Thermal dechlorination of PCB-209 over Ca species-doped Fe₂O₃

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HIGHLIGHTS

- 1% mol Ca species enhanced the activity of Fe₂O₃ in the degradation of DecaCB.
- Dominant Nona-MonoCB isomers were determined during hydrodechlorination reaction.
- Thermodynamic and/or steric effects drive conversion.
- Steric effect prevented the hydrodechlorination at ortho-positions.

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ABSTRACT

Degradation reaction of decachlorobiphenyl (PCB-209) was investigated over the synthesized Ca species-doped Fe₂O₃ at 300 °C. The 1%Ca-Fe₂O₃ exhibited the highest activity among the four catalysts prepared with the pseudo-first order reaction at $k_{obs} = 0.103 \text{ min}^{-1}$. PCB-207, PCB-197, PCB-176, PCB-184, PCB-150, PCB-136, PCB-148, PCB-104, PCB-96, PCB-54, PCB-19, PCB-4 and PCB-1 were identified as the dominant isomers in their respective nonachlorobiphenyl (NonaCB) to monochlorobiphenyl (MonoCB) homologue groups. Analysis of the hydrodechlorination products indicated that dechlorination was much more favored on *meta*- and *para*-than on *ortho*-positions. The formation of significantly predominant NonaCB and octachlorobiphenyl (OctaCB) isomers was attributed to lower energy principles and to the 90° dihedral angles of two aromatic rings which prevented the hydrodechlorination at *ortho*-positions. When the number of chlorine atoms is not more than 7, the steric effect supports the formation of predominant PCB isomers having chlorines at four *ortho*-positions. During the dechlorination of tetrachlorobiphenyl (TetraCB) formed to generate monochlorobiphenyl (MonoCB) isomers, the chlorine atoms fully substituted at the *ortho*-positions have to be successively removed, with the first two dechlorinations preferentially occurring at the two different benzene rings. This is dissimilar to that of octachloronaphthalene (PCN-75) in which the hydrodechlorination reaction happened preferentially at *ortho*-position due to the existence of steric effects. The opposite roles of the steric effect in *ortho*-position between PCB-209 and PCN-75 might be due to the difference of the π -conjugated plane caused by the dihedral angle of 90° and 0° of the two aromatic rings.

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1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants that have 209 possible compounds, featuring 1–10 chlorine atoms. PCBs were proposed for inclusion into Annex A and C of the Stockholm Convention (SC) on POPs (The 12 initial POPs under the Stockholm Convention), which are extremely harmful to human health and the environment because of their high toxic-

ity and bioaccumulation through the food web. They have been widely used as dielectric fluids in electrical transformers and capacitors, plasticizers in paints, and dye carriers in carbonless copy paper (Abramowicz, 1990). Although the production of PCBs has been banned since the mid-1970s, large amounts of PCBs have been released into the environment because of their historically widespread use. According to the estimation in 2008, the global quantity of PCBs amounted to 2.9 million tonnes (The PCBs elimination network: the information exchange platform created for the risk reduction of polychlorinated biphenyls). Once released into the environment, those PCBs can be transported and distributed on a global scale by the global fractionation and grasshopper effect (Wania, 2003; Gouin et al., 2004). The reducing of PCBs is

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therefore a matter of public concern in the context of environmental protection.

According to Annex A part II of the Stockholm Convention, Parties to the Convention are obliged to eliminate PCBs wastes from use by 2025 and bring these under environmentally sound waste management by 2028 (PCBs Elimination Network). High-temperature incineration is currently the principal method of PCBs destruction (Lee and Huffman, 1989). However, there are considerable problems, including the high cost and the possible generation of more toxic polychlorinated dibenzodioxins/polychlorinated dibenzofurans during incineration (Addink and Olie, 1995). Catalytic degradation at lower temperature involving metal oxides as a safe alternative technology is thought as the most promising method, due to its relatively low costs, high levels of activity (Subbanna et al., 1988; Tanaka et al., 2005; Huang et al., 2013). Numerous metal oxides exhibited high activity in the decomposition of PCBs, including Cr_2O_3 , Co_3O_4 , CuO , Al_2O_3 , La_2O_3 (Subbanna et al., 1988; Tanaka et al., 2005). Subbanna et al. (1988) reported that the activity of 10% CuO supported on $\alpha\text{-Al}_2\text{O}_3$ in the decomposition of Aroclor 1254 was better than those of supported 4% Cr_2O_3 and 6% Co_3O_4 , with a destruction efficiency of 97.3%. However, most of these metal oxides are expensive or difficult to obtain, and their applications in catalytic degradation of PCBs are limited.

