ENHANCED DECHLORINATION OF OCDD ON MSWI FLY ASH IN THE PRESENCE OF ETHANOLAMINE: KINETICS AND PATHWAYS

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Introduction

As well known, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are present in flue gases and fly ashes from municipal solid waste incinerators (MSWI)[1]. Because more than 95% of PCDD/Fs can be absorbed on fly ashes, in the European Union (EU), MSWI fly ash is classified as hazardous waste[2]. Under oxygen deficient condition, fly ash catalyses the dechlorination/hydrogenation of PCDD/Fs at the temperature range of 250~450 ^{o}C[3]. So the low temperature thermal treatment is a promising technology for the detoxification of PCDD/Fs in fly ash. It is postulated that two reaction pathways, dechlorination and decomposition, operate simultaneously when fly ash is heated[4]. Although a variety of investigations on the low temperature thermal treatment of fly ash have been performed[2, 5], the detoxification efficiency is not high as expected. In order to enhance the detoxification efficiency, some additives such as iron oxide, calcium hydroxide and triethanolamine[6] and sodium hypophosphite[7] were used. However, these additives operated at the temperature around 350 ^{o}C. In addition, the dechlorination and decomposition kinetics and detailed pathways of the dechlorination have not been clearly elucidated.

The objectives of this study is to develop a low temperature thermal treatment technology of MSWI fly ash at the temperature below 300 ^{o}C, using ethanolamine (MEA) as additive, and to determine the kinetics and pathways of OCDD dechlorination.

Materials and methods

Fly Ash Sample. The fly ash was collected from a grate incinerator in China. In the MSWI, calcium hydroxide was sprayed to neutralize acid gases. In order to remove native PCDD/Fs and PCB, fly ash was Soxhlet-extracted with toluene twice for 24 hours each time. After this treatment, the fly ash was "dioxin free". The elemental components of the fly ash were: Ca 13.95%, Al 9.96%, Fe 7.55%, K 2.96%, Na 1.57%, Ti 1.33% and Mg 1.19% in wt%, Zn 5.34, Ba 3.54, Cu 3.03, Cr 1.51, Mn 1.40, Sn 1.58, Pb 1.01 and Ni 0.63 in mg/g.

Experiments. OCDD hexane solution (2 mg/L) with certain volume was added to the fly ash, and then the hexane evaporated to dryness under purified nitrogen at room temperature. The spiked concentration of OCDD on fly ash was 700 ng/g. Prior to thermal treatment, the methanol solution of MEA was added dropwise to the spiked fly ash. The concentration of MEA in fly ash was 2 wt%. Then the spiked fly ash (0.2 g) was treated at the predetermined temperatures (200 ^{o}C, 225 ^{o}C, 250 ^{o}C, 300 ^{o}C) for 30~180 min. All experiments were conducted in glass ampules (volume, 1.5 mL) sealed under atmospheric air. The fly ashes contained no MEA were treated at the same conditions and taken as contrast experiments.

Product Analysis. After the thermal treatment, the glass ampules were cooled down to room temperature without any quenching, and the samples were then extracted with an accelerated solvent extraction system (ASE 350, Dionex). [13]C labeled 2,3,7,8-substituted PCDDs were added as internal standards. The extract was cleaned on a multilayer silica gel column and an alumina column as described in Japanese Industry Standard JIS K0311. The eluate was concentrated and evaporated to dryness with a stream of nitrogen. 10 μL of nonane containing the recovery standard (^{13}C-1,2,3,4-TCDD, 100 pg/μL) was added. Analysis for PCDDs were carried out using an Autospec Ultima high resolution mass spectrometer interfaced with a Hewlett-Packard 6890 Series gas chromatograph. A DB-5 MS capillary column (60 m × 0.25 mm × 0.1 μm) was employed. The further instrument analysis method was reported elsewhere[8].

