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### Decomposition of 2,2',4,4',5,5'-hexachlorobiphenyl with iron supported on an activated carbon from an ion-exchange resin

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#### ABSTRACT

An activated carbon (AC) containing a high concentration (374 mg g<sup>-1</sup>) of Fe was prepared by carbonization of an ion-exchange resin. To examine its chemical reactivity as a catalyst to decompose 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153), the decomposition parameters of temperature and time were varied under air or N<sub>2</sub>. Decomposition at 350 °C was achieved within 15 min under air and 30 min under N<sub>2</sub>, and the efficiency of PCB-153 decomposition was 99.7% and 98.0%, respectively. An analysis of inorganic chloride ions revealed that PCB-153 was mineralized effectively during the decomposition. The Brunauer–Emmett–Teller (BET) surface area and pore volume of the AC were measured to assess the adsorption capacity before and after the decomposition. The differences between decomposition under air and N<sub>2</sub> reflected the differences in the BET surface and pore volume measurements. A decomposition pathway was postulated, and the reactive characteristics of chlorine atoms loaded on the benzene rings followed the order of *para* > *meta* > *ortho*, which agrees with the calculated results from a density functional theory study.

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#### 1. Introduction

Polychlorinated biphenyls (PCBs) were first produced commercially in the US in 1929 (Wentz, 1989). With highly stable and excellent thermal properties, they have been used as a medium for heat transfer and a component of insulation oil in electrical transformers and capacitors (Wentz, 1989). Approximately, 1.5 million tons of PCBs had been produced over a 50-year period worldwide (Hosomi, 2000). Since PCBs persist in environment and bioaccumulate in fatty tissues, they cause skin lesions and tumors in animals. Thus, the manufacture of PCBs was halted in developed countries in the 1970s. In China, 10000 tons of PCBs had been produced before 1980 (Ministry of Environmental Protection of the People's Repubic of China, 1991; Chen et al., 2008). Due to poor storage, soil was largely contaminated. The contamination soil with high-concentration PCBs (>500 ppm) and low-concentration PCBs (50-500 ppm) was about 50000 and 500000 tons (Ministry of Environmental Protection of the People's Repubic of China, 1991; Chen et al., 2008). In 2004, China joined the "Stockholm Convention on Persistent Organic Pollutants," which mandated that PCB wastes must be disposed of before 2028.

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PCBs are destroyed primarily by incineration and chemical disposal in some developed countries, and the decomposition of highconcentration PCBs has reached 99.9999%. However, during the disposal process, large amounts of exhaust gas containing residual PCBs is generated. Activated carbon (AC) has been used to adsorb these PCBs and then be disposed of by incineration. However, problems arise during incineration, like the high cost of construction and maintenance of high-temp equipments, generation of dioxins in incinerators, and risk of exposure to AC-adsorbed PCBs during the conveyance and pulverization prior to incineration. Therefore, it is necessary to find an inexpensive and safer way to treat the low-concentration residual PCB wastes.

Since the 1980s, zero-valent metals have been reported as reducers to dechlorinate organic halogen compounds, and the technique has been used widely in environmental engineering. Chuang et al. reported that zero-iron (Fe) destroys PCBs to biphenyl in 10 min at 400 °C (Chuang et al., 1995). Zero-valent metals, mainly Fe, tin, and zinc (Boronina et al., 1995), offer the treatment of halogenated hydrocarbons. Li et al. used nano-sized Fe powder as the catalyst to destroy 1,1',2,2'-tetrachloroethane as follows:

$$C_2Cl_4 + 5Fe + 6H^+ \to C_2H_6 + 5Fe^{2+} + 4Cl^-$$
(1)

where zero-valent Fe reacts as a electron donor oxidized to  $Fe^{2+}$ , while  $C_2Cl_4$  gains an electron and is dechlorinated (Li et al., 2006). Commercial nickel-molybdenum (Ni-Mo) catalysts have been