CaO and Fe_2O_3 as facile resource on the earth, their activities on the destruction of chlorinated organic compounds have been examined (Hooker and Klabunde, 1994; Li et al., 1994; Koper et al., 1997; Jia et al., 2011). Li et al. (1994) reported that the presence of CaO allowed the destruction of chlorinated benzenes at lower temperatures than those needed in simple pyrolysis or combustion processes. Jia et al. (2011) synthesized flower-like $\alpha\text{-Fe}_2\text{O}_3$ with relatively high activity in the destruction of hexachlorobenzene (HCBz). Further studies have shown that the reaction efficiencies can be significantly improved by the presence of Ca and Fe composite oxides because of their synergic effects (Jiang et al., 1998; Decker et al., 2002; Ma et al., 2005b). Decker et al. (2002) found that the presence of a small amount of Fe_2O_3 on CaO improved the reaction efficiency. Ma et al. (2005a, 2005b) reported that both physical mixture of $\alpha\text{-Fe}_2\text{O}_3$ and CaO and Ca-Fe composite oxides prepared by coprecipitation had synergic effects on HCBz decomposition. However, to the best of our knowledge, no studies on the activities of Ca-Fe composite oxides with different Ca doping amount in the decomposition of PCBs have been reported. Furthermore, the driving force during hydrodechlorination of PCBs over metal oxides was rarely discussed.

In the present work, Ca species-doped Fe_2O_3 samples with different Ca/Fe molar ratios were prepared and characterized. The activities of the materials were investigated based on their degradation efficiencies toward PCB-209, with fully chlorine-substituted compound as a model PCB. The kinetics of the degradation of PCB-209 over Fe_2O_3 doped with 1 mol% Ca was studied. Series of hydrodechlorination products were identified using gas chromatograph-mass spectrometry. The driving force of PCB hydrodechlorination reaction during different steps was discussed on the basis of the isomer distribution pattern in combination with thermodynamic data and steric effect. The results generated in the present study were compared with those obtained from PCN-75 degradation reported in our previous work under similar reaction conditions (Su et al., 2014).

2. Material and methods

2.1. Materials

All chemicals, including $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, urea, and polyethylene glycol (PEG) 10000 were analytic grade and pur-

chased from Beijing Chemical Co. (Beijing, China), and used without further purification. PCB-209 was purchased from Dr. Ehrenstorfer GmbH, Germany. Hexane of pesticide grade was purchased from Dikma Technologies Inc.

2.2. Preparation of $\alpha\text{-Fe}_2\text{O}_3$ and Ca species-doped Fe_2O_3 with different Ca/Fe molar ratios

Iron oxide was synthesized by an ethylene glycol-mediated reaction using a previously reported method (Zhong et al., 2006; Jia et al., 2011). In a typical procedure, 1.9 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.7 g urea, and 1.5 g PEG 10000 were added to 180 mL ethylene glycol. The mixture was magnetically stirred and refluxed at 230 °C for 30 min, and then cooled to room temperature. The precipitated precursor was centrifuged and washed three times with ethanol, then dried in an oven at 105 °C overnight. $\alpha\text{-Fe}_2\text{O}_3$ was obtained by calcination of the above precursor at 350 °C in tube furnace under air atmosphere.

Ca species-doped Fe_2O_3 with different Ca/Fe molar ratios was prepared by impregnating the above iron oxide precursor with $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. A known amount of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in ethanol, then the iron oxide precursor was added with Ca/Fe molar ratios of 1:99, 5:95, and 50:50. The mixture was mixed with ultrasonic wave, and then dried in an oven. The dried precursor was calcined at 350 °C for 3 h in air, giving Ca species-doped Fe_2O_3 . The Ca species-doped Fe_2O_3 samples with Ca/Fe molar ratios of 1:99, 5:95, and 50:50 were denoted by 1% $\text{Ca-Fe}_2\text{O}_3$, 5% $\text{Ca-Fe}_2\text{O}_3$, and 50% $\text{Ca-Fe}_2\text{O}_3$, respectively.

2.3. Characterization of Ca species-doped Fe_2O_3

The materials were characterized using scanning electron microscopy (Hitachi S-3000N), thermogravimetric analysis and differential scanning calorimetry (TGA-DSC, microcomputer differential thermal balance, Hengjiu, Beijing, China). TGA/DSC experiments were performed between ambient temperature and 800 °C, with a heating rate of 20 °C min^{-1} in an air flow. The surface area and pore characterization of the materials were obtained from N_2 adsorption/desorption analysis at -196 °C using a Quantachrome Quadrasorb SI-MP. XRD patterns of the samples were obtained with a Rigaku D/max 2500 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056$ nm, 40 kV, 200 mA).

2.4. Activity measurements

The reaction activities of the prepared metal oxides were tested in sealed glass ampoules. Prior to the reaction, 0.4 mL of a hexane solution of PCB-209 (0.4 mg PCB-209) were injected into an ampoule, evaporated to dryness at room temperature, and then mixed with 50 mg $\alpha\text{-Fe}_2\text{O}_3$ or Ca species-doped Fe_2O_3 . The ampoule was sealed in the atmosphere and heated at 300 °C for 10–60 min. The sealed ampoule was then cooled to room temperature, crushed and extracted with hexane under ultrasonic condition for product analysis and reaction activity evaluation. All experiments were performed in triplicate to ensure the repeatability of the results, and the average values were used. The relative standard deviations of all experimental data were lower than 8%.

