Influence of metal oxides on PCDD/Fs formation from pentachlorophenol

Yong Qian ^{a,b}, Minghui Zheng ^{a,*}, Wenbin Liu ^a, Xiaodong Ma ^a,
Bing Zhang ^a

^a Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

^b Department of Environmental Science and Engineering, University of Science and Technology of Suzhou, Suzhou 215011, China

Received 17 June 2004; received in revised form 19 December 2004; accepted 24 December 2004

Available online 10 February 2005

Abstract

Chlorophenols (ClPhs) are considered as important precursors for PCDD/Fs formation. The influences of series of metal oxides including MgO, Al₂O₃, CaO, BaO, TiO₂, V₂O₅, MnO₂, Fe₂O₃, Co₃O₄, CuO, Ag₂O, ZnO, HgO, SnO, PbO, La₂O₃, CeO₂, and Eu₂O₃ on PCDD/Fs formation from pentachlorophenol (PCP) were investigated in a laboratory-scale reactor. The results indicated that most of the above metal oxides have obvious suppressing effects on the total amount of PCDD/Fs formation from precursor PCP except for CuO, ZnO, MnO₂, TiO₂ and Co₃O₄ with promotion effects at 280 °C for 2 h. Although MgO, Al₂O₃, Fe₂O₃, PbO, La₂O₃ and Eu₂O₃ could reduce the amount of octachlorinated dibenzo-*p*-dioxin (OCDD), they promote the formation of more toxic 1,2,3,4,6,7,8-HpCDD at the same time. The total suppressing efficiencies of several metal oxides including CaO, BaO, PbO, Ag₂O, HgO and SnO which have lower Z/r (charge to radius ratio) <2 are all over 90%. The theories of generalized acid–base and atomic parameter (Z/r) were used to speculate the effecting mechanisms. The factors including time and temperature on suppressing efficiencies of CaO, BaO and PbO have also been studied in the present paper. The results showed that the total suppressing efficiencies of CaO, BaO and PbO increase with the increase of heated time and temperature.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: PCDD/Fs; Formation; Precursor; PCP; Inhibition

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have been the subject of acute public concern for their highest toxicity (Hays and Aylward, 2003). The mechanisms of PCDD/Fs formation in MSWI have been elucidated as the following

three paths: (i) high-temperature pyrosynthesis, (ii) low-temperature de novo synthesis, (iii) formation from different organic precursors such as chlorophenols, chlorobenzenes, etc., and PCDD/Fs formation from (iii) is 10²–10⁵ times faster than from (ii) (Addink and Olie, 1995; Tuppurainen et al., 1998; McKay, 2002; Stanmore, 2004). Model studies also showed that PCDD/Fs formation from precursors is likely the predominance of the two proposed pathways (ii) and (iii) (Dickson et al., 1992). Chlorophenols (ClPhs) are structurally closely related to PCDD/Fs and thought as important

* Corresponding author. Tel.: +86 10 628 49 172; fax: +86 10 629 23 563.

E-mail address: zhengmh@mail.rcees.ac.cn (M. Zheng).

precursors for PCDD/Fs formation (Dickson and Karasek, 1987; Milligan and Altwicker, 1996). Some mechanisms of PCDD/Fs formation from CIPhs as precursors have been reported (Weber and Hagenmaier, 1999; Tuppurainen et al., 2000). Among the possible precursors for the formation of PCDD/Fs, it seems that PCP has the highest potential to generate PCDDs (Altwicker and Milligan, 1993; Addink et al., 1995). As far as MSWI which is considered as the major PCDD/Fs emission source is concerned, the precursors for PCDD/Fs come from many paths. Besides the introduction via the MSWI feed, the precursors could be formed through de novo synthesis in incomplete combustion or through heterogeneous catalyzed reaction during the cooling of flue gases in the post-combustion zone (Ballschmiter et al., 1988). Suppressing the PCDD/Fs formation from precursors may be more efficient than end-of-pipe technology for PCDD/Fs in MSWI in the future.

