

Synergic effect of calcium oxide and iron (III) oxide on the dechlorination of hexachlorobenzene

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Abstract

Dechlorination of hexachlorobenzene (HCB) was achieved by a mixture of commercial CaO and α -Fe₂O₃ (CaO/ α -Fe₂O₃) in closed systems at temperatures of 300 °C and 350 °C, which exhibited a synergic effect compared to CaO or α -Fe₂O₃ alone, and the dechlorination efficiency was dramatically enhanced. When CaO and α -Fe₂O₃ coexisted, HCB was dechlorinated by about 98% after 0.5 h reaction at 300 °C. All TeCB-, TrCB-, and DCB-isomers were detected, showing the presence of more than one dechlorination pathway. The pathway to form 1,2,4-TrCB must be a major pathway because the greatest amount of 1,2,4-TrCB was detected. There existed discrepancy of the material balance between the starting and dechlorinated materials. It implies that besides dechlorination other decomposition processes may be present. The mechanism of synergic effect of calcium and iron oxides was investigated.

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1. Introduction

It is well known that halogenated organic compounds have been used on a large scale in the chemical, petrochemical, and electronic industries. Due to leak and release from industrial sources, they inevitably contaminate environments such as soil and groundwater. The disposal of organic wastes containing halogen has become a major environmental and social problem, because most of them are toxic and very stable, accumulating in the surrounding for long periods. Polychlorinated

aromatic compounds are environmentally persistent chemicals, recalcitrant toward degradation, which bioaccumulate in fatty tissue and show carcinogenic and mutagenic activity, so they are a class of pollutants of special environmental concern (Alonso et al., 2002).

The most extensively used method to destroy unwanted chlorocarbons is by incineration (Lee and Huffman, 1989; Hawnrl et al., 1992). Toxic chlorinated compounds appear to be completely destroyed by high-temperature thermal oxidation; however, it is related to the release of even more toxic compounds such as chlorinated dioxins and furans. The development of a highly efficient, safe alternative technology for detoxifying organic halides has been anticipated.

Reductive methods can be considered as alternatives to be taken into account prior to their safe but

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controversial incineration. Electrochemical (Wirtz et al., 2000; Atsushi and Akio, 2003), photochemical (Betterton et al., 2000; Hu et al., 2000), ultrasonic (Hung and Hoffmann, 1998; Lin and Ma, 1999), microbial (Chang et al., 1998), radiolytic and thermal (Yamamoto and Tagawa, 2001) reductive methods have been reported. The chemical reduction of organic halides involving the replacement of halogen by hydrogen is the so-called hydrogenolysis of the carbon–halogen bond or hydrodehalogenation reaction, which is known to be promoted by noble metals of group VIII. Literature data have shown that successful dechlorination of polychlorinated aromatic compounds by using Ni catalysis requires severe reaction conditions, high temperature and high hydrogen pressure. Pd, Ru catalysis permitting successful dechlorination of polychlorinated aromatic compounds under mild conditions is not adapted to large-scale applications because of their high cost (Hagh and Allen, 1990).

In related work, some methods have been reported in regard to metal oxide method. Representative ones include the following: oxidative catalysis over metal oxides and noble metals, for example, catalytic decomposition of hydrochlorocarbons over high surface area γ -alumina (Ballinger et al., 1992). Iron (III) oxide as a destructive reagent was used to decompose carbon tetrachloride (Hooker and Klabunde, 1994) and PCDD/F (Weber et al., 2002).

Previous studies have revealed that the presence of CaO allows the destruction of chlorinated benzenes at lower temperatures than simple pyrolysis or combustion processes (Li et al., 1994). While, even CaO particles with very large surface areas was employed, the reaction temperature was still higher than 500 °C in the H₂ atmosphere for decomposing completely. If in the air, the temperature was even greater.

An additional promising method that at relatively low temperatures (400–500 °C) converts halocarbons to CO_x and calcium halides in one step was reported. The process is based on X⁻/O²⁻ exchange on the surface of CaO (or MgO or Fe₂O₃). Thus, oxidizing conditions are not needed. Since the process is based on a surface solid–gas reaction, large surface areas and intrinsic reactivities are beneficial. Ultrafine (nanoscale) particles of CaO has been synthesized and studied for destruction of chlorocarbons (Koper and Klabunde, 1993; Koper

et al., 1997). In the temperature range of 300–500 °C, solid nanocrystalline oxides react nearly stoichiometrically with numerous halocarbons. By the presence of a small amount of transition-metal oxide as catalyst, for example, Fe₂O₃ on CaO, the reaction efficiencies can be improved. However the cost of preparation of nanocrystalline oxides is high and synthetic method is complicated. Few studies on polychlorinated aromatic compounds were conducted.

