

## XAFS investigation of chromium chloride catalysed formation of dioxins

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### Introduction

Heterogeneous or catalytic formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) and other chlorinated aromatic compounds, at the surface of solid carbon (e.g., soot, charred materials) on fly ash particles, requires specific metal ions as catalysts. Copper (speciation of CuCl and CuCl<sub>2</sub>) was already studied intensively and has been identified as strongest catalyst in PCDD/F formation<sup>1</sup>. Its dynamic change in chemical state and reaction mechanisms during the formation of chlorinated aromatics have been systematically investigated using X-ray absorption fine structure (XAFS) spectroscopy<sup>2,3</sup>. Other metals, such as iron, zinc and lead, have also been studied for their effects on the formation of chlorinated aromatics<sup>4,5</sup> and the accompanying reaction mechanisms<sup>6-8</sup>. However, chromium, a known catalyst of the Deacon process<sup>9</sup>, with concentration in the same order of magnitude as copper and lead in municipal solid waste (MSW) fly ash, has seldom been discussed systematically for its influence and potential role during dioxins formation.

Only few studies reported on the correlation between chromium and dioxins. Öberg et al. statistically correlated the elemental composition of incinerator fly ash and the concentration of chlorobenzenes (CBz), chlorophenols (CP) and PCDD/F, suggesting that chromium could contribute to the de novo formation of these chlorinated aromatics<sup>10</sup>. Conversely, their later tests showed that the addition of CrCl<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> actually decreased the formation of CBz and PCDD/F<sup>11,12</sup>. However, in a previous experimental study, we found that CrCl<sub>3</sub> ranked as second most active catalyst for PCDD/F formation, just following CuCl<sub>2</sub>, among the chlorides and oxides of five metals (Cu, Cr, Ni, Zn and Cd); moreover, Cr<sub>2</sub>O<sub>3</sub> was also listed as a potent oxide catalyst, only less active than CuO<sup>13</sup>. In order to draw a consolidated conclusion on the effect of Cr (especially CrCl<sub>3</sub>) on PCDD/F and other chlorinated aromatics, a comprehensive study identifying both the influence on PCDD/F yields and elucidating the reaction mechanisms on a molecular basis is still required.

In this study, firstly, a model fly ash (MFA) doped with chromium chloride was heated in a flow of gas (N<sub>2</sub> + 10 % O<sub>2</sub>) at temperatures ranging from 250 to 550 °C to explore the effect of temperature on the PCDD/F-yield from CrCl<sub>3</sub>-catalysed system. Then, in situ Cr K-edge and in situ Cl K-edge XAFS were applied for detecting the changes in chemical states of chromium and chlorine during the heating processes. The resulting XAFS spectra and the data analyses provide strong evidences for the formation of chlorinated aromatics catalysed by CrCl<sub>3</sub> and substantial information for speculating on the nature of potential reactions of PCDD/F-formation.

### Materials and methods

**Sample preparation.** Two kinds of MFA were prepared. The sample of MFA1 used for forming PCDD/F was composed from activated carbon (AC) as source of carbon (3 wt. %), sodium chloride (NaCl; 10 wt. % Cl) as source of chloride, and chromium chloride hexahydrate (CrCl<sub>3</sub>·6H<sub>2</sub>O; 0.2 wt.% Cr) as catalytic precursor; the matrix material was silica (SiO<sub>2</sub>). The MFA2 used for XAFS measurements consisted of only AC, CrCl<sub>3</sub>·6H<sub>2</sub>O and boron nitride (BN), with BN constituting 80 wt. % and the remaining 20% composed of AC and CrCl<sub>3</sub>·6H<sub>2</sub>O (in the same weight ratio as in MFA1). In both cases, CrCl<sub>3</sub>·6H<sub>2</sub>O was dissolved into distilled water and the solution was mixed with the other components, by wet grinding them together in a mortar for about 20 min. Then the mixture was dried for 36 h at 30 °C and sealed for later experiments.

