Synergetic inhibition of PCDD/F formation from pentachlorophenol by mixtures of urea and calcium oxide

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HIGHLIGHTS

- Mixed CaO/urea have a synergetic inhibition effect for PCDD/Fs formation from PCP.
- 5–20% urea reaction systems obtained the better synergetic inhibition effect.
- 2,3,7,8-PCDD congeners were the dominant products in eight reaction systems.
- Intermediates could promote the acid-base reaction to realize synergetic inhibition.

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ABSTRACT

Chlorophenols are structurally similar to PCDD/Fs and have been considered as highly potential precursors for PCDD/Fs formation. The suppressing effects of PCDD/F formation from pentachlorophenol (PCP) were investigated on various mass ratios of CaO and urea. The total concentration of 2,3,7,8-PCDD/Fs, mostly dominated by OCDD, was determined to be 48.58–10186 ng/mg in inhibitor-reaction systems, being much lower than that in blank reaction system (75654 ng/mg). Interestingly, compared with pure CaO and urea reaction system, the concentration and TEQ of formed 2,3,7,8-PCDD/Fs in mixed urea/CaO reaction system were lower, especially with 5–20% urea reaction systems being respectively at decrease by 96.5–99.4% and 99.2–99.7%. The suppression efficiency of TEQ in 5–20% urea reaction systems could be always approximately 100% under 250–350 °C. These results suggested that mixed inhibitors, especially 5–20% urea inhibitors, have a synergetic inhibition effect for PCDD/Fs formation from PCP. Mixed inhibitor generated several intermediates, involving CO₂, H₂O, NH₃, Ca(OH)₂, CaCO₃, HNCO, biuret and ammelide. The complex between PCP and Ca, N-doped species, lower chlorinated phenols and benzenediol, and organic acids were also determined. Synergetic inhibition mechanism may be attributed to accelerated facilitation of acid-base reaction and N doping. The decomposition of PCP itself also contributes to prevent PCDD/Fs formation.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are notorious owing to their toxicity, persistence, and bioaccumulation. Thermal industrial processes such as incin-

eration and steelmaking are major sources of PCDD/F emissions [1,2]. About 10.2 kg TEQ of dioxins annual emissions from various sources were estimated in China [2]. Research has shown that there are two possible mechanisms of PCDD/F formation in MSWI, i.e., via precursor formation or de novo formation [3].

The de novo synthesis hypothesizes that the PCDD/Fs are formed in the presence of carbon source, organic or inorganic chlorine donors and suitable metal catalyst [4]. The precursor pathway involves the formation of PCDD/Fs from precursors with similar structural features, such as chlorophenols [5] and chlorobenzenes [6]. The concentrations of these compounds have been correlated with those of PCDD/Fs in the stacks of gas incinerators [7,8]. In the

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precursor pathway, PCDD/Fs could be formed from heterogeneous surface-catalyzed reactions, which typically occur at 200–400 °C in the post-flame and cooling zones of combustors [9]. Chlorophenols, in particular, are structurally similar to PCDD/Fs and have been identified as the main potential precursors for PCDD/F formation [10,11]. Vallejo et al. [12] reported that toxic PCDD/Fs could be formed during remediation of 2-chlorophenol via Fenton oxidation. Liu et al. [13] found that PCDDs, especially OCDD, were the mainly formed congeners during inhibition of PCDD/Fs formation from PCP by calcium oxide. Therefore, suppression of PCDD/F formation from chlorophenol precursors could be significant in the thermal processes.

Chemical inhibition is a popular option because it efficiently prevents formation of PCDD/Fs at source. Various chemical inhibitors for reducing PCDD/F formation have been tested on both laboratory- and pilot-plant-scales. The alkali earth metal oxides (CaO, BaO and MgO) have been reported to suppress PCDD/F formation from PCP in a laboratory-scale reactor [5,14]. However, the suppressing efficiencies of them is $\text{CaO} \approx \text{BaO} > \text{MgO}$. Liu et al. [13] also reported that CaO can efficiently inhibit the formation of PCDD/Fs from dioxin precursors. Nitrogen-containing compounds, including NH_3 , urea, and dimethylamine, also effectively inhibit PCDD/F formation [15–19]. Kasai et al. [17] reported that the addition of urea did not significantly affect the concentration of NO_x in the stack gas. Sulfur-based suppressants (e.g., SO_2 , SO_3 , Na_2S , mercaptans and sulfur-amine/ammonium compounds) have been studied [20–22], which probably suppress PCDD/F formation by changing the balance of the Deacon reaction [23]. Fujimori et al. [24] also investigated the inhibition effects of thiourea during the thermochemical formation of PCDD/Fs in model and real fly ashes. Calcium oxides and nitrogen-containing compounds are efficient, non-toxic, low cost, and environmentally friendly. However, the possibility of synergy between calcium oxides and nitrogen-containing compounds in the inhibition of PCDD/F formation from precursors has not been studied. Their roles and effecting mechanisms on PCDD/F formation from PCP are not yet clear.

