The dynamic changes of copper in model fly ash using SiO2 during de novo synthesis

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Introduction

In our previous study, we reported on *in situ* X-ray absorption near edge spectroscopy (XANES) experiments that used a type of real fly ash, which originated from a municipal solid-waste incinerator (MSWI), and two types of model fly ash to investigate the behavior of copper in fly ash at temperatures that are suitable for *de novo* synthesis, which is the major route of formation for polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and other chlorinated aromatics during waste incineration and other thermal processes.[1] We found strong evidence that oxychlorination, the fundamental mechanistic step in the formation of PCDDs, PCDFs, and other chlorinated organics, occurred in both real MSWI and model fly ash. However, the study was limited because the model fly ash was composed of a mixture of $CuCl_2 \cdot 2H_2O$, activated carbon (AC), and boron nitride (BN). Other researchers have not used BN as a supporting material.[2-4] Generally, materials composed of silica, such as Florisil or fused silica, are used to support copper compounds. Therefore, we conducted *in situ* XANES experiments in this study using a model fly ash that was typical of other previous studies to investigate the effect of supporting materials and copper content in fly ash on the dynamic changes of copper and amount of dioxins generated.

Materials and Methods

We prepared a model fly ash by mixing the following components: $CuCl_2 \cdot 2H_2O$, activated carbon (AC), KCl, and SiO_2 (BN). The fly ash contained 0.2% Cu, 10% Cl, and 3.0% AC; the remaining fraction was composed of SiO_2 and K. After grinding the fly ash using a mortar for 10 min, 200 mg were pressed into disks that were 13 mm in diameter.

The direct speciation of copper in the fly ash was examined using XANES with an *in situ* cell as shown in Fig. 1. XANES was performed using beamline BL01B1 in SPring-8, a synchrotron radiation facility in Japan[5], while a disk of fly ash was heated in the *in situ* cell. The heating procedure and atmospheric conditions are shown in Fig. 2. The spectra were collected in fluorescence mode using a 19-element Ge solid-state detector for model fly ash with a Si (111) monochromator. The data were analyzed using REX 2000 ver. 2.3.3 (Rigaku Co. Ltd.).

Fig.1 in situ cell

A pattern-fitting analysis of the XANES spectra was conducted, which assumed that the unknown spectra were linear combinations of reference spectra from our library [Cu, Cu_2O, CuCl, CuO, $CuCl_2 \cdot 2H_2O$, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, CuS, $Cu(OH)_2$, $CuSO_4$, $CuFeO_4$, $Cu_3(PO_4)_2 \cdot H_2O$, and $CuCl_2 \cdot 3Cu(OH)_2$].[1,6] The residual value (R) calculated using Eq. (1) was used to evaluate the fit of the model predictions to the experimental data.
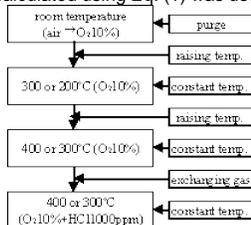
R: residual value
$$R = \frac{\sum \left(XANES_{Measured} - XANES_{Calculated} \right)^2}{\sum \left(XANES_{Measured} \right)^2}$$
(1).

A 5-g sample of model fly ash was heated in a tubular electric furnace under a 10% O_2 (90% N_2) atmosphere while the temperature was raised to 300°C and held at 300°C for 30 min. PCDDs/PCDFs that were expelled in the outlet gas were collected by passing the gas through an impinger containing 100 mL of toluene. Toluene was also used to clean the inside of the quartz tube and was mixed with the solution from the impinger. The fly ash was acid-treated and dried at room temperature for 48 h, and soxhlet was extracted with toluene for 24 h. The cleanup, concentration procedures, and analysis of PCDDs/PCDFs were based on the manual of the Japan Industrial Standard (JIS K 0311 and 0312). GC/MS (HP -6890/Autospecultima by Agilent/Micromass) with two columns, SP-2331 and DB-17HT, was used to measure the concentration of PCDDs/PCDFs. Samples of model fly ash A ($CuCl_2 \cdot 2H_2O$+AC+BN) from our previous study[1] were also heated, and the amounts of PCDDs/PCDFs generated were measured.

