Influence of iron and copper oxides on polychlorinated diphenyl ether formation in heterogeneous reactions

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Abstract Polychlorinated diphenyl ether (PCDE) has attracted great attention recently as an important type of environmental pollutant. The influence of iron and copper oxides on formation of PCDEs was investigated using laboratory-scale flow reactors under air and under nitrogen at 350 °C, a temperature corresponding to the post-combustion zone of a municipal solid waste incinerator. The results show that the 2,2',3,4,4',5,5',6-octachlorodiphenyl ether (OCDE) formed from the condensation of pentachlorophenol (PCP) and 1,2,4,5-tetrachlorobenzene (Cl₄Bz) is the predominant congener formed on the SiO₂/Fe₂O₃ surface with and without oxygen. This indicated that HCl elimination between PCP and 1,2,4,5-Cl₄Bz molecules formed 2,2',3,4,4',5,5',6-OCDE in the presence of Fe₂O₃. On the other hand, decachlorodiphenyl ether, nonachlorodiphenyl ether, and OCDE were the dominant products on the SiO₂/CuO surface without oxygen, although the 2,2',3,4,4',5,5',6-OCDE was the dominant product on the SiO₂/CuO surface with oxygen. Therefore, the presence of Fe₂O₃ and CuO influences the formation and homologue distribution of PCDEs, which shifted towards the lower chlorinated species. Fe₂O₃ can promote both the condensation and dechlorination reaction without oxygen. On the contrary, with oxygen, Fe₂O₃ suppresses the condensation of chlorobenzene and chlorophenol to form PCDEs and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). CuO

can increase the formation of lower chlorinated PCDEs and PCDDs without oxygen. In conclusion, the different fly ash components have a major influence on PCDE emissions.

Keywords Polychlorinated diphenyl ethers (PCDEs) · Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) · Polychlorophenol · Polychlorobenzene · Metal oxide · Model fly ash · Heterogeneous reactions

Abbreviations

Cl ₄ Bz	Tetrachlorobenzene
MSWI	Municipal solid waste incinerator
HxCDD	Hexachlorodibenzo- <i>p</i> -dioxin
HxCDE	Hexachlorodiphenyl ether
HxCDF	Hexachlorodibenzofurans
HpCDD	Heptachlorodibenzo- <i>p</i> -dioxin
HpCDE	Heptachlorodiphenyl ether
HpCDF	Heptachlorodibenzofuran
OCDD	Octachlorodibenzo- <i>p</i> -dioxin
OCDE	Octachlorodiphenyl ether
NonaCDE	Nonachlorodiphenyl ether
DecaCDE	Decachlorodiphenyl ether
PCDDs	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDEs	Polychlorinated diphenyl ethers
PCDFs	Polychlorinated dibenzofurans
PCP	Pentachlorophenol

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Introduction

Polychlorinated diphenyl ethers (PCDEs) are a group of halogenated aromatic compounds that are structurally located between polychlorinated biphenyls (PCBs) and polychlorinated dibenzofuran (PCDFs). PCDEs mainly arise as by-products of technical chlorophenols and chlorinated phenoxyacetic acids during incomplete combustion (Nevalainen and Koistinen 1994). PCDEs are a group of ubiquitous pollutants, which have

been detected in a number of environmental samples including sediments, mussels, fish, birds, seals, foodstuffs, and human tissue (Sinkkonen and Paasivirta 2000; Stanley et al. 1990; Koistinen et al. 1995a, 1997; Niimi et al. 1994). Wide distribution, high lipophilicity, and persistence of PCDEs have raised concern about their bioaccumulation, their potential biomagnification in the food webs, and their adverse effects (Domingo et al. 2006; Xu et al. 2010). Hence, PCDEs have attracted great attention recently as an important type of environmental pollutant.