Many inorganic and organic compounds have been studied for control of PCDD/Fs. These studies mostly focus on the deactivation of the catalysts mainly Cu compounds with inorganic or organic N- or S-compounds (Ruokojärvi et al., 1998; Samaras et al., 2000; Xhrouet et al., 2002), and reduction of the acid chlorine resources such as HCl and Cl₂ with basic compounds such as CaO, CaCO₃, Ca(OH)₂, Mg(OH)₂, NaOH, Ba(OH)₂, BaCO₃, etc. in MSWI (Gullett et al., 1994; Jozewicz and Gullett, 1995; Shemwell et al., 2001). The prevention of sulfur or compounds containing sulfur on PCDD/Fs formation through impacting the balance of Deacon Reaction has been reported (Raghunathan and Gullett, 1996). Certain complex catalysis systems such as V₂O₅, Cr₂O₃, Fe₂O₃ and MgO supported with TiO₂ have been used to decompose PCDD/Fs in laboratory-scale and real municipal waste incinerator (Bonte et al., 2002; Cho and Ihm, 2002; Lomnicki and Dellinger, 2003; Okumura et al., 2003). The inhibition of PCDDs formation by alkaline substances has been demonstrated by some research groups (Dickson et al., 1989; Naikwadi and Karasek, 1989; Ross et al., 1990). These researchers found many basic compounds such as ammonium hydroxide, calcium oxide, 2-aminoethanol, and triethylamine could inhibit PCDD/Fs formation. But the inhibition mechanism was not well understood.

There are many kinds of metals in MSW components, and these metals mostly exist as their basic compounds respectively in MSWI fly ash (Karamanov et al., 2003). The fractions of the common oxides in

typical MSWI fly ash can be seen in Table 1. The catalysis of some transition metal compounds containing copper, zinc and iron on PCDD/Fs formation has been studied extensively. In particular, copper compounds may promote the PCDD/Fs formation remarkably through catalysis of the Deacon Reaction and biaryl synthesis (Ullmann reaction) (Stieglitz et al., 1991; Gullett et al., 1992). The roles and their possible effecting mechanisms of more common metal oxides on PCDD/Fs formation from PCP have not yet been investigated roundly. In view of that the chemical interaction between the metal element and organic compounds maybe take place, the systemic research on the effects of most familiar metal compounds on PCDD/Fs formation seems very essential for the possible controlling measures in the future.

The objective of this paper is to investigate the influence and effecting mechanisms of series of metal oxides on PCDD/Fs formation from model precursor PCP. The results are expected to be useful for understanding the formation of PCDD/Fs and control and abating PCDD/Fs emission from MSWI.

2. Materials and methods

2.1. Materials

HCl, NaOH, MgO, Al₂O₃, CaO, BaO, TiO₂ (anatase), V₂O₅, MnO₂, Fe₂O₃, Co₃O₄, CuO, Ag₂O, ZnO, HgO, SnO, PbO, La₂O₃, CeO₂ and Eu₂O₃ were all of analytical grade (Beijing Chemical Reagents Company, China). With the exception of HgO, V₂O₅, BaO and Ag₂O with high toxicity or degradability by light, the particle sizes of metal oxides (HORIBA, Laser Scattering Particle Size Distribution Analyzer LA-920, Japan) and specific surface area (NOVA 4200 Surface Area and Pore Size Analyzer Quantachrome, USA) were analyzed before use. Toluene, *n*-hexane, dichloromethane were all of pesticide grade (Fisher Scientific, USA). OCDD was synthesized from pentachlorophenol using chlorine as initiator according to Kulka (1961) in our laboratory, and its purity (above 98%) was determined through quantitative analysis with ¹³C-labelled PCDD/Fs as internal criteria. ¹³C-labelled PCDD/Fs standards were obtained from Cambridge Isotope Laboratories (USA). PCP, whose purity has been described by the manufacturer as 99%, was purified to remove impurities of PCDD/Fs as follows: PCP was quantitatively dissolved

Table 1

The fractions of some common oxides in typical MSWI fly ash (wt.%) (Karamanov et al., 2003)

CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	BaO	ZnO	PbO	CuO	TiO ₂
30.0	4.21	2.35	11.52	0.14	1.42	0.14	0.05	1.91

in 2 mol/l NaOH. This solution was first extracted four times with toluene. Then the aqueous solution was acidified with concentrated HCl and subsequently extracted with times of toluene. The solvent was removed from the unified organic phases of the second extraction contained the PCP, and the residue was re-crystallized from acetone (Vollmuth et al., 1994).

