

Dechlorination reaction of hexachlorobenzene with calcium oxide at 300–400 °C

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ABSTRACT

Hexachlorobenzene (HCB) was thermally treated with calcium oxide (CaO) at 300–400 °C. Analyses of chloride ions and residual HCB confirmed that a dechlorination reaction had occurred. The dechlorination mechanism was investigated with a series of analytical methods including X-ray fluorescence (XRF), X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The final products detected were CaCO₃ by XRD and Raman spectroscopy, amorphous carbon by Raman spectroscopy, and CaCl₂ by XPS. The newly produced species of CaCO₃ and amorphous carbon were thought to be the ultimate fate of the C element of HCB. After identification of the final dechlorination products, we can conclude that the reaction of HCB with CaO at 300–400 °C is through a dechlorination/polymerization pathway, which is induced by electron transfer. An overall reaction formula for HCB reaction with CaO was proposed and was energetically quite favorable. The results are helpful for the further comprehension of the reaction mechanism for thermal dechlorination of PCDD/Fs in CaO rich matrices.

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1. Introduction

To implement the goal of worldwide elimination of the “dirty dozen” persistent organic pollutants (POPs) listed in Stockholm Convention, more attention must be paid to unintentionally produced POPs (UPOPs, including polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB)) due to their numerous sources, their potentially huge increase in developing countries, and their serious adverse health effects on humans.

Low-temperature dechlorination has been employed to destroy UPOPs in fly ash from waste incinerators. The catalytic potential of fly ash from a municipal solid waste incinerator (MSWI) for the dechlorination of UPOPs in oxygen deficient conditions at 300–400 °C was observed in the 1980s [1] and this technology was developed and rapidly commercialized [2]. From all of the related references, the high-efficiency degradation of PCDD/Fs in MSWI fly ash by low-temperature dechlorination (300–400 °C) can be easily achieved, but the mechanistic interaction of PCDD/Fs with fly ash and the ultimate fate of any potential reaction products are still not well understood.

During low-temperature dechlorination of PCDD/Fs, the levels of lower chlorinated congeners produced are very small and mass imbalances are often observed. Octachlorodibenzo-*p*-dioxin (OCDD) was added to fly ash (5.5×10^6 ng/kg) to observe the dechlorination/hydrogenation and destruction reactions of PCDD/Fs with

fly ash [3]. A reduction in toxic equivalent (TEQ) for PCDDs by more than 99% was achieved in fly ash by the vacuum heat treatment at 650 K for 4 h (the total amount of OCDD and lower chlorinated PCDD congeners in fly ash was 26 ng/g after treatment). However, the total amount of PCDDs and dibenzo-*p*-dioxin detected in the liquid nitrogen-cooled trap relative to that of added OCDD was about 17%, which indicated that the conversion reactions of OCDD to species with higher molecular weight might have occurred in fly ash.

Although the catalytic potential of MSWI fly ash was initially assigned to its transition metals (e.g. Cu, Fe, and Ni), the reaction of PCDD/Fs with calcium oxide was also of interest. Koper and co-workers [4–6] found a destructive adsorption of chlorinated hydrocarbons (CCl₄, CHCl₃, and C₂Cl₄) on ultrafine particles of CaO at about 300–400 °C, indicating that CaO was effective in the dechlorination of chlorinated aliphatic hydrocarbons. The thermal treatment of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) by reaction with Ca-based sorbents was conducted at 23–300 °C [7]. At 160–300 °C, a 50–100% conversion of TCDD to higher molecular weight, chlorinated products with both aromatic and aliphatic components was observed. As well, the researchers found CaO was more effective than CaCO₃.