Many chlorinated aromatic compounds are emitted by thermal processes and subsequently persist in the environment. PCDEs may be converted to more toxic polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) by photolysis or pyrolysis (Norström et al. 1977; Lindahl et al. 1980; Nito et al. 1997). Of particular note are those produced from municipal solid waste incinerators (MSWIs) (Koistinen et al. 1995b; Passivirta et al. 1986; Kurz and Ballschmiter 1995; Olie et al. 1977), which are known to be major sources of PCDEs and PCDD/Fs. PCDEs and PCDD/Fs become concentrated in fly ash by post-combustion processes, forming in the presence of oxygen, their precursors, and chlorine sources (Liu et al. 2008, 2011; Addink and Olie 1995; Tuppurainen et al. 1998). Therefore, an understanding of the post-combustion mechanism that generates chlorinated aromatic compounds, including PCDEs and PCDD/Fs, is essential for protecting human health, given the persistence of these compounds in the environment. However, there are far fewer accounts of the formation of PCDEs compared with PCDD/Fs.

Some work has been done to describe the formation of PCDEs in the post-combustion zone of MSWIs (Liu et al. 2011). The combustion temperature of MSWIs is usually very high (700–900 °C), whereas chlorinated aromatic compounds are formed readily at the lower temperature (250–400 °C) of post-combustion zones (Milligan and Altwicker 1996; McKay 2002), and their formation is strongly influenced by traces of metallic compounds in the real fly ash of MSWIs (Fujimori et al. 2009). PCDEs were formed from the precursor condensation on the simulated fly ash surface, including SiO₂, SiO₂/FeCl₃, and SiO₂/CuCl₂ surfaces. However, fly ash is an extremely complex material, and there are not only metal chlorides but also metal oxides in municipal solid waste (Chin et al. 2012; Öberg et al. 2008; Fujimori et al. 2009; Altarawneh et al. 2009; Weber et al. 2002a, b; Lomnicki and Dellinger 2003a). Nevertheless, the less pronounced effects of the metal oxides on the PCDEs formation were reported. In the present study, the influence of fly ash ingredients such as Fe₂O₃ and CuO on the formation of PCDEs was investigated under air and nitrogen. Chlorophenol and chlorobenzene have been discussed as potential precursors of PCDEs (Liu et al. 2008), which were found in the effluents from MSWIs (Ballschmiter et al. 1988). Moreover, the tetrachloro- to hexachloro-benzene and tetrachloro- to pentachloro-phenol are dominating over the

lower chlorinated congeners in the combustion effluents. Thus, pentachlorophenol (PCP) and 1,2,4,5-tetrachlorobenzene (1,2,4,5-Cl₄Bz) were chosen as the model compounds. The study may get an initial understanding of the formation of PCDEs during post-combustion reactions. Therefore, it is important for the development of control techniques and strategies to reduce the emission of PCDEs in MSWIs.

Experimental section

Materials

The reagents, silicon dioxide (SiO₂; Beijing Chemical Reagents Company, Beijing, China), Fe₂O₃ (Shantou Xilong Chemical Plant, Shantou city, Guangdong, China), CuO (Beijing Hongxing Chemical Plant, Beijing, China), and 1,2,4,5-tetrachlorobenzene (1,2,4,5-Cl₄Bz; Schuchardt-Munchen Co., Germany) were all of analytical reagent grade. Pentachlorophenol (PCP) was purified to remove PCDE and PCDD/F impurities (Qian et al. 2005). Prior to the experiments, the silicon dioxide was Soxhlet extracted with toluene, air-dried at room temperature, and then heated at 700 °C for 6 h. The copper oxide was ground in a mortar before use. The synthetic fly ash (95 % SiO₂ and 5 % metal oxide) was prepared by mechanical mixing. All solvents used in this study were pesticide grade (Fisher Scientific, USA).

Experimental procedures

The experiments on the effects of fly ash composition on PCDE and PCDD/F formation were carried out in a flow reactor system at the temperature of 350 °C. A schematic diagram of the experimental apparatus is shown in Fig. 1. The quartz reaction tube (60 cm × 6 mm i.d.) was placed in the heated zone of a tube furnace. A total of 20 g [19 g SiO₂ and 1 g metal oxide, metal oxide 5 % (m/m)] of the granulated simulated fly ash was packed in a reaction tube, and the

