

Chlorinated aromatics in municipal-solid-waste fly ash inhibited by thermochemical zinc behavior

Zinc is a major heavy metal produced anthropogenically in solid-phase compounds such as municipal solid waste (MSW) fly ash. Researchers have reported that the zinc content in fly ash correlated positively with the concentrations of toxic chlorinated aromatic compounds (aromatic-Cl), such as polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs), and benzenes (CBzs). During postcombustion, zinc was considered to be generated as zinc chloride ($ZnCl_2$) or an oxidelike compound [1]. Zinc oxide (ZnO) and $ZnCl_2$ showed a weak thermal catalytic activity in aromatic-Cl formation via particulate carbon [2]. However, we cannot conclude that Zn compounds promote aromatic-Cl formation because real systems are more complex than such models. In fact, Hinton and Lane reported data that refuted such a conclusion [3]. They studied the catalytic behavior of zinc using zinc compounds added to real fly ash. When zinc nitrate was added, high concentrations of PCDDs were generated. However, PCDD concentration decreased with the addition of both zinc nitrate and copper nitrate. Their results suggested that zinc nitrate acted as an inhibitor when zinc coexisted with stronger metal promoters in real fly ash. In our previous study [4], to determine whether zinc acts as a promoter, we performed systematic quantitative X-ray spectroscopic experiments under coexistent conditions with $ZnCl_2$ at the temperature of aromatic-Cl formation.

Real fly ash (RFA) samples obtained from municipal solid waste incinerators (MSWIs) were used to determine the major chemical forms and thermal behavior of zinc. We prepared model fly ash (MFA) to understand the thermochemical interaction between zinc and metal chlorides ($CuCl_2$ and $FeCl_3$). Gas chromatography/mass spectrometry (GC/MS) experiments provided quantitative information on aromatic-Cl [2]. The thermochemical states of zinc and chlorine were determined by X-ray absorption fine structure (XAFS) at beamline BL01B1 in SPring-8 and Photon Factory, respectively. During Zn *K*-edge XAFS measurement, the sample disk was heated from room temperature to 300°C and 400°C in a T-type *in situ* cell [5] under a flow of 10% oxygen/90% nitrogen delivered at 50 mL/min. Surface analysis by X-ray photoelectron spectroscopy (XPS) revealed a characteristic zinc behavior in the solid phase. We discuss the coexistent-specific effects of zinc on the basis of our results.

The nearest-neighbor elements of zinc in RFAs were chlorine or oxygen, according to the peak positions of Zn *K*-edge Fourier-transformed extended XAFS (EXAFS) spectra. We previously reported that ZnO had zero or negative potential to promote the thermochemical formation of aromatic-Cl [2]. In the present study, we used $ZnCl_2$ as a promoter to generate aromatic-Cl. We found that the coexistence of zinc with other trace metals ($CuCl_2$ and $FeCl_3$) was more effective for aromatic-Cl formation than zinc alone. When zinc chloride coexisted with cupric or ferric chloride, the concentrations of Σ CBzs (Σ PCBs) were inhibited to 54% (92%) or 33% (52%), compared with those of MFA added $CuCl_2$ or $FeCl_3$, respectively. T4- and P5-chlorobenzenes showed a higher inhibitory effect, greater than 75% ($ZnCl_2+CuCl_2$) and 47% ($ZnCl_2+FeCl_3$), than other congeners (Fig. 1(a)). Inhibitory effects greater than 92% and 64% were observed for PCBs from P5 to O8 in the $ZnCl_2+CuCl_2$ model and from H6 to O8 in the $ZnCl_2+FeCl_3$ model, respectively (Fig. 1(b)). Figure 1 shows visually that zinc chloride inhibited the generation of PCBs (two aromatic rings) at higher rates than CBzs (one ring) owing to coexistence, indicating that the bridged structure of the aromatic ring did not form readily.

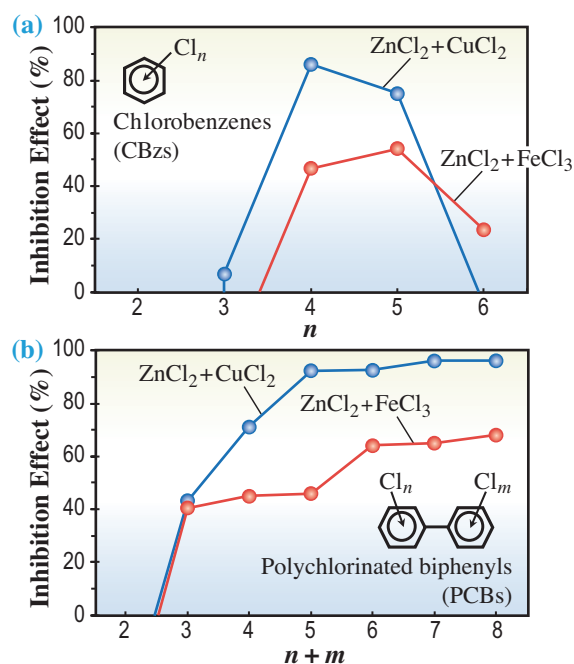


Fig. 1. Inhibition effects of (a) chlorobenzenes (CBzs) and (b) polychlorinated biphenyls (PCBs) after heating model fly ash at 300°C under coexistent conditions of zinc chloride ($ZnCl_2$) with other metal promoters such as $CuCl_2$ and $FeCl_3$.