2.2. Apparatus

The experiment was carried out in a laboratory-scale reactor shown in Fig. 1. The reactor consists of electro-motor for driving central axle tree, namely sample tubes supporting bearing, driving gear wheel, rotate speed adjustor, heater of combustion chamber, temperature sensor and temperature controller and control panel.

2.3. Experimental methods

Thirty milligrams metal oxides and 1 mg PCP were sealed in a glass tube (60×4.2 mm i.d.) in air to prepare a sample. Four to five sample tubes sheathed with high-temperature resist rubber linings were fixed in the holes of central axle tree of the reactor. The power switch of driving electromotor was turned on to make the sample tube rotate at 50 r/min for scheduled time under experimental temperature.

In succession, the experimental apparatus was cooled to room temperature. The sample tube was crushed and the reaction mixture was extracted twice by ultrasonic with 30 ml (5% v/v toluene in *n*-hexane) for 30 min each time. The extraction solutions were merged into a separatory funnel, 20 ml 0.2 mol/l NaOH solution was added to the funnel to remove the PCP remained from the reaction mixture, and 25 ml distilled water was added to wash the unwanted NaOH for three times. A column filled with anhydrous sodium sulfate was used to dry and remove water from the organic phase. The organic phase was concentrated to 1–2 ml with rotary-evaporation in vacuo 7 kPa at bath temperature 65 °C and chromatographed on a column of basic Al_2O_3 activated at 650 °C for 6 h. The column was first eluted with 60 ml hexane/ CH_2Cl_2 (98:2) and the eluant was discarded.

PCDD/Fs were then eluted with 40 ml of hexane/ CH_2Cl_2 (1:1). This fraction was concentrated to 2–3 ml on a rotary evaporator under vacuum control, and then transferred into a K–D concentrating tube to be concentrated to about 1 ml. Finally the solvent was removed under a gentle stream of nitrogen and toluene was added to dissolve the PCDD/Fs for GC–MSD analysis.

2.4. Analysis

An Agilent 6890 GC/5973N MS was used for analyses of the PCDD/Fs. The capillary column was an HP-5 MS (60 m $\times$ 0.32 mm, Agilent). A mixture of ^{13}C -labelled PCDD/Fs (Cambridge Isotope Laboratories) was added as standards for qualitative and internal criteria quantitative analysis of samples. Quantitative of PCDD/Fs was performed in selected ion monitoring mode using two most abundant ion clusters.

A blank experiment was run under the same experimental conditions to avoid any contamination. The method recovery experiment was carried out as: 40 μl (1 ppm) solution of OCDD in acetone was injected to 30 mg CaO in the sample tube, the solvent was permitted to volatilize. Then the sample was treated as mentioned above. All experiments were carried out in duplicates at least.

The total suppressing efficiency was defined as follows: Total suppressing efficiency = $[(\sum \text{PCDD/Fs formation from 1 mg PCP}) - (\sum \text{PCDD/Fs formation from 1 mg PCP with 30 mg metal compounds})] / (\sum \text{PCDD/Fs formation from 1 mg PCP})$.

3. Results and discussion

3.1. Effects of metal compounds on PCDD/Fs formation

The method recovery experiment showed that the recovery was about 80% in this study. The relative standard deviations (RSD) of parallel tests for all species are below 10.0%. The particle sizes and specific surface areas of metal oxides and the average amount and homologue profile of PCDD/Fs formation from PCP or PCP with metal oxides at 280 °C for 2 h were showed in Table 2. PCDFs and lower chlorinated PCDDs whose number of chlorine is less than five under the temperature range 280–340 °C were not detectable. Although some PCDFs and lower chlorinated PCDDs would be detected in samples through high-resolution GC–MS, since significant quantities of OCDD and HpCDDs were formed, the analysis carried out on low-resolution GC–MS with a high detection limit (10 ng/mg PCP) was suitable to observe the trend of OCDD and HpCDDs formation in this study. There are certain PeCDDs and HxCDDs except for OCDD and HpCDDs formed only on condition that PCP was heated with TiO_2 , V_2O_5 , Co_3O_4 , CuO

Fig. 1. Schematic diagram of the laboratory reactor.