In this study, the prevention of PCDD/F formation from PCP by various mixtures of urea and CaO was investigated. The effect of mixture ratios on the pattern and TEQ level of formed PCDD/Fs was assessed. The suppression efficiencies of different mass ratios of urea and CaO on PCDD/F formation from PCP was also estimated. The mechanism of synergetic suppression was explored based on the results of in-situ Fourier transform infrared spectrometer (FT-IR) and the X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), gas chromatography-mass spectra (GC-MS) and ion chromatography (IC). The results will be useful in developing potential control measures for the PCDD/Fs emission from thermal processes.

2. Materials and methods

2.1. Materials

Urea, CaO, NaOH, K_2CO_3 , Na_2SO_4 , and acetic anhydride (all analytical grade) were obtained from the Beijing Chemical Reagents Company (Beijing, China). Toluene, *n*-hexane, and dichloromethane (all pesticide grade) were obtained from Fisher Scientific (Waltham, Massachusetts, USA). ^{13}C -labeled PCDD/Fs were obtained from Cambridge Isotope Laboratories (USA). PCDD/F impurities were removed from PCP (purity 99%) as follows. PCP (2.0 g) was quantitatively dissolved in NaOH solution (2 mol/L). This mixture was extracted three times with toluene. The aqueous solution was acidified with concentrated HCl to pH 1 and then extracted three times with toluene. The solvent was removed from the com-

bined organic phases from the second extraction; PCP was obtained by recrystallizing the residue from toluene [25].

2.2. Inhibition experiments

Samples were prepared by mixing PCP (1 mg) with different mass of urea and CaO (50 mg) in glass tubes (length 10 cm, i.d. 0.4 cm). There were eight reaction systems including a blank (without any inhibitor), CaO (50 mg pure CaO), 2% urea (1 mg urea and 49 mg CaO), 5% urea (2.5 mg urea and 47.5 mg CaO), 10% urea (5 mg urea and 45 mg CaO), 20% urea (10 mg urea and 40 mg CaO), 50% urea (25 mg urea and 25 mg CaO), and urea (50 mg urea). The sample tube was placed in an oven at 250, 300, or 350 °C for 2 h. After cooling to room temperature, the sample tube was crushed and the reaction mixture was extracted ultrasonically three with 5% (v/v) toluene in *n*-hexane (30 mL) for 30 min each time. The extraction solutions were concentrated to 1 mL with rotary-evaporation in vacuo 7 kPa at water-bath temperature (65 °C). All experiments were performed in triplicate to ensure repeatability of the results, and the average values were used.

2.3. Products analysis

In this study, 17 kinds of 2,3,7,8-substituted PCDD/Fs were identified by gas chromatography-mass spectrometry (Agilent 6890 GC/5973 N MS, HP-5 MS capillary column, 30 m × 0.25 mm × 0.25 μm), on the basis of U.S. EPA Method 1613. A mixture of ^{13}C -labeled PCDD/Fs was added as standards for qualitative and internal criteria quantitative analyses of samples. The quantities of PCDD/Fs were determined using selected-ion-monitoring mode, based on the two most abundant ion clusters. The identification of chlorinated phenols and benzendiols by GC-MS based on derivatization experiments using acetic anhydride, and the analysis of organic acids undertaken by ion chromatography, were added into Supplementary Material.

2.4. Sample characterization

XRD patterns of the samples were scanned on a Rigaku D/max 2500 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$, 40 kV, 200 mA). Surface reaction products of PCP and inhibitor were characterized with a Varian 3100 in situ Fourier transform infrared spectrometer (FT-IR) equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. XPS analyses were taken on an ESCALAB 250 instrument using monochromatized Al K radiation (200 W, 200 eV) as the X-ray source. The solid-state ^{13}C NMR spectra were acquired at 75.5 MHz on a Bruker AV300 (Switzerland), employing cross-polarization and magic-angle spinning techniques.

