it will damage the food chain and endanger human life. Aluminosilicates and silica sand are the main inorganic constituents of the earth's upper crust and they are acceptors of heavy metal contaminants.

There are four general technologies to remedy heavy metal-contaminated soils: extraction with appropriate reagents; concentration in the vicinity of an *in situ* electrode with an applied voltage followed by a pump-and-treat process; encapsulation with cement- or polymer-based materials; and heating at high temperature to stabilize most heavy metals. These technologies

work based on the reduction of either the content or the mobility of heavy metals in soils. Previous reports have shown that most heavy metals could be effectively immobilized in soil and sorbents, including aluminosilicates and silica, through heating at 200–1300 °C (Wei 1995, 1996, Wei and Huang 1998, Wei *et al* 2001, Ho *et al* 1992, Uberoi and Shadman 1990, 1991, Edding and Lighty 1992, Rink *et al* 1995). CdO or PbO reacted with various sorbents at temperatures greater than 700 °C; $CdAl_2O_4$ or $PbAl_2O_4$ was detected as the reaction product by the x-ray diffraction (XRD) technique (Uberoi and Shadman 1990, 1991).

It was previously reported that copper could be thermally immobilized with silica or kaolinite (Wei *et al* 2001). After heating at 500–900 °C for 1 h, nearly two thirds of the copper nitrate contaminant in silica was transformed into cupric oxide, while in kaolinite about 80% of copper nitrate was in various forms of oxide (Wei *et al* 2001). They suggested the formation of a less soluble copper solid phase containing CuO in the copper-contaminated kaolinite (40 000 mg Cu^{2+} per kg kaolinite) heated at 900 °C for 1 h (Wei *et al* 2001). Due to the lack of appropriate reference compounds no satisfactory speciation of the less soluble copper solid phase was proposed (Wei *et al* 2001). In contrast, because $CuAl_2O_4$ is commercially available and a high-temperature reaction between CuO and alumina may form it, this study includes $CuAl_2O_4$ as a reference compound to investigate the species distribution of copper in copper-contaminated alumina heated at 100–900 °C for 1 h with the XAS technique.

2. Materials and method

To prepare the artificially copper-contaminated Al_2O_3, a slurry containing 0.75 l of 0.420 M $Cu(NO_3)_2$ solution and 1.0 kg alumina was end-to-end rotated in a bottle at a speed of 30 rev min^{-1} for 1 day. After the mixing, the slurry was dried at 105 °C in an electric oven for 3 days. The copper content contained in alumina was 20 000 mg Cu^{2+} per kg alumina. The dried sample was then ground to less than 0.297 mm and was ready for heating at 500–900 °C. An electrically heated fluidized-bed incinerator operated in fixed-bed mode was used to heat the Cu^{2+}-doped alumina. The air inlet and outlet were closed. Upon reaching the pre-set temperatures of 500 and 900 °C, the Cu^{2+}-contaminated alumina was batch-fed into the incinerator and heated for 1 h at that temperature. After the heating process, the sample was discharged, cooled, and stored for Cu K-edge XAS spectrum recording.

XAS spectra were recorded on the wiggler C (BL-17C) beam line at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan. The ring storage energy was 1.5 GeV with a beam current of 120–200 mA and a range of the monochromator of 4–15 keV. The energy resolution $\Delta E/E$ was 1.9×10^{-4}. The Cu K-edge, 8979 eV, was used in this study. All sample spectra were collected in fluorescence mode and all references in transmission mode at room temperature. The references were $Cu(NO_3)_2$, $Cu(OH)_2$, CuO, and $CuAl_2O_4$. WinXAS 2.0 software (Ressler 1998) was used for XAS data reduction. One of the options of this software is to simulate a sample XANES spectrum with a linear combination of a set of reference spectra to quantify species in a multi-species sample based on their fingerprints in the near-edge region (Ressler 1998). It uses a least-squares procedure, and two parameters (i.e., partial concentration and energy correction) are determined for each reference compound (Ressler 1998). The purpose of energy correction is to correct for small differences in energy calibration between sample and reference compounds; the small differences may cause considerable differences in the fit (Ressler 1998).