Fig. 1 Schematic of experimental apparatus

reaction tube was then placed in the tube furnace. The carrier gas (either nitrogen or air) was carried into the reactor in a Teflon tube from compressed gas cylinders at flow rates of 40 ml/min controlled by a calibrated rotameter. The chlorinated organic precursors (4 mg PCP and 4 mg 1,2,4,5-Cl₄Bz) were fed into the reactor by blowing N₂ at a velocity of 10 ml/min through a heated miniature impinger. The tube furnace temperature and the gas flow rate were kept constant throughout the experiment for 2 h. For the sampling of the PCDEs and PCDD/Fs, the outlet gas from the reaction tube was passed through an ice-cooled XAD-2. Between runs, the glassware was rinsed with detergent and water, followed by toluene and acetone. The feed system was cleaned with flowing air at the temperature of 250 °C. A blank test was performed before each experiment to check the contamination levels. Each experiment was performed in triplicate to ensure the repeatability of the experiments.

Analytical methods

The inside of the tubing was rinsed with dichloromethane and this rinsate was combined with the XAD-2 extract. The reaction products were extracted, identified, and then quantified using an Agilent 6890 GC equipped with a 5973 MSD (Liu et al. 2011).

Results and discussion

The PCDE distribution on the surface of SiO₂/Fe₂O₃

The PCDE content formed by the condensation of PCP and 1,2,4,5-Cl₄Bz on the surface of SiO₂/CuO and SiO₂/Fe₂O₃ in air and in nitrogen (with and without oxygen) is presented in Table 1. The homologue profiles of the PCDEs are shown in Fig. 2. The dominant PCDE homologue on the surface of

Table 1 Formation of PCDEs from condensation of PCP and 1,2,4,5-Cl₄Bz at 350 °C (PCP/Cl₄Bz = 1:1)

Congeners	PCDE content (ng/mg, <i>n</i> =3)					
	SiO ₂		SiO ₂ /Fe ₂ O ₃		SiO ₂ /CuO	
	N ₂	Air	N ₂	Air	N ₂	Air
DecaCDE	53±3	46±2	38±5	9±4	91±3	90±4
2,2',3,3',4,5,5',6,6'-NonaCDE	n.d.	13±3	n.d.	n.d.	22±3	2.2±2
2,2',3,3',4,4',5,5',6-NonaCDE	n.d.	11±2	26±3	n.d.	25±2	88±2
2,2',3,3',4,4',5,6,6'-NonaCDE	n.d.	32±3	73±2	n.d.	34±3	111±3
ΣNonaCDE	n.d.	56±2	99±7	0	81±3	201±2
OCDE (1) ^a	n.d.	3.7±0.6	n.d.	n.d.	5.5±1	n.d.
2,2',3,4,4',5,5',6-OCDE	1,134±9	152±6	1,116±5	27±1	30±2	804±3
OCDE (3) ^a	n.d.	2.6±0.5	n.d.	n.d.	9.4±2	n.d.
OCDE (4) ^a	n.d.	1.7±0.4	n.d.	n.d.	17±2	n.d.
OCDE (5) ^a	n.d.	n.d.	n.d.	n.d.	4.6±1	n.d.
OCDE (6) ^a	n.d.	n.d.	n.d.	n.d.	6.0±1	n.d.
ΣOCDE	1,134±9	160±5	1,116±5	27±1	72±2	804±3
HpCDE (1) ^a	10±2	12±3	48±2	n.d.	n.d.	7.1±1
HpCDE (2) ^a	n.d.	4.2±0.5	166±3	n.d.	8.2±2	12±1
HpCDE (3) ^a	n.d.	2.7±0.6	n.d.	n.d.	n.d.	n.d.
HpCDE (4) ^a	63±4	3.6±0.5	n.d.	n.d.	n.d.	n.d.
HpCDE (5) ^a	n.d.	36±3	33±2	n.d.	n.d.	n.d.
HpCDE (6) ^a	n.d.	n.d.	45±2	n.d.	6.2±2	7.5±1
ΣHpCDE	73±3	59±2	293±3	n.d.	14.4±2	27±1
HxCDE (1) ^a	n.d.	44±3	17±2	n.d.	n.d.	n.d.
HxCDE (2) ^a	n.d.	n.d.	5.7±1	n.d.	n.d.	n.d.
HxCDE (3) ^a	n.d.	n.d.	10±2	n.d.	5.3±1	6.2±1
HxCDE (4) ^a	n.d.	n.d.	6.8±1	n.d.	n.d.	n.d.
HxCDE (5) ^a	n.d.	n.d.	3.9±1	n.d.	n.d.	n.d.
HxCDE (6) ^a	n.d.	n.d.	8.3±1	n.d.	n.d.	n.d.
ΣHxCDE	n.d.	44±3	52±2	n.d.	5.3±1	6.2±1
ΣPCDEs	1,260±10	365±4	1,598±4	36±4	265±4	1,128±3