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applied to dehalogenate PCB waste (Brinkman et al., 1995; Murena and Schioppa, 2000; Murena et al., 2000). Hagenmaier et al. reported that copper dechlorinated polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at low temperature by 99.99% decomposition efficiency (Hagenmaier et al., 1987). Fe or Fe compounds have been used as catalysts to decompose deca-PCBs with 99% decomposition efficiency (Kainuma et al., 2000). On the other hand, AC is not merely a strong adsorbent; it is also a catalyst support in many reactions, including those reducing the concentrations of organic compounds (Derbyshire et al., 2001). A catalyst of Pd loaded on AC has been applied to decompose dioxin-like materials; the decomposition efficiency reached 98.8% under certain conditions (Zhang et al., 2008; Cobo et al., 2009). Kume et al. reported the practical degradation of PCBs using Pd/Ccatalyzed at room temperature (Kume et al., 2008). In addition, several catalysts supported on alumina or AC have been compared with respect to the reaction of o-dichlorobenzene (Frimmel and Zdrazil, 1997).

Of the most commonly studied zero-valent metals, Fe is the cheapest and the most environmentally friendly. We attempted to utilize the synergism between AC and Fe by making AC-supported Fe to destroy low-concentration PCBs. In a previous study, AC-supported Fe was created using an impregnation method and decomposition experiments were conducted under various conditions (Sun et al., 2006a). The Fe concentrations was identified as an important parameter for influencing the decomposition efficiency of PCBs, especially under N<sub>2</sub> atmosphere (Sun et al., 2006a).

Furthermore, we investigated the effects of temperature, time, and atmosphere on the decomposition efficiency. Then, to figure out the adsorption capacity of AC under air and N<sub>2</sub> atmospheres, the Brunauer–Emmett–Teller (BET) surface area and the Barrett–Joyner–Halenda (BJH) pore volume of the AC were measured before and after the decomposition respectively. Finally, the decomposition pathways were studied under different atmospheric conditions. A density functional theory (DFT) study was carried out to investigate the C–Cl bond energy of the *ortho, meta* and *para* positions in PCBs, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy. The information of C–Cl bond energy, and the energy gap between HOMO and LUMO, was related to the dechlorination order of PCB isomers.

#### 2. Experimental

#### 2.1. Preparation of AC-supported high-concentration Fe using an ionexchange resin

Different with activated carbon impregnated with iron ion (Sun et al., 2006a), in this study, the author used a metacrylic acid-type resin (DIAION WK11; Mitsubishi Chemical, Tokyo, Japan) as catalyst supporter. Since the resin was a weak acid type, it had to be exchanged under an alkaline aqueous solution. Twenty-six grams of ion-exchange resin was treated in 200 mL of 1 M NaOH solution, and then the cation resin was poured with 200 mL of 1 M FeSO<sub>4</sub> solution for 1 h. The ion-exchange resin was rinsed with deionized water and vacuum-dried at 70 °C for 24 h. The Fe ion-exchanged resin was heated to 700 °C at a rate of 10 °C min<sup>-1</sup> and held at 700 °C for 20 min in a N<sub>2</sub> stream (300 mL min<sup>-1</sup>) to carbonize it (Nakagawa et al., 1999). The reaction is shown in



This kind of AC-supported Fe is called IRFe-C, which was decomposed in a digestion apparatus (MDS-2000; CEM, Matthews, NC, USA) using 6 mL of 36% HCl and 2 mL of 65% HNO<sub>3</sub>. The solution was then analyzed using inductively coupled plasma-atomic emission spectrometry (IRIS-Intrepid ICAP; Thermo Electron Corporation, Waltham, MA, USA) to measure the amount of Fe supported with the AC. The Fe concentration was 374 mg g<sup>-1</sup>.