Results and discussion:

Kinetics of OCDD Dechlorination and Decomposition. Analysis of OCDD dechlorination on fly ash treated with and without MEA showed that MEA accelerated dechlorination of PCDDs at 200 ^{o}C (Figure 1a). 46%~86% of the OCDD was removed after the fly ash was treated with MEA at 200 ^{o}C for 30~180 min. HpCDD and HxCDD were major dechlorination products. In contrast, 5%~41% of the OCDD was removed

after the fly ash without MEA was treated at the same conditions, and the dechlorination products were not detected out. At 250 °C, 97% of the OCDD on the fly ash treated with MEA was removed in 30 min. The dominant dechlorination products were HxCDD and PeCDD. With the increase of time, HxCDD decreased, while TCDD was increased. This suggested that the dechlorination of OCDD proceeded stepwise. However, at 250 °C, only 37% of the OCDD on the fly ash without MEA was removed in 30 min, and no abvious dechlorination reaction was observed. This indicated that MEA could accelerate the dechlorination of OCDD at 250 °C. The additives employed in the previous studies[6, 7] accelerated dechlorination of PCDD/Fs at high temperatures (≥300 °C), which showed that MEA was a promising additive for the dechlorination of PCDD/Fs.
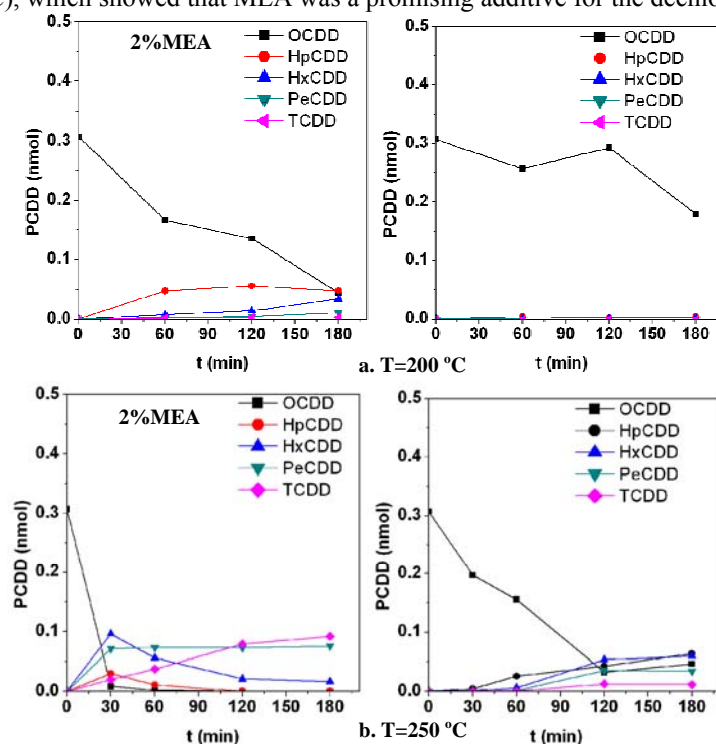

Figure 1 Distribution of OCDD dechlorination products in thermally-treated fly ash contained 2% MEA (left) or not contained MEA (right) at different conditions

A first-order kinetic equation was used to fit the experimental data regarding the decrease of the OCDD concentration. Table 1 reported the kinetic constants estimated for the OCDD reaction at different temperatures (200 °C, 225 °C, 250 °C, 300 °C). The removal rate of OCDD on fly ash treated with MEA was rapider than that of OCDD on fly ash without MEA at the same temperature. At 250 °C, the ratio of the two reaction rates obtained with and without MEA was 9, indicating that the influence of MEA on the removal rate of OCDD seemed to be the most significant.

Table 1 First-order kinetic constants fitted for the removal of OCDD

	2%MEA-fly ash			Fly ash		
$T(°C)$	$k_{obs}(min^{-1})$	$t_{1/2}(min)$	R^2	$k_{obs}(min^{-1})$	$t_{1/2}(min)$	R^2
200	$1.14×10^{-2}$	60.8	0.6147	$1.78×10^{-3}$	389.4	0.4635
225	$4.15×10^{-2}$	16.7	0.9816	$6.34×10^{-3}$	109.3	0.8318
250	$1.18×10^{-1}$	5.9	0.9999	$1.35×10^{-2}$	51.3	0.9684
300	$1.36×10^{-1}$	5.1	0.9995	$3.78×10^{-2}$	18.3	0.9884

It is verified that two reaction pathways, dechlorination and decomposition, operated simultaneously when fly ash was heated[4]. In order to get a better understanding of the kinetic mechanism, we hypothesized that: (1) the dechlorination and decomposition of OCDD are both considered as pseudo-first-order reaction; (2) the mass balance is completed by the products of the decomposition reaction; (3) the decomposition reaction products are treated as a single compound.