^aSubstitution pattern of congener not identified. Mono- to PentaCDE was below detection limit *n.d.* <1.0 ng/mg

Fig. 2 PCDEs homologue patterns under nitrogen and air

SiO₂/Fe₂O₃ at 350 °C in air was 2,2',3,4,4',5,5',6-octachlorodiphenyl ether (OCDE), with small amounts of decachlorodiphenyl ether (DecaCDE). Two nonachlorodiphenyl ether (NonaCDE), four heptachlorodiphenyl ether (HpCDE), and six hexachlorodiphenyl ether (HxCDE) isomers were also detected besides OCDE and DecaCDE, on the surface of SiO₂/Fe₂O₃ under nitrogen. HCl elimination between PCP and 1,2,4,5-Cl₄Bz molecules formed 2,2',3,4,4',5,5',6-OCDE, while DecaCDE was produced by the elimination of H₂O between two PCP molecules. The content of 2,2',3,4,4',5,5',6-OCDE was consistently higher than that of DecaCDE. However, more congeners, including NonaCDE, HpCDE, and HxCDE, were formed on the SiO₂/Fe₂O₃ surface than on the surface of SiO₂ under nitrogen. It can be concluded that the dechlorination reaction occurs more easily on the surface of SiO₂/Fe₂O₃ than SiO₂ under nitrogen.

HpCDE and HxCDE were not detected in reactions that occurred under air, while more isomers of HpCDE and HxCDE were formed under nitrogen. However, no congeners of monochlorodiphenyl ether to pentachlorodiphenyl ether (mono- to pentaCDE) were detected in any experiment. The substitution pattern for some isomers could not be identified under the analytical conditions, so the serial number was used to denote the various isomers. Both of the number of PCDE congener species and the amount of total PCDEs were greater under nitrogen than under air on the surface of SiO₂/Fe₂O₃. This indicates that the presence of oxygen can prevent the production of PCDEs during the reactions of PCP and 1,2,4,5-Cl₄Bz on the SiO₂/Fe₂O₃ surface, which was consistent with the results on the surface of SiO₂ (Liu et al. 2011). Other competitive reaction pathways may be available in the reaction system. It has been reported that on metal oxides, chlorinated benzenes and chlorinated phenols can decompose directly via ring-cracking into small organic molecules such as formates and acetates, and even into CO₂, CO, and H₂O, particularly in the presence of oxygen (Zhang et al. 2008; Krishnamoorthy et al. 2000; Hetrick et al. 2008, Lomnicki and Dellinger 2003b). The addition of oxygen to the system

may have promoted the reaction toward the direct oxidative ring-cracking decomposition of PCP and 1,2,4,5-Cl₄Bz, and thus the formation of PCDEs is reduced.