#### 2.2. Experimental decomposition system

This study used 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153), which is the main component of Kanechlor 600, a commercial mix of PCBs manufactured in Japan. The experimental decomposition system was based on a pulse-injection method, which was same as our previous study (Sun et al., 2006a). The length and inner diameter of the quartz tube was 700 and 20 mm, respectively. To insulate the thermal of system, ribbon heater used to keep the gas introducing to the impingers. AC chip and silica gel were safety devices to keep the flue gas from the system clean. One gram of IRFe-C was placed in the middle position in the furnace and 1 mL of a hexane solution of PCB-153 ( $10 \ \mu g \ mL^{-1}$ ) was injected and vaporized at the electrical furnace inlet. The decomposition process was allowed to proceed for 15, 30, 60, and 120 min under air or N2. The furnace temperature was set at 200 °C, 250 °C, 300 °C, or 350 °C. We confirmed that the PCB-153 was vaporized instantaneously and adsorbed by the AC. When the time allowed for decomposition had elapsed, the furnace was rapidly air-cooled to room temperature for 30 min. The exhaust gas was introduced into impingers filled with 100 mL of toluene to collect the decomposition products from the gas phase.

After decomposition, the AC-supported Fe was extracted for 20 h with 200 mL toluene using a Soxhlet apparatus (Sun et al., 2005, 2006b) to quantify the decomposition products in the AC phase. PCB homologs and biphenyl within this extract and in the toluene solution were analyzed by gas chromatography–mass spectrometry (GC–MS) (Sun et al., 2005, 2006b) using a GCMS-QP2010 series gas chromatograph (Shimadzu, Kyoto, Japan) equipped with an HP-5MS capillary column (60 m length × 0.250 mm i.d.; film thickness, 0.25  $\mu$ m; Hewlett Packard, Palo Alto, CA, USA). The carrier gas was helium at a constant flow rate of 1 mL min<sup>-1</sup> (Sun et al., 2005, 2006b). Inorganic chloride ions were introduced to 50 mL of distilled water and analyzed by ion chromatography (DX-500, AS9-HC column; Dionex, Sunnyvale, CA, USA) at a flow rate of 0.7 mL min<sup>-1</sup>.

## 2.3. BET surface area and BJH pore volume of AC-supported high-concentration Fe

The BET surface area and BJH pore volume of IRFe-C were measured after the decomposition under different conditions. The BET and BJH measurements were derived from N<sub>2</sub> adsorption–desorption isotherms at 77 K using an ASAP 2400 vacuum volumetric sorption instrument (Shimadzu, Kyoto, Japan). Prior to the N<sub>2</sub> sorption analysis, samples (0.15 g) were preheated to 403 K for ~15 h to remove any physically sorbed material from the pores.

## 2.4. Fourier transform infrared spectroscopy and thermogravimetry/ differential thermal analysis

To investigate changes in the functional groups of IRFe-C, Fourier transform infrared spectroscopy (FT-IR) was used. All IR spectra were measured at 4 cm<sup>-1</sup> resolution on a FT-IR spectrometer (FT-IR8400; Shimadzu, Kyoto, Japan). The samples were prepared in the standard manner in KBr using a modified pitch (D15) with a KBr ratio of 1:100. Thermogravimetry (TG) and differential thermal analysis (DTA) were used to measure the mass change and the thermal condition change simultaneously while the sample was subjected to a controlled temperature program under N<sub>2</sub> atmosphere at a flow rate of 50 mL min<sup>-1</sup>.

#### 3. Results and discussion

The efficiency of PCB-153 decomposition using AC-supported Fe was calculated, as follows:

Decomposition efficiency (%) = 
$$\left(1 - \frac{c}{c_0}\right) \times 100$$
 (4)

where  $c_0$  is the amount of PCB-153 before decomposition and c is the total amount of PCB-153 on AC within the toluene trap after decomposition. All experiments were conducted twice under the same experimental conditions.