2.5. Product analysis

The samples were extracted with hexane and dehydrated using anhydrous sodium sulfate. The extract was then analyzed for unreacted PCB-209 and newly formed PCBs, using an Agilent 6890 gas chromatograph equipped with a DB-5MS capillary column (30 m $\times$ 0.25 mm i.d., 0.25 μm film thickness), coupled with an Agilent 5973N mass selective detector. Helium carrier gas

was used during gas chromatography ($\geq 99.999\%$) at a flow rate of 1 mL min^{-1} . In each run, a $1.0\text{-}\mu\text{L}$ aliquot of the diluted sample was injected in the splitless mode. The injector was set at 280°C while the column temperature was initially held at 50°C for 5 min, gradually increased to 80°C at 3°C min^{-1} , then to 180°C at 5°C min^{-1} and finally to 280°C at 8°C min^{-1} . The qualitative and quantitative determinations of PCBs were conducted according to EPA method 1668B. Qualitative determinations of produced PCBs were based on the m/z data, the retention times of $^{13}\text{C}_{12}$ -labeled PCBs standards and the relative retention time intervals between adjacent congeners. Quantitative determinations were performed in the selected ion monitoring mode, using two most abundant ions of the molecular ion clusters combined with those of the corresponding or adjacent $^{13}\text{C}_{12}$ -labeled PCB standards.

3. Results and discussion

3.1. Characterizations of Ca species-doped Fe_2O_3

The thermal behaviors of the Ca species-doped Fe_2O_3 precursors were studied using TGA/DSC (Fig. 1). The 1%Ca- Fe_2O_3 and 5%Ca- Fe_2O_3 samples exhibited two weight loss steps. The first step, up to 200°C , was caused by removal of physisorbed water, crystal water in $\text{Ca}(\text{NO}_3)_2$ hydrates, and residual solvent in the pores (Zhou et al., 2012), and the weight loss was about 3%. The second step, between 200 and 350°C , corresponded to the removal of nitrate groups and the decomposition of iron alkoxides (Larcher et al., 2003). In contrast, for the 50%Ca- Fe_2O_3 sample, there were three weight loss steps. The significant weight loss before 100°C was mainly the results of the removal of crystal water in hydrates and physisorbed water, with a weight loss of about 17%. The second step, between 100 and 200°C , was assigned to the further removal of crystal water and evaporation of residual solvent in the pores, with a weight loss of about 3%. The significant weight loss in the temperature range $200\text{--}350^\circ\text{C}$ could be attributed to the removal of nitrate groups and the decomposition of iron alkoxides, with a weight loss of about 71% (Larcher et al., 2003). Since the precursor's weight did not decrease greatly above 350°C , the Ca species-doped Fe_2O_3 was obtained by precursor calcination at 350°C in air. Two distinct regions, corresponding to the weight loss steps in the TGA curves, were observed in the DSC profiles in the temperature range $25\text{--}350^\circ\text{C}$ (Fig. 1b). The first region, up to 200°C , was characteristic of an endothermic peak which was only observed in 50%Ca-doped Fe_2O_3 precursor, and confirmed the removal of physisorbed and crystal water from the precursors (Zhou et al., 2012). The second region, ranging from 200 to 350°C , included prominent exothermic peaks, indicating

the formation of Ca species-doped Fe_2O_3 (Lu et al., 2008; Zhou et al., 2012). The exothermic peak in 50%Ca-doped Fe_2O_3 precursor was obviously lower than those in the other two samples. Since the Fe_2O_3 precursor was confirmed to be iron alkoxide in previous work (Zhong et al., 2006), its decomposition during the thermogravimetry process was exothermic. However, the decomposition of $\text{Ca}(\text{NO}_3)_2$ was an endothermic process. The higher percentage of $\text{Ca}(\text{NO}_3)_2$ in 50%Ca-doped Fe_2O_3 precursor led to the significant decrease of exothermic peak.

The morphologies of the synthesized Ca species-doped Fe_2O_3 as compared to that of $\alpha\text{-Fe}_2\text{O}_3$ samples are shown in Fig. 2. As previously reported, the synthesized $\alpha\text{-Fe}_2\text{O}_3$ consisted of many uniform, flower-like structures of diameter $1.0\text{--}1.5 \mu\text{m}$ (Fig. 2a), and the flower-like architecture was built up from many nanopetals (Jia et al., 2011). After little addition of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ to the Fe_2O_3 precursor and calcination at 350°C , the morphology of the material was not changed obviously (Fig. 2b). The formed Ca-contained compounds dispersed well on the surface of Fe_2O_3 , due to the impregnation during the preparation process of ultrasonic treatment. It was reported that ultrasound made sample thin and resistant to reunion due to the propagation of ultrasonic wave through liquid media and the collapse of cavitation bubbles (Zhu et al., 2007). When the Ca molar ratio increased to 5%, the material surface turned into vague (Fig. 2c). When the molar ratio of Ca was further increased to 50%, the petals completely disappeared (Fig. 2d), and were replaced by smooth surface. The material on the surface covering the gaps between the petals might be a newly formed Ca-containing composite metal oxide.