Table 2

The particle size and specific surface area of each metal oxide and the average of PCDD/Fs formation from PCP with series of metal oxides under 280 °C for 2 h (10^3 ng/mg PCP)

	D_{50} (μm)	S_{BET} (m^2/g)	ΣPeCDDs	ΣHxCDDs	1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,9-HpCDD	OCDD	ΣPCDDs
PCP	—	—	ND	ND	0.13	0.30	26.7	27
PCP + MgO	12.26	35.03	ND	ND	0.75	0.36	15	16
PCP + Al_2O_3	1.31	24.27	ND	ND	0.33	0.64	8.9	9.9
PCP + CaO	44.16	3.40	ND	ND	0.04	0.06	1.6	1.7
PCP + BaO	NT	NT	ND	ND	ND	ND	2.2	2.2
PCP + TiO_2	0.52	9.66	ND	0.14	2.7	2.5	32	37
PCP + V_2O_5	NT	NT	0.13	0.08	0.11	0.19	11	12
PCP + MnO_2	0.30	50.08	ND	ND	0.17	1.0	29	30
PCP + Fe_2O_3	11.51	4.46	ND	ND	0.25	0.24	17	17
PCP + Co_3O_4	16.16	2.48	ND	0.014	0.49	0.49	30	31
PCP + CuO	20.60	6.88	0.88	0.05	0.96	2.2	58	62
PCP + Ag_2O	NT	NT	ND	ND	ND	ND	0.13	0.13
PCP + ZnO	1.36	3.35	ND	0.017	0.81	0.70	27	29
PCP + HgO	NT	NT	ND	ND	ND	ND	1.2	1.2
PCP + SnO	8.19	17.46	ND	ND	ND	ND	0.56	0.56
PCP + PbO	10.25	4.93	0.20	0.05	0.15	0.17	1.0	1.6
PCP + La_2O_3	0.90	6.91	ND	ND	0.21	0.24	15	15
PCP + CeO_2	6.51	4.57	ND	ND	0.09	0.17	27	27
PCP + Eu_2O_3	3.23	8.47	ND	ND	0.26	0.13	25	25

ND denotes not detectable (<10 ng/mg PCP), NT denotes not tested.

or PbO. The major product is highly chlorinated OCDD. The amount of 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,9-HpCDD is much lower than that of OCDD. The amount of 1,2,3,4,6,7,9-HpCDD is basically more than that of toxic congener 1,2,3,4,6,7,8-HpCDD in all experiments. It is worth noting that despite the capacity of reduction on the amount of OCDD, some oxides such as MgO, Al_2O_3 , PbO, Fe_2O_3 and La_2O_3 have certain simultaneous promoting effects on the formation of 1,2,3,4,6,7,8-HpCDD, which is more toxic than OCDD.

The total suppressing efficiencies of all metal oxides studied can be seen in Fig. 2. Al_2O_3 , alkali earth metal oxides (MgO, CaO and BaO) and transition metal oxides (Ag_2O , HgO, SnO, V_2O_5 and PbO) have obvious

suppressing effect on PCDD/Fs formation from PCP. The suppressing effects of transition metal oxide Fe_2O_3 and partial rare earth metal oxides (La_2O_3 , CeO_2 and Eu_2O_3) are not obvious. Partial transition metal oxides (TiO_2 , MnO_2 , Co_3O_4 , ZnO, CeO_2 and CuO) have certain promotion effects on PCDD/Fs formation from PCP, especially the strongest promotion effect of CuO was observed. The suppressing efficiencies of alkali earth metal oxides CaO and BaO are larger than that of Al_2O_3 and Fe_2O_3 . As for alkali earth metal oxides, the suppressing efficiencies of them increase basically according to period number, that is $\text{MgO} < \text{CaO} \approx \text{BaO}$. The previous findings suggested that Al_2O_3 plays a unique catalytic role in the formation of aromatic rings from

Fig. 2. The total suppressing efficiencies of metal compounds researched under 280 °C for 2 h.

aliphatic hydrocarbons. Al_2O_3 selectively catalyzes the formation of non-chlorinated aromatics through chlorine substitution reactions whereas CuO promote the chlorination of aliphatic intermediates followed by ring formations (Froese and Hutzinger, 1997). It should be pointed out the result that Fe_2O_3 and Al_2O_3 have certain suppressing effects on PCDD/Fs formation from precursor PCP in this study is in apparent contradiction to the work of Gullett et al. (1992) in which Fe_2O_3 and Al_2O_3 were found to obviously promote the formation of PCDD/Fs through de novo process.