#### 3.1. Decomposition efficiency of PCB under an air atmosphere

To determine the appropriate temperature and time required to destroy PCBs using IRFe-C under an air atmosphere, we varied the decomposition temperature from 200 °C to 350 °C in increments of 50 °C and decomposition time from 15 to 120 min. The decomposition efficiencies under these experimental conditions are presented in Fig. 1a. When the decomposition temperature was increased from 200 to 350 °C, the decomposition efficiency increased from 61.3–99.7% to 76.3–99.8% (ranges varied according to decomposition time). When the decomposition temperature was increased to 350 °C, the decomposition temperature than 98%, even when the decomposition time was 15 min.

The amount of residual PCB-153 in the gas phase and AC phase after decomposition is shown in Fig. 1b. When the decomposition temperature was increased from 200 °C to 350 °C, the ratio of residual PCB-153 within the gas phase increased after decomposition due to a decrease in the adsorption capacity of AC at high temperatures. The amount of residual PCB-153 in the gas phase also increased with increasing decomposition time, indicating that the adsorption of PCB-153 to AC-supported Fe occured prior to decomposition; then decomposition proceeded with time, and finally, the products and residual PCB-153 desorbed from the AC whose pore volume changed. Therefore, the process of adsorption–reaction–desorption was assumed under an air atmosphere. The ratios of PCB homologs, biphenyl, and inorganic substances in the products after decomposition are presented in Fig. 1c. At 300 °C and 350 °C,



**Fig. 1.** Efficiency of decomposition of polychlorinated biphenyl-153 (PCB-153) under an air atmosphere at different temperatures and decomposition times. (a) Influence of temperature when decomposition time was 15 ( $\blacksquare$ ), 30 ( $\blacktriangle$ ), 60 ( $\square$ ), and 120 min ( $\triangle$ ). (b) Residual PCB-153 ratio in the activated-carbon (AC) and gas phases. (c) Ratio of decomposition products after decomposition.

PCB-153 was almost completely destroyed. Under an air atmosphere, whether the more toxic PCDD/PCDFs are formed during this decomposition process was the key question. Roland and Sakurai showed that at low temperature during PCB destruction, no PCDD/PCDFs were formed with certain oxidation catalysts (Roland and Sakurai, 2001). Chloride ions were analyzed after decomposition at 200 and 350 °C with a decomposition time of 30 min. Ion chromatography revealed that the concentration of chloride ions under the aforementioned conditions was 0.091 and 0.161 µmol, respectively. Because 10 µg of PCB-153 was injected into the furnace, the concentration of chloride ions within the PCB-153 solution injected at the inlet was 0.166 µmol. This indicated that 55% and 97% of the PCB-153 was dechlorinated to inorganic substances at 200 and 350 °C, respectively. As the decomposition efficiency under this condition was 65.8% and 98.1% at 200 and 350 °C, then 84% and 99% of the products decomposed into inorganic substances, respectively. Therefore, product of others could be confirmed as inorganic substances at 350 °C.

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**Fig. 2.** Influence of reaction temperature on the efficiency of PCB-153 decomposition under air or  $N_2$ . (a) Decomposition rate. (b) Residual PCB-153 ratio in the AC and gas phases. (c) Ratio of decomposition products. Decomposition time was 30 min.

#### 3.2. Influence of different atmospheres

Under an air atmosphere, the decomposition results for PCB-153 at 200 °C, 250 °C, 300 °C, and 350 °C were comparable with those under a N<sub>2</sub> atmosphere, which showed decomposition efficiencies of 85.4% and 98.0% at 300 °C and 350 °C, respectively (Fig. 2). Decomposition was allowed to proceed for 30 min. Under air, an increase in temperature from 200 °C to 350 °C increased the decomposition efficiency from 65.8% to 98.1%, whereas that under a N<sub>2</sub> improved from 74.6% to 98.0% (Fig. 2a).

