UNDERSTANDING ATACAMITE AS A COPPER CATALYST FOR DE NOVO SYNTHESIS BY HEATING EXPERIMENT AND DISPERSIVE XAFS

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Abstract

The copper chlorides, $CuCl$, $CuCl_2$, and $CuCl_2 \cdot 2H_2O$, are important catalysts that generate large amounts of dioxins in fly ash. Most copper in real fly ash is present as atacamite by X-ray absorption fine structure (XAFS). Atacamite is thought to possess copper-chloride-like properties because of its double salts of cupric chloride and cupric hydroxide. In this study, we investigated the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) in model fly ash A [atacamite + activated carbon (AC) + potassium chloride (KCl) + silicon dioxide (SiO_2)] at 300ºC suitable for *de novo* synthesis. We also examined the chemical state of atacamite in model fly ash B [Atacamite + AC + boron nitride (BN)] using *in situ* dispersive XAFS experiments. By heating experiment the concentration of dioxins in model fly ash A was as high as that from $CuCl_2 \cdot 2H_2O$, which has the highest catalytic activity for dioxin formation. Model fly ash A heated from 200 to 400ºC for 30 minutes, the concentration of PCDDs/Fs was the highest at 300ºC. Dispersive XAFS experiments indicated that the critical temperature at which dioxin formation catalyzed by atacamite begins is 300ºC. Catalytic impact of atacamite was very strong and important for dioxin formation in real fly ash.

Introduction

An understanding of the mechanisms involved in dioxin formation in fly ash is a prerequisite to controlling dioxin emissions. Dioxins are formed secondarily on and in fly ash in the post-combustion zone, and *de novo* synthesis is the key mechanism of dioxin formation. Copper compounds are thougut to be the chief catalysts in this *de novo* synthesis. In heating experiments involving model fly ash, copper chlorides ($CuCl_2 \cdot 2H_2O$, $CuCl_2$, and $CuCl$), in particular, have been demonstrated to be important catalysts in generating chlorinated aromatics such as dioxins[1].

Previously, we reported that the majority of copper in real fly ash is present as atacamite [copper chloride hydroxide: $Cu_2(OH)_3Cl$ or $CuCl_2 \cdot 3Cu(OH)_2$], based on *in situ* X-ray absorption fine structure (XAFS) experiments[2]. Although model fly ashes generated in conventional heating experiments using various copper compounds have been evaluated for dioxin amounts, few studies have reported on the formation of dioxins by atacamite, which is thought to have copper-chloride-like properties because of its double salt of cupric chloride and cupric hydroxide[2,3]. To understand the behavior of dioxin formation in real fly ash, the contribution of atacamite to dioxin formation was examined. We investigated the formation of chlorobenzenes (CBzs), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) in model fly ash A [atacamite + activated carbon (AC) + potassium chloride (KCl) + silicon dioxide (SiO_2)] at the temperatures suitable for *de novo* synthesis and the chemical state of atacamite in model fly ash B [atacamite + AC + boron nitride (BN)], using *in situ* dispersive XAFS experiments.

Materials and Methods

Samples

We prepared model fly ash A to evaluate the amount of dioxins generated in conventional heating experiments and model fly ash B to investigate the dynamic changes in copper in model fly ash during heating. Model fly ash A was a mixture of atacamite (copper chloride hydroxide: $Cu_2(OH)_3Cl$ or $CuCl_2 \cdot 3Cu(OH)_2$: Nichika Corp., Kyoto, Japan), activated carbon (AC: Takeda Pharmaceutical Co., Ltd., Osaka, Japan), potassium chloride (KCl: Nacalai Tesque, Inc., Kyoto, Japan), and silicon dioxide (SiO_2: Nacalai Tesque, Inc., Kyoto, Japan), containing 0.2% Cu, 10% Cl, and 3.0% AC, with the remainder almost entirely SiO_2. This fly ash was ground using a mortar for 10 min. Model fly ash B was a mixture of atacamite, AC, and boron nitride (BN: Wako Pure Chemical Industries, Ltd., Osaka, Japan), containing 1.8% Cu, 2.0% Cl, 5.0% AC, with the remaining 91.2% almost entirely BN. It was ground using a mortar for 10 min, and an agate mortar for 10 additional minutes, after which 70 mg of the fly ash was pressed into a disk 7.0 mm in diameter.

