

Chlorination of Carbon during Thermochemical Behavior of Lead by Using X-Ray Absorption Spectroscopy

We examined the thermochemical role of Pb in the formation of chlorinated aromatics (aromatic-Cl_s) in MSW fly ash at a key temperature window for maximum yield by using X-ray absorption spectroscopy. In the presence of lead oxide alone, aromatic-Cl_s formation was suppressed. Promotion can occur by the thermochemical partial oxidation of PbCl₂. Real complex solid phase increases the thermochemical oxidation reactivity of PbCl₂. The presence of PbCl₂ influences the balance of the bonding state of chlorine with Cu and Fe atoms at various temperatures. So, Pb in real MSW fly ash functions as an “adjuster” in the generation of aromatic-Cl_s.

Regarding the toxicity and resource recovery of lead, various speciation studies have reported 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 (PbCl₂) 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), after heating of model fly ash. Lead oxide (PbO) inhibits the formation of PCDDs, PCDFs, PCBs, and CBzs. Lead metallurgical processes can also be used to generate PCDDs, PCDFs, and PCBs. The thermochemical behaviors of metals in the solid phase likely play a role in the formation and inhibition of aromatic-Cl_s, which is supported by 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.

We prepared single-addition and coexistence-addition model fly ashes (MFAs) and real fly ashes (RFAs). Three RFAs from MSW incineration plants were analyzed by Pb L₃-edge X-ray absorption near-edge structure (XANES) spectroscopy to identify the chemical forms of lead. Concentrations of PCBs and CBzs in MFAs under single and coexistence conditions were quantified using gas chromatography/mass spectrometry (GC/MS). Thermochemical chlorine behaviors of MFAs were analyzed using Cl K-edge near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at BL-11B and BL-9A.

Aromatic-Cl_s formation was suppressed in the presence of lead oxide alone. One of the mechanisms of suppression was partial chlorination of PbO by an inorganic chlorine source in the solid phase, based on in situ Pb L₃-edge XANES data. In contrast, we found that aromatic-Cl_s formation was promoted by the coexistence of PbCl₂ with other metal catalysts more effectively at 400°C than at 300°C (Fig. 1). One possible mechanism of this promotion is related to the thermochemical partial oxidation of PbCl₂. More specifically, real complex solid phase increases the thermochemical oxidation reactivity of PbCl₂.

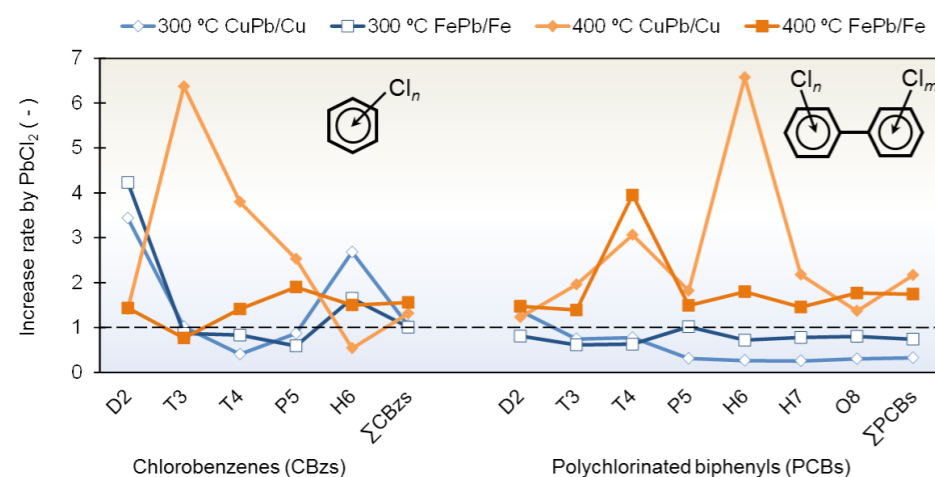


Figure 1: Mixed effect of PbCl₂ in the solid phase according to the concentrations of CBzs and PCBs after heating.