In general, free CaO exists in MSWI fly ash due to the excess addition of CaO from air pollution control systems. The free CaO contents of four MSWI fly ash samples were measured to be 1.6–3.1% (the samples were collected from four large-scale incineration plants in China). In the current study, we assumed that the mass imbalances of PCDD/Fs and the dechlorination pathway were related to the reactions with CaO, and a series of experiments were carried out to elucidate the dechlorination reaction of UPOPs with CaO. In our previous research, the main dechlorination pathway hypothesis

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had included dechlorination/hydrogenation induced by hydrogen transfer from hydrogen donors and dechlorination/polymerization induced by electron transfer from surface defects [8]. In this paper, we will study further into these pathways as well.

2. Experimental

2.1. Chemicals

Hexachlorobenzene (HCB, purity 99%; China Medicine, Inc.) was used as a model compound to investigate the dechlorination reaction with CaO. Prior to use, CaO (purity 98%; BET surface area 7.3 m²/g; Beijing Modern Orient Fine Chemicals Co., Ltd.) was heated at 800 °C for 2 h and stored in a dryer. Hexane, toluene and anhydrous sodium sulfate were all analytical grade (purity 99%; Beijing Modern Orient Fine Chemicals Co., Ltd.).

2.2. Thermal dechlorination

The thermal dechlorination process was investigated at a HCB content of 1%. All experiments were conducted in sealed glass ampoules. HCB was dissolved in hexane at 2.5 g/L. 100 mg CaO powder and 400 μL HCB solution were added to a glass ampoule to obtain an accurate 1% HCB content. The ampoule was dried at 100 °C in a ventilating cabinet for 24 h to remove the hexane, then sealed under nitrogen atmosphere (nitrogen was used to sweep the ampoules and nitrogen flowed lightly during the sealing process). The ampoule was immersed into a salt bath that had been preheated to a specified temperature (300–400 °C), and the dechlorination experiments were performed for a chosen time. The ampoule was kept still during the reaction. After the specified reaction time, the ampoule was cooled down in air to room temperature.

SiO₂, which is inert to HCB dechlorination [8], was used in control experiments.

2.3. Product analytical methods

Using a magnetic stirrer, the sample (together with the cracked glass ampoule) was agitated in deionized water at 80 °C for 20 min. The resulting suspension was subjected to ultrasonic treatment for 20 min, then filtered through a 0.45 μm fiber filter, and the residue was extracted two more times in the same manner. To confirm dechlorination of the HCB, the filtrates were analyzed for chloride ions by ion chromatography (DX-100, DIONEX Co., USA) equipped with an IonPac AS4A-SC anion exchange column.

Another parallel sample (together with the cracked glass ampoule) was Soxhlet-extracted with 200 mL toluene for 24 h for analyses of residual HCB and degradation intermediates. The degradation intermediates were determined by a gas chromatography/mass spectrometry (Shimadzu GC/MS-QP2010 Plus, Japan) in full scan mode using a DB-5 MS capillary column (30 m × 0.25 mm × 0.25 μm). The column temperature was programmed as follows: 60 °C, 10 °C min⁻¹ to 120 °C, 4 °C min⁻¹ to 200 °C, 20 °C min⁻¹ to 280 °C, then holding for 5 min at 280 °C. The temperatures of injector and mass spectrum were both controlled at 280 °C. The qualitative analyses of possible organic products were carried out by comparing the mass spectrum patterns with standard patterns in the U.S. National Institute of Standards and Technology (NIST) mass spectral library (NIST 05 and NIST 05s).

Duplicate runs were conducted and the relative standard deviation (RSD) was <5%.

2.4. Identification of the final products

The products from the reaction of 1% HCB with CaO were below the detectable limits of some analytical methods. We therefore

Table 1
Dechlorination efficiencies of HCB dechlorination.