As mentioned above, the dechlorination of OCDD was stepwise,

$$R'' \xrightarrow{k_{Cl}} HpCDD \xrightarrow{k_{Hp}} HxCDD + PeCDD + TCDD$$

The following differential equation could be used to describe the formation rate of HpCDD,

$$d[HpCDD]/dt = k_{Cl}C_{R''} - k_{Hp}[HpCDD] \tag{1}$$

For fitting data, Eq. (1) was integrated, yielding the following equation,

$$[HpCDD] = C_{Hp,0}\exp(-k_{Hp}t) + C_{R'',0}[k_{Cl}/(k_{Hp}-k_{Cl})][\exp(-k_{Cl}t) - \exp(-k_{Hp}t)] \tag{2}$$

$C_{R'',0}$ represented the initial concentration of OCDD for dechlorination reaction. $C_{Hp,0}$ was the initial concentration of HpCDD on the fly ash. Eq. (2) was used to fit the experimental data for dechlorination reaction of OCDD on fly ash treated with and without MEA. The rate constants (k_{Cl}) were listed in Table 2. The dechlorination of OCDD on fly ash without MEA was not fitted when the temperature was below 250 °C, since the data for the HpCDD concentration were comparative to the detection limit. It could be observed that the rates of OCDD dechlorination on fly ash treated with MEA were significantly faster than that of OCDD dechlorination on fly ash without MEA. At 250 °C, the dechlorination rate of OCDD on fly ash treated with MEA was almost 2 orders of magnitude greater than that of fly ash without MEA.

The decomposition of OCDD could be described as follows,

$$R' \xrightarrow{k_D} P_D$$
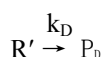
The pseudo-first-order equation for OCDD decomposition was

$$C_D = C_{R',0}[1 - \exp(-k_D t)] \tag{3}$$

C_D was the concentration of the decomposition reaction products and $C_{R',0}$ was the initial concentration of OCDD for decomposition reaction. Eq. (3) was used to fit the experimental data for decomposition reaction of OCDD on fly ashes. Table (3) showed the rate constants (k_D). The decomposition rates of OCDD on fly ash treated with and without MEA were almost similar. The data implied that MEA had no effect on the decompostition of OCDD.

Table 2 Pseudo-first-order reaction rate constants for dechlorination of OCDD

T(°C)	2%MEA-fly ash		Fly ash	
	$k_{Cl}(min^{-1})$	R^2	$k_{Cl}(min^{-1})$	R^2
200	7.27×10^{-3}	0.9992	—	—
225	1.34×10^{-2}	0.9997	—	—
250	5.62×10^{-2}	0.9978	1.67×10^{-4}	0.9540
300	4.27×10^{-2}	0.9994	4.14×10^{-2}	0.9940

Table 3 Pseudo-first-order reaction rate constants for decomposition of OCDD

T(°C)	2%MEA-fly ash		Fly ash	
	$k_D(min^{-1})$	R^2	$k_D(min^{-1})$	R^2
200	2.61×10^{-3}	0.9092	1.06×10^{-2}	0.7776
225	6.39×10^{-2}	0.9952	2.81×10^{-2}	0.9583
250	3.79×10^{-2}	0.9724	5.22×10^{-2}	0.9930
300	—	—	2.02×10^{-2}	0.9853

