

## Thermochemical behavior of lead during formation of chlorinated aromatics determined by X-ray absorption spectroscopy

Regarding the toxicity and resource recovery of lead, various speciation studies have revealed the redox chemical state of lead in postcombustion fly ash from thermal processes such as municipal solid waste (MSW) incineration and coal combustion. A large amount of lead exists as chloride, oxide, or sulfide in the thermal solid phase. Lead chloride ( $\text{PbCl}_2$ ) promotes the formation of toxic chlorinated aromatic compounds (aromatic-Cl)s, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs), and benzenes (CBzs). In contrast, lead oxide ( $\text{PbO}$ ) inhibits the formation of aromatic-Cl)s. Lead metallurgical processes can also be used to generate PCDDs, PCDFs, and PCBs. The thermochemical behavior of metals in the solid phase likely plays a role in aromatic-Cl formation and inhibition, which is supported by the results of our recent mechanism-based thermochemical studies of strong metal catalysts (Cu [1,2] and Fe [3]) and a metal inhibitor (Zn [4]). In the present study [5], we evaluated the thermochemical behavior of lead using quantitative and X-ray spectroscopic techniques.

Real fly ashes (RFAs) from municipal solid waste incinerators (MSWIs) were used to determine the major chemical forms and thermal behavior of lead. We prepared model fly ashes (MFAs) to understand the thermochemical interaction between lead and metal chlorides ( $\text{CuCl}_2$  and  $\text{FeCl}_3$ ). Gas chromatography/mass spectrometry (GC/MS) experiments provided quantitative information on aromatic-Cl)s such as PCBs and CBzs. The thermochemical state of lead was analyzed by X-ray absorption near-edge structure (XANES) measurements at beamline BL01B1. During the Pb  $L_3$ -edge XANES measurement, the sample disk was heated from room temperature to 300°C and 400°C in a T-type *in situ* cell under a flow of 10% oxygen/90% nitrogen delivered at 50 mL/min. After background removal and normalization, spectral analyses were performed by a linear combination fit (LCF) using reference materials of Pb [ $\text{Pb}$ ,  $\text{PbCl}_2$ ,  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}\cdot\text{Pb}(\text{OH})_2$ , and  $\text{PbS}$ ].

The chemical states of Pb in three raw RFAs (at room temperature) were analyzed on the basis of the spectral shapes and LCFs of the Pb  $L_3$ -edge XANES spectra. The XANES spectral shape of Pb in each RFA was similar to that of the reference chloride ( $\text{PbCl}_2$ ), as shown in Fig. 1. Pb existed mainly as a combination of chloride and oxide according to the

LCFs of the XANES spectra (Table 1). Only RFA-B contained a notable quantity of lead sulfide (31%). According to previous studies, the three RFAs were representative mixtures of Pb chemical forms in MSW fly ash.

We prepared simplified MFAs admixed with  $\text{PbCl}_2$  (1.0% Pb) and  $\text{PbO}$  (1.0% Pb) with KCl (10% Cl), activated carbon (3.0%), and  $\text{SiO}_2$  (remainder), denoted as MFA- $\text{PbCl}_2$  and MFA- $\text{PbO}$ , respectively, to examine the thermochemical behaviors of the two major Pb compounds in MSW fly ash. We observed small changes of MFA- $\text{PbCl}_2$  in the spectra from room temperature to 300°C and 400°C, as shown in Fig. 1. The LCF results indicated that the  $\text{PbCl}_2$  composition at room temperature (60%) decreased slightly to 55–56% at higher temperatures. Therefore, the thermochemical oxidation of trace  $\text{PbCl}_2$  in the model solid phase could promote the chlorination of the carbon matrix. Heating at 300°C and 400°C lifted the characteristic spectrum dip of MFA- $\text{PbO}$  at ~13067 eV, as shown in Fig. 1. The analysis of

