

Chemosphere 57 (2004) 73-79

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Role of copper chloride in the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans during incineration

Takeshi Hatanaka *, Akio Kitajima, Masao Takeuchi

Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba-shi, Ibaraki 305-8569, Japan

Received 12 June 2003; received in revised form 31 December 2003; accepted 22 April 2004

Abstract

Combustion experiments in a laboratory-scale fluidized-bed reactor were performed to elucidate the role of copper chloride in formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) during model waste incineration. The amounts of PCDDs and PCDFs formed, the homologue profiles, and the isomer distributions were measured in the flue gas from incineration of model wastes containing various levels of copper. A correlation was found between the Cu content of the waste and the proportion of each congener. An increase in copper enhanced the formation of certain congeners, showing that copper acts as a catalyst for formation of PCDDs and PCDFs. An increase in the copper content of the waste decreased the CO concentration in the flue gas and reduced the formation of PCDDs and PCDFs during incineration. This indicates that copper also works as an oxidation catalyst to promote combustion, leading to lower concentrations of products of incomplete combustion. It is indispensable to consider both roles of the catalyst, i.e., enhancement and suppression, in the formation of PCDDs and PCDFs during waste incineration, which are estimated separately from the isomer distributions and the amounts of PCDDs and PCDFs formed.

Keywords: PCDD/F formation; Oxidation catalyst; Copper content; Isomer distribution

1. Introduction

Municipal waste incinerators are an important source of emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs, together: PCDD/ Fs). Many researchers have studied PCDD/F formation during municipal waste incineration (Addink and Olie, 1995; Tuppurainen et al., 1998). Experiments using fly ash or model mixtures showed that copper in the waste plays a significant role in PCDD/F formation (e.g., Stieglitz et al., 1989; Gullett et al., 1990; Hinton and Lane, 1991; Altwicker and Milligan, 1993; Luijk et al., 1994). Copper chloride catalyzes ring condensation and

*Corresponding author. Tel.: +81-29-861-8228; fax: +81-29-861-8229.

E-mail address: t.hatanaka@aist.go.jp (T. Hatanaka).

chlorination of the dibenzofuran and dibenzo-*p*-dioxin rings (Addink et al., 1990). Mattila et al. (1992) cocombusted a mixture of coal, bark, and plastics in a fullscale incinerator and found that the presence of copper in the mixture led to increased PCDD/F formation. Akimoto et al. (1997) reported that the accumulation of metals in worn-out sand in a fluidized-bed municipal waste incinerator led to increased PCDD/F formation.

Copper also functions as an oxidation catalyst (Mul et al., 1995; Fullana et al., 2002). It directly contributes to PCDD/F formation by assisting oxidative decomposition of carbon (Schoonenboom et al., 1995). Copper can also promote combustion by functioning as an oxidation catalyst, leading to the suppression of the formation of polycyclic aromatic hydrocarbons (PAHs) (Wang et al., 2002).

The decrease in PAHs could be related to the suppression of PCDD/F formation, because PAHs are

^{0045-6535/\$ -} see front matter @ 2004 Elsevier Ltd. All rights reserved. doi:10.1016/j.chemosphere.2004.04.058

considered strong candidates as the starting material for PCDD/F formation (Iino et al., 1999a,b; Weber et al., 2001). This means that copper exerts an indirect influence on PCDD/F formation during incineration through affecting combustion reactions themselves. Consequently, the addition of copper chloride may result in both enhancement and suppression of PCDD/F formation during incineration.

The aim of this study is to elucidate the effects of copper chloride on PCDD/F formation in municipal waste incineration. We focus on the roles of copper as both a formation catalyst and an oxidation catalyst. The amounts of PCDD/Fs formed, the homologue profiles, and the isomer distributions were measured in the flue gas from combustion experiments on model wastes containing various amounts of copper, using a laboratory-scale fluidized-bed reactor.