	Conditions	Dechlorination efficiencies (%)
Run 1	300 °C, 4 h, 1% HCB	32.3 ± 0.7
Run 2	350 °C, 0.5 h, 1% HCB	47.7 ± 1.0
Run 3	350 °C, 1 h, 1% HCB	58.8 ± 0.8
Run 4	350 °C, 4 h, 1% HCB	64.6 ± 1.3
Run 5	400 °C, 4 h, 1% HCB	90.8 ± 1.5
Run 6	350 °C, 1 h, 20% HCB	14.8 ± 0.4
Run 7	350 °C, 4 h, 20% HCB	34.7 ± 0.8
Run 8	350 °C, 16 h, 20% HCB	50.3 ± 1.1

attempted to increase the concentration of the final products, and found that 20% HCB yielded measurable results. 100 mg CaO with 20 mg HCB (weighed with an electronic balance) was added into a glass ampoule and sealed under nitrogen atmosphere. The ampoule was heated at 350 °C for 1 h, 4 h, or even as long as 16 h.

For the identification of the final products, some standard analytical methods were used. The chemical compositions of the heated samples were measured by X-ray fluorescence spectrometer (XRF, Shimadzu Lab Center XRF-1700, Japan) to confirm that the C and Cl of HCB were qualitatively maintained in the solid phase. Crystalline products were measured by X-ray powder diffraction (XRD, Rigaku D/max-r B, Japan) at the following settings: Cu Kα radiation, 40 keV accelerating voltage, 80 mA current, 10–70° 2θ scanning range, 0.02° step and 6° min⁻¹ scan speed. Raman spectra were recorded at room temperature using a microscopic confocal Raman spectrometer (Renishaw RM 2000, UK) with a He–Ne laser beam at the 632.8 nm line. The elements and species on the surface were detected by X-ray photoelectron spectroscopy (XPS, PHI-5300, Japan). A vacuum of 6.7 × 10⁻⁸ Pa was maintained during analyses. All samples analyzed were adhered on double-sided tape on a sample rod and then placed in the analysis position. The C_{1s} peak (289.6 eV) of CaCO₃ was used for the calibration of binding energies. Photoelectron lines for Cl_{2p}, Ca_{2p}, O_{1s}, and C_{1s} were acquired for all samples.

3. Results and discussion

3.1. Thermal dechlorination of HCB

Dechlorination of 1% HCB with CaO was performed at 300–400 °C for 0.5–4 h. After the reaction, chloride ions and residual HCB were measured. Dechlorination efficiencies were calculated from the measured amount of chloride ions and the amount of chlorine initially added as HCB. These results are shown in Table 1. The chloride ions increased with the reaction temperature and time, indicating that the dechlorination reaction occurred under these experimental conditions.

The levels of residual HCB after different time at 350 °C are shown in Fig. 1. The organic compounds after dechlorination, as analyzed by GC/MS, consisted only of residual HCB. There were no lower chlorinated benzenes or lower polymerized products (e.g. PCBs), which indicated that the dechlorination/hydrogenation reaction did not occur and that the ultimate fate of the carbon of HCB might be the formation of either small molecules through a ring-cracking process [9] or high-molecular-weight compounds through polymerization [8]. In the scientific references regarding PCDD/F dechlorination in MSWI fly ash, a decrease in PCDD/Fs and carbon mass imbalances of the carbon had been observed by many researchers [10–12], but the reactions underlying these have not yet been well elucidated. At this point, little is known about the fate of carbon during PCDD/F dechlorination in fly ash.

The control experiments using SiO₂ showed that a loss of about 20% of HCB could be expected, which might be due to self-degradation of HCB response to heating.

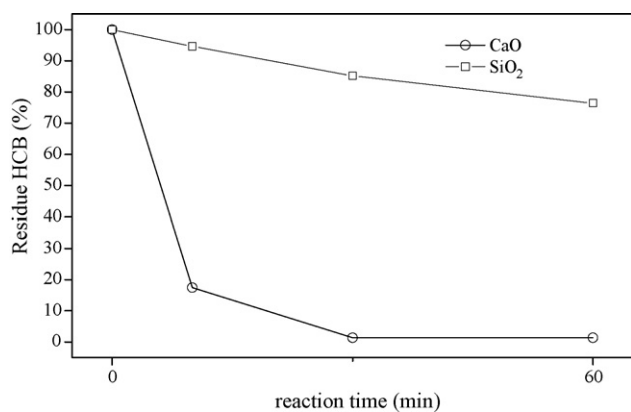


Fig. 1. The levels of residual HCB after 1% HCB reaction with CaO and SiO₂ for different time at 350 °C.

