

in a digestion apparatus MDS-2000 (CEM, Mathews, NC). The iron concentration in IRFe-C was 374 mg/g-AC, which was eight times more than that in LaFe-C (45.1 mg/g-AC).

The decomposition system in this study was shown in Fig.1. One milliliter of a PCB-153 solution (10 $\mu\text{g/ml}$ -hexane) was injected and vaporized at the inlet of the electrical furnace, and the decomposition process was allowed to proceed for 15, 30, 60, 120, or 180 min under air or N_2 at a space velocity (SV) of 600 h^{-1} . The furnace temperature was set at 200, 250, 300, 350, or 400°C . We confirmed that the PCB-153 was vaporized instantaneously and adsorbed by the AC. After 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. The AC-supported iron was extracted after decomposition using a Soxhlet apparatus to quantify the decomposition products from the AC phase. PCB homologs and biphenyl within this extract and in the toluene solution were analyzed by gas chromatography mass spectrometry ⁶ using a GCMS-QP2010 series gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a HP-5MS capillary column (length and inside diameter, $60 \text{ m} \times 0.250 \text{ mm}$, respectively; film thickness, $0.25 \mu\text{m}$; Hewlett Packard, Palo Alto, CA, USA). The carrier gas was helium at a constant flow rate of 1 ml/min ⁶.

Results and Discussion

Decomposition Effect on Different Catalysts under Multi-temperature

The effects of temperature on the decomposition of PCB-153 catalyzed by LaFe-C and IRFe-C under an air or N_2 atmosphere are presented in Fig. 2. According to the previous study, decomposition was allowed to proceed for 120 min and 250 to 400°C using LaFe-C as a catalyst, while 30 min and $200\text{--}350^\circ\text{C}$ was conducted when IRFe-C used as a catalyst. Under air, an increase in temperature from 250 to 400°C increased decomposition efficiency from 25.7 to 100.0%, while decomposition efficiency under N_2 improved from 49.8 to 99.7% using LaFe-C (Fig. 2a). When IRFe-C used as a catalyst, an increase in temperature from 200 to 350°C increased decomposition efficiency from 65.8 to 98.1% under air;