**PCDD/F formation tests.** The PCDD/F-formation experiments were conducted in a vertical tubular reactor surrounded by an electric furnace and operating substantially at atmospheric pressure<sup>4</sup>. A sample of 2 g of MFA was placed into a vertical quartz tube, which was then introduced into a preheated electric furnace for 60 min (at

250 °C for 120 min) at eight different temperatures (250, 290, 320, 350, 380, 420, 460 and 550 °C, respectively), in a gas stream supplied at 100 ml/min (10% O<sub>2</sub>/90% N<sub>2</sub>). After heating, the PCDD/F remaining in the MFA residue and those in the gas phase and collected by XAD-2 and the impinger, with ca. 125 ml of toluene, were analysed together.

**In situ Cr K-edge and in situ Cl K-edge XAFS.** The dynamic changes in the chemical states of chromium and chlorine were detected by in situ Cr K-edge XAFS (BL01B1 in SPring-8, Hyogo, Japan) and in situ Cl K-edge X-ray Absorption Near Edge Structure (XANES) (BL-9A in Photon Factory, Tsukuba, Japan), respectively. After milling the MFA2 in an agate mortar for 15 min, 150-200 mg of MFA2 was pressed into a disk (10 mm in diameter). The disk was then placed and heated in a T-type in situ cell<sup>4</sup> in a gas stream of 10% O<sub>2</sub> (+ 90% N<sub>2</sub> for Cr-XAFS; + 90% He for Cl-XAFS) delivered at 50 ml/min. The sample disk was gradually heated by a mantle heater, from room temperature (RT) to 550 °C at a rate of 5 °C/min. The temperature was successively held at eight steps (250, 290, 320, 350, 380, 420, 460 and 550 °C) during the heating process sustained for measuring Cr-XAFS and Cl-XANES. The Cl-XANES was not measured at 420, 460 and 550 °C due to the excessive volatility of chlorine at high temperatures and thus the low chlorine signal intensity. Two individual in situ Cl-XANES test campaigns were also conducted for studying the influence of reaction time at two different temperatures, by heating the sample disk from RT to 250 and 350 °C, respectively, in 30 min, and keeping the temperature thereafter. Cl-XANES was measured continuously during the whole heating process.

The XAFS spectra of chromium in CrCl<sub>3</sub>·6H<sub>2</sub>O, CrCl<sub>3</sub>·6H<sub>2</sub>O solution, Cr, Cr<sub>2</sub>O<sub>3</sub> and CrO<sub>3</sub> were measured as reference spectra, for comparing shapes and identifying chromium species. Three categories of chlorine species were selected as Cl-references: (i) chlorine bonded with chromium (CrCl<sub>3</sub>·6H<sub>2</sub>O and CrCl<sub>3</sub>·6H<sub>2</sub>O solution), (ii) chlorine connected to aromatic carbon (2,6-, 2,3,4,6-CP and PeCBz) and (iii) chlorine connected to aliphatic carbon (polyvinyl chloride, PVC). Some other chromium compounds which may be generated during the heating process, e.g. CrCl<sub>2</sub> and CrO<sub>2</sub>Cl<sub>2</sub>, failed to be tested for their spectra, due to their high reactivity.

## Results and discussion

**Formation of PCDD/F.** Figure 1 shows the PCDD-, PCDF- and PCDD/F-output (in ng/g MFA) from the CrCl<sub>3</sub>-catalysed system, as a function of temperature. Except for the test at 250 °C for 120 min, both PCDD and PCDF reach their summit at 350 °C. The highest yields observed (at 350 °C) are 16.4 ng PCDD/g and 217 ng PCDF/g. The behaviour of PCDD is slightly different from that of PCDF: PCDD considerably can still be produced from CrCl<sub>3</sub>-MFA even at relatively low temperatures (250 and 290 °C). Formation of PCDF is greatly favoured over that of PCDD. The ratio-PCDF/PCDD varies between a deep low of 1.4 at 250 °C, up to 18 at 550 °C, albeit with a slight dip at 460 °C. The PCDD/F-output data from CrCl<sub>3</sub>-MFA in this study are inconsistent with those in the study of Öberg et al.<sup>11</sup> using CrCl<sub>3</sub>-added real electrostatic precipitator (ESP) fly ash from a biofuel incinerator. One explanation is that CrCl<sub>3</sub> can largely promote the formation of PCDD/F and reach the highest reactivity at 350 °C, while it may also interact with other transition metals contained in real fly ash and lead to less formation of dioxins from the mixture.