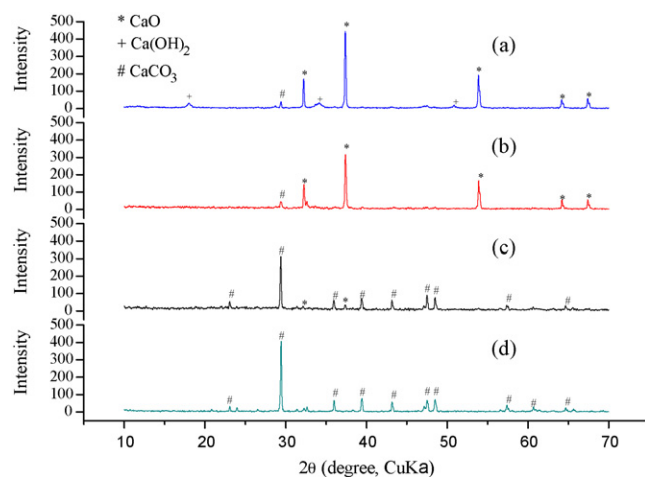


Fig. 2. XRD patterns of (a) CaO, (b) sample heated at 350 °C for 1 h, (c) sample heated at 350 °C for 4 h, and (d) sample heated at 350 °C for 16 h. The dechlorination reaction was done at 20% HCB with CaO.

3.2. Identification of the final dechlorination products

After the reaction of 20% HCB with CaO, the samples were analyzed to identify the final products. These experiments yielded following results.

3.2.1. The chemical compositions of the heated samples

The chemical compositions of the heated samples were measured by XRF. For samples treated for 1 h, 4 h and 16 h, the elemental contents of C (including both inorganic species and organic species)