3. Results and discussion

3.1. Effects of different mass ratios of CaO and urea on concentrations and congener patterns of PCDD/Fs

PCDD/F formation from PCP in eight different reaction systems at 300 °C for 2 h was studied. Table 1 shows the concentration levels of the detected 2,3,7,8-PCDD/F congeners in these systems. In the blank reaction system, a large amount of newly formed OCDD, a smaller amount of 1,2,3,4,6,7,8-HpCDD, and trace amount of 1,2,3,7,8-PeCDD, 2,3,7,8-TCDD, OCDF, and 2,3,7,8-TCDF were detected with $\sum 2,3,7,8\text{-PCDD/Fs}$ at 75654 ng/mg. PCDD could be formed by condensation of chlorophenol precursors, which was analogous to the Ullmann reaction [26]. Ryu et al. [27] reported the formation of 1,3,7,9-TCDD and 1,3,6,8-TCDD from the 2,4,6-trichlorophenol (TriCP) via the steps such as oxygen-carbon

Table 1
The concentrations levels of 2,3,7,8-PCDD/Fs in eight reaction systems following heating for 2 h at 300 °C.

congener	PCP blank reaction	CaO reaction system	2% urea reaction system	5% urea reaction system	10% urea reaction system	20% urea reaction system	50% urea reaction system	urea reaction system
2378-TCDF	1.85	ND	ND	ND	ND	ND	ND	ND
12378-PeCDF	ND	ND	ND	ND	ND	ND	0.08	ND
23478-PeCDF	ND	ND	ND	ND	ND	ND	0.15	ND
123478-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND
123678-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND
234678-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND
123789-HxCDF	ND	ND	ND	ND	ND	ND	ND	ND
1234678-HpCDF	ND	0.34	ND	ND	ND	ND	ND	ND
234789-HpCDF	ND	2.05	ND	ND	ND	ND	ND	ND
OCDF	1.55	0.98	ND	ND	ND	ND	ND	ND
2378-TCDD	1.96	0.31	ND	ND	ND	ND	ND	ND
12378-PeCDD	7.95	ND	ND	ND	ND	ND	0.31	ND
123478-HxCDD	ND	ND	ND	ND	ND	ND	43.71	14.80
123678-HxCDD	ND	ND	ND	ND	ND	ND	2.08	3.45
123789-HxCDD	ND	ND	ND	ND	ND	ND	13.16	9.15
1234678-HpCDD	248	179	44	9.89	ND	ND	10.35	38.46
OCDD	75393	10003	2458	328	87.11	48.58	29.24	1128
∑2,3,7,8-PCDF	3.40	3.37	ND	ND	ND	ND	0.23	ND
∑2,3,7,8-PCDD	75651	10182	2502	338	87.11	48.58	98.85	1194
∑2,3,7,8-PCDD/Fs	75654	10186	2502	338	87.11	48.58	99.08	1194
∑I-TEQ	83.99	12.13	2.90	0.43	0.087	0.049	6.26	4.25

ND <0.01 ng/mg PCP.

coupling at a chlorinated ortho position and the loss of two chlorine atoms. In the present study, OCDD could be easily formed by the similar condensation of structurally closely related PCP. TCDD to HpCDD could be further produced from the hydrodechlorination of OCDD during the thermal reaction. Tuppurainen et al. [8] reported that tetra- and penta-congeners may be formed from hexa- and hepta-PCDD/Fs by dechlorination in incineration processes. One trichlorophenol isomer (2,3,5-TriCP) and three tetrachlorophenol isomers (2,3,4,5-, 2,3,5,6- and 2,3,4,6-TetraCP) were detected by GC–MS with the derivatization method in the blank reaction system (See Fig. S1 and its explanation). It indicated that lower chlorinated phenols were produced through the hydrodechlorination of PCP. These lower chlorinated phenols could also lead to the formation of TCDD to HpCDD via similar condensation pathway. However, Ryu et al. found that 2,4,6-triCP and 2,3,4,6-teCP with both ortho site chlorinated could not form any PCDF by condensation with themselves and other chlorophenol [28]. Therefore, it is presumed that PCP with both ortho sites pre-chlorinated, might be difficult to form the PCDFs via its direct condensation reaction. However, 2,3,5-TriCP and 2,3,4,5-teCP produced by the hydrodechlorination of the parent PCP, feature only one ortho-substituted chlorine atom, possibly resulting in the formation of PCDF. Lomnicki et al. [29] reported that 2-chlorophenol with only one ortho-substituted chlorine atom formed 4,6-dichlorodibenzofuran (DCDF) via the condensation on a CuO/silica surface.