The purpose of this study was to present investigation on the synergic effect of commercial CaO and α -Fe₂O₃ on the dechlorination of hexachlorobenzene which was taken as a model compound of polychlorinated aromatic hydrocarbons, and to investigate a predominant dechlorination pathway. The mechanism of synergic effect of calcium and iron oxides was discussed.

2. Experimental

2.1. Materials

Hexachlorobenzene, hexane, CaO and α -Fe₂O₃ were all analytical grade. CaO was ground to ~300 mesh, and heated at 900 °C for 2 h. α -Fe₂O₃ was ~300 mesh, and was heated at 120 °C for 2 h.

2.2. Dechlorination of HCB

2.0 mg of HCB was added to 200 mg CaO/Fe₂O₃, or 200 mg CaO and 200 mg Fe₂O₃, respectively. The mixture was transferred into a small glass tube (11 cm length, 0.4 cm i.d.), which was then sealed under air atmosphere and was heated in an oven. Dechlorination experiments were performed at 300 °C or 350 °C. Details of reaction conditions were shown in Table 1.

2.3. Sample analysis

After finishing the dechlorination reaction, the glass tubes were cooled to the room temperature, wrapped by aluminum foil, and then they were carefully crushed and subjected to extraction. The samples were extracted with 15 ml hexane twice for 15–20 min each time in an ultrasonic extractor. The solutions were transferred into a separatory funnel and then each solution was washed

Table 1
Reaction conditions for dechlorination of HCB

	Run 1	Run 2	Run 3	Run 4	Run 5
Amount of HCB (mg)	2	2	2	2	2
Amount of CaO (mg)	200	0	100	100	100
Amount of Fe ₂ O ₃ (mg)	0	200	100	100	100
Reaction temperature (°C)	300	300	300	300	350
Period of heating (h)	1	1	0.5	1	1

three times with 15 ml of water. The hexane layers were dried with anhydrous sodium sulfate. The solution was used for the measurement of parent HCB remaining and lower chlorinated benzenes newly formed. The analyses of chlorobenzenes were performed by an Agilent 6890 gas chromatograph equipped with a DB-5 capillary column (30 m length, 0.25 mm i.d., 0.25 μ m film thickness) and interfaced to Agilent 5973N MSD. Quantitative analyses of chlorobenzenes were performed in selected ion monitoring mode using two most abundant ions of the molecular ion clusters.

3. Results and discussion

3.1. Yield of dechlorination

The dechlorination efficiency (DE, %) was calculated using Eq. (1).

$$DE = 1 - \frac{\sum_{i=0}^6 iN_i}{6N_0} \quad (1)$$

where N_i is the molar number of chlorinated benzene containing i chlorine atoms in the molecule and N_0 is the initial molar number of HCB. The results were demonstrated in Fig. 1. The intermediates formed in the experiments were given in Table 2.

3.2. Dechlorination of HCB by CaO

It could be seen from Table 2 that HCB was partially dechlorinated by CaO (Run 1). After 1 h reaction, the dechlorination efficiency was up to 52%, while the only intermediate was trace amounts of pentachlorobenzene, and no lower chlorinated benzenes were detected. This means that besides dechlorination, other degradation

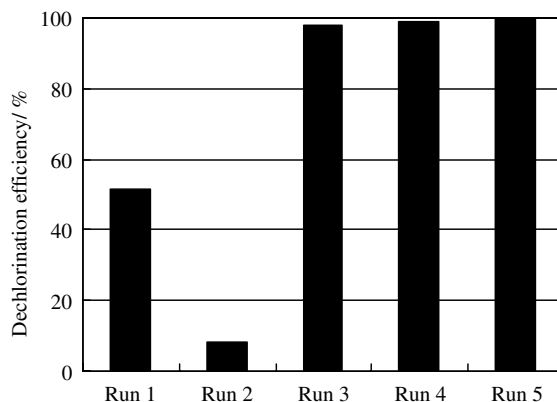


Fig. 1. Dechlorination efficiency in the different experiments.

processes may be present. Similar conclusion was also drawn by Li et al. (1994).