The Arrhenius rate parameters for the dechlorination of OCDD on fly ash with MEA and the decomposition of OCDD on fly ash without MEA were determined. The activation energies for OCDD dechlorination and OCDD decomposition were 24 kJ/mol and 6 kJ/mol, respectively. The pre-exponential factors of OCDD dechlorination and OCDD decomposition were 7 min^{-1} and 0.12 min^{-1}, respectively. The activation energy and pre-exponential factor of OCDD dechlorination were higher than that of OCDD decomposition, which was in agreement with the results about OCDF in previous studies[4]. As we know, for a heterogeneous reaction, a sequence of physical and chemical steps are involved: (1) transport of reaction molecules into the interfacial region by convection and diffusion; (2) diffusion of reactant molecules within the interfacial region; (3) surface chemical reaction; (4) desorption of products through the pores and away from the surface. Reaction rates governed by chemical step usually have activation energies exceeding 25 kJ/mol, and diffusion limitation reactions have an activation energy that may be as low as 15 kJ/mol[9]. According to the activation energies obtained in this study, it could be postulated that the dechlorination of OCDD was determined by chemical step, and the decomposition of OCDD was determined by diffusion.

Dechlorination mechanism. Under the catalysis of fly ash, the amino group and hydroxyl group contained in MEA could be oxidized to the intermediates, aldehyde group and cyano group, and to release hydrogen, simultaneously. The reaction were depicted as follows,

$$HOCH_2CH_2NH_2 \xrightarrow{\triangle} OHCCH_2NH_2 + H_2$$

$$HOCH_2CH_2NH_2 \xrightarrow{\triangle} HOCH_2CN + H_2$$
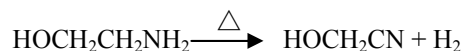
The generation of hydrogen gas might cause the dechlorination of OCDD on fly ash at the temperature range of 200~300 °C.

Dechlorination pathways of OCDD. The dechlorination pathway of OCDD on fly ash treated with MEA was proposed (Figure 2). Some PCDD isomers such as 1,2,3,6,8,9-HpCDD/1,2,3,6,7,9-HxCDD, 1,2,4,6,8,9-HxCDD /1,2,4,6,7,9-HxCDD, 1,2,4,7,9-PeCDD/1,2,4,6,8-PeCDD could not be completely separated by GC (DB-5 column) and thus they were considered as a whole group. The lateral chlorine atoms (2,3,7,8) had a preference over the longitudinal chlorine atoms (1,4,6,9), which was consistent with the result of theoretical study[10]. Therefore, it was not likely to result in a dominant formation of the toxic congeners. Moreover, from Figure 2 it could be found that successive dechlorination seemed to take place preferably on the benzene ring of higher degree of chlorination, which was similar to the phenomena observed by other researchers[11, 12]. Besides, the dechlorination was liable to eliminate the chlorine atom which was the most crowded by ortho-substituted chlorines.
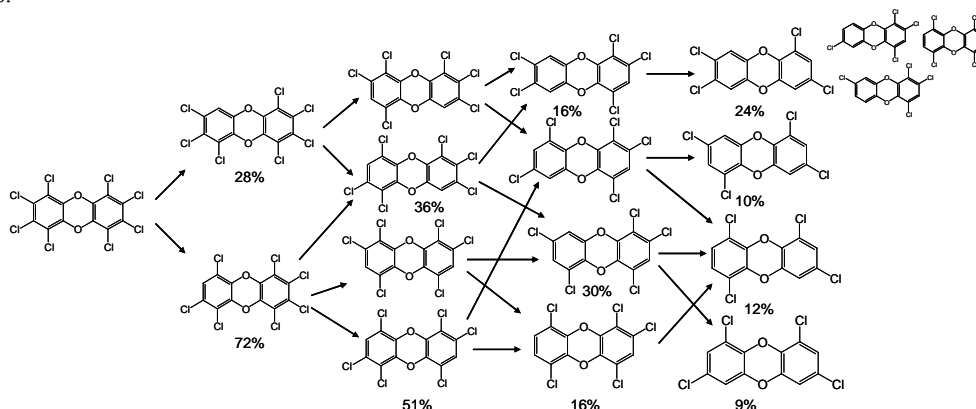

Figure 2 The postulated dechlorination pathway of OCDD

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