

Chlorine Behavior during Formation of Chlorinated Aromatic Compounds in a Thermal Process Promoted by Oxychlorination of Ferric Chloride

Takashi FUJIMORI¹, Masaki TAKAOKA^{*1}, Shinsuke MORISAWA¹
¹Kyoto University, Katsura, Nishikyo-ku 615-8540, Japan

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 and iron ore sintering plants. Ash collected from the post combustion zone, called fly ash, has the highest concentration of organo-Cl compounds. Unburned carbon and chlorine sources in fly ash and surrounding oxygen are known to be essential factors for the formation of organo-Cl compounds. In addition, iron and copper chlorides with low concentrations in fly ash promote the formation of organo-Cl compounds. Previously, we revealed the behavior of Cl in fly ash mixed with copper chloride using Cl K-edge X-ray absorption near edge structure (XANES)[1].

In present study, we also discussed the behaviors of Cl in fly ash. Based primarily on XAFS spectroscopy, we provide basic information on the chlorination mechanism of carbon by iron chloride[2].

Experimental

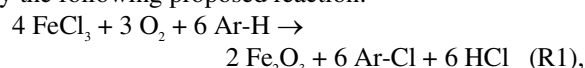
To determine the behavior of Cu and Cl, we prepared a model fly ash (MFA), which was a mixture of iron(III) chloride (FeCl₃), activated carbon (AC), and boron nitride (BN) contained 2% Fe, 3.8% Cl, 5.0% AC, and the remaining was almost entirely of BN.

The Cl forms present after MFA was heated were determined by measuring the Cl K-edge 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% O₂ (90% N₂) at 50 mL/min and heated for 30 minutes in an electric furnace preheated to 200, 300, and 400 °C. After heating, 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

Although chlorine bonded only with iron atoms at room temperature in the MFA, the interaction of chlorine atoms with the carbon matrix after the dechlorination process can be examined using the Cl K-edge XANES technique. Figure 1 shows the Cl K-edge XANES spectra at each temperature. The specific acute peak at ca. 2821 eV of chlorine connected with aromatic carbon was confirmed visually from the Cl -XANES shape at 400°C.

A linear combination fit of Cl K-edge XANES showed a rise in the aromatic-Cl ratio, with a maximum at 400°C (aromatic-Cl, ca. 30%). Combining other characterization, oxychlorination of ferric chloride primarily occurred to generate chlorinated aromatic compounds over ca. 300°C, by the following proposed reaction:



where Ar-H and Ar-Cl are aromatic and chlorinated aromatic compounds, respectively. We suggest that the oxychlorination reaction (R1) of ferric chloride is a key mechanism contributing to the formation of chlorinated aromatics in the solid phase of a thermal process.

References

- [1] T. Fujimori and M. Takaoka., *Environ. Sci. Technol.* 43, 2241 (2009).
- [2] T. Fujimori *et al.*, *Environ. Sci. Technol.* 44, 1974 (2010).

* takaoka@environ.mbox.media.kyoto-u.ac.jp

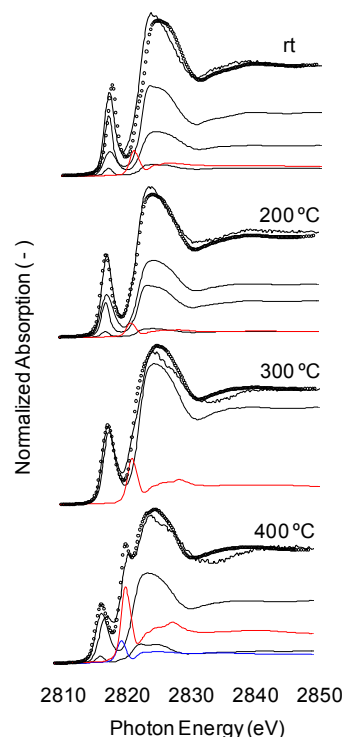


Figure 1. Cl-K edge XANES spectra at room temperature (rt), 200°C, 300°C, and 400°C, indicated by the bold solid line. Dotted circles indicate calculated spectra from combined Cl references (thin solid line). Red and blue thin lines indicate aromatic- and aliphatic-Cl, respectively.