3.2. Impacts of heating time and temperature on suppressing efficiencies

High suppressing efficiencies (over 90%) of CaO, BaO and PbO on PCDD/Fs formation indicate their applying perspectives. The influences of temperature and time on their suppressing effects are showed in Fig. 3. The total suppressing efficiencies of CaO, BaO and PbO all increase with the increase of time and temperature under experimental conditions.

3.3. Discussion on possible effecting mechanisms

Although there are no lower chlorinated PCDDs (HxCDDs, PeCDDs, TCDDs) for most metal oxides (MgO, CaO, BaO, Al_2O_3 , Fe_2O_3 , etc.), it is the case for some transition metal oxides (CuO, ZnO, TiO_2 , V_2O_5 , Co_3O_4 , PbO, etc.). The results may be explained by the fact that there are always some $\text{H}^\cdot$ and $\text{HO}^\cdot$ free radicals in the indoor air, but the amount of them is usually very low about at the level of 10^6 mol/cm^3 (Ingrosso, 2002). Only less of 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,9-HpCDD maybe forms through chlorine abstraction reaction with little amount of $\text{H}^\cdot$ free radicals in the closed sample tube, as can be seen in Fig. 4 (Fueno et al., 2002). There are no TCDDs, PeCDDs and HxCDDs detected for most cases maybe owing to the absence of

additional $\text{H}^\cdot$ free radicals in the reaction system. As for CuO, its strong catalysis activities are not only on PCDD/Fs formation through biaryl condensation but also on the dechlorination of PCDD/Fs newly formed (Hagenmaier et al., 1987). Thereafter, comparatively more OCDD, HpCDDs and even lower chlorinated PeCDDs and HxCDDs formed. The anatase TiO_2 is a catalyzing species, thus maybe resulting in its promoting effect on PCDD/Fs formation from PCP. For some transition metal oxides such as Co_3O_4 and PbO maybe have the similar complex catalysis action under heated conditions, thus there is less amount of OCDD formed, but more 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,9-HpCDD, and certain PeCDDs and HxCDDs formed according to similar chlorine abstraction processes. The considerable higher total suppressing efficiency (55.6%) of V_2O_5 may have relation with its higher catalysis destruction and oxidization effect. Further studies should be conducted to elucidate their more detailed processes.

The total suppressing efficiencies were calculated per number of moles and per surface area of each metal oxide to make clear the relationship between suppressing effects and the physical and mechanical characteristics of metal oxides. However, no obvious surface effects on the formation of PCDDs could be found. Naikwadi and Karasek (1989) found CaO mixed with fly ash could inhibit PCDD/Fs formation under laboratory-scale test, but the possible catalysis of fly ash was not analyzed and the effecting mechanism was not discussed in their study. Strömberg (1991) found the inhibition of basic sorbents (CaO, KOH, Na_2CO_3 , Al_2O_3 , Dolomite and NH_3) with fly ash or silica sand on chlorinated compounds including PCDD/Fs formation from CO_2 and HCl through the neutralization of the HCl. Since PCP is an acid and the metal oxides are bases according to the generalized acid–base theory, the chemical reaction of basic metal oxides abstract the proton of PCP and give the anion probably takes place thus prevent PCP to form PCDD/Fs, as can be seen in Fig. 5. In this study,

Fig. 3. Influence of time and temperature on the total suppressing efficiencies of CaO, BaO and PbO. (a) Reaction temperature: 280 °C. (b) Reaction time: 2 h.

Fig. 4. Schematic picture of the possible courses of HpCDDs formation under the experimental condition.

the effects of MgO , Al_2O_3 , CaO , BaO , V_2O_5 , Fe_2O_3 , Ag_2O , HgO , SnO , PbO and La_2O_3 on PCDD/Fs formation from PCP mostly relate to the acid–base reaction mechanism. The alkalinescence of CaO and BaO are stronger than that of Al_2O_3 and Fe_2O_3 , accordingly the total suppressing efficiencies of CaO and BaO are larger than that of Al_2O_3 and Fe_2O_3 . As for alkali earth metal oxides, the total suppressing efficiencies increase basically according to their alkalinescence, that is $\text{MgO} < \text{CaO} \approx \text{BaO}$. However, Ag_2O , HgO and SnO who are typical soft bases have higher total suppressing efficiencies. Therefore, the suppressing effect of one metal oxide is not only determined by its basic strength.

