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Chemosphere 59 (2005) 1497–1505

CHEMOSPHERE

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The effect of copper speciation on the formation of chlorinated aromatics on real municipal solid waste incinerator fly ash

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Received 19 January 2004; received in revised form 22 November 2004; accepted 14 December 2004

Abstract

A limited amount of information exists regarding the relationship between the chemical form of copper and the formation of chlorinated aromatics in fly ash. To understand the effects of the various forms of copper on the formation of chlorinated aromatics in real fly ash, we determined the chemical forms of copper present in various types of real fly ash using X-ray absorption near edge structure (XANES) and evaluated the relationship between the chemical forms of copper and the formation of chlorinated aromatics. Copper chloride hydroxide ($CuCl_2 \cdot 3Cu(OH)_2$) and cuprous chloride (CuCl) were the predominant copper species found in real fly ash. Although pure cupric chloride ($CuCl_2$) is known to be the most active catalyst for the formation of chlorinated aromatics under experimental conditions with synthetic fly ash, $CuCl_2$ was not found in every real fly ash sample. The amount of copper chloride hydroxide was positively correlated with the formation of chlorinated aromatics in real fly ash and is, consequently, considered to be one of the key species involved in the formation of chlorinated aromatics.

Keywords: XAFS; Copper; Chemical forms; PCBs; Formation; Copper chloride hydroxide

1. Introduction

Understanding the mechanisms involved in the formation of chlorinated aromatics in fly ash is necessary in order to control the emission of dioxins and other toxic organic compounds; such compounds are secondarily formed in a post-combustion zone which is considered to occur primarily on and in fly ash, as first described by Stieglitz and Vogg (1986).

According to many studies, copper compounds are regarded as influential catalysts; large amounts of polychlorinated dibenzo-*p*-dioxin/dibenzofuran (PCDD/DF) and related compounds have been found to be generated in experiments involving heat, synthetic fly ash, and copper chloride (Stieglitz et al., 1989; Luijk et al., 1994; Addink and Olie, 1995; Schoonenboom et al., 1995;

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0045-6535/$ - see front matter
doi:10.1016/j.chemosphere.2004.12.049

Addink and Altwicker, 1998). On the other hand, some studies on the relationship between the amount of PCDD/DF generated and the changes in copper compounds in synthetic fly ash under conditions similar to those leading to the deactivation of catalysts have reported that the catalytic activities for the formation of chlorinated aromatics differed among copper compounds (Lippert et al., 1991; Gullett et al., 1992; Raghunathanm and Gullett, 1996). In a similar manner, much research has been performed using synthetic fly ash, but only limited information on the relationship between the chemical forms of copper in real fly ash and the formation of chlorinated aromatics is available from the literature. Although the results of experiments investigating the formation of PCDD/DF using synthetic fly ash have established that copper chloride acts as a catalyst in real fly ash, the presence and potential of copper chloride in real fly ash are yet to be confirmed.

Our purpose for this study was to investigate the effect of the chemical form of copper present in real fly ash on the formation of chlorinated aromatics. Chlorobenzene (CBz) and polychlorinated biphenyls (PCBs) were chosen as representative chlorinated aromatic compounds for this study because they have been found to react similarly to PCDDs and DFs in heating experiments involving fly ash (Stieglitz et al., 1989; Huang and Buekens, 1995), are well known precursors of dioxin (Kato et al., 2000; Heger et al., 2001), and are easily managed and analyzed. We determined the chemical forms of copper present in various types of real fly ash using X-ray absorption near edge structure (XANES) and evaluated the relationship between the formation of chlorinated aromatics and the chemical form of copper.

2. Materials and methods

2.1. Samples

Samples of several types of fly ash were obtained from eight stoker-type municipal solid waste incinerators (MSWIs) as shown in Table 1. The composition of the fly ash was measured by using an inductively coupled plasma atomic emission spectrometer (ICP-AES; Shimadzu model ICPS-8000) or an X-ray fluorescence spectrometer (XRF; Shimadzu model XRF-1700). The total organic carbon (TOC) in the fly ash was analyzed using a TOC analyzer (Shimadzu model TOC-5000) after inorganic carbon was removed by the addition of 2 M HCl. The procedures are described in detail by Takaoka et al. (2000a). In other experiments involving de novo synthesis, researchers have pretreated the fly ash with heat or with extraction methods to remove organic compounds from the fly ash before experimentation. However, in this study, neither thermal nor extractive pretreatment were performed before conducting the heating experiments. Instead, we prevented the chemical forms of copper in the fly ash from changing from their original form to other forms by thermal or extractive pretreatment.

2.2. Heating experiment with fly ash and analysis of PCBs and CBzs

Fly ash was heated in a tubular electric furnace under an air atmosphere at 300 °C for 30 min. PCBs and CBzs 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 mixed toluene solution and fly ash were analyzed separately. The heating experiments were performed twice for each condition. The fly ash was acid-treated and dried at room temperature for 48 h, and ^{13}C-PCBs and ^{13}C-CBzs (Wellington, Ontario, Canada) were added as internal standards prior to the mixture undergoing soxhlet extraction with toluene for 24 h using toluene. The extracts were cleaned by passage through a multilayer silica column and were concentrated to 100 μl on a rotary evaporator using nitrogen. The mixed solution was also cleaned and concentrated in the same way after the addition of the internal standards. The concentrations of PCBs (D2CBs-O8CBs) and CBzs (D2CBzs-H6CBz) were measured by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS; Agilent model 6890/5973).

2.3. Copper speciation by X-ray absorption near edge structure

The speciation of copper in the fly ash was determined by using XANES. As the wavelength of the X-rays is gradually decreased, the absorbance generally decreases until a certain critical wavelength is reached, at which point the absorbance increases abruptly by several-fold. This discontinuity in absorbance is called the absorption edge. In proximity to or below the edge, absorption peaks generally appear owing to the excitation of core electrons of some bound forms of copper (Teo, 1986). XANES is an elemental speciation technique that uses the measurement of the X-ray absorbance in the vicinity of an absorption edge of the element of interest. The basic principle is based on Beer–Lambert's Law, and it is believed that XANES spectra reflect the local structure around the absorbing atom.

The XANES measurements were carried out at beam line BL01B1 in SPring-8, which is a synchrotron radiation facility in Japan (Uruga et al., 1999). The spectra of reference materials as well as fly ash were measured to compare their spectral shapes and to identify major