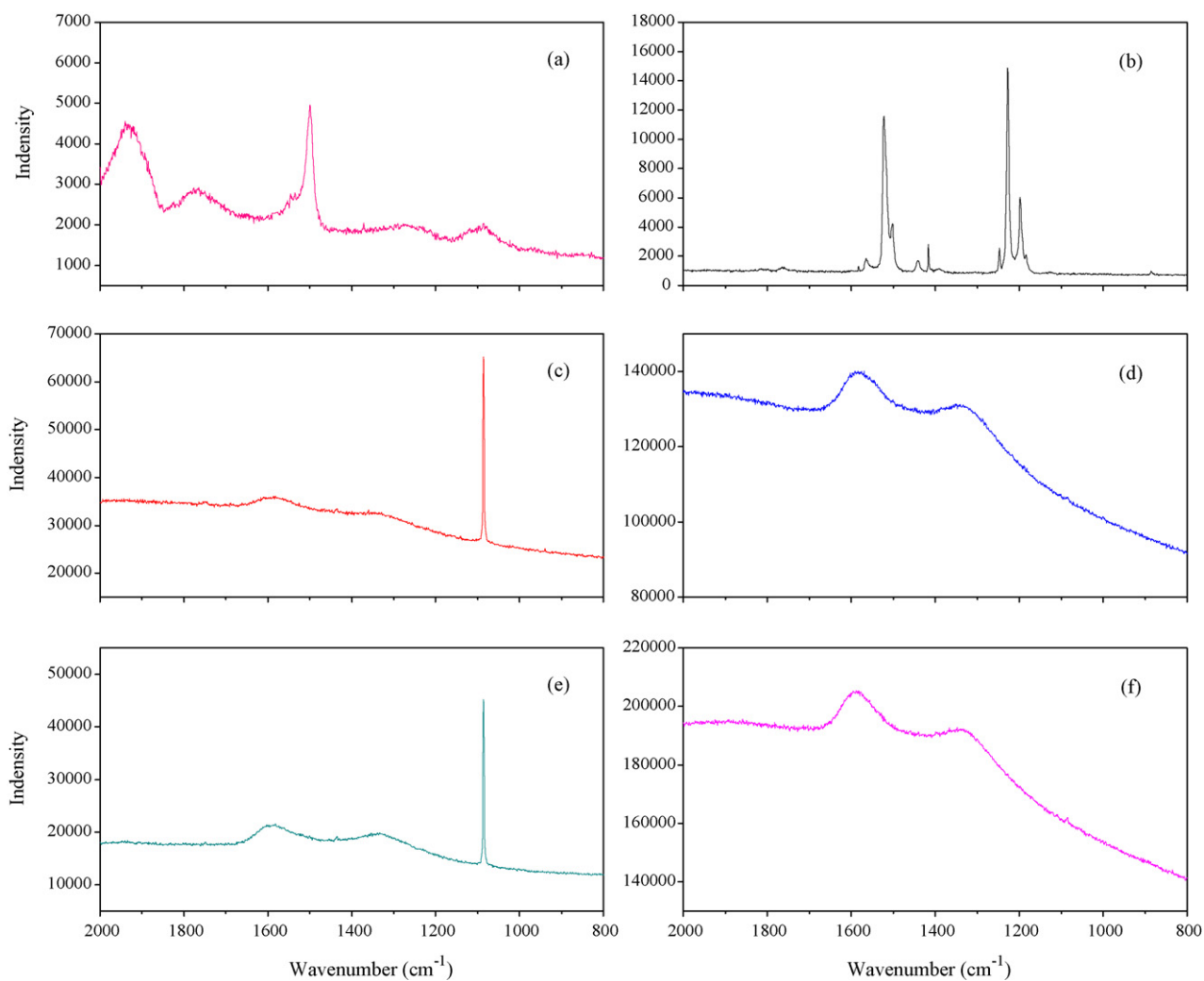


Fig. 3. Raman spectra of (a) CaO, (b) HCB, (c) white particle of sample heated at 350 °C for 4 h, (d) black particle of sample heated at 350 °C for 4 h, (e) white particle of sample heated at 350 °C for 16 h, and (f) black particle of sample heated at 350 °C for 16 h. The dechlorination reaction was done at 20% HCB with CaO.

were 4.03%, 4.49% and 5.56%, while the contents of Cl were 1.54%, 4.42% and 6.48%, respectively (the accurate chloride ion contents were listed in Table 1). The increase of C and Cl in the solid phase with the reaction time indicated that the C and Cl of HCB were qualitatively maintained in the solid phase. The increased C content was a signal that other C species were being formed. Therefore, to elucidate the fate of carbon, the species containing carbon in heated samples were of great importance.

3.2.2. XRD patterns of the heated samples

The XRD patterns of heated samples are shown in Fig. 2. As the only inorganic compound used, CaO was observed in a blank CaO sample from the XRD patterns. As well, small amounts of Ca(OH)₂ and CaCO₃ were observed, which arose due to the hydration and carbonation of the CaO with water and CO₂ in the air during the operation. With the increasing treatment time, the XRD peaks showed CaCO₃ to be the major inorganic product of the dechlorination reaction, while the peaks of CaO and Ca(OH)₂ disappeared gradually. There were no peaks related to inorganic chlorine products, which indicated that the chlorine products formed after the heating operation were amorphous species. A similar phenomenon was observed in the products from trichlorobenzene mechanochemical grinding with CaO [13]. From the XRD results, it was reasonable to conclude that the formation of CaCO₃ was related to the dechlorination reaction of HCB and CaO. In other words, the CaCO₃ was one type of newly formed species that could account for the fate of C.