As shown in Fig. 3a, the product obtained by calcining the iron oxide precursor at 350°C in air was pure $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 01-089-0599). Besides the dominated $\alpha\text{-Fe}_2\text{O}_3$ phase, little $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS 00-025-1402) and $\text{Ca}_2\text{Fe}_2\text{O}_5$ (JCPDS 00-018-0286) (Ma et al., 2005a) was formed in 1%Ca- Fe_2O_3 , as showed in Fig. 3b. When the Ca/Fe molar ratio was 5:95, the Fe_2O_3 peaks turned broad and the $\gamma\text{-Fe}_2\text{O}_3$ (maghemite, JCPDS 00-024-0081) was the dominant phase, as showed in Fig. 3c. The reason would be that the decomposition of iron alcoholate was in a hypoxia environment due to the covering of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ on the surface, resulting in the phase transformation to $\gamma\text{-Fe}_2\text{O}_3$ (Zhong et al., 2006). When the Ca/Fe molar ratio was increased to 50:50, the dominant phase changed to $\text{Ca}_2\text{Fe}_2\text{O}_5$ (JCPDS 00-019-0222), and only a few Fe_2O_3 diffraction peaks were detected, as showed in Fig. 3d.

Table 1 provides a summary of the pore structure data for the Ca species-doped Fe_2O_3 and $\alpha\text{-Fe}_2\text{O}_3$ sample series. The specific surface area of $\alpha\text{-Fe}_2\text{O}_3$ was $25 \text{ m}^2 \text{ g}^{-1}$. When 1% Ca was adopted onto Fe_2O_3 , the specific surface area increased dramatically to $61 \text{ m}^2 \text{ g}^{-1}$. The significantly larger BET surface area of the

Fig. 1. TGA curves (a) and DSC curves (b) of prepared Ca species-doped Fe_2O_3 precursors.

Fig. 2. SEM images of Ca species-doped Fe_2O_3 : (a) Fe_2O_3 ; (b) 1%Ca- Fe_2O_3 ; (c) 5%Ca- Fe_2O_3 ; and (d) 50%Ca- Fe_2O_3 .

Fig. 3. XRD patterns of prepared materials: (a) Fe_2O_3 ; (b) 1%Ca- Fe_2O_3 ; (c) 5%Ca- Fe_2O_3 ; and (d) 50%Ca- Fe_2O_3 .

1%Ca- Fe_2O_3 compared to $\alpha\text{-Fe}_2\text{O}_3$ might be attributed to the increase in the pore volume from 0.21 to 0.35 $\text{cm}^3 \text{g}^{-1}$. In combination with the XRD results, these results might be related to the formation of new $\text{Ca}_2\text{Fe}_2\text{O}_5$. Similar case was reported during the preparation of Mg_xSiO via the impregnation method with SiO_2 and an aqueous solution of MgCl_2 (Zou et al., 2015). It was

found that the BET surface area of $\text{Mg}_{0.1}\text{SiO}$ significantly increased to 254 $\text{m}^2 \text{g}^{-1}$, compared to that of SiO_2 at 197 $\text{m}^2 \text{g}^{-1}$, and this change was related to the formation of MgSiO_3 . However, in the Ca species-doped Fe_2O_3 sample series, the specific surface areas and pore volumes both decreased with increasing Ca/Fe molar ratios, being for 5%Ca- Fe_2O_3 at 47 $\text{m}^2 \text{g}^{-1}$ and 0.25 $\text{cm}^3 \text{g}^{-1}$, and

Table 1
Pore structure parameters of different materials.

	Surface area (m ² g ⁻¹)	Average pore diameter (nm)	Pore volume (cc g ⁻¹)
Fe ₂ O ₃	25	31.5	0.21
1%Ca-Fe ₂ O ₃	61	23.34	0.35
5%Ca-Fe ₂ O ₃	47	21.44	0.25
50%Ca-Fe ₂ O ₃	11	19.96	0.06

50%Ca-Fe₂O₃ at 11 m² g⁻¹ and 0.06 cm³ g⁻¹, respectively. It is possible that additional increases in the amount of Ca₂Fe₂O₅ lead to greater coverage of the surface of the materials, blocking the pores between the Fe₂O₃ nanopetals, as can be seen in SEM images (Zou et al., 2015).

