

Observation of Carbon Chlorinated by Oxychlorination of Ferric Chloride in a Thermal Process

In thermal processes, metal chlorides are known to promote the formation of chlorinated aromatic (aromatic-Cl) compounds such as dioxins, PCBs, and chlorobenzenes. The relationship between the formation of such compounds and ferric chloride motivated us to study the chemical characteristics of iron. Atomic-scale evidence of the chlorination of aromatic carbon was detected by Cl-K X-ray absorption near edge structure (XANES) spectroscopy. We attribute the formation of aromatic-Cl compounds to the chlorination of carbon, based on the oxychlorination reaction of FeCl_3 at temperatures over 300°C. Chemical changes of trace iron in a thermal process may offer the potential to generate aromatic-Cl compounds.

Toxic and trace chlorinated aromatic (aromatic-Cl) compounds are produced unintentionally by humans and persist in the environment. Dioxins, PCBs, and chlorobenzenes 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 aromatic-Cl compounds. Unburned carbon and chlorine sources in fly ash and surrounding oxygen are known to be essential factors for the formation of such compounds. In addition, iron and copper chlorides with low concentrations in fly ash promote the formation of aromatic-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) spectroscopy [1].

In the present study, we examined the behavior of Fe and Cl in fly ash. Based primarily on XAFS spectroscopy, we obtained basic information on the chlorination

mechanism of carbon by iron chloride [2].

To determine the behavior of Fe and Cl, we prepared a model fly ash (MFA), which was a mixture of iron (III) chloride (FeCl_3), activated carbon (AC), and boron nitride (BN) containing 2% Fe, 3.8% Cl, 5.0% AC, and the remainder was almost entirely BN.

After MFA was heated, the Cl forms were determined by measuring the Cl K-edge XANES. The MFA was ground using a mortar for 10 minutes, then the MFA powder was placed on a quartz boat in a 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, 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. Cl K-edge XANES spectra of chlorobenzenes and chlorophenols were measured under atmospheric pressure by the conversion electron yield (CEY) method at BL-9A.

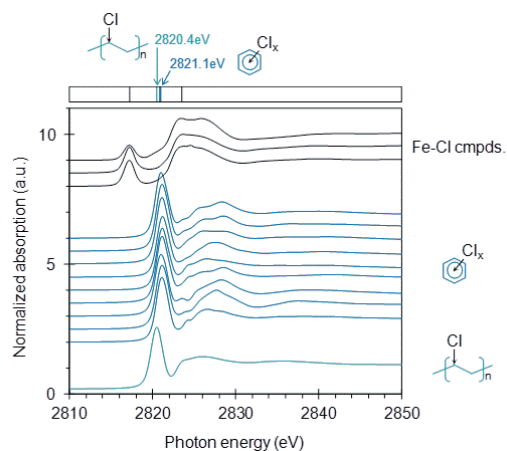


Figure 1
Cl K-edge XANES of reference Cl materials related to iron and aromatic and aliphatic carbon, which have different maximum peak positions.

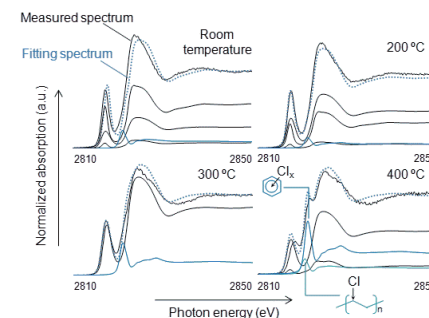
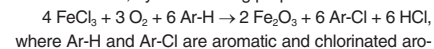


Figure 2
Cl-K edge XANES spectra at room temperature, 200°C, 300°C, and 400°C, indicated by the bold solid lines. Dotted plots indicate calculated spectra from combined Cl references (thin solid line). Blue and light-blue thin lines indicate aromatic-Cl and aliphatic-Cl, respectively.

The energy position of the maximum peak depended on whether chlorine was bonded with organic or inorganic compounds (Fig. 1). Compared with iron compounds, the lower energy positions of the maximum peak derived for aromatic-Cl and aliphatic-Cl compounds were at 2821.1 and 2820.4 eV, respectively. Cl K-edge XANES spectra were useful for directly revealing “carbon–chlorine” bonds (C–Cl bonds) as found in the structures of aromatic-Cl compounds [3].

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 of iron can be examined using the Cl K-edge XANES technique. Figure 2 shows the Cl K-edge XANES spectra at each temperature. The specific acute peak at ca. 2821 eV of chlorine related to 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 characterizations, oxychlorination of ferric chloride primarily occurred to generate chlorinated aromatic compounds over ca. 300°C, by the following proposed reaction:



matic compounds, respectively.

In the thermal-solid phase, the mixture of carbon and trace iron might have serious potential to generate harmful aromatic-Cl compounds in the environment. We need to rethink and assess trace iron in solid phases, such as fly ash, in thermal processes. Furthermore, eliminating the inflow of metals including iron to thermal facilities or chemically inhibiting metals at the atomic level might decrease the unintentional creation of aromatic-Cl compounds and thereby have beneficial effects on the environment and human health.

REFERENCES

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BEAMLINES

9A and 11B

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