

Mechanistic investigation of chromium-chloride-promoted formation of dioxins by *in situ* XAFS

Ever since the discovery of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F), or, in brief dioxins, in emissions from municipal solid waste incineration (MSWI), numerous endeavors have been launched for determining their mechanisms of formation. The catalytic formation of PCDD/F requires specific metal ions as catalysts [1]. Chromium is widely contained in municipal solid wastes and is commonly used in MSWI superheater metal alloys. Although present in fly ash in concentrations comparable to that of the strongest catalyst, copper, chromium has been less investigated regarding its influence and role during dioxin formation. X-ray absorption fine structure (XAFS) spectroscopy is one of the best-known techniques for determining the chemical forms of the target element. *In situ* XAFS spectroscopy enables the measurements of XAFS spectra of target elements only during the thermochemical reaction process without altering the original conditions of the test. A combination of both *in situ* and *ex situ* XAFS techniques has been applied to elucidating the formation mechanisms of chlorinated aromatics from MSWI model fly ash (MFA) catalyzed by the metals Cu, Fe, Zn and Pb [1-4]. In this study, the *in situ* XAFS technique was used to investigate the reaction mechanisms of PCDD/F formation promoted by Cr compounds [5].

Firstly, model fly ash (MFA₁) doped with chromium chloride (CrCl₃·6H₂O, 0.2wt% Cr; activated carbon, 3wt%; NaCl, 10wt% Cl; SiO₂, remainder) was heated over a wide range of temperatures to confirm the effects of CrCl₃ on PCDD/F formation (Fig. 1). MFA₁ was heated in a tubular furnace for 60 min at each temperature except for 120 min at 250°C in a gas stream of 10% O₂ + 90% N₂ and the resulting PCDD/F were collected and analyzed. A blank MFA₁ without

the addition of CrCl₃·6H₂O was also tested at 350°C. Both PCDD and PCDF yields were highest at 350°C, being 16.4 ng PCDD/g and 217 ng PCDF/g, attaining factors of 9.7 (PCDD) and 17.9 (PCDF) compared with those of the blank MFA₁. This result confirmed the appreciable promoting effect of CrCl₃ on the formation of PCDD/F.

The dynamic changes in the chemical states of chromium and chlorine were detected by *in situ* Cr K-edge XAFS at SPring-8 BL01B1 and *in situ* Cl K-edge X-ray absorption near edge structure (XANES) at BL-9A in Photon Factory, respectively. The MFA used for XAFS measurements (MFA₂) consisted of activated carbon, CrCl₃·6H₂O, and boron nitride (BN), with BN constituting 80% and the remaining 20% being composed of activated carbon and CrCl₃·6H₂O in the same weight ratio as in MFA₁. MFA₂⁻ was heated in an *in situ* cell in a gas stream with 10% O₂ (+90% N₂ for Cr-XAFS; +90% He for Cl-XANES) from room temperature (RT) to 550°C at a rate of 5°C/min. During heating, the temperature was successively sustained at eight stages (250, 290, 320, 350, 380, 420, 460 and 550°C) for measuring Cr-XAFS and Cl-XANES spectra.

As the temperature increased from RT to 550°C, most changes in the Cr K-edge XANES spectra were observed in the pre-edge region (-3 to 9 eV from the Cr K-edge position at 5989 eV Fig. 2(a)). The pre-edge region of the spectrum at RT featured only one weak peak at ~5989 eV, similar to the spectrum of the CrCl₃·6H₂O standard. A second peak at around 5992 eV emerged at 250°C, grew with increasing temperature, slightly decreased at 350°C, peaked at 380°C, and then rapidly declined, finally to the level of Cr₂O₃ (Fig. 2(a)). The appearance of this peak suggests that the CrCl₃ in MFA₂ was oxidized to Cr₂O₃ and even to Cr(VI)-O during heating. The fraction of Cr(VI) in Cr was estimated by peak fitting in the pre-edge region (Fig. 2(a)). The analysis of Cr K-edge EXAFS data (Fig. 2(b)) further confirms the results of Cr-XANES. The peak at ~1.6 Å (denoted as Peak 1) is mainly attributed to the Cr(III)-O bond, while the second peak at ~2.5 Å (denoted as Peak 2) arises from Cr-Cr scattering. As temperature increased, Peak 1 initially dropped owing to the dehydration of chromium chloride hydrate and subsequently increased owing to oxidation to Cr₂O₃. With increasing temperature, Peak 2 exhibited an increasing trend, providing further proof of the gradual formation of Cr₂O₃.