The distribution of 2,3,7,8-substituted PCDD/F congeners in the reaction products differed depending on the mass ratios of CaO and urea with ∑2,3,7,8-PCDD/Fs in the range of 48.58–10186 ng/mg. In CaO reaction system, the similar congeners were identified. The ∑2,3,7,8-PCDD concentration was determined to be 10182 ng/mg, decreased by 86.5%, compared with those in the PCP blank reaction system. ∑2,3,7,8-PCDF concentration became more less with a decrease by 8.8%. These comparison results indicate that the CaO inhibitor has an obviously negative effect on PCDD/F formation. This is consistent with previous reports [13], which showed that the ∑2,3,7,8-PCDD/F concentration decreased sharply with the CaO inhibitor. When the mass percentages of urea were 2% and 5%, only 1,2,3,4,6,7,8-HpCDD and OCDD were detected respectively with ∑2,3,7,8-PCDD/Fs at 2502 ng/mg and 338 ng/mg. In the 10% urea and 20% urea reaction systems, only OCDD was detected respec-

tively with ∑2,3,7,8-PCDD/Fs at 87.11 ng/mg and 48.58 ng/mg. However, when the mass percentage of urea increased to 50%, all 2,3,7,8-PCDDs, except 2,3,7,8-TCDD, were detected, namely OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, and 1,2,3,7,8-PeCDD, while two 2,3,7,8-PCDF congeners, i.e., 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, were detected. ∑2,3,7,8-PCDD/Fs was determined to be 99.08 ng/mg. Except for 1,2,3,4,6,7,8-HpCDD and OCDD, the 2,3,7,8- PCDD/F congeners detected in the pure urea reaction system differed from those of the pure CaO system with their concentration at 1194 ng/mg. It is worth noting that the ∑2,3,7,8-PCDD/Fs concentration was lower in all reaction systems containing inhibitor than that of the blank reaction system. Furthermore, the ∑2,3,7,8-PCDD/Fs concentrations in mixed inhibitor reaction system were tentatively compared to that of urea alone combined with CaO alone. Fig. S2 shows the concentrations of ∑2,3,7,8-PCDD/Fs formed over mixed urea/CaO (2–50% urea reaction systems), and the combined concentrations of formed ∑2,3,7,8-PCDD/Fs over corresponding quality of urea alone and CaO alone, which were calculated from Table 1. When compared with the corresponding combination of individual urea and CaO reaction systems, the concentration of ∑2,3,7,8-PCDD/Fs in the mixed urea/CaO (2–50% urea reaction systems) decreased by 75.0%, 96.5%, 99.1%, 99.4% and 98.3%, respectively. This indicated that the mixtures of different mass of urea and CaO all exhibited the synergetic effect on PCDD/F formation from PCP, particularly the 5–50% urea reaction systems.

2,3,7,8-substituted PCDD congeners were the dominant products in the eight reaction systems. The distributions of the produced PCDD congeners were evaluated by normalizing the PCDD congener concentrations with the percentage of the sum of 2,3,7,8-substituted PCDD congeners. Fig. 1 shows the distribution patterns for the 2,3,7,8-PCDD congeners in the eight reaction systems after heating for 2 h at 300 °C. The OCDD fraction predominated in the blank reaction system, representing 99.66% of the total 2,3,7,8-substituted PCDD congeners. Similar trends were observed in the CaO, 2% urea, 5% urea, 10% urea, 20% urea, and urea reaction systems. In the 2% urea and 5% urea reaction systems, only 1,2,3,4,6,7,8-HpCDD was produced in addition to OCDD, at levels of 1.76% and 2.93%, respectively. In the 10% urea and 20% urea reaction systems, OCDD was the only 2,3,7,8-substituted PCDD

Fig. 1. 2,3,7,8-PCDD congener profiles in the eight reaction systems following heating for 2 h at 300 °C.

congener produced. In contrast, OCDD was not the dominant component of the total 2,3,7,8-substituted PCDD congeners in the 50% urea reaction system. The congener fractions decreased as follows: 1,2,3,4,7,8-HxCDD (44.22%) > OCDD (29.58%) > 1,2,3,7,8,9-HxCDD (13.31%) > 1,2,3,4,6,7,8-HpCDD (10.47%) > 1,2,3,6,7,8-HxCDD (2.10%) > 1,2,3,7,8-PeCDD (0.31%). The 2,3,7,8-substituted PCDD congener profiles showed more clearly that different mass ratios of CaO and urea have different inhibitory effect on PCDD formation from PCP. The distribution of produced PCDD congeners patterns is different in eight reaction systems, which might be caused by the different interaction between the different mass ratios of CaO and urea.