It can be seen that the PCDE homologue profiles were different in air and under nitrogen (Fig. 2). The amount of ΣOCDE comprised 70 % and 75 % of the total PCDEs, while DecaCDE comprised 2.4 % and 25 % of the total PCDEs under nitrogen and air, respectively. The amount of ΣNonaCDE, ΣHpCDE, and ΣHxCDE comprised 6.2 %, 18 %, and 3.2 % of the total PCDEs, respectively, under nitrogen on the SiO₂/Fe₂O₃ surface. Therefore, the condensation of PCP with 1,2,4,5-Cl₄Bz to form OCDE was the predominant reaction in the system, while the condensation of two PCP molecules to form DecaCDE occurred less on the SiO₂/Fe₂O₃ surface, which was consistent with the results from the condensation of PCP with 1,2,4,5-Cl₄Bz on the surface of SiO₂ (Liu et al. 2011). This result was also consistent with the findings of Liu et al. (2008), who described the formation mechanism of PCDEs in homogeneous gas phase reactions. The presence of Fe₂O₃ does not change the reaction processes of PCP and 1,2,4,5-Cl₄Bz. However, there were more PCDE congener species on the SiO₂/Fe₂O₃ surface than on the SiO₂ surface under nitrogen. The condensation of polychlorophenol and polychlorobenzene generating PCDEs can be a radical/molecule reaction mechanism (Louw and Ahonkhai 2002; Bozzelli et al. 1991). Polychlorophenoxy radicals were formed on the simulated fly ash under heated condition and polychlorophenoxy radical addition reactions to polychlorobenzene formed the ether linkages, and following the elimination of chlorination, PCDEs were formed. Under nitrogen atmosphere, Fe₂O₃ can react with hydrogen chloride, which was eliminated between polychlorophenol and polychlorobenzene molecules; therefore, Fe₂O₃ catalyzes the formation of PCDEs without oxygen. On the other hand, the lower chlorinated PCDEs congeners were formed due to Fe₂O₃ dechlorination action under nitrogen atmosphere.

The PCDE distribution on the surface of SiO₂/CuO

Over the SiO₂/CuO surface, DecaCDE, NonaCDE, and OCDE were the main PCDE homologues under nitrogen, while OCDE was the main PCDE homologue under air. Three isomers of NonaCDE, six isomers of OCDE, two isomers of HpCDE, and one isomer of HxCDE were detected on the SiO₂/CuO surface under nitrogen, whereas other OCDE isomers in addition to 2,2',3,4,4',5,5',6-OCDE were not detected under air. The amounts of total PCDEs were 265 ng/mg and 1,128 ng/mg under nitrogen and air, respectively. There were more PCDE products without oxygen than with oxygen, but the amount of total PCDEs formed was lower under nitrogen than air on the SiO₂/CuO surface. On the SiO₂/CuO surface under oxidative condition, the formation of PCDEs involves

two different surface-mediated mechanisms (Lomnicki and Dellinger 2003a), which are Eley–Rideal and Langmuir–Hinshelwood. Eley–Rideal mechanism involves the reaction between the adsorbed species and a gas-phase molecule, while Langmuir–Hinshelwood is the reaction between two surface-adsorbed species. The experiment confirms that upon adsorption of chlorophenol over copper oxide, the interaction of adsorbed phenolate species with the surface results in the formation of phenoxy radical (Shi and Yuan 1996; Lomnicki and Dellinger 2003a). The surface-associated chlorophenoxy can react with gas-phase chlorobenzenes to form PCDEs, which are produced as a result of an Eley–Rideal mechanism. Pyrolytic condition resulted in the significant surface oxygen deficit, and this resulted in PCP remaining adsorbed on the surface rather than being oxidized into phenoxy radical. Oxygen affects the rate of formation. Therefore, the addition of oxygen could increase PCDEs formation on the SiO_2/CuO surface.

The content of total PCDEs was significantly higher on the SiO_2/CuO surface than on the $\text{SiO}_2/\text{CuCl}_2$ surfaces under both atmospheres (Liu et al. 2011). Therefore, CuO can promote PCDE formation more effectively than CuCl_2 from precursors in heterogeneous reactions.

The proportions of DecaCDE, NonaCDE, and OCDE to total PCDEs were 34 %, 31 %, and 27 %, on the SiO_2/CuO surface under nitrogen, while their proportions were 8 %, 18 %, and 71 % under air, respectively (Fig. 2). 2,2',3,4,4',5,5',6-OCDE is the dominant PCDE homologue product formed on the surface of SiO_2/CuO under air. However, the proportions of DecaCDE were 94 % and 77 % on the $\text{SiO}_2/\text{CuCl}_2$ surface under nitrogen and air, respectively (Liu et al. 2011). Thus, the presence of CuO and CuCl_2 influenced the PCDE homologue profiles, and the distribution shifted toward the less substituted chlorinated congeners on the surface of SiO_2/CuO than $\text{SiO}_2/\text{CuCl}_2$.