3.2.3. Raman spectra of the heated samples

The Raman spectra of the heated samples are shown in Fig. 3. Compared with spectra obtained from a blank CaO sample and a blank HCB sample, two kinds of particles, white and black, were observed in the heated samples. For the white particles, the peaks at 1086 cm⁻¹ were assigned to CaCO₃ [13]. There were two specific absorption peaks at 1582 cm⁻¹ and 1335 cm⁻¹ corresponding to the typical Raman peaks of amorphous carbon [13,14] for both the white and blank particles. The 1582 cm⁻¹ peak is associated with the optically allowed E_{2g} zone center of crystalline graphite structures and involves bond-stretching motion of pairs of C-sp² atoms. The 1335 cm⁻¹ peak is a breathing mode of A_{1g} symmetry involving phonons near the K zone boundary, which becomes active in the presence of disorder in graphitic structures [15]. Both the amorphous peak at 1335 cm⁻¹ and the crystalline peak at 1582 cm⁻¹ were Raman characteristic peaks of amorphous carbon. At this point, we concluded that the white particles consisted primarily of CaCO₃ and residual CaO, while the black particles consisted mainly of amorphous carbon. In this amorphous carbon, the formation of graphitic structures was of importance for elucidating the dechlorination pathway. From the Raman spectra, it was reasonable to conclude that the amorphous carbon was a second type of newly formed species related to the fate of C.

3.2.4. XPS analyses of the heated samples

Data from XPS are shown in Table 2. The peak identification in XPS data was conducted using the NIST X-ray Photoelectron Spectroscopy Database. Further support for the presence of CaCl₂ can be inferred from the binding energies of 199.4–199.6 eV for Cl_{2p}. Since XPS only analyzes the surface, it would appear that CaCl₂ was the major solid surface component, as would be expected from the reaction of surface CaO with HCB. In the experimental conditions, the dechlorination would be a gas/solid reaction, and the products would be expected to cover the surface of the residual CaO, leading to high contents of Cl and C on the surface.

The C_{1s} XPS spectra of the samples are shown in Fig. 4. The peak at 284.6 eV was assigned to common organic pollutants in the XPS device (also observed in the spectrum of a CaO blank sam-