At 200 °C, the decomposition efficiency under N<sub>2</sub> was higher than that under air. The decomposition efficiencies under an air atmosphere were higher than those under a N<sub>2</sub> atmosphere at 250 °C and 300 °C, but no obvious differences in decomposition efficiencies were observed at 350 °C. Under air atmosphere, the active ingredient in the catalyst was partly oxidized by O<sub>2</sub> when hated and became lower reactivity. The tendencies were the same as those observed in the decomposition of PCB-153 using LaFe-C (Sun et al., 2006a). Fig. 2b shows the detected amounts of residual PCB-153 within the AC and gas phases after decomposition. Under air, the amount of residual PCB-153 within the gas phase increased from 0 to 0.004  $\mu$ mol as the experimental time increased from 15 to 120 min at 200 °C; in contract, the ratio of residual PCB-153 within the gas phase increased as the temperature increased from 200 °C to 350 °C. Under N<sub>2</sub>, however, almost all of the residual PCB-153 was detected within the AC phase although the residual PCB-153 decreased from 0.007 to 0.001  $\mu$ mol in association with the increasing decomposition efficiency.

Fig. 2c shows the ratios of all products after decomposition, including other compounds that were not detected by GC–MS. The figure indicated the presence of about 5.7% biphenyl under a  $N_2$  atmosphere, whereas no biphenyl was detected under air. Inorganic substances were considered to be products of the other substances.

Chloride ions were analyzed after decomposition under a N<sub>2</sub> atmosphere at 200 °C and 350 °C with a decomposition time of 30 min. Ion chromatography revealed that the concentrations of chloride ions under the aforementioned conditions were 0.091 and 0.161 µmol, respectively. Because 10 µg of PCB-153 was injected into the furnace, the concentration of chloride ions within the PCB-153 solution injected at the inlet was 0.166 µmol, indicating that 55% and 97% of the PCB-153 were dechlorinated to inorganic substances at 200 °C and 350 °C, respectively. Given that the decomposition efficiency values under these conditions was 74.6% and 98.0% at 200 °C and 350 °C, 74% and 99% of the products were decomposed into inorganic substances, respectively. Therefore, the products of other substances could be confirmed to be inorganic substances at 350 °C. Integrating these results with those of Fig. 2c, PCB-153 was effectively converted to biphenyl and inorganic substances under N2 at 350 °C.

As the decomposition temperature increased, more residual PCB-153 was detected in the gas phase under an air atmosphere. Conversely, all of the residual PCB-153 was detected in the AC phase at all the temperatures investigated. These results are likely due to the BET surface area changing after decomposition under an air or N<sub>2</sub> atmosphere, revealing a difference between the catalytic activity of AC-supported Fe under air and N<sub>2</sub>. The amount of residual PCB-153 in the gas phase after decomposition under air increased with temperature and decomposition time and as the reaction conditions changed to favor decomposition, whereas almost all of the residual PCB-153 under a N<sub>2</sub> atmosphere and the same experimental conditions was detected in the AC phase after decomposition. The adsorption capacity influenced the variation in the amount of residual PCB-153 detected in the AC and gas phases under the different atmospheres. Although we mentioned that an adsorption-reaction-desorption process was assumed under the air atmosphere, the process under N<sub>2</sub> seemed to be an adsorption-reaction, because most residual PCB-153 was detected in the AC phase after decomposition.

The changes under air indicate that the adsorption of PCB-153 was greatest at low temperatures and became progressively weaker as the temperature increased to  $350 \,^{\circ}$ C.

#### 3.3. Influence of decomposition time

To investigate the influence of time on decomposition, the decomposition time was varied from 30 to 120 min while the decomposition temperature was held at 300 °C or 350 °C. The decomposition efficiencies of PCB-153 were relatively low at the beginning of the 30-min decomposition period under both air and N<sub>2</sub> (92.0% and 86.9%, respectively). The decomposition efficiencies under both air and N<sub>2</sub> appeared to be 99% within 120 min. Given that the relative standard deviation of the decomposition efficiencies for 30 min under the N<sub>2</sub> atmosphere was 3.6%, and it was <1.5% under the other conditions, the reproducibility under this experimental condition was satisfactory.

