

## Synchrotron X-Ray Spectroscopic Evidence of Dioxin Formation Mechanism in Solid Waste Incinerator – Direct Chlorination of Carbon by Copper Chloride –

Thermal processes are a major anthropogenic source of chlorinated aromatic compounds (aromatic-Cls, see I in Fig. 1 or Fig. 2) such as dioxins and PCBs. Many of them are toxic to both humans and wildlife. Therefore, understanding the mechanisms of the formation of aromatic-Cls in solid waste incinerators is necessary in order to control the emission of aromatic-Cls. Ash collected from the postcombustion zone, called fly ash, has high concentrations of aromatic-Cls. Unburned carbon and chlorine sources in fly ash and surrounding oxygen are essential factors for aromatic-Cl formation. In addition, trace metal compounds in fly ash promote aromatic-Cl formation. Copper in particular has a strong potential, and its chlorination mechanism has been proposed by various researchers. However, limited experimental data to support the predicted behavior of copper at the atomic level have been acquired. Although X-ray absorption spectroscopy has recently been used to monitor the redox change of copper in fly ash upon heating [1], the atomic environment of copper has not yet been clarified fully and little direct evidence exists to clarify the formation mechanism of aromatic-Cls with copper at the atomic level and to describe the chlorination mechanism in

detail. In this work [2], we determine the behavior of copper in fly ash.

To examine the behavior of copper, we prepared a model fly ash (MFA) consisting of a mixture of copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), activated carbon (AC), and boron nitride (BN) containing 1.9% Cu, 2.0% Cl, 5.0% AC; the remaining 91.1% was almost entirely BN. After the MFA was ground, 200 mg was pressed into a disk. Cu *K*-edge XAFS was performed at beamline BL01B1. The MFA disk was heated in a T-type cell [1] for *in situ* experiment. The temperature of the sample was increased gradually from room temperature to 400°C. A 10%  $\text{O}_2$  (90%  $\text{N}_2$ ) gas simulating the condition of the postcombustion zone 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 9820 eV of Cu *K*-edge extended X-ray absorption fine structure (EXAFS) could be measured within 2.5 min by a quick scan mode. The EXAFS spectra of a MFA disk were collected in the transmission mode with a Si(111) monochromator. The chemical forms in the MFA were determined by powder X-ray diffraction analysis using synchrotron radiation (SR-XRD) at beamline BL02B2. The MFA was packed in a quartz capillary column and sealed.

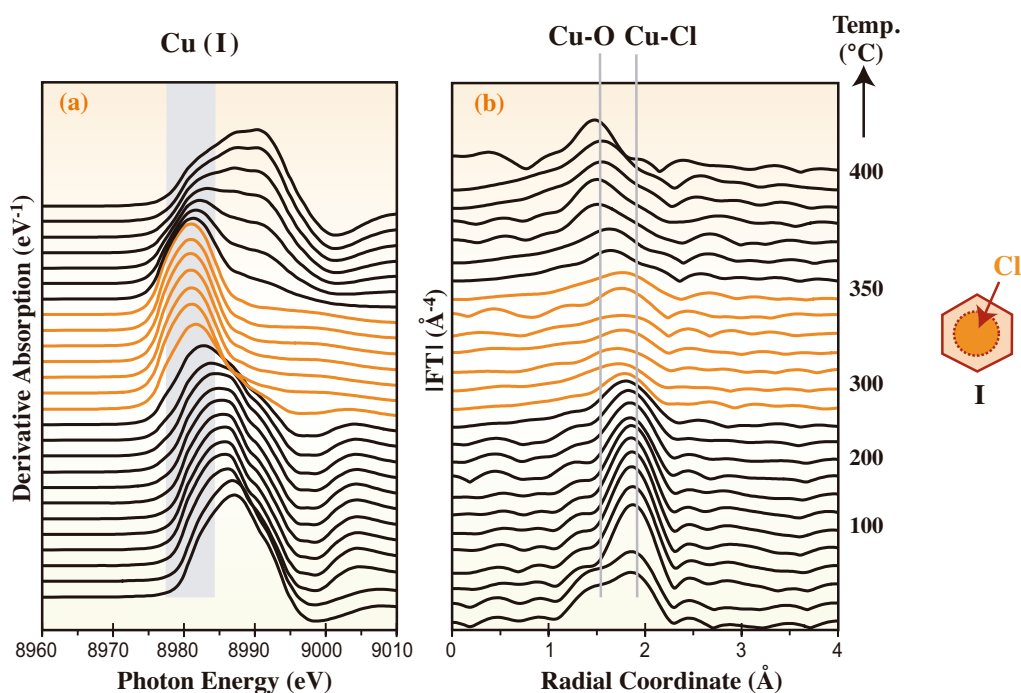


Fig. 1. Derivative Cu-K XANES spectra (a) and Fourier-transformed spectra (b) at each temperature during heating MFA. Maximum amounts of chlorinated aromatic compounds (I) were generated at 300-350°C.