Conventional heating experiment

We inserted 5 g of model fly ash A on a quartz boat into a quartz tube (120 cm $\times$ 4 cm internal diameter) filled with 10% O_2 (90% N_2) at 50 mL/min and heated for 30 minutes in an electric furnace preheated to 200, 300, and 400 ºC. CBzs, PCBs, and PCDDs/Fs that were expelled in the outlet gas were collected by passing the gas through an impinger containing 100 mL of toluene. Fly ash residue and the toluene in an impinger were analyzed separately by using gas chromatography/mass spectrometry (GC/MS). The heating experiments were performed twice for each condition.

in situ dispersive XAFS experiment

Dispersive XAFS (DXAFS) has a greater temporal resolution than conventional XAFS, with an exposure time of a few milliseconds. We used DXAFS with an *in situ* cell to examine the direct speciation of copper in model fly ash. DXAFS was performed using beamline BL28B2 in SPring-8 (a synchrotron radiation facility in Hyogo, Japan), as a model fly ash disk was heated in the *in situ* cell under a flow of 10% O_2 (90% N_2) at 50 mL/min. Figure 1 shows the general time and temperature profile of the heating procedure. First, we placed a disk of model fly ash B in the *in situ* cell and turned on a heater to raise the temperature to 210ºC, 300ºC, and then 400ºC. XAFS data were collected both as the temperature increased and while it was held constant. Each measurement in the XAFS region required 12 sec. In about 180 min, 1000 spectra were collected, with each spectrum detecting approximately 1ºC intervals.

The DXAFS system consisted mainly of a polychromator with a bent silicon crystal, a higher-harmonic-rejecting mirror, and a charge-coupled device (CCD), coupled with a scintillating screen and a lens system. DXAFS allows the collection of continuous wavelength (or energy) data at one place on the sample disk because of the curve in the polychromator. When X-rays with continuous energy are passed through the sample, the X-ray transmittance differs according to the energy, and differently shaded stripes occur at the pre- and post-edge of the XAFS, as shown in Figure 2. A CCD detects the light variations.

The X-ray absorption near edge structure (XANES) spectrum can be used as a fingerprint that reflects the local environment of elements within a material. We measured the spectra of reference materials and the model fly ash to compare spectral shapes and identify major species. Species can also be distinguished using the linear combination fit (LCF) technique, in which spectra of known reference species [*e.g.*, Cu, Cu_2O, CuCl, CuO, atacamite ($CuCl_2\cdot3Cu(OH)_2$), and $CuCl_2\cdot2H_2O$] are fitted to the spectrum of the unknown sample. We conducted LCF of the XANES spectrum to determine the major species using REX 2000 ver. 2.3 software (Rigaku, Japan).

Results and Discussion

Conventional heating experiment

The PCDD and PCDF concentrations after heating at 200, 300, and 400ºC is shown as Table 1. Concentration of PCDDs and PCDFs was the highest 19100 and 14300 ng/g at 300ºC which was the temperature of maximum concentration of PCDDs and PCDFs by *de novo*
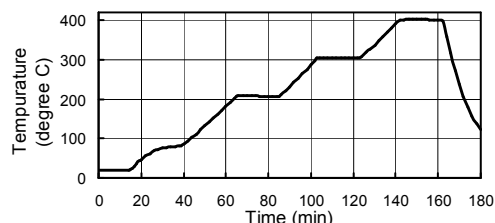

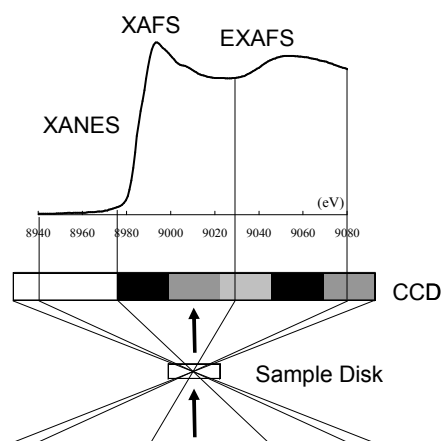Figure 1. General time and temperature profile of the heating procedure.

Figure 2. XAFS spectrum using DXAFS.

Table 1. Concentrations of PCDDs, and PCDFs at 200, 300, and 400ºC.

ng/g	Cl	Temperature (ºC)		
		200	300	400
PCDDs	T4	0.141	68	1
	P5	0.081	230	2.2
	H6	0.11	2000	18
	H7	0.083	3800	140
	O8	0.14	13000	2100
	Sum	0.55	19100	2260
PCDFs	T4	0.1	440	34
	P5	0.076	750	98
	H6	0.084	1700	410
	H7	0.12	3500	1900
	O8	0.16	7900	4300
	Sum	0.54	14300	6740

synthesis[4]. The average number of chloride in PCDDs and PCDFs increased with temperature rising.