The ratio of residual PCB-153 in the gas phase increased as the decomposition time increased under an air atmosphere, indicating that the adsorption of PCB-153 to AC-supported Fe occurred before decomposition as the decomposition time improved. In contrast,

although decomposition occurred within 120 min under N<sub>2</sub>, almost all of the residual PCB-153 was detected in the AC phase for all reaction times. Ion chromatography confirmed that when the decomposition time was increased to 120 min, at 350 °C, almost all of the decomposition products appeared as biphenyls and inorganic substances.

Compared with AC-supported Fe by impregnated method (called LaFe-C), which Fe concentration was 40 mg g<sup>-1</sup>, IRFe-C showed higher catalytic activity than LaFe-C (Sun et al., 2006a). With experimental times of 30, 60, and 120 min, all the decomposition rate with IRFe-C were over 99%. On the other hand, using LaFe-C as a catalyst, the decomposition rate increased with the reaction time improved, and the amount of residual PCB was reduced as the reaction time increased. For experimental times of 30, 60, and 120 min, the decomposition rate with LaFe-C were 64.5, 77.5, and 93.9%. Therefore, decomposition reaction was fast when IRFe-C used as a catalyst, and 30 min was sufficient for PCB-153 decomposition. While LaFe-C was used as a catalyst, the decomposition process was slowly.

#### 3.4. Mechanistic aspects of PCB degradation

The BET surface area and pore volume values before and after the decomposition at 250 °C, 300 °C, and 350 °C under an air and N<sub>2</sub> atmospheres are presented in Table 1. The BET surface area of IRFe-C before decomposition was  $119 \text{ m}^2 \text{ g}^{-1}$ ; this value did not change substantially after decomposition under N<sub>2</sub> at each temperature, whereas under air it decreased to 43, 63, and 72  $m^2 g^{-1}$  at 250 °C, 300 °C, and 350 °C, respectively. In contrast, after decomposition under air, the pore volume of micropores less than 20 Å in diameter decreased from 0.04 to 0.01 cm<sup>3</sup> g<sup>-1</sup>, whereas no such change occurred under a N2 atmosphere. In addition, after decomposition under air, the pore volume of mesopores (20-500 Å in diameter) increased from 0.03 to 0.09 and 0.11 cm<sup>3</sup> g<sup>-1</sup> at 250 °C and 350 °C, respectively, whereas decomposition under a N<sub>2</sub> atmosphere caused no change in the mesopore pore volume. Because micropores determine the adsorption capacity and mesopores determine catalyst support, these results indicated that the capacity of AC to adsorb PCB-153 under an air atmosphere was weaker than that under N<sub>2</sub> and that the reaction capacity became greater under an air atmosphere. Table 1 shows that the BET surface area and pore volume did not change during decomposition; consequently, the adsorption capacity of AC-supported Fe was comparable to that of AC.

The FT-IR results (Fig. 3a) showed that functional groups changed when ion-exchanged resin carbonized to IRFe-C. IRFe-C contains ether (1650 cm<sup>-1</sup>) and ketone (1220 cm<sup>-1</sup>) groups. After reaction, the hydroxyl bond (1100 cm<sup>-1</sup>) was generated. Tachimoto and Abe reported that these functional groups could damage the oxygen bridge in dioxin. The functional groups on AC-supported Fe may contribute the decomposition effect of PCBs. Fig. 3b and c shows the TG-DTA spectra of IRFe-C and resin WK11. The reduced weight of resin WK11 at 100C indicated the dewatering process.



**Fig. 3.** FT-IR and TG-DTA spectra of IRFe-C or ion exchange resin (WK-11). (a) FT-IR spectra of IRFe-C before (IRFe-C-BR) or after (IRFe-C-AR) reaction, and ion exchange resin (WK-11); (b) TG-DTA spectra of IRFe-C; (c) TG-DTA spectra of ion exchange resin (WK-11).