3.2. I-TEQ level and TSE_{TEQ} of 2,3,7,8-PCDD/Fs in different reaction systems and at different temperatures

The suppression efficiency of the total international toxic equivalent quantity (TSE_{TEQ}) was calculated using the following equation:

$$TSE_{TEQ} = \left[(TEQ \text{ of } \sum \text{PCDD/Fs formed from 1 mg PCP without any inhibitor}) - (TEQ \text{ of } \sum \text{PCDD/Fs formed from 1 mg PCP with 50 mg inhibitor}) \right] / (TEQ \text{ of } \sum \text{PCDD/Fs formed from 1 mg PCP without any inhibitor})$$

The corresponding total I-TEQ ($\sum$ I-TEQ) values in the different systems following reaction for 2 h at 300 °C are presented in Table 1. The $\sum$ I-TEQ levels in seven reaction systems containing inhibitor were much lower than that of the blank reaction. In particular, the $\sum$ I-TEQ values for the 5%, 10% and 20% urea reaction systems (i.e., 0.43, 0.087, and 0.049 ng/mg, respectively) were 195–1714 times lower than that of the PCP blank reaction system (i.e., 83.99 ng/mg). Lu et al. [14] reported that I-TEQ levels of adding CaO inhibitor were 29 times lower than that of no sorbent on PCP forming PCDD/Fs. Meanwhile, the $\sum$ I-TEQ of formed 2,3,7,8-PCDD/Fs in mixed urea/CaO reaction system was compared to that of corresponding combination of urea alone and CaO alone according to the calculation from Table 1 above. As shown in Fig. S3, relative to the corresponding combination of urea and CaO alone reaction systems, the $\sum$ I-TEQ in a series of mixed urea/CaO reaction systems (2–50% urea reaction systems) were lower, especially with 5–20% urea reaction systems being at decrease by 99.2–99.7%. This also suggested that the mixtures of urea and CaO showed the excellent synergetic inhibition effect to reduce the toxicity of formed 2,3,7,8-PCDD/Fs from PCP. The distribution trend of TEQ values is slightly

different from the PCDD/Fs concentration, which was caused by the different TEF values of different congeners.

The effect of the reaction temperature on the I-TEQ values and TSE_{TEQ} of 2,3,7,8-PCDD/F congeners formed in eight reaction systems after reaction for 2 h is shown in Fig. 2 (The concentrations levels of 2,3,7,8-PCDD/Fs at 250 and 350 °C were seen in Tables S1 and S2). As observed in Fig. 2a, the $\sum$ I-TEQ at 350 °C, 1061.11 ng/mg in the blank reaction system was higher than those at 300 and 250 °C, i.e., 83.99 and 75.81 ng/mg, respectively. In contrast, the CaO reaction system gave a slightly higher $\sum$ I-TEQ at 350 °C than at 300 °C (12.9 and 12.13 ng/mg, respectively). However, both values were much lower than that at 250 °C (45.98 ng/mg). The same trend was observed in the 100% urea reaction system with increasing temperature (i.e., 16.60, 4.25, and 6.15 ng/mg, at 250, 300, and 350 °C, respectively). The I-TEQ values for the systems with adding inhibitor were much lower than those for the blank reaction system at the three different temperatures. Compared with the pure CaO and urea reaction system, the mixed 2–50% urea reaction systems, especially 5–20% urea reaction systems, obtained the lower TEQ amount of the formed 2,3,7,8-PCDD/Fs following heating for 2 h at the three different temperatures. The trend in TSE_{TEQ} was consistent with that of I-TEQ for the different reaction systems and temperatures (Fig. 2b). In particular, TSE_{TEQ} values are almost approximately 100% under the temperature of 250–350 °C in 5–20% urea reaction systems. As mentioned above, the 5–20% urea reaction systems obtained the outstanding performance in reducing the concentration and $\sum$ I-TEQ of formed 2,3,7,8-PCDD/Fs, as well as increasing TSE_{TEQ} among all reaction systems containing inhibitor.