3. Results and discussion

Figure 1 depicts the reference XANES spectra (see the left-hand column) of $Cu(NO_3)_2$, $Cu(OH)_2$, CuO, and $CuAl_2O_4$, and their corresponding first derivatives (right-hand column).
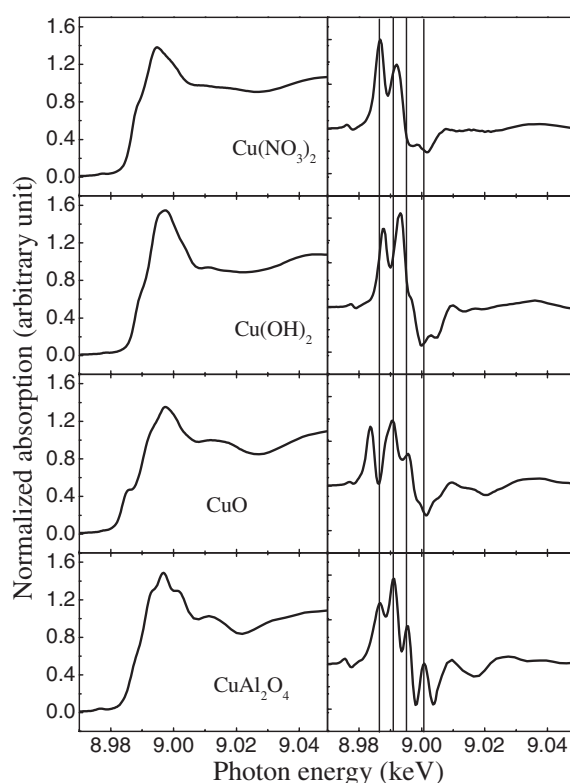
Figure 1. XANES and the first derivative spectra of copper reference compounds.

The vertical lines running through the derivative curves are intended for convenient comparison of peak positions. There are obvious differences among these derivatives.

Figure 2 shows the simulation of normalized sample XANES spectra with the references CuO, $Cu(OH)_2$, and $Cu(NO_3)_2$ (see the left-hand column). The right-hand column of figure 2 demonstrates their corresponding first derivatives. Fractional XANES spectra of reference compounds are shown in each compartment of the left-hand column. All fractional reference XANES spectra were summed to generate the fitted spectrum (open circle). The experimental sample spectrum (solid curve) is satisfactorily simulated by the fitted spectrum. The simulation indicates that $Cu(OH)_2$ is the main copper species in the 105 °C-dried sample due to the hydroxylation reaction of Cu^{2+}. After heating at 500 or 900 °C for 1 h, CuO becomes the dominant species (ca. 85–90%) because of the decomposition of $Cu(OH)_2$ and $Cu(NO_3)_2$ into CuO. However, examination of the derivative curve of the 900 °C-heated sample (see the right-hand side of figure 2) reveals that the peak at 8995 eV is noteworthy. This small peak seems to be associated more with $CuAl_2O_4$ than with CuO (see figure 1).

Figure 3 shows the simulation of the 900 °C sample XANES spectra with references CuO and $CuAl_2O_4$. The derivative simulation is improved, and this suggests that partial formation of $CuAl_2O_4$ might have occurred after heating at 900 °C for 1 h.

Figure 4 shows the first-shell fitting of Fourier transformed EXAFS spectra using CuO feff1. The solid curve denotes the sample EXAFS spectrum and the open circle is the fitting result. Table 1 lists the structural parameters for the first shell derived from the fitting of EXAFS spectra of all heated samples and references $Cu(OH)_2$, CuO, and $CuAl_2O_4$. The coordination
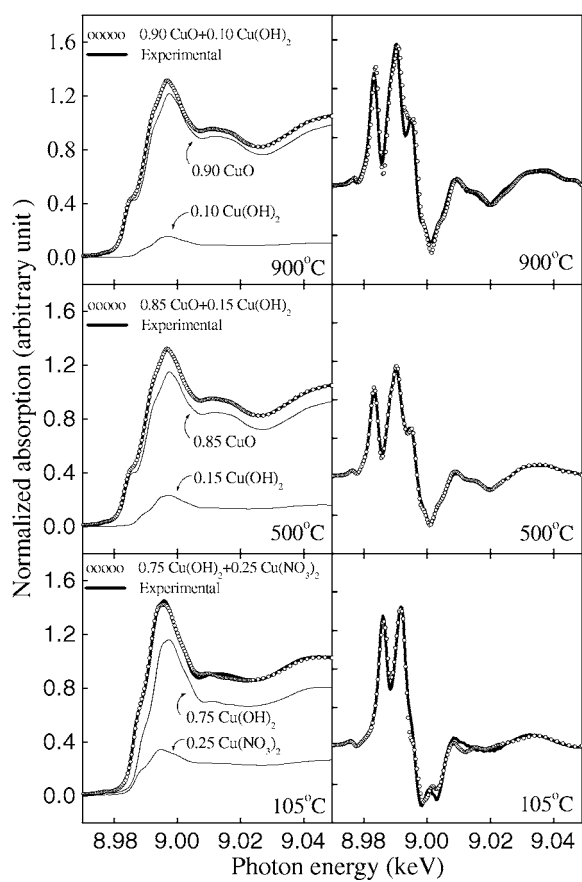
Figure 2. XANES simulation of 105, 500, and 900 °C Cu-doped Al_2O_3 samples using references $Cu(OH)_2$, $Cu(NO_3)_2$, and CuO.
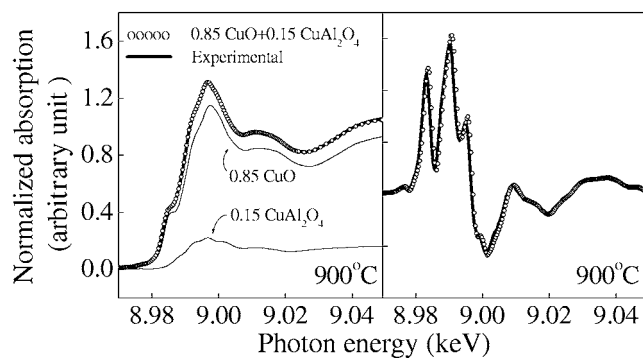