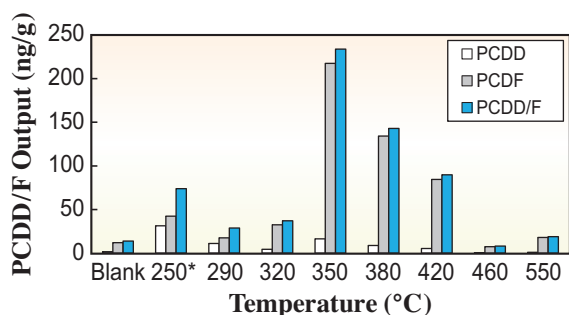


Fig. 1. Formation of PCDD, PCDF, and PCDD/F (ng/g) as a function of temperature at 10% oxygen. *MFA₁ at 250°C was heated for 120 min.

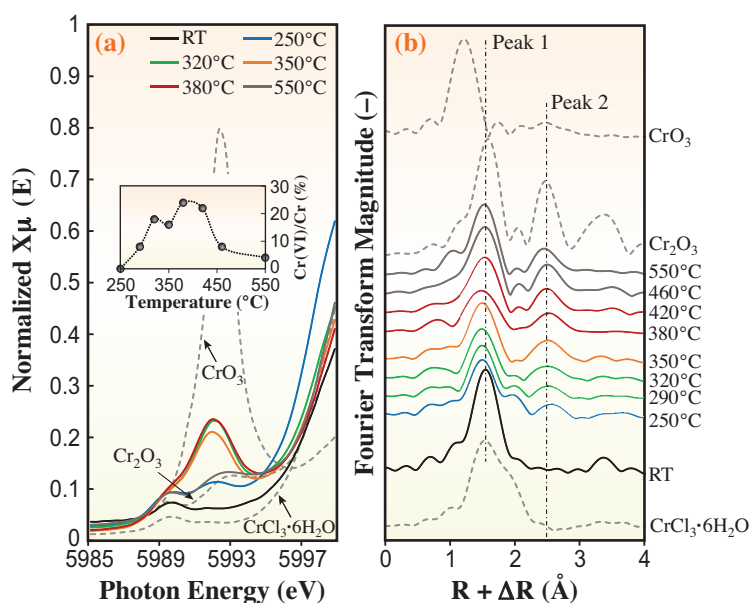


Fig. 2. Pre-edge region of Cr K-edge XANES spectra of MFA₂ during the temperature increase and of reference standards (a). Fourier transform of k^3 -weighted Cr K-edge EXAFS spectra as a function of temperature (b).

The dynamic changes of chlorine species were observed in *in situ* Cl K-edge XANES spectra (only RT to 350°C owing to the indiscernibility of higher-temperature spectra) and an *ex situ* spectrum measured from MFA₂ heated at 460°C for 60 min (Fig. 3). As temperature increased a peak at around 2821 eV, a typical feature of chlorine connected to carbon (Cl to aliphatic carbon, aliphatic-Cl: 2820.6 eV; Cl to aromatic carbon, aromatic-Cl: 2821.1–2821.3 eV), occurred and gradually increased. Ratios of different Cl species (%) in MFA₂ were estimated by linear combination fitting. The conversion of Cl in $CrCl_3$ to that bound to carbon (Fig. 3) occurred simultaneously with the oxidation of $CrCl_3$ (Fig. 2), providing direct evidence for carbon chlorination through $CrCl_3$ oxidation and dechlorination.

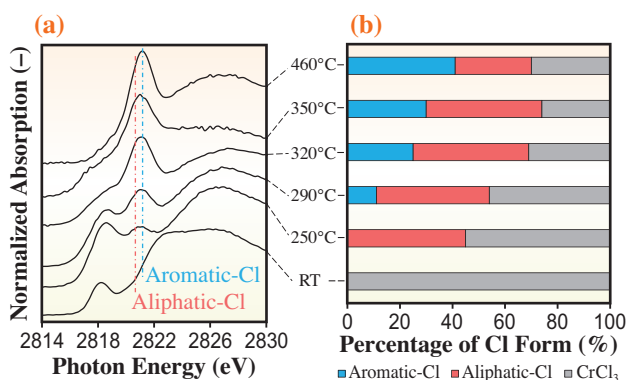


Fig. 3. Cl K-edge XANES spectra of MFA₂ during the temperature increase (a) and the percentage of Cl species as a function of temperature (b).

Overall, chromium compounds play two key roles during dioxin formation: the chlorination of carbon by the chlorine derived from the oxidation of $CrCl_3$ to Cr_2O_3 and to Cr(VI)-O, and facilitating the oxidative destruction of the carbon matrix by the reduction of Cr(VI)-O as well as the end-product Cr_2O_3 . As a result, chloro-aromatic compounds including PCDD/F are generated. The XAFS technique provides visual evidence of the invisible chemical reactions and proves to be a very useful tool for understanding the mechanistic aspects in various thermochemical processes.

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