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Chlorine Behavior during Formation of Chlorinated Organic Compounds in a Thermal Process Using Cl-K XANES

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Introduction

Toxic and trace chlorinated organic (organo-Cl) compounds are produced unintentionally by humans and persist in the environment. Polychlorinated dibenzo-p-dioxins, furans, and biphenyls are known to be emitted from municipal solid waste incinerators. Ash collected from the post combustion zone, called fly ash, has the highest concentration of organo-Cl compounds, and unburned carbon and chlorine sources in fly ash and surrounding oxygen are known to be essential factors for organo-Cl formation. In addition, copper chlorides with low concentrations in fly ash promote organo-Cl formation.

X-ray absorption spectroscopy has recently been used to monitor the redox change of copper in fly ash upon heating[1]. The behavior of chlorine was not clarified in these studies. The chlorination mechanism can be better described if the behavior of chlorine atom is observed. In the present work[2], we reveal the behavior of Cl in fly ash and provide basic information on the chlorination mechanism of carbon by copper that produces organo-Cl compounds during thermal processes.

Experimental

To determine the behavior of Cu and Cl, we prepared a model fly ash (MFA), which was a mixture of copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), activated carbon (AC), and boron nitride (BN) contained 1.9% Cu, 2.0% Cl, 5.0% AC, and the remaining 91.1% was almost entirely of BN.

The Cl forms present after MFA was heated were determined by measuring the Cl K-edge X-ray absorption near edge structure (XANES). A MFA was ground using a mortar for 10 minutes. And then we inserted MFA powder on a quartz boat into quartz tube filled with 10% O_2 (90% N_2) at 50 mL/min and heated for 30 minutes in an electric furnace preheated to 200, 250, 300, 350, and 400 ºC. After heating procedure, MFA powder was sealed as quickly as possible and supplied to the measurement of Cl K-edge XANES performed using BL-11B in Photon Factory (Tsukuba, Japan). Cl K-edge XANES spectra of chlorobenzenes and chlorophenols were measured under atmospheric pressure by conversion electron yield (CEY) method at BL-9A.

Results and Discussion

When the dechlorination reaction of Cu occurred, we found strong evidence of the C-Cl bond. The Cl K-edge XANES spectrum of the MFA at 300ºC, the first dechlorination of copper, had the lowest energy position of the absorption maximum at 2821.1 eV (Figure 1A). Copper chlorides have a larger energy position at 2822.0 eV than the MFA at 300ºC. The absorption maximum of the MFA at 300ºC is the same energy as Cl connected to an aromatic carbon. The ratio of Cl connected to aromatic and aliphatic carbons was the maximum at 300ºC based on analyses of Cl K-edge XANES spectra (Figures 1B and 1C). The C-Cl bond was derived from the dechlorination of copper because the only chlorination source in MFA was copper(II) chloride, i.e., the direct chlorination of carbon by copper occurred. Chlorides from reduced copper chloride directly bonded aromatic or aliphatic carbon at the temperature that most of the chlorinated organic compounds formed.

References

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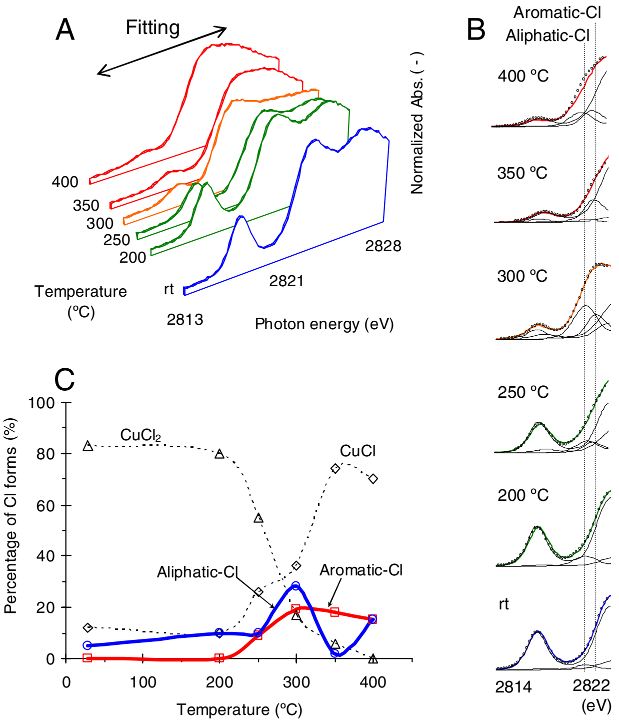

Figure 1. Cl K-edge XANES spectra (A) after MFA was heated. Linear combination fit using reference materials of chlorine shown in (B). The percentage of Cl-species as a function of temperature is shown in (C)