2. Materials and methods

The main combustion section in the experimental setup consisted of primary and secondary combustion zones (Fig. 1). The primary combustor was a laboratory-scale fluidized-bed reactor (60 mm i.d., 300 mm length). This small size suppressed the radial distribution of combustion intensity in the reactor. The fluidized material was 100–140 μ m silica sand, and the static bed height was 100 mm. The secondary combustor was a freeboard section (30 mm i.d., 1450 mm length). All parts of the main combustion section coming in contact with flue gas were made of quartz. The postcombustion



Fig. 1. Schematic diagram of experimental setup.

section consisted of 3 glass tubes (30 mm i.d., 300 mm length). Air was supplied to the primary and secondary combustors by a compressor. The excess air ratio was set to 1.3 in the primary combustor and 0.7 in the secondary combustor; in total, air was supplied at twice the stoichiometric ratio. The temperature was independently kept at 900 $^{\circ}$ C in the main combustion section and 350 $^{\circ}$ C in the postcombustion section with electric heaters.

Fresh sand was used for the fluidized material in each experiment, because even trace amounts of residues such as chlorine and catalyst in the sand and on the inner surfaces of the reactor strongly affect PCDD/F formation (Akimoto et al., 1997). After each experimental run, the inner surfaces of the reactor in contact with flue gas were washed to prevent memory effects. In case washing could not remove the contamination, the quartz parts were replaced with new material. Actually, the reactors were remade in most cases because copper compounds adhered to it. Sampling for PCDD/F analysis was carried out for 4 h or more in the postcombustion section (point X in Fig. 1). Solids in the flue gas were trapped with a filter of a wad of glass wool and were Soxhletextracted with toluene for 24 h. The flue gas sample was also collected in an ice-cooled water trap and a Florisil (60-100 mesh, Wako Pure Chemical Industries, Osaka, Japan) trap and was extracted with hexane. All the extracted samples were cleaned by silica-gel and activatedcarbon column chromatography. PCDD/Fs in the samples were analyzed by gas chromatography-mass spectrometry (Hitachi M-80B or JEOL JMS-700). The analysis was conducted twice for each sample. Details for the analysis and identification of PCDD/Fs are described elsewhere (Imagawa and Lee, 2001).

A model waste was used, so as to have a strictly defined waste composition. Four kinds of model wastes (designated A to D and containing different levels of Cl and Cu) were used in this study (Table 1). The Cl contents of the model wastes are comparable to those of the municipal waste because the typical value of the municipal waste because the typical value of the municipal waste is less than 1.0% in Japan. The base ingredients of the model waste were 45% unbleached pulp powder, 40% unbleached flour, and 15% wood powder. The properties and elementary composition of the model waste containing only the base ingredients are described elsewhere (Hatanaka et al., 2000). In addition to the base ingredients, PVC (degree of polymerization)

Table 1

Cl and Cu contents in model wastes, based on analysis of dry material

Model waste	А	В	С	D
Cl content (%)	0.97	$1.00^{\rm a}$	0.64	1.24
Cu content (%)	n.d. ^b	$0.007^{\rm a}$	0.07	0.07

^a Calculated values.

^bn.d.: not detected.

 $n \cong 1100$, Wako) was mixed with model wastes A, C, and D as a chlorine source. Copper chloride (CuCl₂· 2H₂O, Wako) was added as a catalyst to model wastes C and D. All ingredients were ground separately, mixed mechanically, and then pelletized into particles (1–3 mm i.d.). Model waste B was prepared by mixing wastes A and D in a ratio of 9 to 1, so that waste B contained onetenth the level of Cu of waste D. The Cu content of waste A was assumed to be zero because copper was not detected. Model wastes were supplied to the fluidizedbed reactor at 100 g h⁻¹. The combustion experiment was performed once for each model waste.