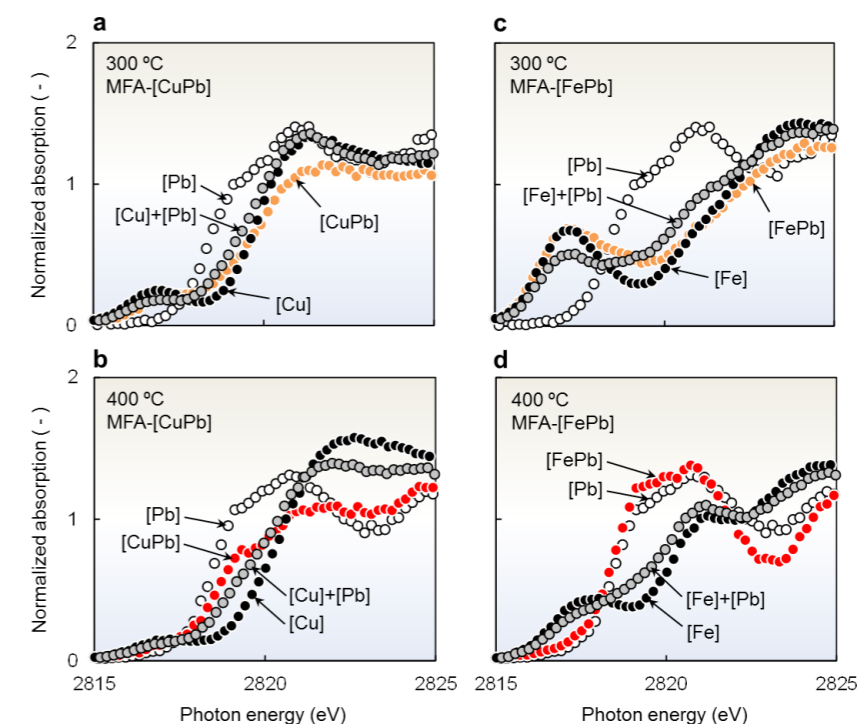


Figure 2: Cl K-edge NEXAFS spectra of various MFAs. MFA-[CuPb] after heating at (a) 300°C and (b) 400°C. MFA-[FePb] after heating at (c) 300°C and (d) 400°C. Reference spectra of MFA-[Cu], -[Fe], and -[Pb] after heating at each temperature are also shown. [Cu] + [Pb] and [Fe] + [Pb] indicate theoretical spectra generated by linear combinations of MFA-[Cu] and -[Fe], respectively, with MFA-[Pb].

We performed Cl K-edge NEXAFS measurements to explore the thermochemical mechanism of PbCl₂ in the presence of other metal catalysts. According to a comparison of the measured spectrum with the theoretical spectrum, Cl K-edge NEXAFS analyses revealed the coexistence effect of PbCl₂ with other metal catalysts, such as CuCl₂ and FeCl₃ (Fig. 2). The shapes of the MFA-[CuPb] and MFA-[FePb] spectra were closer to those of MFA-[Cu] (Fig. 2a) and MFA-[Fe] (Fig. 2c), respectively, at 300°C. This suggests that the observed amounts of chlorine bonded with copper and iron were greater than the theoretical amounts. So, the relatively mild inhibition of aromatic-Cl_s at 300°C is caused in part by decreased dechlorination by metal catalysts. At 400°C, both the spectra of MFA-[CuPb] (Fig. 2b) and MFA-[FePb] (Fig. 2d) were similar to that of MFA-[Pb]. The chlorine amounts bonded with Pb and Cu/Fe were higher and lower, respectively, than in the theoretical spectrum. The promotion at 400°C is caused by increased dechlorination by metal catalysts. Thus, the coexistence of PbCl₂ influences the imbalance of the bonding state of chlorine caused by heating temperature.

In real MSW fly ash, Pb exists in both oxide and chloride forms. Aromatic-Cl_s formation depends on the

balance between inhibition by lead oxide and promotion by lead chloride. Because Pb coexists with other metal catalysts in real MSW fly ash, the coexistence effect of PbCl₂ had to be considered. Overall, our mechanism-oriented study suggests that Pb in MSW fly ash functions as an “adjuster” in the generation of aromatic-Cl_s, depending on the lead oxide/chloride ratio and coexistence conditions with metal catalysts.

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BEAMLINES

BL-11B and BL-9A

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