According to the atomic parameter theory, the ratio of charge to radius, or Z/r , is essentially a measure of how highly focused charge is in an ion—the larger the ratio, the more intense the charge. If Z/r is small, a cation has weakly focused charge and so only weakly bonds to O^{2-} . The Z/r of one metal cation represents the affinity of the metal element bonding to chlorine or to oxygen. The lower the Z/r value of one cation is, the easier it bonds to chlorine and the more difficult it bonds to oxygen. The Z/r values of metal cations in the corresponding oxides calculated according to Pauling's radius are

listed in Table 3 (Pauling, 1960). It can be seen that the total suppressing efficiencies of those metal compounds which contain the cations ($Z/r < 2$) are basically over 90%, while most metal oxides whose cations has the Z/r values above 2 have lower suppressing effects or even certain promotion effects on PCDD/Fs formation from PCP. Therefore, besides the acid–base reaction between PCP and metal oxides, it could be speculated that certain integrative physical and chemical interactions probably take place between metal oxides and precursor PCP in the course through the affinity of the metal element bonding to chlorine (or similar metal–chlorine bond), which could inhibit PCP to form PCDD/Fs by double-molecule condensation. The stronger the integrative interaction, the higher total suppressing effects the metal oxide possess. Moreover, PCDFs formation from PCP may be suppressed according to the same mechanism on speculation under higher temperature. To discuss the previous studies on the adding acid absorbent to reduce chloride source thus prevent PCDD/Fs formation in MSWI, it could be concluded that the influence of those basic compounds (CaO , BaO , $\text{Ca}(\text{OH})_2$, etc.) on PCDD/Fs formation may attribute to: (i) reduction on chlorine source through absorbing HCl , (ii) suppressing

Fig. 5. Schematic diagram of acid–base interaction (CaO is taken as an example).

Table 3

The values of Z/r of metal cations in the corresponding oxides researched

M^{n+}	Mg^{2+}	Al^{3+}	Ca^{2+}	Ba^{2+}	Ti^{4+}	V^{5+}	Mn^{4+}	Fe^{3+}	Co^{3+}	Cu^{2+}	Ag^{+}	Zn^{2+}	Hg^{2+}	Sn^{2+}	Pb^{2+}	La^{3+}	Ce^{4+}	Eu^{3+}
Z/r	2.08	4.84	2.02	1.40	5.90	8.48	4.55	4.60	4.76	2.78	0.79	2.70	1.82	1.82	1.67	2.61	3.96	2.94

PCDD/Fs formation through acid–base reaction and other integrative physical and chemical interaction between precursor ClPhs and basic metal compounds.

4. Conclusion

The suppressing effects of series metal oxides on PCDD/Fs formation from PCP were investigated. Some of them have obvious suppressing effects on PCDD/Fs formation from PCP while others have promotion effects under experimental conditions. For their higher suppressing efficiencies over 90%, alkali earth metal oxide CaO and BaO have certain promising application. The total suppressing efficiencies of CaO, BaO and PbO on PCDD/Fs formation all increase with the increase of heated time and heated temperature. The main effecting mechanisms are speculated as acid–base interaction and the integrative physical and chemical interaction between precursor PCP and metal oxide thus prevent the PCDD/Fs formation from PCP.

Although this study has no directive relevance to the full-scale municipal solid waste incineration, the results of the present experiments can help an understanding the mechanisms of the formation of PCDD/Fs from precursors in the presence of metal oxides. The results of the present study may be taken into account to make measures to control and reduce PCDD/Fs emission from MSWI.

Acknowledgement

This study was supported by National Basic Research Program of China (2003CB415006) and National Natural Science Foundation of China (Grant No. 20177031, 20122202).

Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2004.12.068](https://doi.org/10.1016/j.chemosphere.2004.12.068).