3. Results and discussion

3.1. PCDD/F concentrations and homologue profiles

The experimental results are presented in figures as the average values of the duplicate analysis. The difference of the total PCDD/F concentrations between the analyses was 1% in wastes A and B, 3% in waste C, and less than 1% in waste D. Adding copper chloride to the model waste makes the more-chlorinated species of both PCDDs and PCDFs formed in the experiments on wastes B, C, and D (Fig. 2). This is the result of the strong effect of copper chloride as a chlorination catalyst, because tetra- to hexa-chlorinated species were the principal species formed in the experiment on the waste not containing copper chloride (waste A). This demonstrates that even a small amount of copper in waste sufficiently functions as a catalyst. The degree of chlorination of PCDDs and PCDFs in waste B with 0.007% Cu content is between those in waste C and D with 0.07% Cu content. The ratio of the amounts of O8CDF to H7CDFs formed, for example, was 1.8 in waste B, 1.5 in waste C, and 2.9 in waste D. The degree of chlorination coincides with the order of the Cl contents of these wastes. Chlorination seems to be promoted as the Cl content of the waste increases with no relation to the Cu content in these experiments.

The total PCDD/F concentrations in the experiment on waste B were about 5 times as high as for waste A (Fig. 3), even though these wastes have almost the same Cl contents. Obviously, just a small amount of copper in waste B acts as a formation catalyst. A comparison of the results for waste B with those for wastes C and D, to examine the effects of Cu content, shows that the PCDD/F concentration in the experiment on waste B is the highest among wastes B, C, and D. This was an unexpected result. Assuming a hypothetical waste E in which the Cl content is the same as in waste B (1.00%) and the Cu content is 0.07%, the PCDD/F concentration is expected to be between those for wastes C and D (as indicated in Fig. 3), because there is a strong positive correlation between their concentration and the Cl



Fig. 2. Homologue profiles of PCDDs and PCDFs.



Fig. 3. Total PCDD/F concentration in flue gas vs. Cu content of model waste. Assuming the hypothetical waste E contained 1.00% Cl and 0.07% Cu, its PCDD/F concentration is estimated to be between those of wastes C and D.

content when the other experimental conditions are the same (Hatanaka et al., 2000). Then, the PCDD/F concentration in the experiment on waste B is about triple that for waste E though the waste B contains the same Cl content and only one-tenth the Cu content as in waste E.

The results show that the amount of PCDD/Fs formed during incineration differs greatly with different Cu contents in the waste even if the Cl content is the same, probably because of the influence of copper on combustion itself. Copper acts as an oxidation catalyst to promote combustion, as mentioned above. Wikstrom et al. (1999) and Blumenstock et al. (2000) reported that PCDD/F formation is strongly related to combustion conditions in the furnace. We plotted the average CO concentration in the flue gas against the Cu content of the waste (Fig. 4), because the CO concentration is usually used as a practical parameter for indicating changes in combustion conditions in a furnace. Higher levels of copper in the waste are associated with decreased CO concentration in the flue gas, which means that copper promotes combustion. This suggests that the amount of other products of incomplete combustion (PICs) should also decrease with increasing copper. This is probably the reason that less PCDD/Fs were formed during incineration of wastes C and D than for waste B (Fig. 3) because PICs such as PAHs are considered strong candidates as the starting material for PCDD/F formation as mentioned above.

3.2. Isomer distribution patterns

Detailed examination of isomer distributions of PCDDs and PCDFs is important for understanding the mechanisms of PCDD/F formation. Specific PCDF congeners are selectively formed in the presence of copper in the waste (Hatanaka et al., 2001); these



Fig. 4. Relations between CO concentration in flue gas and Cu content of model waste.

congeners have a common Cl-substituted pattern and their formation appears to be via the similar pathways catalyzed by copper. In this section, the ratio of each isomer to the sum of all in the homologue is compared for wastes A, B, and C.

Figs. 5 and 6 show the proportions of tetra- through hexa-chlorinated dibenzofuran congeners (T4CDFs through H6CDFs) and dibenzo-p-dioxins (T4CDDs through H6CDDs) for wastes A, B, and C. These substitution patterns show similarities to the fluidized-bed pattern reported by Weber and Hagenmaier (1999). The differences in PCDF congener proportions between wastes A and C (Fig. 5) indicate that 2,3,4,6,7-P5CDF was predominantly formed, and 3,4,6,7-, 2,3,4,6-, and 1,6,7,8-/1,2,3,4-T4CDFs were major congeners formed in the presence of copper. For PCDDs (Fig. 6), some clear differences in congener proportions were found between wastes A and C. These results (Figs. 5 and 6) show that copper functions as a formation catalyst and certainly affects the formation of some PCDD/F congeners.