Fig.2 Heating procedure in in situ XAFS experiment

Results and Discussion

The change in the chemical form of copper in model fly ash($CuCl_2 \cdot 2H_2O$+AC+KCl+SiO_2)
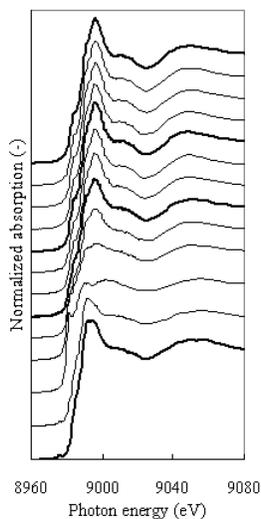
The changes in the chemical forms of copper in model fly ash after heating from room temperature to 300 and 400°C are shown in Fig. 3. The percentages relative to the total Cu obtained by linear combination fitting (LCF) for the XANES spectra of model fly ash during heating are shown in Table 1. At room temperature, the copper compounds consisted of 73% $CuCl_2 \cdot 2H_2O$ and 27% CuO. Therefore, some of the $CuCl_2 \cdot 2H_2O$ changed into CuO while we were grinding and pressing the model fly ash into a disk. During the first temperature increase, the CuO disappeared, while CuCl and Cu_2O appeared, and the ratio of $CuCl_2 \cdot 2H_2O$ slightly decreased. In the second temperature increase, no $CuCl_2 \cdot 2H_2O$ was observed, and CuCl, Cu_2O, and Cu were the predominant species. In the third temperature increase, the ratio of CuCl reached 50%, which suggests that the $CuCl_2 \cdot 2H_2O$ in the new model fly ash is strongly reduced at low temperatures. This change is the same as the change observed in our previous work using a mixture with BN. Also, this change in the chemical form of copper in this model fly ash agrees with the change observed in real fly ash.

In the fourth temperature increase, although the ratio of CuCl was highest among the distribution, CuO, a cupric compound, appeared, which suggested that the atmosphere inside the fly ash was changing from a reductive to an oxidative atmosphere. At a constant temperature of 300°C, the ratio of Cu_2O and CuCl decreased to 12 and 25%, respectively, whereas the ratio of CuO increased to 63%. In the second temperature increase from 300 to 400°C, the residual value of $CuCl_2$ was low, and the spectra fit was adequate. However, cupric chloride is not stable at high temperatures. Copper compounds not included in our data set will likely be present. However, we conclude that about 90% of the total Cu was from cupric compounds in this model fly ash at approximately 400°C.

Fig.3 Cu K-edge XANES spectra in model fly ash during heating from room temperature to 300 and 400°C. Bold: spectra at constant temperature under constant gas composition
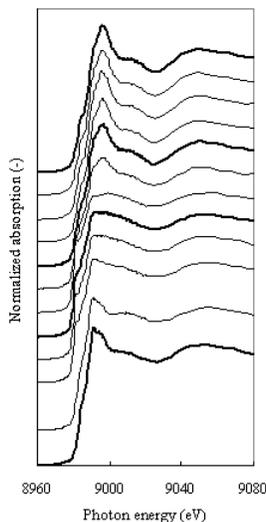
The atmosphere was then changed from 10% O_2 (90% N_2) to 10% O_2 + HCl 1000 ppm (balance of N_2) to observe the effect of chlorination by HCl at 400°C. The XANES spectra and the distribution of copper compounds did not change. The addition of 1000 ppm HCl in this temperature region did not significantly influence the chemical form of copper.

Table 1 The percentages to total Cu obtained by LCF for the XANES spectra of model fly ash during heating from room temperature to 300 and 400°C

No.	step	starting temp.	Cu	Cu_2O	CuCl	$CuCl_2 \cdot 2H_2O$	CuO	R
1	rt	35				73	27	0.025
2	rt→300℃ 1st loop	41		25	16	59		0.037
3	rt→300℃ 2nd loop	170	30	37	33			0.072
4	rt→300℃ 3rd loop	306	21	29	50			0.042
5	rt→300℃ 4th loop	298		22	42		36	0.020
6	300℃	298		12	25		63	0.018
7	300℃→400℃ 1st loop	313		8	17		75	0.015
8	300℃→400℃ 2nd loop	390			13	11	76	0.014
9	400℃	390			7	11	82	0.011
10	→ 1000ppmHCl 1st loop	392			8	10	82	0.012
11	→ 1000ppmHCl 2nd loop	388			9	10	81	0.012
12	→ 1000ppmHCl 3rd loop	390			11	9	80	0.013
13	400℃at1000ppmHCl	392			8	9	84	0.012

To confirm the temperature at which the reaction starts, the same model fly ash was heated from room temperature to 200°C. The change in the chemical form of copper in model fly ash A after heating from room temperature to 200 and 300°C is shown in Fig. 4. The percentages relative to the total Cu obtained by LCF for the XANES spectra of model fly ash during heating are shown in Table 2. At room temperature, the ratio of $CuCl_2 \cdot 2H_2O$ was 71%, which was almost the same as the above experiment. In the second temperature increase, no $CuCl_2 \cdot 2H_2O$ was observed, and CuCl made up 54% of the total Cu. At approximately 200°C, the distribution of CuCl, Cu, and Cu_2O did not change, which indicates that the atmosphere inside the fly ash remained reductive. During the second temperature increase from 200 to 300°C, CuO appeared, but the ratio of CuCl was highest among the distribution. At a constant temperature of 300°C, the ratio of Cu_2O and CuCl dramatically decreased to 16 and 29%, respectively, whereas the ratio of CuO increased to 55%. This distribution of copper compounds was similar to that observed at the same temperature in the above experiment. While the atmosphere was changed from 10% O_2 (90% N_2) to 10% O_2 + HCl 1000 ppm (balance of N_2), the ratios of CuO were about 70%. At the constant gas composition, the ratio of CuO increased to 78%.