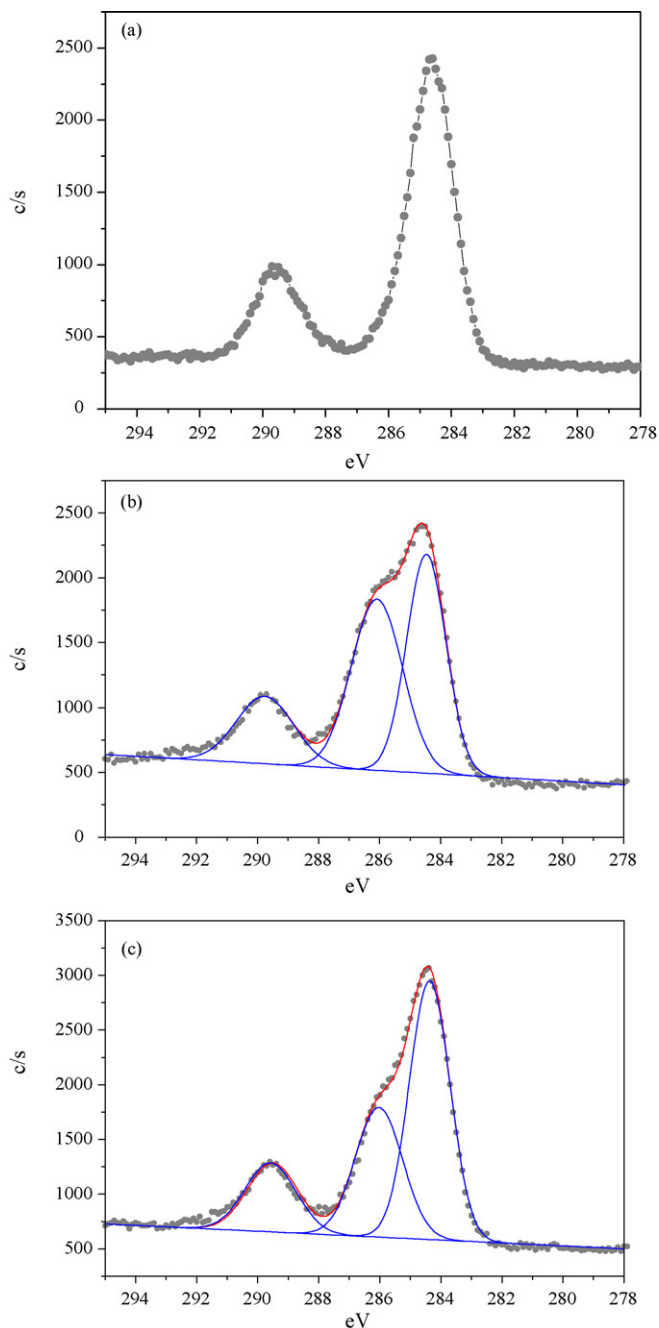


Fig. 4. The C_{1s} XPS spectra of (a) CaO, (b) sample heated at 350 °C for 4 h, and (c) sample heated at 350 °C for 16 h. The dechlorination reaction was done at 20% HCB with CaO.

ple), while the peak at 289.6 eV was due to CaCO₃, which was used for charge shift correction. For the samples heated for 4 h and 16 h, there was a new peak at 286.0 eV, which was probably due to the newly produced amorphous carbon.

3.3. Proposed reaction of HCB with CaO

Through this research, inorganic chlorine (in the form of CaCl₂), CaCO₃ and amorphous carbon were confirmed as the products of the reaction of HCB with CaO. Hence, the potential overall reaction of HCB with CaO can be written as the following:



Table 2
XPS analyses of the heated samples for 4 h and 16 h (20% HCB reaction with CaO).

Sample Region App. (%)	CaO (4 h)				CaO (16 h)			
	Ca _{2p}	Cl _{2p}	C _{1s}	O _{1s}	Ca _{2p}	Cl _{2p}	C _{1s}	O _{1s}
	6.94	11.65	56.97	24.45	8.04	11.63	57.31	23.01

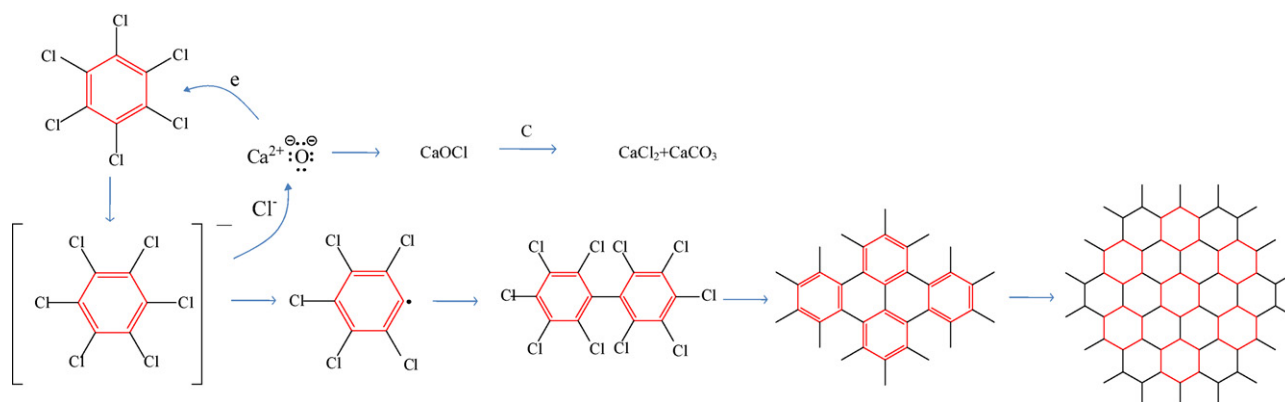


Fig. 5. The dechlorination/polymerization pathway of HCB reaction with CaO at 300–400 °C.