References

- Addink, R., Olie, K., 1995. Mechanisms of formation and destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in heterogeneous systems. *Environmental Science and Technology* 29, 1425–1435.
- Addink, R., Cnubben, P.A.J.P., Olie, K., 1995. Formation of polychlorinated dibenzo-*p*-dioxins/dibenzofurans on fly ash from precursors and carbon model compounds. *Carbon* 33 (10), 1463–1471.
- Altwickler, E.R., Milligan, M.S., 1993. Formation of dioxins: competing rates between chemically similar precursors and de novo reactions. *Chemosphere* 27 (1–3), 301–307.
- Ballschmiter, K., Braunmiller, I., Niemczyk, R., Swerev, M., 1988. Reaction pathways for the formation of polychlorodibenzodioxins (PCDD) and dibenzofurans (PCDF) in combustion processes: II. Chlorobenzenes and chlorophenols as precursors in the formation of polychlorodibenzodioxins and dibenzofurans in flame chemistry. *Chemosphere* 17 (5), 995–1005.
- Bonte, J.L., Fritsky, K.J., Plinke, M.A., Wilken, M., 2002. Catalytic destruction of PCDD/F in a fabric filter: experience at a municipal waste incinerator in Belgium. *Waste Management* 22, 421–426.
- Cho, C.-H., Ihm, S.-K., 2002. Development of new vanadium-based oxide catalysts for decomposition of chlorinated aromatic pollutants. *Environmental Science and Technology* 36 (7), 1600–1606.
- Dickson, L.C., Karasek, F.W., 1987. Mechanisms of formation of polychlorinated dibenzo-*p*-dioxins produced on municipal incinerator flyash from reactions of chlorinated phenols. *Journal of Chromatography* 389, 127–137.
- Dickson, L.C., Lenoir, D., Hutzinger, O., 1989. Inhibition of chlorinated dibenzo-*p*-dioxin formation on municipal incinerator fly ash by using catalyst inhibitors. *Chemosphere* 19 (8–9), 1435–1445.
- Dickson, L.C., Lenoir, D., Hutzinger, O., 1992. Quantitative comparison of de novo and precursor formation of polychlorinated dibenzo-*p*-dioxins under simulated municipal solid waste incinerator postcombustion conditions. *Environmental Science and Technology* 26 (9), 1822–1828.
- Froese, K.L., Hutzinger, O., 1997. Mechanisms of the formation of polychlorinated benzenes and phenols by heterogeneous reactions of C₂ aliphatics. *Environmental Science and Technology* 31 (2), 542–547.
- Fueno, H., Tanaka, K., Sugawa, S., 2002. Theoretical study of the dechlorination reaction pathways of octachlorodibenzo-*p*-dioxin. *Chemosphere* 48 (8), 771–778.
- Gullett, B.K., Bruce, K.R., Beach, L.O., Drago, A.M., 1992. Mechanistic steps in the production of PCDD and PCDF during waste combustion. *Chemosphere* 25 (7–10), 1387–1392.
- Gullett, B.K., Lemieux, P.M., Dunn, J.E., 1994. Role of combustion and sorbent parameters in prevention of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran formation during waste combustion. *Environmental Science and Technology* 28 (1), 107–118.
- Hagenmaier, H., Kraft, M., Brunner, H., Haag, R., 1987. Catalytic effects of fly ash from waste incineration facilities on the formation and decomposition of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. *Environmental Science and Technology* 21 (11), 1080–1084.
- Hays, S.M., Aylward, L.L., 2003. Dioxin risks in perspective: past, present, and future. *Regulatory Toxicology and Pharmacology* 37 (12), 202–217.
- Ingrosso, G., 2002. Free radical chemistry and its concern with indoor air quality: an open problem. *Microchemical Journal* 73 (1–2), 221–236.
- Jozewicz, W., Gullett, B.K., 1995. Reaction mechanisms of dry Ca-based sorbents with gaseous HCl. *Industrial Engineering Chemical Research* 34 (2), 607–612.