We studied the chemical state of zinc chloride at the temperature of aromatic-Cl formation to understand the thermochemical behavior of zinc. Zn K-edge EXAFS analysis (Fig. 2) using a model and real fly ash confirmed that the thermochemical state of zinc chloride changed slightly and was thermally stable (i.e., no energy shift of the peak position) at ~300°C, the temperature at which the maximum aromatic-Cl formation occurs in real fly ash. Although Zn-Cl bonding was stable in the complex solid phase, we observed an unstable chlorine behavior with coexisting strong promoters by Cl K-edge near-edge XAFS (NEXAFS) analysis. By comparing the spectrum of the ZnCl₂+CuCl₂ model sample with the theoretical linear combination spectrum Calc(ZnCl₂+CuCl₂), a low-temperature transition of chlorine to the gas phase (low-Cl(g)) with CuCl₂ was found to occur (a, in Fig. 3(a)) and aromatic-Cl formation was also found to be inhibited at 300°C (b, in Fig. 3(a)). In addition, under the coexistent conditions (ZnCl₂+CuCl₂), XPS analysis results for the near-surface concentrations of Zn (Fig. 3(b)) and Cl (no figure) indicated a weak reactivity between the catalysts and the carbon matrix. FeCl₃ also showed a similar behavior to CuCl₂ when coexisting with ZnCl₂. From these findings, we suggest the importance of

studying a “coexistent complex system” to understand the interaction between trace metals and aromatic-Cl_s in a real thermal solid phase such as MSW fly ash.

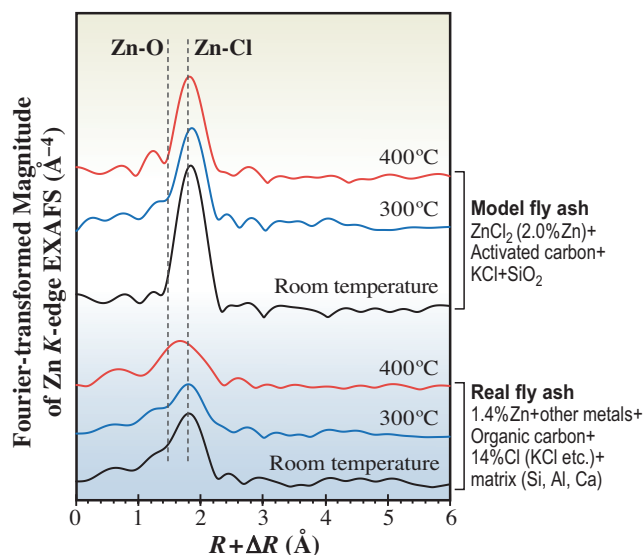


Fig. 2. *In situ* Fourier-transformed k^3 -weighted Zn K-edge extended X-ray absorption fine structure (EXAFS). Real and model fly ashes admixed with zinc chloride at room temperature, 300°C, and 400°C.

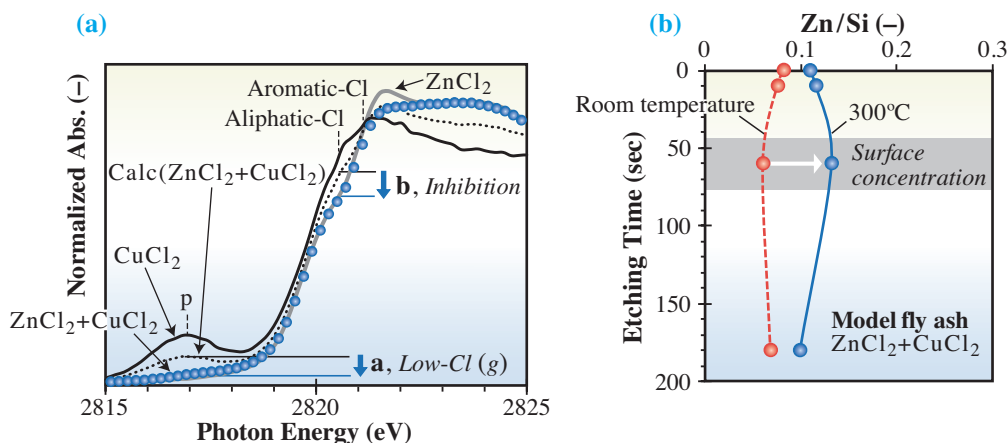


Fig. 3. (a) Cl K-edge near-edge X-ray absorption fine structure (NEXAFS) for three model fly ashes (ZnCl₂, CuCl₂, and ZnCl₂+CuCl₂) after heating at 300°C and theoretical linear combination spectrum of two models (ZnCl₂ and CuCl₂), Calc(ZnCl₂+CuCl₂). (b) Near surface concentration of zinc measured by in-depth X-ray photoelectron spectroscopy (XPS).

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