3.3. Possible mechanism of synergetic inhibition

As observed in Fig. 3, surface reaction studies were carried out using FT-IR to understand the synergetic inhibition mechanism of PCDD/F formation from PCP by mixed CaO and urea. Fig. 3a shows the FT-IR spectra of the urea, CaO, and 20% urea reaction systems before heating. The broad bands at 3447, 1597, and 782 cm^{−1} can be attributed to urea [30], and the peaks at 1429 and 873 cm^{−1} can be assigned to CaO. The intense band at 3643 cm^{−1} arises from OH groups [31], perhaps from adsorbed H₂O and formed Ca(OH)₂. In the 20% urea reaction system, the reaction species changed with increasing temperature. The FT-IR spectra at room temperature, and 250, 300, and 350 °C, are shown in Fig. 3b. The intensities of the bands at 3447, 1597, and 790 cm^{−1} decreased with increasing temperature, indicating decomposition of urea. The bands at 2360 and

Fig. 2. (a) The TEQ amount of 2,3,7,8-PCDD/Fs congener formed in the eight reaction systems following heating for 2 h at 250 °C, 300 °C and 350 °C; (b) The TSE_{TEQ} of 2,3,7,8-PCDD/Fs congener formed in the seven reaction systems following heating for 2 h at 250 °C, 300 °C and 350 °C.

1610 cm⁻¹ are related to CO₂ [32,33] and NH₃ [34], respectively. The absorption bands at 2204 and 1233 cm⁻¹ correspond to isocyanic acid (HNCO) [35]. The presence of lactam compounds could explain the appearance of the additional band at 1674 cm⁻¹, and the band at 1084 cm⁻¹ is related to biuret (C₂H₅O₂N₂) [36]. CaCO₃ is responsible for the bands at 2873, 2515, 1795, 1429, 873, and 711 cm⁻¹ [31,37]. The increases in the intensities of these peaks in the FT-IR spectrum at 350 °C confirm that more CaCO₃ was formed with increasing temperature. CaO and CaCO₃ both have peaks at 1429 and 873 cm⁻¹.

For further characterizing the intermediate reaction over CaO and urea, the solid intermediates obtained from reaction of the inhibitor were analyzed by XRD (Fig. 4). Fig. 4a shows the XRD patterns of the samples in the CaO reaction system under the untreated condition or following heating for 2 h at 250, 300, and 350 °C. In the untreated reaction system, the crystal phases of CaO and Ca(OH)₂ were observed, which is consistent with the result from FT-IR spectrum. The peaks in the Ca(OH)₂ pattern became more intense and sharp at 350 °C, indicating the formation of more Ca(OH)₂. It should be noted that a weak diffraction peak from CaCO₃ was observed at 350 °C. This is probably because CaCO₃ was formed by the reaction of CaO or Ca(OH)₂ with H₂O and CO₂ adsorbed in the reaction system. Fig. 4b shows the XRD patterns of the samples in the 20% urea

Fig. 3. (a) FT-IR spectra of products in reaction systems of urea, CaO and 20% urea before heating; (b) FT-IR spectra of products in 20% urea reaction system at 250 °C, 300 °C and 350 °C.

reaction system under the untreated condition or following heating for 2 h at 250, 300, and 350 °C. For the untreated reaction system, the crystal phases of CaO, urea, and Ca(OH)₂ were observed. The urea diffraction peak disappeared, as a result of decomposition, at 250 °C. Likewise, urea was not observed in the XRD patterns at 300 and 350 °C. Compared with those in the XRD patterns of Ca(OH)₂ and CaCO₃ in the CaO reaction system, the intensity of the Ca(OH)₂ peak decreased slightly and that of CaCO₃ increased sharply in the 20% urea reaction system with increasing temperature. This indicates that some of the Ca(OH)₂ reacted with produced H₂O and CO₂, resulting in an increased amount of CaCO₃. The XRD patterns of the CaCO₃ in 20% urea reaction system show that addition of urea facilitated formation of CaCO₃. However, no obvious peaks corresponding to inorganic species containing Cl⁻, was observed possibly due to the detection limit. To confirm the formation of such species, the amount of PCP was extremely increased in reaction system. The new phase of CaClOH (JCPDS 01-073-1885) was determined besides the original CaO, Ca(OH)₂ and CaCO₃ (See Fig. S4 and its explanation).

Analysis of the reaction products using FT-IR spectroscopy and XRD showed that urea decomposed to give a series of intermediate products, including H₂O, NH₃, CO₂, HNCO, biuret, and several

Fig. 4. (a) The XRD patterns of the samples under the untreated condition or following heating for 2 h at 250, 300, and 350 °C in the CaO reaction system; (b) The XRD patterns of the samples under the untreated condition or following heating for 2 h at 250, 300, and 350 °C in 20% urea reaction system.

lactam compounds. The evolution of these intermediate products can be interpreted with reference to the main chemical reactions, shown in Scheme 1a. The hydrolysis of HNCO with trace amounts of water could produce NH_3 and CO_2 . The lactam compound might be the ammelide ($\text{C}_3\text{H}_4\text{O}_2\text{N}_4$), which could be formed by the reaction between HNCO and biuret [36,38]. The formation of H_2O and CO_2 could be the reason why addition of urea facilitated the formation of CaCO_3 .