The amount of PCDEs was higher on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ surface than on the SiO_2/CuO surface under nitrogen. Moreover, the amount of PCDEs was higher on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ surface than on the SiO_2 surface under nitrogen, while the amount of PCDEs was lower on the SiO_2/CuO surface than on the SiO_2 surface. Without oxygen, Fe_2O_3 catalyzes the formation of PCDEs, whereas CuO reduces PCDEs formation. In addition, the effect of oxygen on the PCDEs formation needs to be noticed. Compared with reaction condition of nitrogen, the amount of PCDEs remarkably reduced by 71 % and 97.7 %, and increased by 325.7 % under air on the SiO_2 , $\text{SiO}_2/\text{Fe}_2\text{O}_3$, and SiO_2/CuO surfaces, respectively. Reaction atmosphere was an important factor for the formation of PCDEs on simulated fly ash surface. In air, the amount of PCDEs was higher on the SiO_2/CuO surface compared with that on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ and SiO_2 surfaces. However, the amount of PCDEs was lower on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ surface than on the SiO_2 surface. This

indicated that with oxygen, CuO facilitated PCDE formation, while Fe_2O_3 impeded PCDE formation. In heterogeneous reactions with oxygen, Fe_2O_3 reduces the catalytic production of PCDEs, but without oxygen, CuO reduces the catalytic production of PCDEs. This indicates that the presence of Fe_2O_3 and CuO influence PCDE formation from the reactions of PCP and 1,2,4,5- Cl_4Bz in heterogeneous reactions. Fe_2O_3 and CuO have significant different effects on PCDEs formation, with and without oxygen.

PCDEs contents were changed by −36.7 %, 26.8 %, −93.3 %, and −78.96 % under nitrogen atmosphere, and −27.4 %, −90.1 %, −81.9 %, and 209.0 % under air atmosphere on the $\text{SiO}_2/\text{FeCl}_3$, $\text{SiO}_2/\text{Fe}_2\text{O}_3$, $\text{SiO}_2/\text{CuCl}_2$, and SiO_2/CuO surfaces compared to the SiO_2 surface, respectively (Liu et al. 2011). Therefore, the catalytic activities of the Cu and Fe salts should be different on the formation of PCDEs. Fe_2O_3 under nitrogen atmosphere shows catalytic activities, while CuO have higher catalytic activities under air atmosphere on the formation of PCDEs.

The trend and relationship between PCDEs and PCDFs

The contents of PCDD/Fs formed from the condensation of PCP and 1,2,4,5- Cl_4Bz are shown in Table 2. The observed products included octachlorodibenzo-*p*-dioxin (OCDD), heptachlorodibenzo-*p*-dioxin (HpCDD), hexachlorodibenzo-*p*-dioxin (HxCDD), pentachlorodibenzo-*p*-dioxin (PeCDD), heptachlorodibenzofuran (HpCDF), hexachlorodibenzofuran (HxCDF), and pentachlorodibenzofuran (PeCDF). However, octachlorodibenzofuran (OCDF) and tetrachlorodibenzo-*p*-dioxin and dibenzofuran (TetraCDD/F) were not detected in the study. The amounts of OCDD and HpCDD were 44 % and 48 % of the total PCDD/Fs measured on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ surface (Fig. 3), respectively, and their amounts were respectively 54 % and 25 % of the total PCDD/Fs on the SiO_2/CuO surface under nitrogen. On the SiO_2 surface under nitrogen and air, the amounts of OCDD were above 91 % of the total PCDD/Fs measured, and the amounts of OCDD were more than 98 % of total PCDD/Fs on the $\text{SiO}_2/\text{FeCl}_3$ and $\text{SiO}_2/\text{CuCl}_2$ surfaces under both atmospheres (Liu et al. 2011). This indicates that the presence of Fe_2O_3 and CuO contributes to the formation of some less chlorinated PCDDs.