Amounts of PCDDs/DFs generated

Figure 5 shows the amounts of PCDDs/PCDFs generated after the heating experiments using a tubular electric furnace. The total amount of PCDDs/PCDFs in the model fly ash used in this study and model fly ash A from the previous study accounts for 69000 ng/g and 12000 ng/g, respectively. The total amount of PCDDs/PCDFs in the model fly ash was five times higher than in model fly ash A, but the amounts followed the same trend. Although a difference in lower chlorinated compounds was observed between both model fly ashes, their relative distributions of PCDDs/PCDFs were almost identical, which agrees with the pattern using $CuCl_2 \cdot 2H_2O$ reported by Iino et al.[3]

According to *in situ* XANES experiments, the dynamic changes of copper observed in this study are similar to those observed in the previous study using BN as a supporting material. Also, the amounts of PCDDs/PCDFs generated in both model fly ashes are of the same order. Therefore, the mechanisms of formation of PCDDs/PCDFs in both of the model fly ashes are basically the same, and there is not a large difference between the use of BN or

Fig.4 Cu K-edge XANES spectra in model fly ash during heating from room temperature to 200 and 300°C. Bold: spectra at constant temperature under constant gas composition
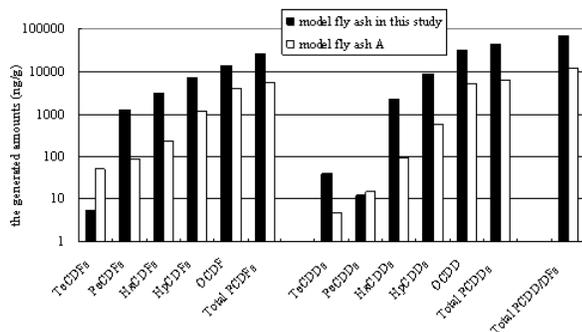
SiO_2 as a supporting material.

However, with regard to the changes in the chemical forms of copper at temperatures of 300°C and higher, the distribution of copper compounds was different between the model fly ashes. In particular, the difference involved the temperature at which CuO appeared. In this study, that temperature was 300°C, but it was approximately 400°C in the previous study. This difference is thought to be attributable to the main

Table 2 The percentages to total Cu obtained by LCF for the XANES spectra of model fly ash during heating from room temperature to 200 and 300°C

No.	step	starting temp.	Cu	Cu$_2$O	CuCl	CuCl$_2$·2H$_2$O	CuO	R
14	rt	35		19	10	71		0.031
15	rt→200°C 1st loop	41		28	29	43		0.047
16	rt→200°C 2nd loop	170	21	25	54			0.035
17	rt→200°C 3rd loop	306	21	24	55			0.036
18	200°C	298	24	18	59			0.035
19	200°C→300°C 1st loop	313	27	27	46			0.048
20	200°C→300°C 2nd loop	390		30	52		18	0.025
21	300°C	390		16	29		55	0.019
22	→1000ppmHCl 1st loop	392		13	19		68	0.016
23	→1000ppmHCl 2nd loop	388		11	17		72	0.015
24	→1000ppmHCl 3rd loop	390		13	17		70	0.015
25	300°C at 1000ppmHCl	392		10	12		78	0.014

component in the fly ash. The carbon, copper, and chlorine contents in model fly ash A are 5% C, 1.86% Cu, and 2% Cl, whereas the new model fly ash contained 3% C, 0.2% Cu, and 10% Cl. The difference in carbon content affects the copper speciation. However, the ratio of C to Cu in the new model fly ash was five times higher than in model fly ash A, which indicates that the new model fly ash can maintain a more reductive atmosphere than model fly ash A. Furthermore, gasification of carbon at 300°C is slower than at 400°C, so the atmosphere at 300°C is more reductive than at 400°C. Stieglitz et al. reported that a significant amount of carbon remained even after heating model fly ash at 300°C for 5 h.[7] Consequently, conclusive remarks are difficult to formulate in this study. Furthermore, heating experiments using model fly ash at 300°C generate PCDDs/PCDFs for extended times. It took about 1 h to progress from room temperature to 200 and 300°C in the *in situ* XANES experiments. At 300°C, it is possible that the fly ash was still forming PCDDs/PCDFs. In other words, it is probable that the final state of copper at 300°C is responsible for the formation of PCDDs/PCDFs. In the future, we need to formulate various mixtures and more copper compounds that are stable at high temperatures. It is also necessary to analyze more precisely the chemical forms of copper by XANES and correspond the results to conventional annealing experiments to understand the formation of PCDDs/PCDFs in greater detail.

Fig.5 The generated amounts of PCDDs/DFs in model fly ash used in this XANES experiment and in model fly ash A in our previous study
Model fly ash consists of CuCl$_2$·2H$_2$O, AC, KCl and SiO$_2$.
Model fly ash A consists of CuCl$_2$·2H$_2$O, AC and BN.

Acknowledgements

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