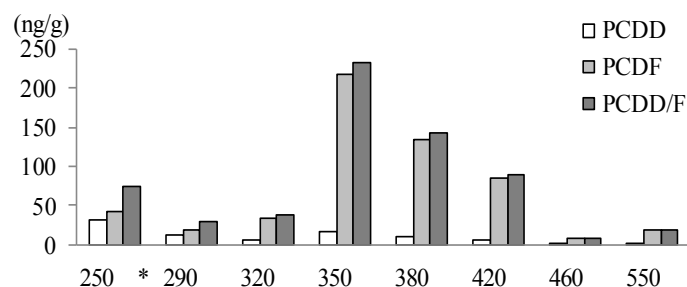


Figure 1. Formation of PCDD, PCDF and PCDD/F as a function of temperature (ng/g).

\*MFA was heated for 120 min at 250 °C.

**Chemical form of chromium varying with temperature.** Cr XANES spectra are shown as a “fingerprint” to present the dynamic changes in Cr-species during heating (Figure 2), with most changes observed in the pre-edge region. The pre-edge region of spectrum at RT is characterised by only a weak peak at about 5989 eV,

same to the spectra of  $\text{CrCl}_3$  standards. A second peak around 5992 eV emerges at 250 °C, grows with rising temperature (although slightly dropping at 350 °C), peaks at 380 °C, and rapidly declines after 420 °C, finally to the similar height as that in  $\text{Cr}_2\text{O}_3$ . The pre-edge feature peak around 5992 eV, almost as intense as the edge step in  $\text{CrO}_3$  while rather weak in  $\text{Cr}_2\text{O}_3$ , has been used for signifying the oxidation state of Cr<sup>14</sup>. Statistical analyses of the pre-edge feature peaks indicate that  $\text{Cr}_2\text{O}_3$  and also  $\text{CrO}_3$  are formed in  $\text{CrCl}_3$ -MFA during heating, with up to about 10% of the Cr oxidised to  $\text{CrO}_3$  (at 380 °C) and finally almost all Cr in form of  $\text{Cr}_2\text{O}_3$  at the highest temperature.

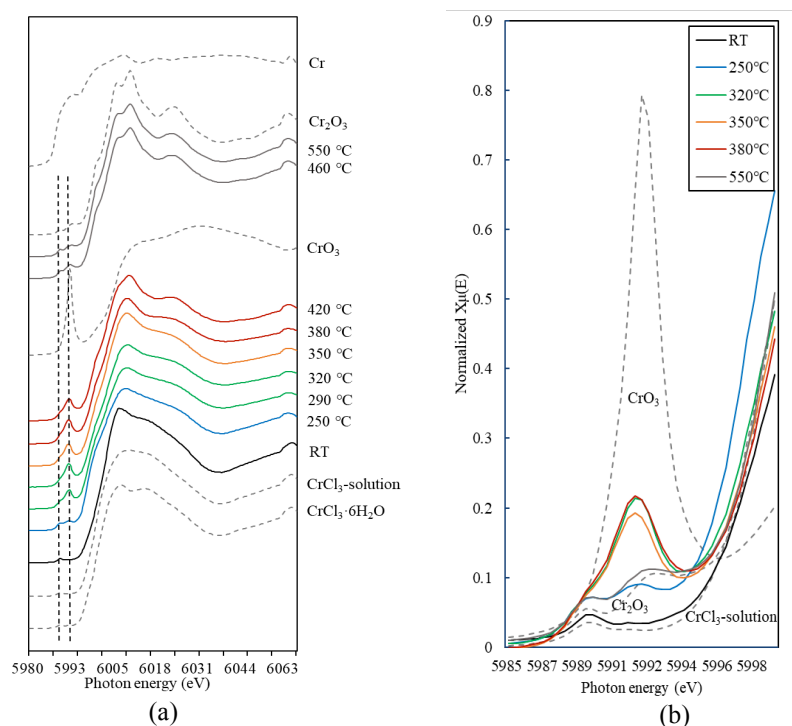


Figure 2. Cr K-edge XANES spectra of MFA2 during the temperature rising process and the reference standards (a) and expansion and superposition of the pre-edge region of selected spectra (b).