The amount of PCDD/Fs formed was higher on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ surface without oxygen than that with oxygen, but this pattern was reversed on the SiO_2/CuO surface. In addition, the amounts of PCDEs and PCDD/Fs were obviously lower on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ surface under air than those under nitrogen. This indicates that the presence of oxygen can prevent the production of PCDEs and PCDD/Fs during the reactions of PCP and 1,2,4,5- Cl_4Bz on the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ surface. Other competitive reaction pathways may be available in the reaction system (Zhang et al. 2008; Krishnamoorthy et al. 2000; Hetrick et al. 2008). The addition of oxygen to the

Table 2 Formation of PCDD/Fs from condensation of PCP and 1,2,4,5-Cl₄Bz at 350 °C (PCP/Cl₄Bz = 1:1)

Congeners	PCDD/Fs content (ng/mg, <i>n</i> =3)					
	SiO ₂		SiO ₂ /Fe ₂ O ₃		SiO ₂ /CuO	
	N ₂	Air	N ₂	Air	N ₂	Air
OCDD	3,359±10	2,568±9	2,453±6	12±2	1,922±5	3,786±6
1,2,3,4,6,7,9-HpCDD	44±6	39±3	1,255±4	n.d.	417±3	48±2
1,2,3,4,6,7,8-HpCDD	175±5	106±6	1,465±3	n.d.	486±3	34±2
ΣHpCDD	219±6	145±5	2720±4	n.d.	903±3	82±2
HpCDF (1) ^a	11±2	10±2	59±2	n.d.	4.5±1	6.2±1
HpCDF (2) ^a	1.8±0.3	2.2±0.4	26±2	n.d.	n.d.	7.1±2
HpCDF (3) ^a	n.d.	2.7±0.5	n.d.	n.d.	n.d.	9.4±2
1,2,3,4,7,8,9-HpCDF	2.4±0.3	3.7±0.4	41±2	n.d.	n.d.	n.d.
HpCDF (4) ^a	4.3±0.5	2.9±0.3	21±1	n.d.	n.d.	n.d.
ΣHpCDF	20±1.5	22±2	148±2	n.d.	4.5±1	22.7±2
HxCDD (1) ^a	4.0±0.5	6.3±0.4	54±2	n.d.	109±3	n.d.
HxCDD (2) ^a	4.6±0.5	n.d.	n.d.	n.d.	310±3	n.d.
HxCDD (3) ^a	n.d.	n.d.	88±2	n.d.	57±2	n.d.
1,2,3,4,7,8-HxCDD	2.6±0.3	15±2	22±2	n.d.	83±2	2.3±1
1,2,3,6,7,8-HxCDD	n.d.	9.1±1.2	24±2	n.d.	61±2	n.d.
HxCDD (7) ^a	n.d.	n.d.	32±2	n.d.	108±2	n.d.
ΣHxCDD	11±0.6	30±0.6	220±2	n.d.	728±3	2.3±1
HxCDF (1) ^a	n.d.	1.1±0.4	21±2	n.d.	n.d.	n.d.
HxCDF (2) ^a	n.d.	1.0±0.3	n.d.	n.d.	n.d.	n.d.
1,2,3,4,7,8-HxCDF	n.d.	1.1±0.3	n.d.	n.d.	n.d.	n.d.
2,3,4,6,7,8-HxCDF	64±3	11±2	63±2	1.5±1	n.d.	18±2
1,2,3,7,8,9-HxCDF	n.d.	1.0±0.3	n.d.	n.d.	n.d.	n.d.
ΣHxCDF	64±3	15±2	84±2	1.5±1	n.d.	18±2
PeCDD (1) ^a	n.d.	n.d.	6.2±1	n.d.	8.5±2	n.d.
PeCDD (2) ^a	n.d.	n.d.	n.d.	n.d.	6.7±1	n.d.
PeCDD (3) ^a	n.d.	n.d.	n.d.	n.d.	4.8±1	n.d.
PeCDD (4) ^a	n.d.	n.d.	n.d.	n.d.	8.5±2	n.d.
PeCDD (5) ^a	n.d.	n.d.	n.d.	n.d.	3.7±1	n.d.
ΣPeCDD	n.d.	n.d.	6.2±2	n.d.	32±2	n.d.
PeCDF	n.d.	n.d.	8.0±2	n.d.	n.d.	n.d.
ΣPCDD/Fs	3,673±8	2,781±5	5,639±6	14±2	3,591±6	3,911±4

