

THE FORMATION OF CHLORINATED AROMATICS AND DYNAMIC CHANGES IN THE CHEMICAL FORM OF COPPER IN MODEL FLY ASHES USING VARIOUS COPPER COMPOUNDS

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Introduction

Previously, we reported *in situ* X-ray absorption near edge structure (XANES) experiments in real fly ash and in two kinds of model fly ash to investigate the behavior of copper at temperatures suitable for *de novo* synthesis.^{1,2} Dynamic changes in copper on heating the fly ash were observed in both the real fly ash and the model fly ash using CuCl₂·2H₂O. We found strong evidence that oxychlorination—the key mechanistic step in the formation of chlorinated aromatics—occurred in both a real municipal solid waste incinerator and model fly ash using CuCl₂·2H₂O.

Many researchers regard CuCl₂·2H₂O as an influential catalyst,^{3–5} although other species might be present in real fly ash.⁶ Since only two kinds of model fly ash were examined in our previous studies,^{1,2} it was necessary to investigate the effects of various copper species in model fly ash on the formation of chlorinated aromatics, such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Some researchers have already prepared model fly ashes using various copper compounds, and have evaluated the amount of chlorinated aromatics generated in conventional heating experiments.^{7–9} Nevertheless, only limited information on the change in copper in model fly ashes during heating is available from the literature.

Therefore, in this study, we prepared ten kinds of model fly ash using various copper compounds and conducted conventional heating experiments to check the formation potentials of chlorobenzenes (CBzs) and polychlorinated biphenyls (PCBs) in each model fly ash. In addition, we conducted *in situ* XANES experiments using nine kinds of model fly ash to investigate the dynamic changes in copper in the model fly ashes during heating. Finally, the relationship between the dynamic changes in copper in the model fly ashes and the amounts and homologs of the chlorinated aromatics generated are discussed.

Materials and Methods

We prepared a model fly ash by mixing the following components: copper compound, activated carbon (AC), KCl, and SiO₂. The fly ash contained 0.2% Cu, 10% Cl, and 3.0% AC; the main remaining fraction was composed of SiO₂ and K. We used Cu, CuO, Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, Cu₂O, CuCl, CuCl₂, CuCl₂·2H₂O, CuS as copper compound. Also model fly ash without copper compound was prepared. After grinding the fly ash using a mortar for 10 min, the fly ash was used as a conventional heating experiment and *in situ* XANES experiment.

A 5-g sample of model fly ash was heated in a tubular electric furnace under a 10% O₂ (90% N₂) atmosphere while the temperature was held at 300°C for 30 min. The gas flow rate was 50 ml/min. CBzs and PCBs 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 was Soxhlet-extracted with toluene for 24 h. The cleanup, concentration procedures, and analysis of CBzs (D2–H6) and PCBs (D2–O8) were presented elsewhere.⁶

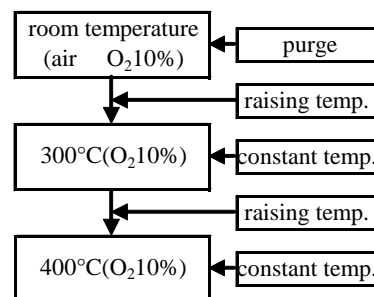


Fig.1 Heating procedure in *in situ* XAFS experiment

The direct speciation of copper in the fly ash was examined using XANES with an *in situ* cell. XANES was performed using beamline BL01B1 in SPring-8, while a disk of fly ash was heated in the *in situ* cell. The heating procedure and atmospheric conditions are shown in Fig. 1. 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.). A linear combination fitting (LCF) for the XANES spectra was conducted, which assumed that the unknown spectra were linear combinations of reference spectra from our library [Cu, Cu₂O, CuCl, CuO, CuCl₂·2H₂O, CuCO₃·Cu(OH)₂·H₂O, CuS, Cu(OH)₂, CuSO₄, CuFeO₄, Cu₃(PO₄)₂·H₂O, and CuCl₂·3Cu(OH)₂].^{1,6,10} The residual value (R) was used to evaluate the fit of the model predictions to the experimental data.

Results and Discussion

Amounts and homologs of CBzs and PCBs generated in various model fly ashes

Figures 2 and 3 show the respective amounts and homologs of CBzs and PCBs generated after heating experiments using a tubular electric furnace. The total amounts of CBzs and PCBs in the model fly ashes containing copper compounds ranged from 43 to 630 µg/g-model fly ash and 230 to 7500 ng/g-model fly ash, respectively. These levels are roughly equal to those in model fly ash using CuCl₂·2H₂O reported by Weber et al.¹¹ The model fly ash without a copper compound contained nine times less CBzs and PCBs than those with copper compounds, which indicates that the copper compounds in model fly ash promote the formation of chlorinated aromatics. The total amounts of CBzs or PCBs in the model fly ashes using CuCl, CuCl₂, CuCl₂·2H₂O, or CuS were eight times greater than those in the model fly ashes using Cu, CuO, Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, or Cu₂O. Although copper chloride is regarded as an influential catalyst, we also found that CuS had extremely high catalytic activity for the formation of chlorinated aromatics.