A comparison of the congener proportions among wastes A, B, and C reveals that the very small amount of copper in waste B apparently is enough to affect the congener proportions. It is interesting that the proportions of almost all the congeners in the experiment on waste B are intermediate between those of wastes A and C even though the PCDD/F concentration in waste B is the highest among the three model wastes. This point will be discussed in the next section.

Examining Figs. 5 and 6 closely, the proportions of many PCDF congeners in waste B seem to be close to those in waste C and, conversely, the proportions of many PCDD congeners in waste B are close to those in waste A. This is probably caused by differences between PCDDs and PCDFs with respect to the major pathways for their catalytic formation via copper compounds (Milligan and Altwicker, 1995; Hell et al., 2001). Additionally, among the PCDF congeners (Fig. 5), the proportions of 3,4,6,7-T4CDF, 2,3,4,6-T4CDF, and 2,3,4, 6,7-P5CDF in waste B are very close to those in waste C, whereas the proportion of 1,6,7,8-/1,2,3,4-T4CDFs in waste B is intermediate between those in wastes A and C. The effects of copper on the proportions differ among congeners. This could show differences in the formation mechanism of each congener.

3.3. Effects of Cu content on PCDD/F formation

Our experiments show that the proportions of PCDD/F congeners correlate closely with the Cu content of wastes (Figs. 5 and 6). The correlation between the congener proportion and the Cu content is reasonable because copper acts as a catalyst for PCDD/F formation. The increase in copper enhances the proportions of the specific congeners of which the major



Fig. 5. Effects of Cu content of model waste on PCDF congener proportions.

pathway is the catalytic formation via copper compounds. This probably indicates that copper functions more strongly as a formation catalyst than as a decomposition catalyst. Actually, the presence of copper led to increased PCDD/F formation. However, the total amount of PCDD/Fs formed was higher for waste with 0.007% Cu content than for wastes with higher (0.07%) content. The main reason could be that copper also acts as an oxidation catalyst to promote combustion in the furnace. The increase of copper lowers the PIC concentration in the flue gas, leading to less PCDD/F formation during incineration. The different roles of copper in incineration, enhancement and suppression of PCDD/ F formation, were estimated separately from two aspects, the isomer distributions and the amount of PCDD/Fs formed. It is indispensable to consider both roles of copper in investigating its effects on PCDD/F formation during waste incineration.



Fig. 6. Effects of Cu content of model waste on PCDD congener proportions.

References

- Addink, R., Olie, K., 1995. Mechanisms of formation and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in heterogeneous systems. Environ. Sci. Technol. 29, 1425–1435.
- Addink, R., Bavel, B.V., Visser, R., Wever, H., Slot, P., Olie, K., 1990. Surface catalyzed formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans during municipal waste incineration. Chemosphere 20, 1929–1934.
- Akimoto, Y., Nito, S., Inouye, Y., 1997. Comparative study on formations of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and related compounds in a fluidized bed solid waste incinerator using long term used sand and fresh sand. Chemosphere 34, 791–799.
- Altwicker, E.R., Milligan, M.S., 1993. Formation of dioxins: competing rates between chemically similar precursors and de novo reactions. Chemosphere 27, 301–307.
- Blumenstock, M., Zimmermann, R., Schramm, K.-W., Kettrup, A., 2000. Influence of combustion conditions on the

PCDD/F-, PCB-, PCBz- and PAH-concentrations in the post-combustion chamber of a waste incineration pilot plant. Chemosphere 40, 987–993.

- Fullana, A., Font, R., Conesa, J.A., Sidhu, S., 2002. Investigation of catalytic activity of sewage sludge combustion ash for PCDD/F formation. Organohalogen Compd. 56, 131– 134.
- Gullett, B.K., Bruce, K.R., Beach, L.O., 1990. The effect of metal catalysts on the formation of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran precursors. Chemosphere 20, 1945–1952.
- Hatanaka, T., Imagawa, T., Takeuchi, M., 2000. Formation of PCDD/Fs in artificial solid waste incineration in a laboratory-scale fluidized-bed reactor: influence of contents and forms of chlorine sources in high-temperature combustion. Environ. Sci. Technol. 34, 3920–3924.
- Hatanaka, T., Imagawa, T., Takeuchi, M., 2001. Effects of copper chloride on formation of polychlorinated dibenzofurans in model waste incineration in a laboratory-scale fluidized-bed reactor. Chemosphere 46, 393–399.