3.2. Activity test

3.2.1. PCB-209 degradation efficiencies over Ca species-doped Fe₂O₃ and α-Fe₂O₃

The PCB-209 degradation efficiencies (DE) over Ca species-doped Fe₂O₃ and α-Fe₂O₃ were calculated using following equation:

$$DE = (1 - R_{PCB-209}/I_{PCB-209}) \times 100\% \quad \text{Eq. (1)}$$

where $I_{PCB-209}$ is the initial number of moles of PCB-209, and $R_{PCB-209}$ is the number of moles of the remained PCB-209 following heating for a given time period. The activities of the materials were evaluated at 300 °C for 30 min in sealed ampoules, and the results are shown in Fig. 4a. The degradation efficiency of PCB-209 over pure α-Fe₂O₃ was 88%. When 1% of Ca was introduced into α-Fe₂O₃, the PCB-209 degradation efficiency increased significantly to 97%. The material's reactivity was primarily related to the number of available surface active sites, and this in turn depended on factors such as the material's surface area, pore volume, and phase composition. The increased surface area would increase the number of active sites, resulting in an increase in the degradation activity (Fan et al., 2011; Huang et al., 2013). Ma et al. (2005a) reported that the formation of Ca₂Fe₂O₅ in Ca-Fe composite oxide promoted the dechlorination of HCB, whose reaction activity was obviously higher than pure Fe₂O₃ and CaO. α-Fe₂O₃ phase in 1%Ca-Fe₂O₃ catalyst acting as catalyst supporter had dispersive, supporting, and promotion effects to active component Ca₂Fe₂O₅ phase (Chen et al., 2006; Wang et al., 2014). α-Fe₂O₃ also promoted the catalytic activity of Ca₂Fe₂O₅, owing to the interaction between supporter and active component (Tauster et al., 1981). The interaction could enhance the mobility of oxygen species in catalyst (Lin et al., 2012). However, when the molar ratio of Ca increased to 5%, the activity of the material decreased significantly, and even lower than that over pure α-Fe₂O₃ which had lower surface area. The reason would be that, on the one hand, the surface of 5%Ca-Fe₂O₃ was covered by small amount of formed Ca₂Fe₂O₅, which blocked the pores and decreased the surface area according to the SEM image as compared to 1%Ca-Fe₂O₃. On the other hand, the major phase of 5%Ca-Fe₂O₃ turned to γ-Fe₂O₃ from α-Fe₂O₃. It was reported that the activity of γ-Fe₂O₃ was obviously lower than that of α-Fe₂O₃ (Zhong et al., 2006; Peng et al., 2007). When the molar ratio of Ca further increased to 50%, the activity of the material decreased significantly, and the PCB-209 degradation efficiency was only 5%. This would be due to the very low surface area of 50%Ca-Fe₂O₃ which could not provide sufficient adsorption and active sites. The above analysis showed that the order of the activities of the prepared materials in PCB-209 degradation was 1%Ca-Fe₂O₃ > α-Fe₂O₃ > 5%Ca-Fe₂O₃ > 50%Ca-Fe₂O₃, which indicated that the proper ratio of active compound to supporter of catalyst

Fig. 4. (a) PCB-209 degradation efficiencies over Fe₂O₃ and Ca species-doped Fe₂O₃ at 300 °C for 30 min; (b) Residual PCB-209 content as a function of reaction time (Inset shows the pseudo-first-order kinetic plot of the reaction).

was an important factor to its activity. It also confirmed that the material activity was affected by both the phase composition and the surface area caused by “Ca-doping effect” (Ma et al., 2014).

As discussed above, the 1%Ca-Fe₂O₃ material showed the highest activity, so the reaction kinetics was studied by evaluating the time-dependent degradation behavior of PCB-209 (802 nmol) over 1%Ca-Fe₂O₃ (50 mg) at 300 °C. As shown in Fig. 4b, PCB-209 rapidly decomposed from 802 to 32.8 nmol in 30 min, and further decreased to be under the detection limit in 60 min. This result suggested that flower-like 1%Ca-Fe₂O₃ was an effective catalyst for the degradation of PCB-209. A linear $\ln(R_{PCB-209}/I_{PCB-209})$ vs time plot was obtained that corresponded to pseudo-first-order reaction kinetics, shown in the inset figure of Fig. 4b. The initial rate of CB-209 decomposition could be described by the pseudo-first-order kinetic law with respect to PCB-209 concentration, as shown in Eq. (2):

$$\ln(R_{CB-209}/I_{CB-209}) = -k_{obs}t + b \quad \text{Eq. (2)}$$

where k_{obs} is the pseudo-first-order initial rate constant (min⁻¹), as calculated from the experimental data. The pseudo-first-order

rate constant for the degradation of PCB-209 over 1%Ca-Fe₂O₃ was 0.103 min⁻¹ ($R^2 = 0.94$), which was comparable with that of PCN-75 degradation over the prepared Fe₃O₄, with pseudo-first-order rate constant of 0.10 min⁻¹ ($R^2 = 0.89$) (Su et al., 2014). The existence of strong π -conjugated effects both in PCB-209 and PCN-75 resulted in their similar reaction rate constants.

3.2.2. Analysis of hydrodechlorination products as compared to that of PCN-75

For studying the mechanism of PCB-209 degradation over the prepared 1%Ca-Fe₂O₃ composite oxide, series of hydrodechlorination products were identified.