For the distributions of both CBz and PCB homologs, fewer chlorinated compounds were observed in the model fly ashes using Cu, CuO, Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, or Cu₂O, while more chlorinated compounds were present in the model fly ashes using CuCl, CuCl₂, CuCl₂·2H₂O, or CuS. Therefore, either (oxy)chlorination is ongoing in the latter group of model fly ashes or the copper compounds in the former group start to dechlorinate CBzs and PCBs.

Since some experimental studies using real fly ash have indicated that the formation of chlorinated aromatics was inhibited by the sulfuration of copper in real fly ash,^{12,13} i.e., the conversion of copper compounds into CuS, it is thought that CuS lacks the potential to form chlorinated aromatics. However, CuS appeared to be an influential catalyst in this study. Future studies must investigate the difference between the sulfuration of copper compounds in real fly ash and the behavior of copper compounds in model fly ash using CuS. Based on the results of homolog distributions, the formation mechanism in model fly ash using CuS appears to be the same as that using copper chlorides.

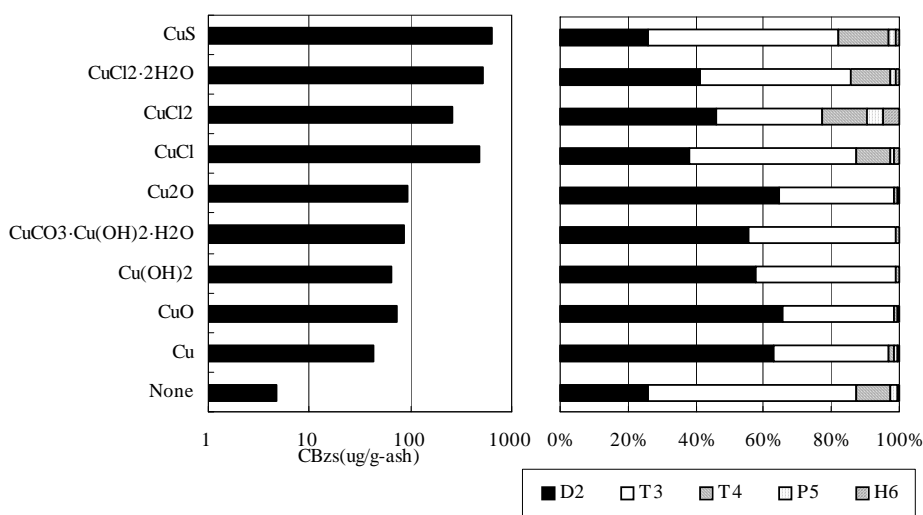


Fig.2 The amounts and homologs of CBzs generated after conventional heating experiments

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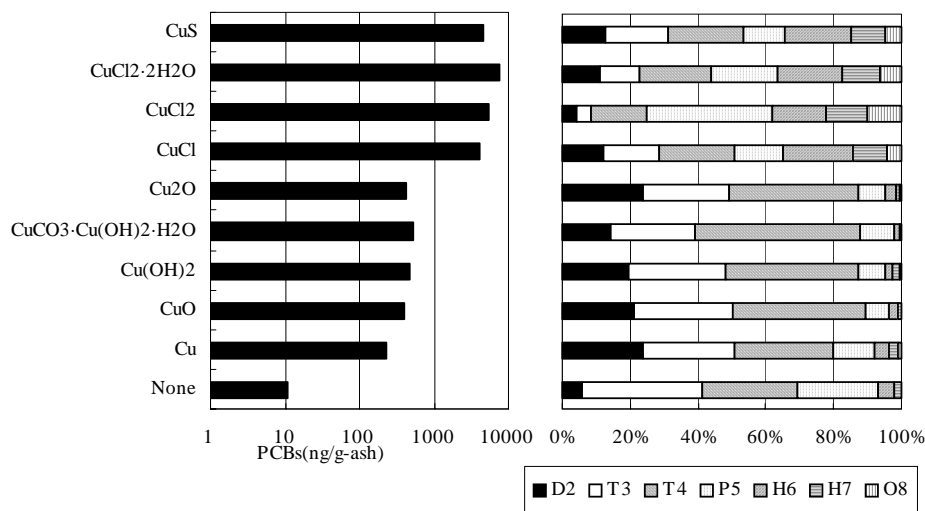


Fig.3 The amounts and homologs of PCBs generated after conventional heating experiments

The change in the chemical form of copper in model fly ashes

The percentages relative to the total Cu obtained by LCF for the XANES spectra of model fly ash during heating are shown in Table 1. For the *in situ* XANES experiments with model fly ashes using Cu, CuO, Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, or Cu₂O, we raised the temperature to 300°C only.