Table 2 shows the CBz, PCB, PCDD, and PCDF concentrations after the heating experiment at 300ºC. "Blank" indicates model fly ash without copper compounds. The CBz and PCB concentrations in model fly ash with $CuCl_2 \cdot 2H_2O$ measured are also shown. CBz, PCB, PCDD and PCDF concentarations generated from the atacamite model fly ash A were much higher than those generated from the blank, and the same as those generated from $CuCl_2 \cdot 2H_2O$ model fly ash. These results demonstrate that atacamite has a catalytic proficiency for dioxin formation.

Table 2. Concentrations of CBzs, PCBs, PCDDs, and PCDFs at 300ºC.

ng/g	Blank	Atacamite	CuCl2·2H2O
CBzs	570	24000	36000
PCBs	32	1000	1400
PCDDs	6.3	19000	43000
PCDFs	1	14000	26000

Figure 3 shows the congener distribution of CBzs, PCBs, PCDDs, and PCDFs. As the number of substituted chlorines in the CBzs increased, the concentration of CBzs in the blank decreased. In contrast, the CBz distribution from atacamite showed the greatest concentration of T4CBz, and was very similar to the profile in $CuCl_2 \cdot 2H_2O$. The similarity in CBz distribution also applied to PCBs: the congener distribution of PCBs in atacamite was the same as that in $CuCl_2 \cdot 2H_2O$, but not that in blank. As chlorination number of PCDDs and PCDFs increased, the concentration in the atacamite and $CuCl_2 \cdot 2H_2O$ increased together, which was also different distribution pattern from blank. These results suggest that the mechanism of dioxin formation by atacamite is similar to that by $CuCl_2 \cdot 2H_2O$.
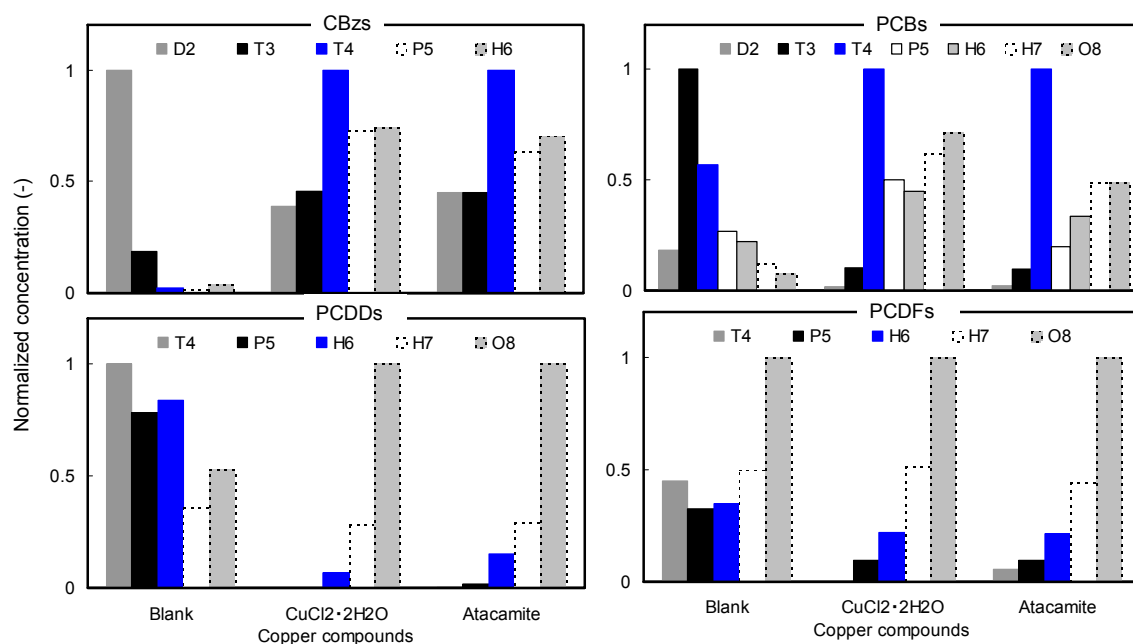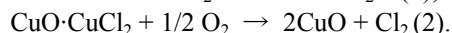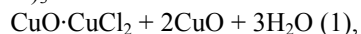

Figure 3. Congener distribution of CBzs, PCBs, PCDDs, and PCDFs. The normalized concentration indicates that each concentration has been divided by the highest concentration of each congener.
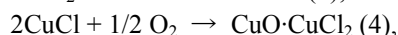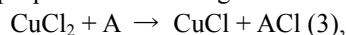
in situ dispersive XAFS experiment