The content of products was calculated using following equation:

$$\text{Content}(\%) = (N_{\text{PCBs}}/I_{\text{PCB-209}}) \times 100\% \quad \text{Eq. (3)}$$

where N_{PCBs} is the number of moles of the newly formed PCBs following heating for a given time period, and $I_{\text{CB-209}}$ is the initial number of moles of PCB-209. As observed in Fig. 5, products were identified that included (a) NonaCBs, (b) OctaCBs, (c) heptachlorobiphenyls (HeptaCBs), (d) hexachlorobiphenyls (HexaCBs), (e) pentachlorobiphenyls (PentaCBs), (f) TetraCBs, (g) trichlorobiphenyls (TriCBs), (h) dichlorobiphenyls (DiCBs), and (i) MonoCBs. With increasing reaction time, the amount of all newly formed lower chlorinated biphenyls increased at the early stages of the reaction before a decrease was noted. The detection of newly formed lower chlorinated biphenyls homologues and their time-dependent distribution pattern indicated the occurrence of successive reductive hydrodechlorination reactions during the degradation of PCB-209 over the prepared 1%Ca-Fe₂O₃. Similar successive reductive hydrodechlorination of PCB-209 over as-prepared Fe₃O₄ was also observed with identification of dechlorinated products from NonaCBs to DiCBs (Huang et al., 2013). Furthermore, it is noted that the sum of the residue PCB-209 and the new formed PCBs took 97.6%, 42.6%, 12.3% and 1.55% of the origin PCB-209 at 10, 20, 30, and 60 min, respectively. The sum of all PCBs was not balanced with the original amount of PCB-209, suggesting other products must have been generated. The other products would most probably be the oxidative products due to the high oxidation activity of metal oxides. The simultaneous existence of hydrodechlorination and oxidation reaction have been often determined during the degradation of chlorinated aromatics over metal oxides. The oxidation products, such as phenolate, acetate, and carbon oxide species, have been detected besides lower hydrochlorinated products (Lin et al., 2011; Ma et al., 2007; Schoonenboom et al., 1995; Weber et al., 2002).

Fig. 5 also showed that the lower chlorinated homologues displayed nonuniform distribution profiles of the PCB isomers. In regard to the three isomers of NonaCBs, as shown in Fig. 5a, the content of PCB-207 was markedly higher than that of PCB-208, while none PCB-206 was observed under the present condition. The content of PCB-207 corresponded to 78.4% of the total amount of NonaCB isomers at a reaction time of 30 min. The amount of intermediate product was determined by both its formation and further degradation rates. The experimental data demonstrated that the stabilities of chlorine atoms substituted on the PCBs were in the order of ortho >> para > meta (Wang et al., 2005; Huang et al., 2013). The reason was that the chlorines on ortho-position had a major influence on the torsional angles and rotational barriers of PCBs, while the effect of adjacent meta chlorine atoms was much smaller (Dorofeeva et al., 2004). Therefore, PCB-209 would proceed to dechlorination on the meta-position preferentially to form PCB-207. Zhai et al. (2005) previously reported the thermodynamic function data for 209 PCB isomers by fully optimized calculation at the B3LYP/6-31G* level, including the total en-

ergy (TE), the standard formation energy (ΔH_f^0), and the formation free energy ($\Delta G_f^{573.15}$). It was found that these thermodynamic parameters were heavily dependent on the number and position of the chlorine atoms. Among the three NonaCB isomers, the calculated $\Delta G_f^{573.15}$ of PCB-207 with 367.28 kJ mol⁻¹ was lower than that of PCB-208 and PCB-206 with 367.88 and 371.19 kJ mol⁻¹, respectively. In addition, the calculated $\Delta_f G_{298}^0$ value of PCB-207 with -22.6 kJ mol⁻¹ was also lower than that of PCB-208 and PCB-206 with -19.2 and -15.3 kJ mol⁻¹ (Dorofeeva et al., 2004). The lower $\Delta G_f^{573.15}$ and $\Delta_f G_{298}^0$ values indicated PCB-207 was more thermally stable than the other two isomers. Therefore, higher formation rate and lower degradation rate of produced PCB-207 led to its largest amount among the three NonaCB isomers. However, as compared to the degradation of PCN-75 over Fe₃O₄, the hydrodechlorination proceeded primarily at the ortho-position to mainly produce PCN-73 (Su et al., 2014).

The produced NonaCB could be further hydrodechlorinated to OctaCBs. As shown in Fig. 5b, PCB-197 was the major isomer and amounted to 46.4% of the total content of OctaCB isomers at 30 min. It was reported that PCBs with chlorines reasonably distributed at two aromatic rings and their substitution position relatively far were more stable (Zhai et al., 2005). Therefore, PCB-197 with symmetrical substituted chlorines was more stable than other OctaCB isomers. Furthermore, the TE, ΔH_f^0 , and $\Delta G_f^{573.15}$ values of -4140.0277, 80.31, and 348.57 kJ mol⁻¹, respectively, were lower than those of other detected OctaCB isomers, except that of PCB-201 and PCB-202 which was closed to PCB-197 (Zhai et al., 2005). As compared to the degradation of PCN-75 over Fe₃O₄, the hydrodechlorination at the second step also happened preferentially at the ortho-position but at the other side to mainly form PCN-66/67 (Su et al., 2014).