- Karamanov, A., Pelino, M., Salvo, M., Metekovits, I., 2003. Sintered glass–ceramics from incinerator fly ashes. Part II. The influence of the particle size and heat-treatment on the properties. *Journal of the Europe Ceramic Society* 23 (10), 1609–1615.
- Kulka, M., 1961. Ocatahalogenodibenzo-*p*-dioxins. *Canada Journal of Chemistry* 39, 1973–1976.
- Lomnicki, S., Dellinger, B., 2003. Development of supported iron oxide catalyst for destruction of PCDD/F. *Environmental Science and Technology* 37 (18), 4254–4260.
- McKay, G., 2002. Dioxin characterization, formation and minimization during municipal solid waste (MSW) incineration: review. *Chemical Engineering Journal* 86 (3), 343–368.
- Milligan, M.S., Altwicker, E.R., 1996. Chlorophenol reactions on fly ash. I. Adsorption/desorption equilibria and conversion to polychlorinated dibenzo-*p*-dioxins. *Environmental Science and Technology* 30 (1), 225–229.
- Naikwadi, K.P., Karasek, F.W., 1989. Prevention of PCDD formation in MSW incinerators by inhibition of catalytic activity of fly ash produced. *Chemosphere* 19 (1–6), 229–304.
- Okumura, M., Akita, T., Haruta, M., Wang, X., Kajikawa, O., Okada, O., 2003. Multi-component noble metal catalysts prepared by sequential deposition precipitation for low temperature decomposition of dioxin. *Applied Catalysis B: Environmental* 41 (1–2), 43–52.
- Pauling, L., 1960. *The Nature of the Chemical Bonds*, third ed. Cornell University Press, Ithaca, New York.
- Raghunathan, K., Gullett, B.K., 1996. Role of Sulfur in Reducing PCDD and PCDF Formation. *Environmental Science and Technology* 30 (6), 1827–1834.
- Ross, B.J., Lacombe, D., Naikwadi, K.P., Karasek, F.W., 1990. Investigation of the effect of water, acids, and bases in the gas stream in the catalytic formation of PCDD and PCDF over MSW fly ash. *Chemosphere* 20 (10–12), 1967–1972.
- Ruokojärvi, P.H., Halonen, I.A., Tuppurainen, K.A., Tarhanen, J., Ruuskanen, J., 1998. Effect of gaseous inhibitors on PCDD/F formation. *Environmental Science and Technology* 32 (20), 3099–3103.
- Samaras, P., Blumenstock, M., Lenoir, D., Schramm, K.W., Kettrup, A., 2000. PCDD/F prevention by novel inhibitors: addition of inorganic S- and N-compounds in the fuel before combustion. *Environmental Science and Technology* 34 (24), 5092–5096.
- Shemwell, B., Levendis, Y.A., Simons, G.A., 2001. Laboratory study on the high-temperature capture of HCl gas by dry-injection of calcium-based sorbents. *Chemosphere* 42 (5–7), 785–796.
- Stanmore, B.R., 2004. The formation of dioxins in combustion systems. *Combustion and Flame* 136 (3), 398–427.
- Stieglitz, L., Vogg, H., Zwick, G., Beck, J., Bautz, H., 1991. On formation conditions of organohalogen compounds from particulate carbon of fly ash. *Chemosphere* 23 (8–10), 1255–1264.
- Strömberg, B., 1991. Low temperature formation and minimization of chlorinated hydrocarbons. *Chemosphere* 23 (8–10), 1515–1525.
- Tuppurainen, K., Halonen, I., Ruokojärvi, P., Tarhanen, J., Ruuskanen, J., 1998. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. *Chemosphere* 36 (7), 1493–1511.
- Tuppurainen, K.A., Ruokojärvi, P.H., Asikainen, A.H., Aatamila, M., Ruuskanen, J., 2000. Chlorophenols as precursors of PCDD/Fs in incineration processes: correlations, PLS modeling, and reaction mechanisms. *Environmental Science and Technology* 34 (23), 4958–4962.
- Vollmuth, S., Zajc, A., Niessner, R., 1994. Formation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans during the photolysis of pentachlorophenol-containing water. *Environmental Science and Technology* 28 (6), 1145–1149.
- Weber, R., Hagenmaier, H., 1999. Mechanism of the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from chlorophenols in gas phase reactions. *Chemosphere* 38 (3), 529–549.
- Xhrouet, C., Nadin, C., DePauw, E., 2002. Amines compounds as inhibitors of PCDD/Fs de novo formation on sintering process fly ash. *Environmental Science and Technology* 36 (12), 2760–2765.