As mentioned above, the addition of CaO and urea to a PCDD/F formation system significantly decreases PCDD/Fs emissions. Liu et al. [13] found that CaO not only absorbed and decomposed dioxin precursors, but also absorbed HCl and prevented the formation of Cl_2 from HCl. Qian et al. [5] speculated that the effects of basic compounds such as CaO, BaO, and $\text{Ca}(\text{OH})_2$ on PCDD/F formation could be attributed to suppression of PCDD/F formation through acid–base reactions and other physical and chemical interactions between the precursor PCP and basic metal compounds. While Ruokojärvi et al. [39] proposed that the urea molecule itself, or NH_3 or HNCO may form the complex with the catalyzing metal. Such complexes can reduce the activity of copper, which is the

main catalyst used to promote oxidation and chlorination reactions of carbonaceous materials to form PCDD/Fs [40,41]. Fujimori et al. [24] investigated the inhibition effects of thiourea during the thermochemical formation of PCDD/Fs via de novo pathway in model and real fly ashes. However, such mechanism cannot explain the effect of urea addition on PCDD/F formation from PCP precursor.

As described above, CaO and urea mixtures have a synergetic inhibition effect for preventing PCDD/Fs formation from PCP. The mechanism of synergetic inhibition of PCDD/F formation could be explained as shown in Scheme 1b. Double-molecule condensation of PCP could form PCDD/Fs through a series of intermediate reactions [3]. Whereas, the chemical reaction of basic compounds and acidic PCP took place by abstracting the proton of PCP based on the generalized acid–base theory. The combination of $\text{Ca}(\text{OH})_2$ and phenol could produce hydroxycalcium phenoxides (PhOCaOH), which could further form calcium phenoxide ($(\text{PhO})_2\text{Ca}$) with continuous removal of water [42]. In order to further justify the formation of such analogous complexes, the ^{13}C NMR was used to probe the chemical binding of pentachlorophenoxy in the reacted samples. As observed in Fig. S5, ^{13}C resonances appeared in the pentachlorophenol (PCP) spectrum at 147.1 ppm for the ipso carbon. While in the solid-state ^{13}C spectrum of degraded sample in 5% urea reaction system, resonances ascribed to the ipso carbons appeared at 153.6 ppm. The ipso carbon of latter shifted upfield by about 6.5 ppm compared with that of the former. Schlosberg et al. [42] reported that the ^{13}C NMR of the ipso carbon of the aromatic ring also shifts upfield by about 7 ppm in either PhOCaOH or $(\text{PhO})_2\text{Ca}$ compared to phenol. These results might indicate the formation of hydroxycalcium pentachlorophenoxides and/or calcium pentachlorophenoxide by the acid–base reaction of CaO or $\text{Ca}(\text{OH})_2$ with PCP, and thus prevented PCP to form PCDD/Fs. In the experimental system, H_2O and CO_2 from the pyrolysis of urea could facilitate the formation of CaCO_3 which covered the surface of CaO to form a complex. It has been reported that CaCO_3 had good absorbability to chlorophenol [30], formaldehyde [43] and heavy metals (Zn, Cr, Pb, Cd, Cu and Fe) [44]. As an effective adsorbent, CaCO_3 covering the complex surface could adsorb more PCP which further resulted in the occurrence of acid–base reaction with CaO and CaCO_3 or $\text{Ca}(\text{OH})_2$ to hinder PCDD/Fs formation. CO_2 adsorption or release from the particulates benefited the transport of PCP molecules, resulting in sufficient contact between PCP and complex, thereby further improving the inhibition effect. Furthermore, the addition of CaO might decrease the decomposition temperature of urea, promoting urea to decompose more H_2O and CO_2 [38], thereby more CaCO_3 was formed. This series of circular reaction explained the synergetic inhibition effect of CaO and urea mixture for preventing PCDD/Fs formation from PCP.