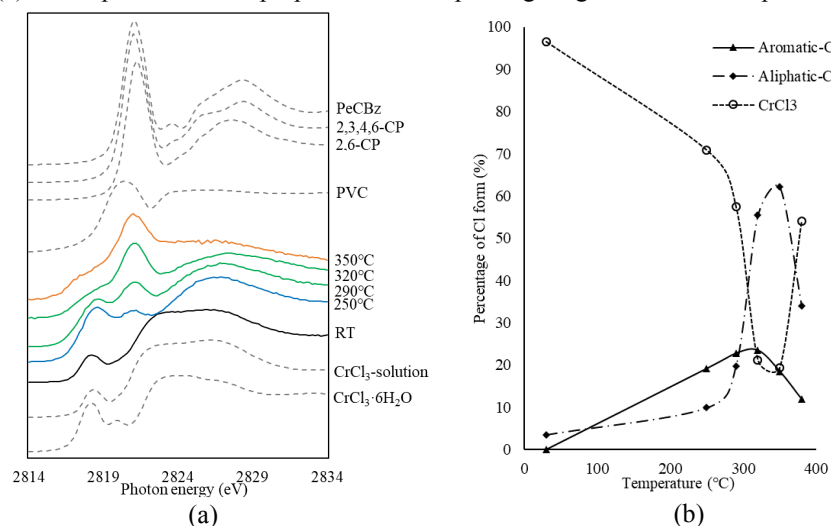


Figure 3. Cl K-edge XANES spectra of MFA2 during the temperature rise and the reference standards (a) and the percentage of Cl-species as a function of temperature (b).

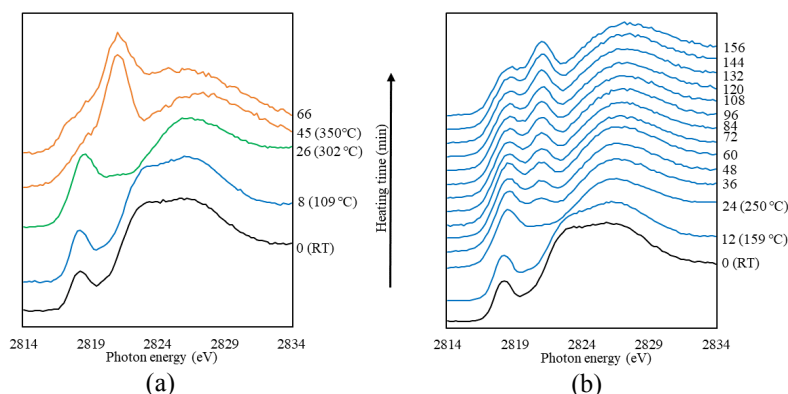


Figure 4. Cl K-edge XANES spectra as a function of time during heating tests to 350°C (a) and to 250°C (b).

**Chlorination of carbon and formation of chlorinated aromatics.** Figure 3a shows the XANES spectra of Cl in MFA varying with temperature and the comparison with the three types of reference standards. At RT, Cl is only bonded with Cr. A small peak occurs around 2821 eV at 250 °C, with its intensity growing higher with rising temperature until 350 °C, and again almost disappears at 380°C (not shown). This peak (2821 eV) is a typical feature of chlorine connected with carbon (Aromatic-Cl: 2821.1-2821.3 eV; Aliphatic-Cl: 2820.6 eV). Visually, the changes in Cl- and Cr-XANES spectra provide direct, non-destructive evidence of carbon chlorination accompanied by CrCl<sub>3</sub> dechlorination. Ratios of different Cl-species (%) in MFA were determined by linear combination fitting using the reference materials (fitting range: 2814-2824 eV). This shows that the contribution of Aromatic-Cl peaks at 300°C and the sum of organic Cl at 350 °C (Figure 3b), consistent with the PCDD/F output. Higher temperature ( $\geq 380^\circ\text{C}$ ) leads to intensive desorption of chlorine (mainly as organic Cl and Cl<sub>2</sub>), failing to produce smooth Cl-spectra due to the low Cl content in solid phase. The chlorination of carbon by CrCl<sub>3</sub> was monitored as a function of time at two different temperatures, progressing rapidly at 350°C (Figure 4a) and marching more slowly but still visibly at 250 °C (Figure 4b).

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