Figure 3. XANES simulation of 900 °C Cu-doped Al_2O_3 sample using $CuAl_2O_4$ and CuO references.

number (N) of the first shell slightly increases from 2.89 to 3.11 when the temperature is raised from 500 to 900 °C. This is probably due to the occurrence of copper sintering and/or formation of $CuAl_2O_4$ that has a greater first shell coordination number than $Cu(OH)_2$, 3.04
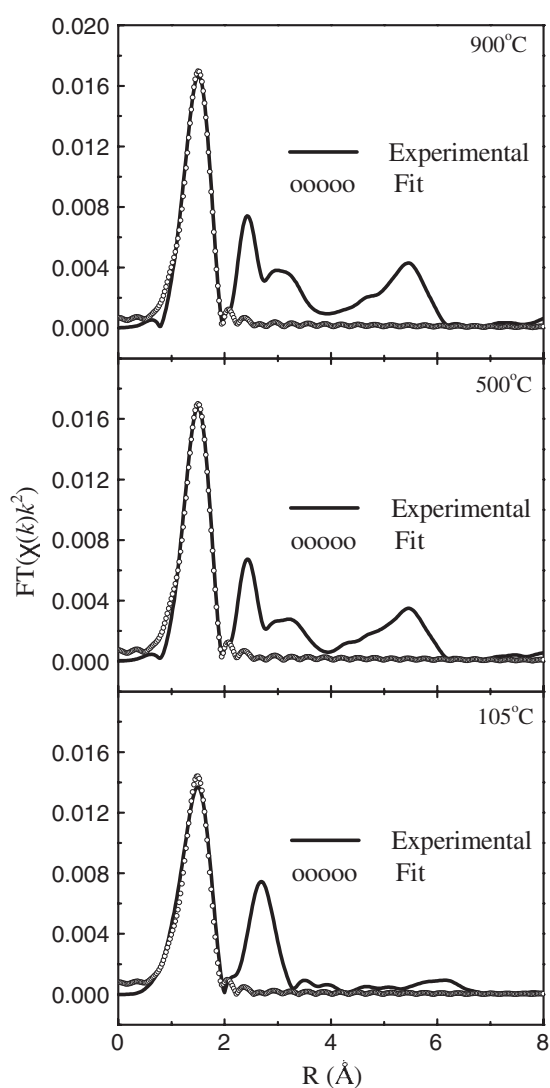
Figure 4. Fitted Fourier transforms of Cu-doped Al_2O_3 heated at 100, 500, and 900 °C.

Table 1. Structural parameters around copper in 500–900 °C heated samples and references: $Cu(OH)_2$, CuO, and $CuAl_2O_4$. (Fourier fitting by CuO feff1.)

Sample	N type at R (Å)	σ^2 (Å^2)
105 °C	2.68 Cu–O at 1.95	0.0012
500 °C	2.89 Cu–O at 1.95	0.0014
900 °C	3.11 Cu–O at 1.95	0.0017
$Cu(OH)_2$	2.80 Cu–O at 1.95	0.0021
CuO	3.25 Cu–O at 1.95	0.0022
$CuAl_2O_4$	3.04 Cu–O at 1.95	0.0040

versus 2.80. The Debye–Waller factor (σ^2) of the 900 °C sample is rather similar to that of the 500 °C sample.

4. Conclusion

The simulation of the 900 °C-heated sample XANES derivative curve suggests that although most copper in Al_2O_3 was in the form of CuO after being heated at 900 °C for 1 h, $CuAl_2O_4$ formed from the chemical reaction of CuO with alumina.

The coordination number of the first shell slightly increased from 2.89 for the 500 °C sample to 3.11 for the 900 °C sample. This was probably due to the occurrence of copper sintering and/or formation of $CuAl_2O_4$ that has a greater first shell coordination number than $Cu(OH)_2$, 3.04 versus 2.80.

Acknowledgments

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