We placed the capillary in the Debye-Scherrer camera for SR-XRD measurement. The capillary was heated using N<sub>2</sub> gas from room temperature to 400°C, and SR-XRD patterns were recorded.

Dynamic changes in the forms of copper in the MFA were clearly observed by X-ray absorption and diffraction analysis using synchrotron radiation (Figs. 1 and 2). The difference in copper form was caused by the reduction of copper near 300°C and the maintenance of its chemical form even at around 350°C as follows: The energy point of the first maximum in the derivative of the Cu K-edge XANES spectrum (called the “edge”) can provide information on the redox state of copper (Fig. 1(a)) [3]. The edge position changed to 8981.0 eV around 300°C, and the valence of copper was shown to be lower than that of Cu(II) by comparing the edges of reference materials. Therefore, copper was reduced from Cu(II) to Cu(I) or Cu(0). The coordination number of the first shell of

Cu-Cl decreased by 1.5±0.3 between 310 and 350°C with half of the CuCl<sub>2</sub> form at 100°C, and the atomic distance was shortened by 2.19±0.02 Å compared with that in CuCl<sub>2</sub> at 100°C, according to analysis of the EXAFS spectra (Fig. 1(b)). On the basis of the SR-XRD pattern, CuCl was clearly identified from 275 to 350°C (Fig. 2). We conclude that most CuCl<sub>2</sub> within the carbon matrix dechlorinated to CuCl at around 300°C and maintained this state up to about 350°C. The C-Cl bond was derived from the dechlorination of copper because the only chlorination source in the MFA was copper(II) chloride, i.e., the direct chlorination of carbon by copper occurred and the aromatic-Cl concentration reaches its maximum in the fly ash. Eliminating the inflow of copper to thermal facilities or chemically inhibiting copper at the atomic level might decrease the creation of aromatic-Cl's by thermal processes and thus have beneficial effects on the environment and human health.

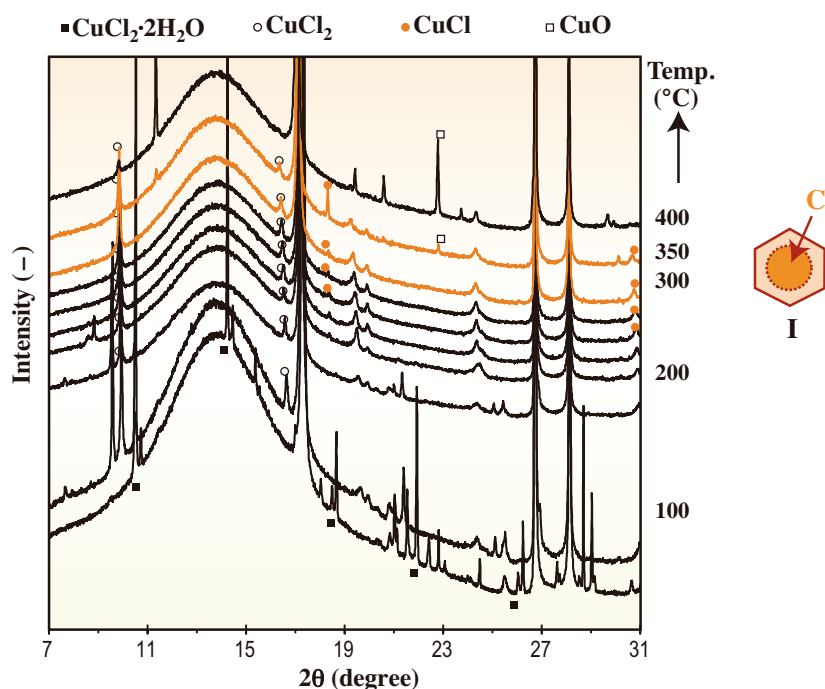


Fig. 2. SR-XRD patterns at each temperature during heating of MFA. Maximum amounts of chlorinated aromatic compounds (I) were generated at 300-350°C.

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#### References

- [1] M. Takaoka *et al.*: *Environ. Sci. Technol.* **39** (2005) 5878.
- [2] T. Fujimori and M. Takaoka: *Environ. Sci. Technol.* **43** (2009) 2241.
- [3] T. Fujimori *et al.*: *X-ray Spectrom.* **37** (2008) 210.