OCDF and Tetra- to PentaCDD/DF were below detection limit
n.d. <1.0 ng/mg

^aSubstitution pattern of congener was not identified

Fig. 3 PCDD/Fs homologous patterns under nitrogen and air

system may have promoted the reaction toward the direct oxidative ring-cracking decomposition of PCP and 1,2,4,5-Cl₄Bz, and thus reduced the formation of PCDEs and PCDD/Fs on the SiO₂/Fe₂O₃ surface.

It can be also seen that PCDDs are generally more common than PCDFs for all the reaction systems. The formation of PCDDs requires that a chlorine is available in the ortho position (Tuppurainen et al. 2003; Louw and Ahonkhai 2002). Because all the ortho positions on PCP are chlorinated, PCDDs become the major product over PCDFs. This is supported by the finding that the predominant PCDDs are formed from 2,4,6-trichlorophenol in heterogeneous reactions (Hell et al. 2000, 2001). The condensation between PCP and 1,2,4,5-Cl₄Bz could also lead to the formation of

PCDEs, which are known to form PCDFs (and to a lesser degree PCDDs) upon pyrolysis (Liu et al. 2008). Therefore, PCDFs are harder to form from PCP and 1,2,4,5-Cl₄Bz in the heterogeneous reactions. However, it is worth mentioning that the yields of PCDEs are significantly lower than those of PCDD/Fs from the condensation of PCP and 1,2,4,5-Cl₄Bz on the SiO₂/CuO and SiO₂/Fe₂O₃ simulated fly ash surfaces in the flow reactor system under nitrogen.

The formation of PCDEs is significantly different from PCDD/Fs formation on SiO₂/Fe₂O₃ and on SiO₂/CuO. This could be induced by a competitive reaction between the absorbed species and a gas-phase molecule (Farquar et al. 2003; Lomnicki and Dellinger 2003a). The surface-associated chlorophenoxyl can react with gas-phase chlorobenzenes to form PCDEs, with another vicinal chlorophenoxyl via a Langmuir–Hinshelwood pathway to form PCDF, and with gas-phase polychlorophenol via an Eley–Rideal pathway to form PCDD. The differences between Langmuir–Hinshelwood and Eley–Rideal mechanisms could result in significant differences in the reaction rates. The differences of the mechanisms can explain the observed differences between the formation of PCDEs and PCDD/Fs.

Conclusions

The present study clearly demonstrated that Fe₂O₃ and CuO affect the formation of PCDEs from the heterogeneous reactions of precursors. The 2,2',3,4,4',5,5',6-OCDE formed from the condensation of PCP and 1,2,4,5-Cl₄Bz is the predominant congener formed on the surface of the SiO₂/Fe₂O₃ with and without oxygen. However, DecaCDE, NonaCDE, and OCDE were the dominant products on the SiO₂/CuO surface without oxygen, although the 2,2',3,4,4',5,5',6-OCDE was the dominant product on the SiO₂/CuO surface with oxygen. The presence of Fe₂O₃ and CuO influences the formation and homologue distribution of PCDEs, and results in an increase in the lower chlorinated PCDEs contribution from heterogeneous reactions. The amount of total PCDEs formed was higher, and the PCDE congener species were more complicated on the surface of SiO₂/Fe₂O₃ without oxygen than on that with oxygen. In contrast, although the PCDEs formed were more complex, the amount of total PCDEs formed was lower on the surface of SiO₂/CuO under nitrogen than on that in air. Fe₂O₃ can catalyze both the condensation and dechlorination reaction without oxygen. On the contrary, with oxygen, Fe₂O₃ suppress the condensation of chlorobenzene and chlorophenol to form PCDEs and PCDD/Fs. CuO can increase the formation of lower chlorinated PCDEs and PCDDs without oxygen. Moreover, abundant PCDD/F was produced from the reactions of PCP and 1,2,4,5-Cl₄Bz during the process of PCDE formation.

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