- Hell, K., Stieglitz, L., Dinjus, E., 2001. Mechanistic aspects of the de-novo synthesis of PCDD/PCDF on model mixtures and MSWI fly ashes using amorphous ¹²C- and ¹³Clabeled carbon. Environ. Sci. Technol. 35, 3892– 3898.
- Hinton, W.S., Lane, A.M., 1991. Synthesis of polychlorinated dioxins over MSW incinerator fly ash to identify catalytic species. Chemosphere 23, 831–840.
- Iino, F., Imagawa, T., Takeuchi, M., Sadakata, M., 1999a. De novo synthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristic isomers of polychlorinated naphthalenes. Environ. Sci. Technol. 33, 1038–1043.
- Iino, F., Imagawa, T., Takeuchi, M., Sadakata, M., Weber, R., 1999b. Formation rates of polychlorinated dibenzofurans and dibenzo-*p*-dioxins from polycyclic aromatic hydrocarbons, activated carbon and phenol. Chemosphere 39, 2749– 2756.
- Imagawa, T., Lee, C.W., 2001. Correlation of polychlorinated naphthalenes with polychlorinated dibenzofurans formed from waste incineration. Chemosphere 44, 1511–1520.
- Luijk, R., Akkerman, D.M., Slot, P., Olie, K., Kapteijn, F., 1994. Mechanism of formation of polychlorinated dibenzo*p*-dioxins and dibenzofurans in the catalyzed combustion of carbon. Environ. Sci. Technol. 28, 312–321.
- Mattila, H., Virtanen, T., Vartiainen, T., Ruuskanen, J., 1992. Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans in flue gas from co-combustion of mixed plastics with coal and bark. Chemosphere 25, 1599–1609.
- Milligan, M.S., Altwicker, E.R., 1995. Mechanistic aspects of the de novo synthesis of polychlorinated dibenzo-*p*-dioxins

and furans in fly ash from experiments using isotopically labeled reagents. Environ. Sci. Technol. 29, 1353–1358.

- Mul, G., Neeft, J.P.A., Kapteijn, F., Makkee, M., Moulijn, J.A., 1995. Soot oxidation catalyzed by a Cu/K/Mo/Cl catalyst: evaluation of the chemistry and performance of the catalyst. Appl. Catal., B 6, 339–352.
- Schoonenboom, M.H., Tromp, P.C., Olie, K., 1995. The formation of coplanar PCBs, PCDDs and PCDFs in a fly ash model system. Chemosphere 30, 1341–1349.
- Stieglitz, L., Zwick, G., Beck, J., Roth, W., Vogg, H., 1989. On the de-novo synthesis of PCDD/PCDF on fly ash of municipal waste incinerators. Chemosphere 18, 1219–1226.
- Tuppurainen, K., Halonen, I., Ruokojarvi, P., Tarhanen, J., Ruuskanen, J., 1998. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. Chemosphere 36, 1493–1511.
- Wang, D., Xu, X., Zheng, M., Chiu, C.H., 2002. Effect of copper chloride on the emissions of PCDD/Fs and PAHs from PVC combustion. Chemosphere 48, 857–863.
- Weber, R., Hagenmaier, H., 1999. PCDD/PCDF formation in fluidized bed incineration. Chemosphere 38, 2643–2654.
- Weber, R., Iino, F., Imagawa, T., Takeuchi, M., Sakurai, T., Sadakata, M., 2001. Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: mechanistic aspects and correlation to fluidized bed incinerators. Chemosphere 44, 1429–1438.
- Wikstrom, E., Tysklind, M., Marklund, S., 1999. Influence of variation in combustion conditions on the primary formation of chlorinated organic micropollutants during municipal solid waste combustion. Environ. Sci. Technol. 33, 4263–4269.