3.3. Dechlorination of HCB by α -Fe₂O₃

α -Fe₂O₃ has been used as a destructive reagent for chlorinated organic compounds (Hooker and Klubunde, 1994). The reaction was carried out between 400 and 620 °C. The higher activity of α -Fe₂O₃ than other metal oxides was found, this can be attributed to the formation of Fe₂Cl₆, a dominant vapor species in the vaporization of solid FeCl₃. The formation and migration of FeCl₃ out of the hot zone are rather rapidly since solid FeCl₃ is known to decompose at about 315 °C. In the case of Run 2, due to the reaction temperature was lower (300 °C), the dechlorination pathway became less efficient. Dechlorination efficiency was just about 8.4%. A tentative explanation is that the surface of the Fe₂O₃ be-

Table 2

Comparison of the amount of formed products in the dechlorination of HCB^a (nmol)

Chlorobenzenes	Run 1	Run 2	Run 3	Run 4	Run 5
1,3-DCB	ND ¹	ND ¹	4.9	ND ¹	ND ¹
1,4-DCB	ND ¹	ND ¹	4.8	ND ¹	ND ¹
1,2-DCB	ND ¹	ND ¹	4.5	ND ¹	ND ¹
1,2,4-TrCB	ND ²	ND ²	33	74	ND ²
1,3,5-TrCB	ND ²	ND ²	6.2	18	ND ²
1,2,3-TrCB	ND ²	ND ²	4.4	6.6	ND ²
1,2,4,5-TeCB	ND ³	ND ³	17	8.5	ND ³
1,2,3,5-TeCB	ND ³	ND ³	16	9.4	ND ³
1,2,3,4-TeCB	ND ³	ND ³	9.2	3.3	ND ³
PeCB	48	ND ⁴	49	6.8	ND ⁴
\sum DPs ^b	48	–	149	127	–
HCB	3724	6431	54	1.8	ND ⁴

ND¹ < 0.8 nmol; ND² < 0.3 nmol; ND³ < 0.2 nmol; ND⁴ < 0.1 nmol.

^a Initial amount of HCB was 7023 nmol.

^b \sum DPs = sum of dechlorination products.

came covered with chloride ions which inhibited further dechlorination. Comparing the dechlorination efficiency in Run 1 and Run 2, the conclusion can be drawn that at lower temperature, CaO is a better dechlorination agent than α -Fe₂O₃.

The difference of dechlorination capacity between CaO and α -Fe₂O₃ could be resulted from the difference of alkalinity. The higher the alkalinity, the higher the dechlorination capacity is.

3.4. Synergic effect of CaO/ α -Fe₂O₃ on the dechlorination of HCB

From the analytical results of intermediate chlorobenzenes in Run 3, it was found that the dechlorination capacity increased greatly when CaO and α -Fe₂O₃ coexisted. The residual amount of HCB was only 54 nmol,

much less than the original 7023 nmol. Dechlorination efficiency was about 98%. Comparing the data in Run 3, Run 4, and Run 5, one can observe that the dechlorination was greater with increasing reaction time or temperature. At 300 °C for 1 h, the dechlorination extent was up to 99%, and 100% at 350 °C for 1 h.

CaO and α -Fe₂O₃ exhibits a remarkable synergic effect on the dechlorination of HCB. Decreasing orders of chlorobenzenes by amount were 1,2,4,5- \approx 1,2,3,5- > 1,2,3,4- for tetrachlorobenzenes (TeCB); 1,2,4- > 1,3,5- > 1,2,3- for trichlorobenzenes (TrCB); the amount of 1,3-, 1,4-, 1,2-dichlorobenzene (DCB) were almost the same. The pathway to form 1,2,4-TrCB must be a major pathway because the greatest amount of 1,2,4-TrCB was detected. All TeCB-, TrCB-, and DCB-isomers were detected, showing the presence of more than one dechlorination pathway.