The weight of resin WK11 and IRFe-C clearly decreased at temperatures from 400 °C. The FT-IR spectra revealed that ketone and ether groups were created. One could postulated that the resin removed water from formyl with a hydrogen atom, and therefore the resin weight decreased.

#### Table 1

Activated carbon pore structure before and after decomposition under an air or  $N_{\rm 2}$  atmosphere.

	Before decomposition	After decomposition					
		250 °C		300 °C		350 °C	
		Air	N <sub>2</sub>	Air	N <sub>2</sub>	Air	N <sub>2</sub>
BET surface area $(m^2 g^{-1})$ <i>t</i> -Plot desorption cumulative pore volume of pores $(cm^3 g^{-1})$	119	43	116	63	117	72	121
Micropores <20 Å	0.04	0.01	0.04	0.01	0.04	0.01	0.04
BJH (desorption) 20–500 Å	0.03	0.09	0.03	0.04	0.04	0.11	0.03
Average pore radius (4 V $A^{-1}$ by BET) (Å)	25.5	76.9	25.9	37.9	26.4	82.9	26.2

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Fig. 4. Decomposition pathway with IRFe-C under air (a) and  $N_2$  (b).



**Fig. 5.** GC–MS chromatogram of diCBzs in the products in the activated-carbon phase following the decomposition of PCB-153 under air.

#### 3.5. Decomposition pathway

Fig. 4 shows the decomposition pathway of PCB-153 at 350 °C under air and N<sub>2</sub>. Under air and N<sub>2</sub> atmospheres, PCB-153 was dechlorinated to tetraCBs, and then dechlorinated to triCBs and diCBs. MonoCBs were not detected by GC-MS. Finally, PCBs were dechlorinated to biphenyl. PentaCBs were not detected for two possible reasons: either the reaction occurred too quickly or the decomposition did not pass the pathway to pentaCBs. The difference between the pathways under air and N2 is that diCBs of PCB-18 and PCB-20 are detected under air; i.e., some tetraCBs are dechlorinated to biphenyl directly under N2. Both pathways, however, showed that chlorine in the para position could be dechlorinated more easily. Due to steric hindrance, the chlorine atom located at the para position in PCB-153 was more reactive than the one at the ortho or meta position. Kume et al. and Lin et al. also found that the chlorine atoms on the all ortho-positions were difficult to be removed during the decomposition of the fully orthosubstituted PCB congeners (Kume et al., 2008; Lin et al., 2011).

#### Table 2

Illustration of the HOMO and LUMO of MonoCB molecular and bond energies.

Isomer	LUMO Energy (a.u.)	НОМО	Energy gap between HOMO and LUMO (a.u.)	Molecular energy (a.u.)	C-Cl bond energy <sup>a</sup> (a.u.)
2-MonoCB			0.2035	-923.0413	0.0461
	-0.0419	-0.2454			
4-MonoCB		•••	0.1893	-923.0456	0.0418
	-0.0493	-0.2386			
5-MonoCB			0.1934	-923.0456	0.0419
	-0.0505	-0.2439			

<sup>a</sup> C–Cl bond energy:  $E_{\rm B} = E_{\rm B-monoCB} + E_{\rm H} - E_{\rm Biphenyl} - E_{\rm Cl}$ .

Thus, we postulate the reactive characteristics of chlorine atoms located on the benzene rings as *para* > *meta* > *ortho*.

Under air, diCBzs were detected in the AC phase of products after decomposition. The chromatogram after GC–MS analyses is shown in Fig. 5. It revealed that the decomposition process is coincident with the oxidation mechanism, which damages the bridge in the PCBs during the decomposition process using IRFe-C as the catalyst. DiCBz was not detected in the products after decomposition under a N<sub>2</sub> atmosphere. The reduction decomposition was confirmed according to this phenomenon.