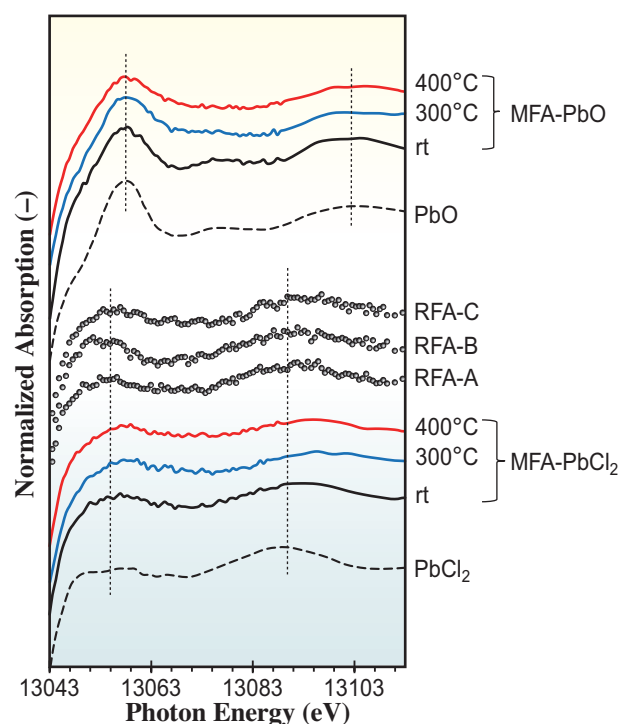


Fig. 1. Pb  $L_3$ -edge XANES spectra of RFAs and MFAs containing  $\text{PbCl}_2$  and  $\text{PbO}$ .

spectra by LCF indicated that lead oxide in MFA-PbO was partially chlorinated to 25–28% PbCl<sub>2</sub> (Table 1). Inorganic chloride (KCl) functioned as a chlorine source for lead oxide. The reduced thermochemical chlorination of carbon by inorganic chloride might be due to the suppression of aromatic-Cls resulting from the prior partial chlorination of PbO using an inorganic chlorine source in the solid phase.

There is a large elemental composition gap between MFA-PbCl<sub>2</sub> and RFA. Thus, using RFA-A (which contained 89% PbCl<sub>2</sub> as the major Pb chemical form at room temperature) (Table 1), we performed *in situ* Pb L<sub>3</sub>-edge XANES analysis. The L<sub>3</sub>-edge spectrum of Pb at room temperature (rt), similarly to that of PbCl<sub>2</sub>, shifted its peak positions to higher energies, such as in the PbO spectrum, upon heating (Fig. 2). The LCF results indicated that the 89% PbCl<sub>2</sub> content in RFA-A decreased to 44–59% after heating at 300°C and 400°, as shown in Table 1. Because the complex solid phase contributed largely to the thermochemical oxidation of PbCl<sub>2</sub>, the formation of aromatic-Cls was promoted.

In real MSW fly ash, Pb exists in both oxide and chloride forms. Aromatic-Cl formation depends on the balance between the inhibition by lead oxide and the promotion by lead chloride. Because Pb coexists with other metal catalysts in real MSW fly ash, the coexistence effect of PbCl<sub>2</sub> has to be considered. Overall, our mechanism-oriented study suggests that Pb in MSW fly ash functions as an "adjuster" in the generation of aromatic-Cls, depending on the lead oxide/chloride ratio and conditions of coexistence with metal catalysts.

Table 1. Lead chloride, oxide, and sulfide components (%) in RFAs and MFAs based on LCF of Pb L<sub>3</sub>-edge XANES.

Pb samples	Chloride (%)	Oxide (%)	Sulfide (%)
RFA-A	89	11	
300°C	44	56	
400°C	59	41	
RFA-B	26	43	31
RFA-C	47	53	
MFA-PbO		100	
300°C	25	75	
400°C	28	72	
MFA-PbCl <sub>2</sub>	60	40	
300°C	55	45	
400°C	56	44	

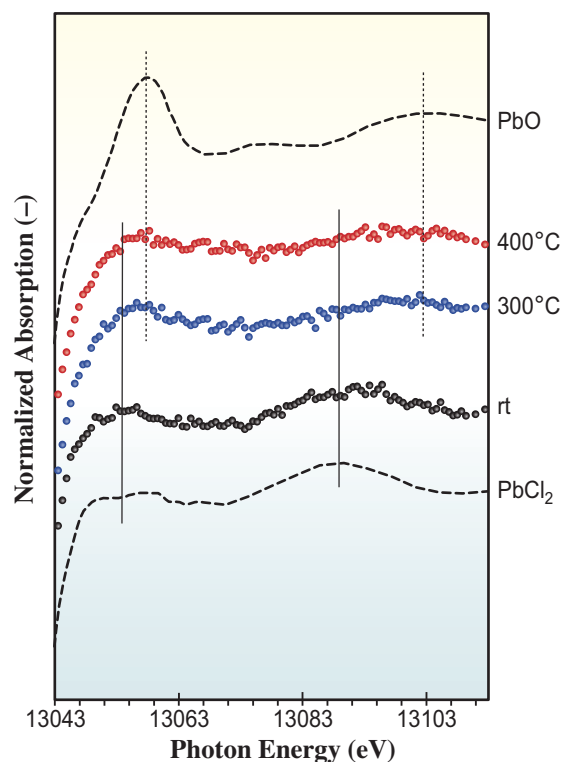


Fig. 2. *In situ* Pb L<sub>3</sub>-edge XANES spectra of lead chloride-rich RFA-A heated from room temperature (rt) to 300°C and 400°C.

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