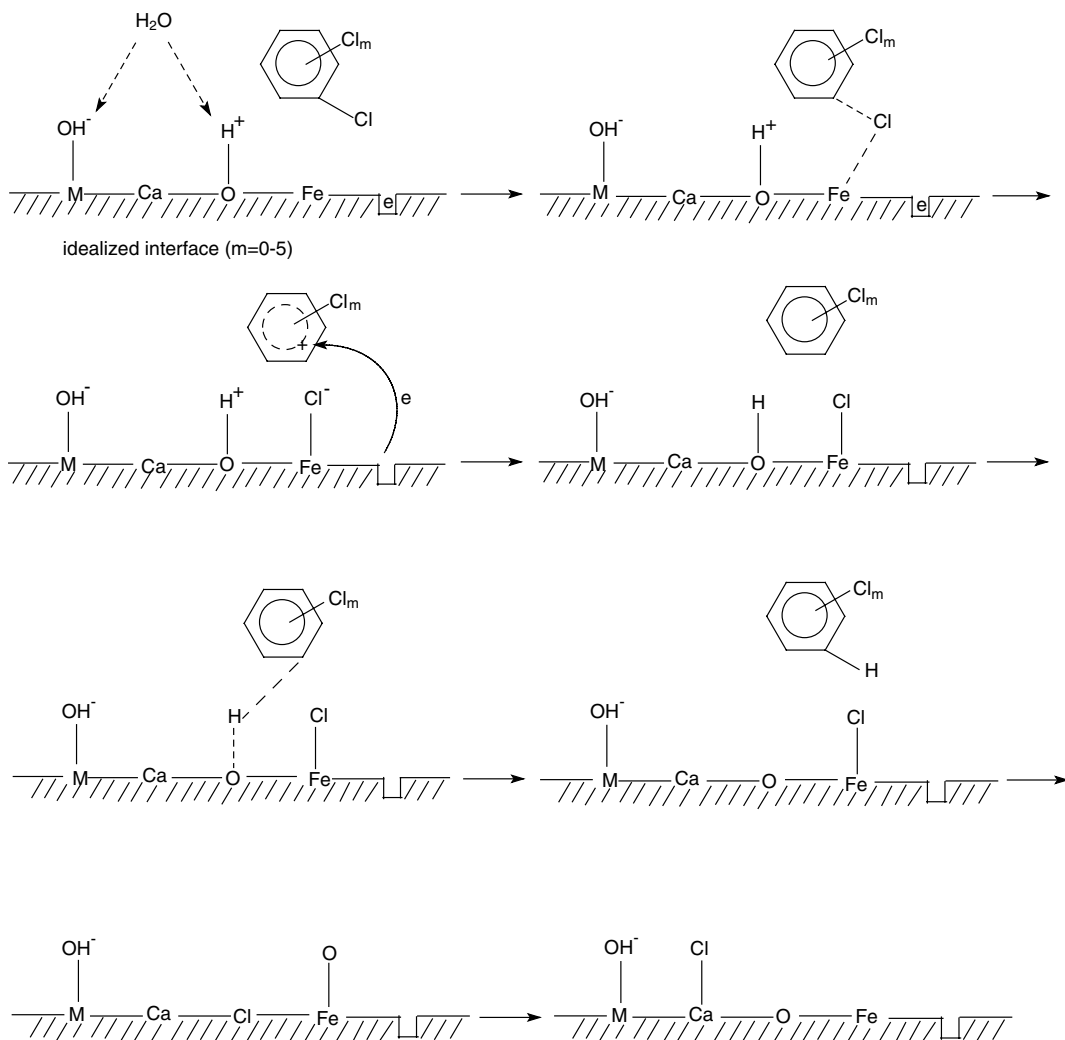


Fig. 2. A proposed mechanism for the dechlorination of HCB over the solid surface of CaO/ α -Fe₂O₃.

When HCB was dechlorinated by CaO/ α -Fe₂O₃, there existed discrepancy in the material balance of the starting and dechlorinated materials. This implies besides dechlorination other decomposition processes may be present. Similar conclusion was also made by Schoonenboom et al. (1995).

Previous studies have revealed that CaO could improve the decomposition of chlorinated hydrocarbons over iron oxide catalysis (Jiang et al., 1998; Decker et al., 2002). This effect is attributed to ion exchange between the CaO and FeCl₃, the latter being formed as a result of interaction of iron oxide with chlorinated hydrocarbons. In that case, calcium serves as a sink for chlorine ions, regenerating iron oxide. For efficient chloride ion exchange between iron and calcium in an interfacial process, good contact between the phases is necessary. The systems discussed in the previous paper (Decker et al., 2002) were composed of transition-metal oxides (Fe, Ni) supported on CaO with intimate contact. In the case of this study, due to the mean particle is relatively larger (50 μ m), the surface area is smaller, so the content of oxides used is excessive in order to ensure interface between iron oxide and calcium oxide.

It is known that metallic ions and O²⁻ on the surfaces of metal oxides are unsaturated according to the coordination theory. They are prone to bond with some functional groups that are absorbed as ligands. For Fe₂O₃ belongs to N type semiconductor, some electrons exist in the vacancies that are from defection of surface O²⁻. Water absorbed is dissociated to produce OH⁻ and H⁺, and they bond with metallic ions and O²⁻, respectively.

On the basis of these established theories, a possible mechanism for the dechlorination of HCB with CaO/ α -Fe₂O₃ is illustrated (Fig. 2). An idealized interface of CaO/ α -Fe₂O₃ is given. It is reasonable to assume a synergic effect of calcium and iron oxides. We speculate that unsaturated iron ions at the surface serve as an initial adsorption sites for HCB, which leads to the breakage of C–Cl bond. Chlorine ions on the iron surface as well as carbonium ions were produced simultaneously. At the next step, electrons from the vacancies of iron oxide are transferred to benzene ring to cause the displacement of H⁺ from the linkage with ligand O²⁻, to form PeCB. The newly formed chloride ion can then migrate over the surface of the particle to perform Cl⁻/O²⁻ exchange. Calcium serves as a sink for chlorine ion in the process of dechlorination. The displacement of chlorine is repeated, until all chloride atoms are converted.

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