The LUMO and HOMO energies of 2-MonoCB, 3-MonoCB, and 4-MonoCB were calculated based on DFT, which was performed with the Gaussian 03 package using the B3LYP exchange correlation function. The base set was  $6-311+G^{**}$  (Frisch et al., 2003). The optimized structures of PCB-153 were calculated. The Energy gap between HOMO and LUMO of MonoCBs, energy of 2-MonoCB, 3-MonoCB, 4-MonoCB with biphenyl were separately optimized by the B3LYP/6-311+G (D,P) method shown in Table 2. The C–Cl bond energy,  $E_{\rm B}$ , of 2-MonoCB, 3-MonoCB, and 4-MonoCB was calculated as follows:

$$E_{\rm B} = E_{\rm B-monoCB} + E_{\rm H} - E_{\rm Biphenyl} - E_{\rm Cl} \tag{5}$$

where  $E_{\rm B}$  is C–Cl bond energy,  $E_{\rm B-monoCB}$  is the molecular energy of monoCB,  $E_{\rm H}$  is the H atom energy,  $E_{\rm Biphenyl}$  is the molecular energy of biphenyl, and  $E_{\rm Cl}$  is the Cl atom energy.

The  $E_{\rm B}$  values of the *ortho*, *meta* and *para* positions were 0.0461, 0.0419 and 0.0418 a.u.; a higher  $E_{\rm B}$  value indicates a more difficult dechlorination. The energy gap between the HOMO and LUMO predicated the molecular stability, *i.e.*, the resistance to electron transfer. The energy gaps between the HOMO and LUMO for the *ortho*, *meta* and *para* positions were 0.2035, 0.1893 and 0.2035 a.u., revealing that the most stable position was *ortho*. The reactive characteristics of chlorine atoms located on the benzene rings followed the order *para* > *meta* > *ortho*, which is in agreement with the calculated results for the C–Cl bond energy order (*para* < *meta* < *ortho*) and the energy gap between the LUMO and HOMO in the DFT study.

#### 4. Conclusions

AC-supported high-concentration Fe produced by ion-exchange resin can be used as a catalyst for the decomposition of PCBs under an atmosphere of air or N<sub>2</sub>. The decomposition process was influenced by temperature, time, and atmosphere. At 350 °C, the decomposition process was almost complete within 15 min under air or 30 min under N<sub>2</sub>, with decomposition efficiencies of 99.7% and 98.0%, respectively. At lower temperatures of 200 °C and 250 °C, adsorption was a primary process; in contrast, decomposition was the main process at 300 °C and 350 °C. The process of PCB decomposition was considered to be adsorption-reaction-desorption under air and adsorption-reaction under N<sub>2</sub>.

The BET surface area and pore volume did not change under a  $N_2$  atmosphere, but changed substantially during decomposition under an air atmosphere, in relation to the adsorption capacity of AC. Therefore, residual PCB-153 was in the AC phase under  $N_2$ , but was transferred from the AC phase to the gas phase under an atmosphere of air when the reaction conditions were changed to favor decomposition. Ether and ketone functional groups on AC-supported Fe influenced the decomposition effect of PCBs.

Under air and  $N_2$  atmosphere, PCB-153 was dechlorinated to tetraCBs, then dechlorinated to triCBs and diCBs, and finally dechlorinated to biphenyl. DiCBzs were detected on the AC phase of products after decomposition under air. The decomposition process is coincident with the oxidation mechanism, which damages the bridge in the PCBs during the decomposition process using IRFe-C as the catalyst. The reduction decomposition was confirmed under a N<sub>2</sub> atmosphere. The reactive characteristics of chlorine atoms located on the benzene rings followed the order *para* > *meta* > *ortho*, which is in agreement with the calculated results for the C–Cl bond energy order (*para* < *meta* < *ortho*) and the energy gap between the LUMO and HOMO in the DFT study.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere. 2012.03.099.

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