The bonding configurations of N atoms in reaction system were further investigated by XPS (See Fig. S6). Four peaks corresponding to the binding energy levels of 398.7, 399.8, 400.1 and 401.9 eV in the samples were assigned to pyridinic, amine, pyrrolic and inorganic nitrogen [45,46]. Possibly, the N-doped species containing pyridinic and pyrrolic structures might be formed by replacing carbon in the six-membered ring with the amine group or NH_3 , thus to also inhibit the formation of PCDD/Fs [17,22]. However, GC–MS analysis of the degraded products indicates that there were no detectable peaks consistent with those of emerging phenazine and cabazole pollutants under the present experiment condition [47].

The alkali earth metal oxides could also exhibit high level of activities toward the degradation of chlorinated aromatics. Su et al. [48] found that the physical mixtures of alkaline earth metal oxides (MgO, CaO, SrO, BaO) and iron oxides could effectively decompose hexachlorobenzene at 300 °C. It is presumed that the decomposition of PCP precursor itself could inhibit the formation of PCDD/Fs in the reaction system. Fig. S7 shows the GC–MS spectrums of the sample in 5% urea reaction system after derivatization in aqueous

Scheme 1. (a) The possible major reactions and intermediate for the pyrolysis of urea and formation process of CaCO₃ in 20% urea reaction system at heating condition; (b) The inhibition mechanism of PCDD/F formation from PCP in 20% urea reaction system.

solution using acetic anhydride. The derivatization products were identified by comparing mass spectra with the NIST02.L standard spectral database, and the elution order of the different standards. The peaks were identified as one trichlorophenylacetates, three tetrachlorophenylacetates and two tetrachlorobenzendiol diacetate. It can be seen that the 2,3,5-TriCP, 2,3,4,5-, 2,3,5,6- and 2,3,4,6-TetraCP, and tetrachloro-Benzenediol (tetrachlorocatechol, TCC; tetrachlorohydroquinone, TCHQ) were detected as the degradation products during the thermal reaction of PCP. This indicated

that lower chlorinated TriCP and TetraCPs were produced through the hydrodechlorination of PCP, which were also found in the blank reaction system. And they could also contribute the formation of PCDD/Fs. Lan et al. [49] reported that TCC and TCHQ were two primary intermediates during heterogeneous photodegradation of PCP with maghemite and oxalate under UV illumination. Su et al. [48] found that the hexachlorobenzene could form PCP which was further converted into TCC and TCHQ via nucleophilic attack by O²⁻. Therefore, it is speculated that the formed lower chlorinated

phenols and PCP could be further oxidized to the quinone species such as TCC and TCHQ. It was reported that chlorinated aromatic compounds containing hydroxyl groups can be easily ring cracked into smaller organic molecules such as formate and acetate [50,51]. In the current study, such ring-cracked products in the 5% urea reaction system at 300 °C for 2 h were detected by ion chromatography (IC). Formic, acetic and propanoic acids were determined as the main ring-cracked products, as shown in Fig. S8. These results further demonstrated that the parent PCP, and formed chlorinated phenols and benzendiols, decomposed finally into small organic acid molecules, to inhibit the PCDD/F formation. This was also presented into Scheme 1b. However, it is found that there is a mass chlorine imbalance between the amounts of the initial and dechlorinated materials. This suggests that other unidentified products should be also available in the reaction system (See Table S3 and its explanation).

4. Conclusion

The synergetic prevention of 2,3,7,8-PCDD/Fs formation was investigated over a series of mixtures containing various mass ratios of CaO and urea. The formation of 2,3,7,8-PCDDs, mostly dominated by OCDD and then 1,2,3,4,6,7,8-HpCDD, was much favored over 2,3,7,8-PCDFs in the eight reaction systems. The total concentration and $\sum$ I-TEQ of formed 2,3,7,8-substituted PCDD/Fs in the mixed CaO/urea reaction systems were lower than those of the corresponding urea alone combined with CaO alone, both of which were lower than those of blank reaction system. In particular, for the 5%, 10% and 20% urea reaction systems, the $\sum$ I-TEQ values were significantly lower in the range of 0.049–0.43 ng/mg. And TSE_{TEQ} values could be always approximately 100% under the temperature of 250–350 °C. The synergetic suppressing effect might be partially attributed to the interaction between CaO and urea during the reaction process, resulting in formation of Ca(OH)₂, CaCO₃, NH₃, HNCO, biuret and ammelide along with CO₂ adsorption and release. This interaction could provide more adsorption and reaction sites for acid–base reaction between PCP and basic compounds, thus significantly preventing the PCDD/Fs formation from PCP. The formation of the N-doped species containing pyridinic and pyrrolic structures, and the decomposition of PCP into organic acids, could also contribute the reduction of the PCDD/Fs generation.

Conflict of interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.05.090>.

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