As shown in Fig. 5c–e, the predominant isomers of the detected HeptaCB, HexaCB, and PentaCB were PCB-176, PCB-184, PCB-150, PCB-136, PCB-148, PCB-104 and PCB-96 at reaction time of 30 min, respectively. On the basis of the thermodynamic data reported by Zhai et al. (2005), the TE, ΔH_f^0 and $\Delta G_f^{573.15}$ of the above main isomers were not the lowest among those obtained for the HeptaCB, HexaCB, and PentaCB isomers. The reason would be that other effects rather than thermodynamic properties were the main driving force of further hydrodechlorination. It was noticed that all the dominant isomers of detected HeptaCBs, HexaCBs, and PentaCBs were fully substituted with chlorines at ortho-position, and the further hydrodechlorination from OctaCBs to PentaCBs preferentially happened at meta- or para-positions. As compared to the degradation of PCN-75 over Fe₃O₄, the main hydrodechlorination pathway of PCN-75 after the elimination of two chlorines at ortho-position happened at meta-positions. At the onward step, no predominant PCN isomers distinguished among the detected TetraCB and TriCB isomers, due to their similar thermodynamic parameters (Su et al., 2014).

The contents of PCB-54, PCB-19, PCB-4 and PCB-1 (Fig. 5f–i) contributed to 79.0%, 83.4%, 77.3% and 72.7% of the total detected TetraCB, TriCB, DiCB and MonoCB isomers at 30 min. All of PCB-54, PCB-19, PCB-4 and PCB-1 isomers with one to four chlorine atoms substituted at C atoms in positions 2, 2', 6, or 6'. However, the thermodynamic data of PCB-54, PCB-19, PCB-4 and PCB-1 isomers were not the lowest among the detected corresponding isomers (Zhai et al., 2005). The reason would be that chlorine at ortho-position was more stable than at other two positions, although the thermodynamic data of those dominant isomers were not the lowest (Zhai et al., 2005). Besides, all main TetraCB to MonoCB isomers featured the substituted chlorines locating at two different benzene rings. Similarly, PCN-75 mainly dechlorinated to PCN-11/8 which featured the substituted chlorines locating at two different

Fig. 5. Distribution of the hydrodechlorination products (a) NonaCBs, (b) OctaCBs, (c) HeptaCBs, (d) HexaCBs, (e) PentaCBs, (f) TetraCBs, (g) TriCBs, (h) DiCBs, and (i) MonoCBs following degradation of PCB-209 over as-prepared 1%Ca-Fe₂O₃ at 300 °C as a function of heating time.

benzene rings (Su et al., 2014). The PCB isomer distribution patterns were quite different with those in transformer oil and global commercial PCB formulations (Takasuga et al., 2006), which might be due to their different formation pathways. PCB-110, PCB-138, PCB-149, and PCB-153 were the main congeners in PCB polluted oil, while the main PCB congeners turned to PCB-3 and PCB-8 in chemically degraded oil (Takasuga et al., 2006).

3.2.3. The hypothesis of hydrodechlorination mechanism of PCB-209 compared with that of PCN-75

According to the above analysis of hydrodechlorinated products, higher amounts of PCB-207, PCB-197, PCB-176, PCB-184, PCB-150, PCB-136, PCB-148, PCB-104, PCB-96, PCB-54, PCB-19, PCB-4 and PCB-1 were determined in their respective homologues. The hydrodechlorination mechanism of PCB-209 over 1%Ca-Fe₂O₃ was shown in Fig. 6a. In newly formed dominant NonaCB and OctaCB isomers, four *ortho*-positions were all substituted with chlorines with their lowest thermodynamic properties. The dechlorination driving force was primarily controlled by thermodynamic stabilities of products and their steric effects which prevent the hydrodechlorination at *ortho*-position. When the number of substituted chlorines of the newly formed PCBs was less than or equal to 7, the chlorines of dominated isomers preferentially substituted at *ortho*-positions. The steric effect keeps the formation of predominant PCB isomers with chlorines at *ortho*-positions. During the dechlorination of the formed TetraCB into MonoCB isomers, the chlorine atoms fully substituted in *ortho*-positions have to be successively removed preferentially at two different benzene rings. The above results meant that chlorines at *ortho*-positions were the most stable, while those at *meta*- and *para*-positions were relatively easier to drop during catalytic degradation of PCB-209 at 300 °C. The dechlorination pattern in our study was similar with that of PCB dechlorination over iron-based spinel at 300 °C (Huang et al., 2013) and microbial reductive dechlorination of PCBs in soils and aquatic sediments under anaerobic conditions (Wiegel and Wu, 2000). The dechlorination pattern described above matches PCB dechlorination Process N, which defined microbiologically mediated dechlorination of PCBs which typically removes *meta* and/or *para* chlorines to generate primarily *ortho*-substituted lower chlorinated biphenyls (Wiegel and Wu, 2000; LaRoe et al., 2014).