The standard formation enthalpies of HCB, CaO, CaCO₃, CaCl₂, and C are –33.89 kJ/mol, –635.1 kJ/mol, –1206.9 kJ/mol, –795 kJ/mol, and 0 kJ/mol [16], respectively. The standard reaction enthalpy could be easily calculated as –2607 kJ/mol. The thermodynamics of the reaction between HCB and CaO were energetically quite favorable. However, since the reaction of HCB with CaO did not occur at room temperature, and was only observed when the temperature was increased to 300–400 °C, this reaction apparently had high activation energy.

Since amorphous carbon with graphitic structures was produced, it is reasonable to conclude that the reaction of HCB with CaO was through a dechlorination/polymerization pathway, as shown in Fig. 5. As described elsewhere [8], this pathway was induced by electron transfer. It is known that metallic ions and O²⁻ on the surfaces of the crystal are unsaturated, and that these form free electrons in the vacancies. The parent chlorinated molecular obtained an electron from the surfaces and formed an anion. This was followed by the dissociation of a chloride ion, which formed a radical. These radicals could then in turn form high-molecular-weight compounds through polymerization, leading to some non-extractable compounds which had not been thus detected by the analytical procedure applied, which was the major reason for the differences in dechlorination efficiencies calculated by chloride ions and residual HCB (e.g., 64.62% and 99.6%, respectively, for 1% HCB reacting with CaO at 350 °C for 4 h).

As HCB is similar to other UPOPs in its characteristic C–Cl bonds, the results from this study are helpful in explaining the dechlorination reaction that occurs during the PCDD/F dechlorination in oxygen deficient conditions at 300–400 °C in CaO rich matrices (e.g. MSWI fly ash). The dechlorination/polymerization pathway might be a major reaction in PCDD/F dechlorination; therefore, knowledge of this reaction is beneficial for clarifying PCDD/F conversion and mass imbalances. The adiabatic electron affinities of PCDD/Fs were important in the formation of radicals. Calculation of adiabatic electron affinities for 15 PCDFs indicated that all values were positive and that the chloride ion dissociation from anions to form radicals was the major pathway for chlorine abstraction [17]. Hence, the dechlorination/polymerization pathway and the production of high-molecular-weight compounds, even carbon materials, can readily explain the mass imbalances observed by previous researchers [10–12].

The dechlorination/polymerization pathway of PCDD/Fs is very favorable for the detoxification of PCDD/Fs because the polymerized products are nontoxic. In the technology that uses hydrogen or other organic hydrogen donors to induce dechlorination/hydrogenation reaction, it is possible that more toxic products might be formed. The dechlorination of OCDD with Pd/C catalysts in ethanol–water solution under mild conditions was investigated, and the results showed that the TEQ of the products increased to 3.68 ng/g, 3.05 ng/g, and 1.05 ng/g for the treatment at 30 °C, 50 °C, and 80 °C, respectively, while the TEQ of the original material was 1.00 ng/g (initial OCDD concentration was 1 ppm) [18]. Therefore, the technology related to dechlorination/polymerization pathway appears to be more promising for eliminating PCDD/F contaminated hazardous waste (especially in CaO rich matrices) in commercialized applications than that related to dechlorination/hydrogenation pathway.

4. Conclusion

This study elucidated the reaction mechanism and the ultimate fate of HCB after its reaction with CaO at 300–400 °C under nitrogen atmosphere. The dechlorination of HCB with CaO occurred, leading to the formation of chloride ions and a decrease in residual HCB. The final products identified were CaCO₃, CaCl₂ and amorphous carbon. The formation of amorphous carbon with graphitic structures indicated that the dechlorination reaction was occurring through a dechlorination/polymerization pathway. The formation of these products also explained previously observed mass imbalances. Based on these results, dechlorination/polymerization was proposed to be a major reaction of low-temperature PCDD/F dechlorination in CaO rich matrices.

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