Considering copper species at room temperature, in model fly ash using Cu, 48, 36, and 16% of the total Cu existed as Cu₂O, CuCl₂·3Cu(OH)₂, and CuCl, respectively. Therefore, all of the Cu changed into other species while we were grinding and pressing the model fly ash into disks. A similar phenomenon was observed in model fly ashes with added Cu⁰ or Cu⁺ compounds. In the other model fly ashes with added Cu²⁺ compounds, the copper species differed from the initial compound before mixing, although some of the initial compound remained after mixing. In the model fly ashes using Cu, Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, Cu₂O, or CuCl, some CuCl₂·3Cu(OH)₂ was observed. A small difference was detected between the model fly ashes using CuCl₂ and CuCl₂·2H₂O, although the predominant species were similar and hydration had no effect.

When the model fly ash was heated to 300°C, in those model fly ashes using Cu, CuO, Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, or Cu₂O, more than 70% of the total Cu changed into CuO. In the model fly ashes using Cu, Cu(OH)₂, or Cu₂O, 11–18% of the copper compounds had a low valence. In the model fly ashes using Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, or Cu₂O, a small amount of CuCl₂·2H₂O was detected at 300°C.

In the model fly ashes using CuCl, CuCl₂, CuCl₂·2H₂O, or CuS, the proportion of CuCl was 19–27% at 300°C, while the model fly ashes using Cu, CuO, Cu(OH)₂, CuCO₃·Cu(OH)₂·H₂O, or Cu₂O contained no CuCl. A large difference was observed in the amount of CuCl generated and the homologs of chlorinated aromatics present between these two groups, implying that CuCl plays an important role in the formation of chlorinated aromatics. The proportion of copper compounds with a low valence in the former group was also higher than that in the latter group, suggesting that the copper compounds in the former group were reduced more. Although the dynamic change in the Cu K edge XANES spectra is not shown here, the change was similar to that reported in our previous studies.^{1,2} There was no difference in the distribution of copper species at 300°C between the model fly ashes using CuCl₂·2H₂O and CuCl₂. The model fly ash using CuS contained 44% CuS at room temperature, but no CuS at 300°C, and it had the same distribution of copper species as that observed in the model fly ash using CuCl. The *in situ* XANES experimental results also suggested that the CuS in the model fly ash was not stable and had extremely high catalytic activity for the formation of chlorinated aromatics.

When the model fly ashes using CuCl, CuCl₂, CuCl₂·2H₂O, or CuS were heated to 400°C, in all of the model fly ashes except that containing CuCl₂, more than 70% of the total Cu changed into CuO. In the model fly

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ash using CuCl_2 , the CuCl_2 fraction remained. Of all the model fly ashes, this one contained the greatest amounts of CBz and PCB homologs, suggesting that (oxy)chlorination continued, even at 400°C .

Table.3 The percentages relative to the total Cu obtained by LCF for the XANES spectra of model fly ashes during heating

Sample*	Temperature**	Cu	Cu_2O	CuO	CuCl	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{Cu}(\text{OH})_2$	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$	$\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$	CuS	R
Cu	rt		48		16				36		0.021
	300°C	18		82							0.014
CuO	rt			100							0.023
	300°C			100							0.015
$\text{Cu}(\text{OH})_2$	rt					10	43		47		0.011
	300°C	15		71		14					0.012
$\text{CuCO}_3 \cdot \text{Cu}(\text{O})$ $\text{H}_2 \cdot \text{H}_2\text{O}$	rt							66	34		0.028
	300°C			88		12					0.035
Cu_2O	rt				13		27		60		0.010
	300°C		11	77		12					0.011
CuCl	rt					28			72		0.015
	300°C	18		57	25						0.017
	400°C	11		76		13					0.011
CuCl ₂	rt		15	14		71					0.028
	300°C		18	40	25	17					0.019
	400°C		13	58	18	11					0.014
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	rt					28			72		0.026
	300°C		15	53	19	13					0.015
	400°C			85		15					0.013
CuS	rt				11			45		44	0.011
	300°C	14		59	27						0.016
	400°C		12	73		15					0.011

* Composition: 0.2% Cu, 3.0% AC, 10% Cl, reminder SiO_2 and K.

** Atmosphere: 10% O_2/N_2 balance)

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