The catalytic role of atacamite for *de novo* synthesis was revealed by DXAFS. $CuCl_2 \cdot 2H_2O$ was not found in the LCF analysis. Atacamite and CuO were the major chemical forms, while CuCl, Cu_2O, and Cu appeared at >300ºC. Figure 4 shows the LCF results for each Cu-K XANES spectrum for atacamite model fly ash B. From room temperature to 300ºC, copper appered as 60 - 70% atacamite and 30 - 40% CuO. At >300 ºC, atacamite was reduced dynamically to Cu(I) (Cu_2O, CuCl) or elemental copper, and CuO increased. Dynamic reduction of atacamite over 300ºC acted as driving force of dioxin formation. Figure 5 shows the change of the Cu-K XANES spectrum above 300ºC, when the copper began to change chemical form. At room temperature (rt: 28ºC), the XANES spectrum was similar to that of atacamite. At >300ºC, the strongest intensity of the XANES spectrum

(white-line) decreased, the intensity at lower and higher energy position of white-line increased gradually, and the spectrum was similar to that of CuO. Sharkey and Lewin[5] reported changes in the chemical form of atacamite. The reaction stages were dehydration and dechlorination:

$$2Cu_2(OH)_3Cl \rightarrow$$
$$CuO \cdot CuCl_2 + 2CuO + 3H_2O \ (1),$$
$$CuO \cdot CuCl_2 + 1/2 \ O_2 \rightarrow 2CuO + Cl_2 \ (2).$$

Reaction (1) is the dehydration of atacamite at 265 - 301ºC. Reaction (2) is the dechlorination of oxychloride ($CuO \cdot CuCl_2$), which ensued at 399 - 442ºC. In our *in situ* DXAFS experiment, the change in the chemical form of copper corresponded to that reported[5]. The dehydration of atacamite (1) began at 300ºC, as CuO increased. The change in the chemical form of model fly ash B held at 400ºC for 20 min indicates that CuO continued to increase. This was followed by dechlorination (2). By the way, it is said that oxychloride ($CuO \cdot CuCl_2$) appears in the oxychlorination cycle[6] and propose the following reactions:

$$CuCl_2 + A \rightarrow CuCl + ACl \ (3),$$
$$2CuCl + 1/2 \ O_2 \rightarrow CuO \cdot CuCl_2 \ (4),$$
$$CuO \cdot CuCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O \ (5).$$

where A and ACl refer to organic compounds and organic chlorinated compounds, respectively.

We suggest that oxychloride was generated >300ºC, but was so unstable in the above

Figure 4. LCF results for each Cu-K XANES spectrum for atacamite model fly ash B.

Figure 5. Change of the Cu-K XANES spectrum above 300ºC.

reactions that $CuCl_2$ was rapidly generated by the reaction described by equation (5). $CuCl_2$ was also too unstable to be observed, and the XANES spectrum showed CuCl. Thus, CuCl was generated as a chemical form of copper by reaction (3). From 200ºC to 400ºC or at a constant temperature of 300ºC, as CuCl increased, atacamite decreased, which indicated that atacamite led to the oxychlorination cycle in fly ash.

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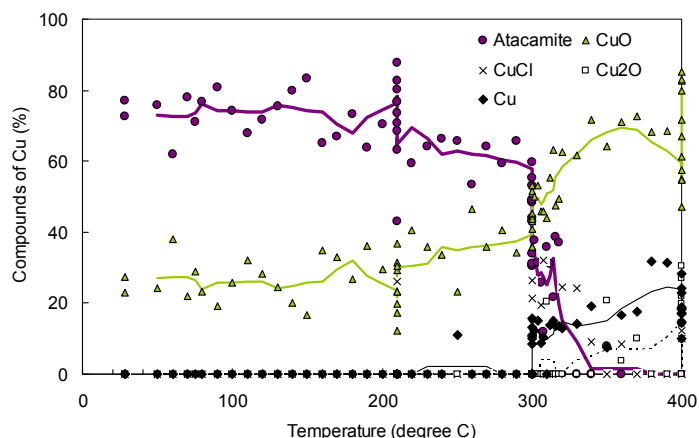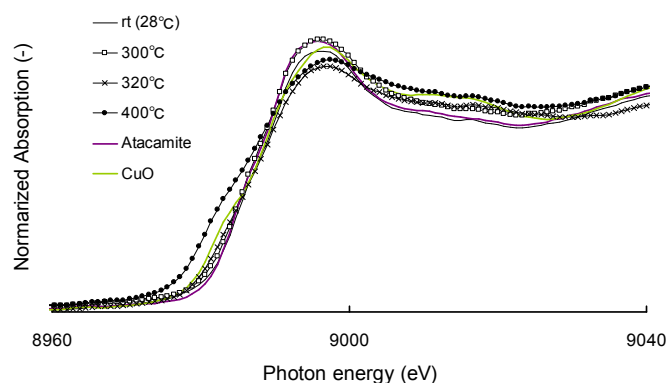6. Lamberti C *et al. Angewandte Chemie International Edition* 2002; 41: 2341.