The reactivity of chlorines at different substituted position in aromatic compounds was quite related with their geometrical

structures. The optimized geometry of the minima states of PCB-209 was calculated by DFT at the B3LYP/6-31g(d) theory level, shown in Fig. 6b. The high Coulombic repulsion and steric hindrance elevate the repulsion between the four chlorine atoms at *ortho*-positions, causing the conformational changes in PCB-209 to be quite distorted, with dihedral angles of two aromatic rings at 90° (Alonso et al., 2008). The activation energy of the rotation around the aryl-aryl bond is over 56 kcal mol⁻¹ for PCB-209 (Alonso et al., 2008). This result indicates that the existence of a coplanar structure in PCB-209 can be completely discarded. The existence of the 90° dihedral angles resulted in the C-Cl bonds at *ortho*-position are stable and resistant to be attacked from any directions. Whereas the chlorines in *meta*- and *para*-position are relatively easy to be sterically attacked from the top and bottom of two aryl planes. This can also be reflected by the higher bond dissociation energy (BDE) of C-Cl bonds at *ortho*-position at 357.28 kJ mol⁻¹ than those of at *meta*- and *para*-position at 353.98 and 351.69 kJ mol⁻¹, respectively. Therefore, in the main dechlorination pathway, chlorines in *meta*- and *para*-position were firstly dropped, while chlorines at *ortho*-position start to eliminate when other chlorines have been removed.

In comparison, in the conformation of PCN-75, shown in Fig. 6c, the two aromatic rings are in the same plane (Su et al., 2014). The dihedral angles of 0° in PCN-75 lead to the existence of steric effect between chlorines at *ortho*-position. The PCN isomers that featured chlorine atoms at either set of positions i.e., 1 and 8, or 4 and 5 were determined as nonstable (Zhai and Wang, 2005; Su et al., 2014). Contrary to PCB-209, the steric repulsion of chlorines at *ortho*-position in PCN-75 results in their instability and been preferentially attacked from the top and bottom of the conjugated aromatic planes. Once one of chlorines in either set of *ortho*-position at 1 and 8, or 4 and 5 removed, the steric repulsion could be weakened. In the thermal degradation of PCN-75 over Fe₃O₄, the first and second hydrodechlorination steps preferentially occurred respectively at 1- and 8-, or 4-, resulting in the successive formation of PCN-73 and 66/67 (Su et al., 2014). Once the steric repulsion at *ortho*-position was weakened, the dechlorination proceeded preferentially at flanked *meta*-position. The dechlorination of PCN-75 was controlled by thermodynamically stabilized products and promoted by steric effects (Su et al., 2014). The opposite roles of the steric effect in *ortho*-position between PCB-209 and PCN-75 might be due to the difference of the π -conjugated plane caused by the dihedral angle of 90° and 0° of the two aromatic rings.

Fig. 6. Hydrodechlorination mechanism of PCB-209 over 1%Ca-Fe₂O₃ (a) and the optimized geometries of the minima states of (b) PCB-209 and (c) PCN-75.

4. Conclusion

Ca species-doped Fe_2O_3 with different Ca/Fe molar ratio was synthesized and characterized. The material activities decreased with the increasing Ca doping amount, in which 1% Ca- Fe_2O_3 exhibited the highest activity on PCB-209 degradation at 300 °C for 60 min with a reaction rate constant of 0.103 min^{-1} of pseudo-first order. PCB-209 proceeded hydrodechlorination pathway producing series of NoCB to MoCB products with the respective predominant isomers of PCB-207, PCB-197, PCB-176, PCB-184, PCB-150, PCB-136, PCB-148, PCB-104, PCB-96, PCB-54, PCB-19, PCB-4 and PCB-1. This indicated the dechlorination was more favored on *meta*- and *para*- than on *ortho*-positions. The dechlorination driving force was different with dechlorination steps. When PCB-209 was dechlorinated stepwise to OctaCBs, all four *ortho*-positions were substituted with chlorines because the dechlorination driving force was controlled by thermodynamic stabilities of products and the steric effects which prevented the hydrodechlorination at *ortho*-positions. When the formed OctaCBs were further dechlorinated to lower chlorinated biphenyls with the number of chlorines not more than 7, the steric effect kept the predominant HeptaCB to MonoCB isomers with chlorines substituted at *ortho*-positions. In comparison, the chlorines at *ortho*-positions in structurally similar PCN-75 were preferentially attacked due to the steric effects. The opposite roles of the steric effect in *ortho*-position between PCB-209 and PCN-75 might be due to the difference of the π -conjugated plane which locates in the two separate conjugated systems in PCB-209 due to the existence of C–C bridge bond, but locates in the same conjugated plane in PCN-75.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.08.022>.

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