A metal mixture lowers the reaction temperature of copper chloride as shown using in situ quick XAFS

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Abstract. Trace chlorinated organic compounds are generated via thermal processes. Their formation is promoted by copper chloride in solid phase such as fly ash, especially in the post-combustion zone in municipal solid waste incineration. Previously, we reported the chemical state and change of copper chloride in a single model using the in situ quick scan x-ray absorption fine structure (QXAFS). However, a real solid phase, which is a complex system involving many elements, was not simulated. In this paper, we measured the Cu-K XAFS of a metal-mixture model upon heating to discuss the effect of mixing. The in situ QXAFS technique revealed that the reaction temperature of copper was lower, compared with the single model, when a mixture was measured. The result shows that the formation mechanism of chlorinated organic compounds derived from anthropogenic thermal sources can be described more correctly.

1. Introduction
In thermal processes, the post-combustion zone ash which called fly ash contains high concentrations of chlorinated organic compounds such as dioxins. Small amounts of metal compounds in fly ash promote the formation of chlorinated organic compounds[1], especially copper(II) chloride. Preparing a simple model fly ash with added copper(II) chloride, we observed the direct chlorination of carbon by copper(II) chloride as a key formation mechanism using in-situ quick-scan x-ray absorption fine structure (QXAFS) spectroscopy[2].

Real fly ash from thermal processes, such as municipal solid waste incineration, contains many elements, and copper is thought to interact with other metal compounds in real fly ash. However, it is difficult to clarify the interaction of copper with other metals (iron, lead, zinc, etc.) in real fly ash using XAFS spectroscopy because of the complexity of real fly ash and the low concentration of copper in it. If the number of metal compounds with the ability to form chlorinated organic compounds equal to that of copper chlorides is limited, the mixing state in real fly ash can be imitated. This makes it possible to measure the change in Cu chemical form using QXAFS spectroscopy.

In this study, we obtained in-situ Cu-K XAFS spectra of a metal-mixture model fly ash on heating to examine the effect of metal mixing and the interaction of copper with other metal chlorides in order to describe the more correct path of chlorinated organic compounds formation in real fly ash.
2. Materials and Method

2.1. Model Fly Ash

We prepared a model fly ash called "Cu+Fe+Pb+Zn ash" that was a mixture of 5 wt % copper(II) chloride (CuCl$_2$), 5 wt % iron(III) chloride (FeCl$_3$), 5 wt % lead(II) chloride (PbCl$_2$), 5 wt % zinc(II) chloride (ZnCl$_2$), 5 wt % activated carbon (AC), and boron nitride (BN) (the remainder). All organic compounds were removed from the AC by heating at 500 ºC for 60 min under a 100 % nitrogen stream. Previously, we performed Cu-K XAFS spectroscopy of a model fly ash called "Cu-only ash" that contained 5 wt % CuCl$_2$·2H$_2$O, 5% AC, and BN [2] and compared the result with Cu+Fe+Pb+Zn ash.

2.2. In situ QXAFS

After grinding the model fly ash using a mortar and agate mortar for 10 min and then pressing it into a disk, in-situ Cu-K QXAFS spectroscopy was performed using BL01B1 in SPring-8 (Hyogo, Japan). The disk of the model fly ash was heated in a T-type cell, as shown in Figure 1. This consisted of a glass cell, mantle heater, and temperature controller. The T-type cell is described in detail elsewhere [2, 3]. The temperature of the sample was increased gradually from room temperature to about 450 ºC, as shown in Figure 2. Then, 10 % oxygen (90 % nitrogen) gas was introduced from the inlet of the T-type cell at 50 mℓ/min and exhausted from the outlet. The energy area from 8730 to 9660 eV of Cu-K extended XAFS (EXAFS) could be measured in 2.5 min in quick scan mode.

3. Results and Discussion

3.1. Change of Copper K-edge EXAFS

The change in the $k^3$ weighted Fourier-transformed Cu-K EXAFS spectra of Cu+Fe+Pb+Zn ash is shown in Figure 3. A peak derived from the Cu–Cl bond of CuCl$_2$ was identified by comparison with the shape of the Fourier-transformed EXAFS spectra of reference copper compounds [CuCl$_2$·2H$_2$O, CuCl$_2$, CuCl, Cu$_2$(OH)$_3$Cl, CuO, Cu$_2$O, and Cu] at near room temperature (Figure 3a). This indicated that the physical procedure used to make the disk did not appreciably affect the form of Cu. The dechlorination reaction progressed according to the increase in temperature because the Cu–Cl peak decreased continuously as the temperature increased (Figure 3b). A two-stage dechlorination reaction was observed, with the first dechlorination occurring at about 80–160 ºC and the second at 270–300 ºC. At temperatures over around 300 ºC, the Cu–Cl peak vanished almost entirely and a Cu–O peak appeared and increased.
Figure 3. Contour plot of $k^3$ Fourier-transform magnitude of Cu-K EXAFS in Cu+Fe+Pb+Zn ash upon heating.

Figure 4. Change in the $k^3$ Fourier-transform magnitude derived from Cu–Cl and Cu–O bonds upon heating. Closed and open circle were Cu+Fe+Pb+Zn ash and Cu only ash respectively.
as shown in Figure 3c. This indicated that the oxidation of copper had started.

3.2. A Metal Mixture Lowers the Reaction Temperature of Copper(II) Chloride

To determine the effect of mixed metals on the formation of chlorinated organic compounds, we compared Cu+Fe+Pb+Zn ash with Cu-only ash. The change in the patterns of the $k^3$ weighted Fourier-transformed magnitudes of the Cu–Cl and Cu–O peaks in Cu-K EXAFS spectra on heating are shown in Figure 4. The magnitude of the Cu–Cl peak decreased by half from 80 to 160 °C, reflecting the first dechlorination step of copper(II) chloride ($\text{CuCl}_2 \rightarrow \text{CuCl}$) [2]. By contrast, the end point of the first dechlorination step in Cu-only ash was at about 300 °C. Therefore, the temperature in the Cu+Fe+Pb+Zn ash at which the first dechlorination step finished was about 140 °C lower than in the Cu-only ash. In addition, the Cu–O peak in Cu+Fe+Pb+Zn ash increased beginning at about 300 °C, which was 50 °C lower than in Cu-only ash. This oxidation process reflects the change from copper(I) chloride to copper(II) oxide[2].

Most of the chlorinated organic compounds in real fly ash are generated at 300–400 °C[1]. In the metal-mixture model fly ash, the oxidation of CuCl → CuO started at 300 °C. This oxidative reaction of copper was thought to promote the chlorination of the carbon matrix in real fly ash. On the other hand, The first dechlorination step ends at 300 °C in the Cu-only ash. This first dechlorination step might occur predominantly in local areas of the fly-ash surface where the density of cupric chloride is high. As a result, the reaction with the metal during the mixing state and in the single state occurs in parts of real fly ash, and trace chlorinated organic compounds are generated in real fly ash.

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