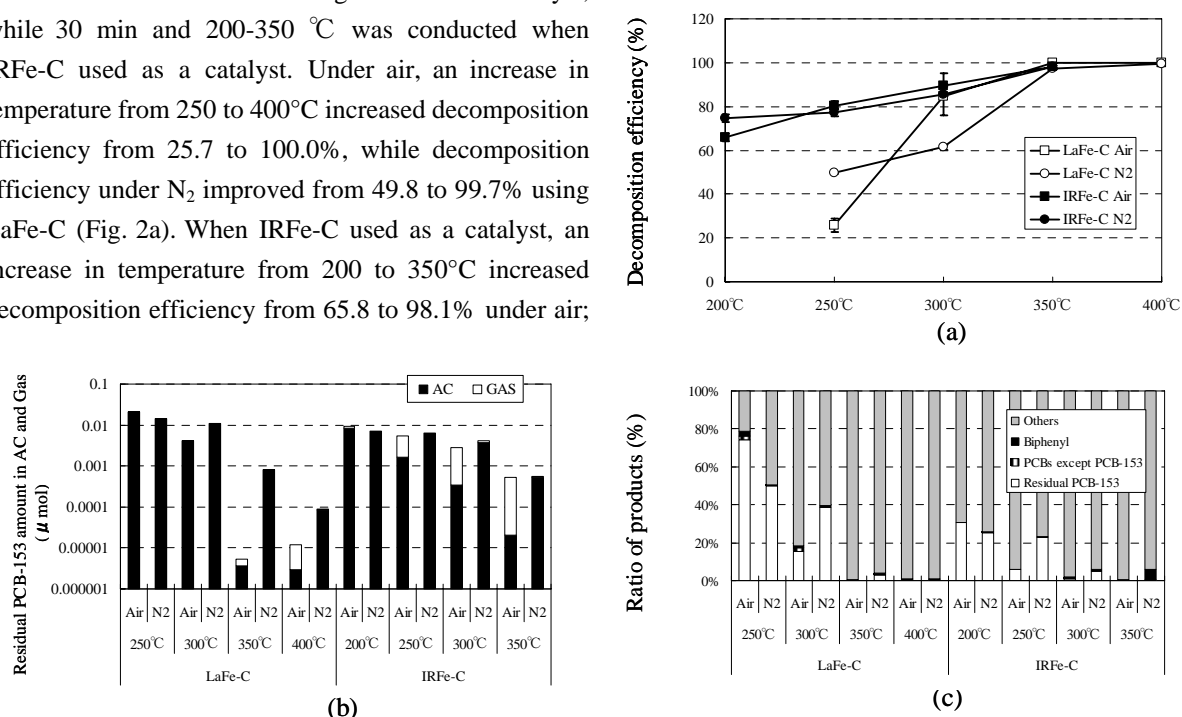


Fig. 2 Influence of reaction temperature on the efficiency of PCB-153 decomposition under air or N_2 with LaFe-C and IRFe-C. (a) Decomposition rate. (b) Residual PCB-153 ratio in the AC and gas phases. (c) Ratio of decomposition products. Decomposition time was 120 min or 30 min with LaFe-C or IRFe-C, respectively.

while decomposition efficiency under N_2 improved from 74.6 to 98.0% (Fig. 2a). At the lowest temperature for each of the catalyst, the decomposition efficiency under N_2 was higher than that under air. While, the decomposition efficiencies at air atmosphere were higher than that at N_2 atmosphere as the temperature increased. And there were no obvious differences in decomposition efficiency at high temperature of 350°C. The average relative standard deviation (RSD) of decomposition efficiencies was about 1.6%. Fig. 2b shows the detected ratio of residual PCB-153 within the AC and gas phases following decomposition. For both catalyst, the ratio of residual PCB-153 within the gas phase increased as temperature increased under air. In contrast, under N_2 almost all of the residual PCB-153 was detected within the AC phase. As seen in Fig. 2c, the results revealed that PCB-153 was converted effectively to biphenyl and others at 350 and 400°C with LaFe-C, at 300 and 350°C with IRFe-C. Chloride ions were analyzed after decomposition under a N_2 atmosphere at 350°C with both catalysts. Ion chromatography revealed that the concentration of chloride ions under the aforementioned conditions was 0.145 and 0.161 μmol with LaFe-C and IRFe-C, 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 87% and 97% of the PCB-153 was dechlorinated to inorganic substances with LaFe-C and IRFe-C, respectively. As the decomposition efficiency under this condition was 97.1% and 98.0%, then 90% and 99% of the products decomposed into inorganic substances, respectively.

Decomposition Pathway

Fig.3 shows the decomposition pathway of PCB-153 at 350°C with LaFe-C and IRFe-C under air and N_2 . Under air atmosphere with LaFe-C, PCB-153 dechlorinated to penta-PCBs, and then dechlorinated to tetra-PCBs, tri-PCBs and di-PCBs. Mono-PCBs were not detected in this study. Under N_2 atmosphere with LaFe-C or under both atmospheres with IRFe-C, the process seemed simple. All the pathways showed that it is easier for para-position to be dechlorinated. Because of steric hindrance, the chlorine atom located at the para-position in PCB-153 was more reactive than the one at the ortho- and meta-position. We postulate the reactive characteristics of chlorine atom located on the benzene rings as: para- > meta- > ortho-. Under air, it has a possibility that the dechlorination process is coincident with the oxidation process, which damages the bridge in the PCBs during the decomposition process using AC-supported iron as the catalyst.

Influence of BET Surface Area and Pore Volume

The BET surface area of LaFe-C and IRFe-C before decomposition was 1,351 and 119 $\text{m}^2 \text{g}^{-1}$; this value was not substantially different after decomposition under air or N_2 . However, after decomposition at 350°C under air, the pore volume of micropores smaller than 20 Å in diameter decreased from 0.44 to 0.38 $\text{cm}^3 \text{g}^{-1}$ with LaFe-C, and from 0.04 to 0.01 $\text{cm}^3 \text{g}^{-1}$ with IRFe-C. However, no such change occurred under a N_2 atmosphere. In addition, after decomposition under air, the pore volume of mesopores (20–500 Å in diameter) increased from 0.19 to 0.24 $\text{cm}^3 \text{g}^{-1}$ and from 0.03 to 0.11 $\text{cm}^3 \text{g}^{-1}$ by using LaFe-C or IRFe-C, respectively. However, decomposition under N_2 atmosphere caused little change in the pore volume of mesopores with both catalysts. Because micropores determine adsorption capacity while mesopores determine the catalyst support⁷, these results indicated that the capacity of AC to adsorb PCB-153 under an air atmosphere was weaker than that under N_2 , and the reaction capacity became greater under air atmosphere.

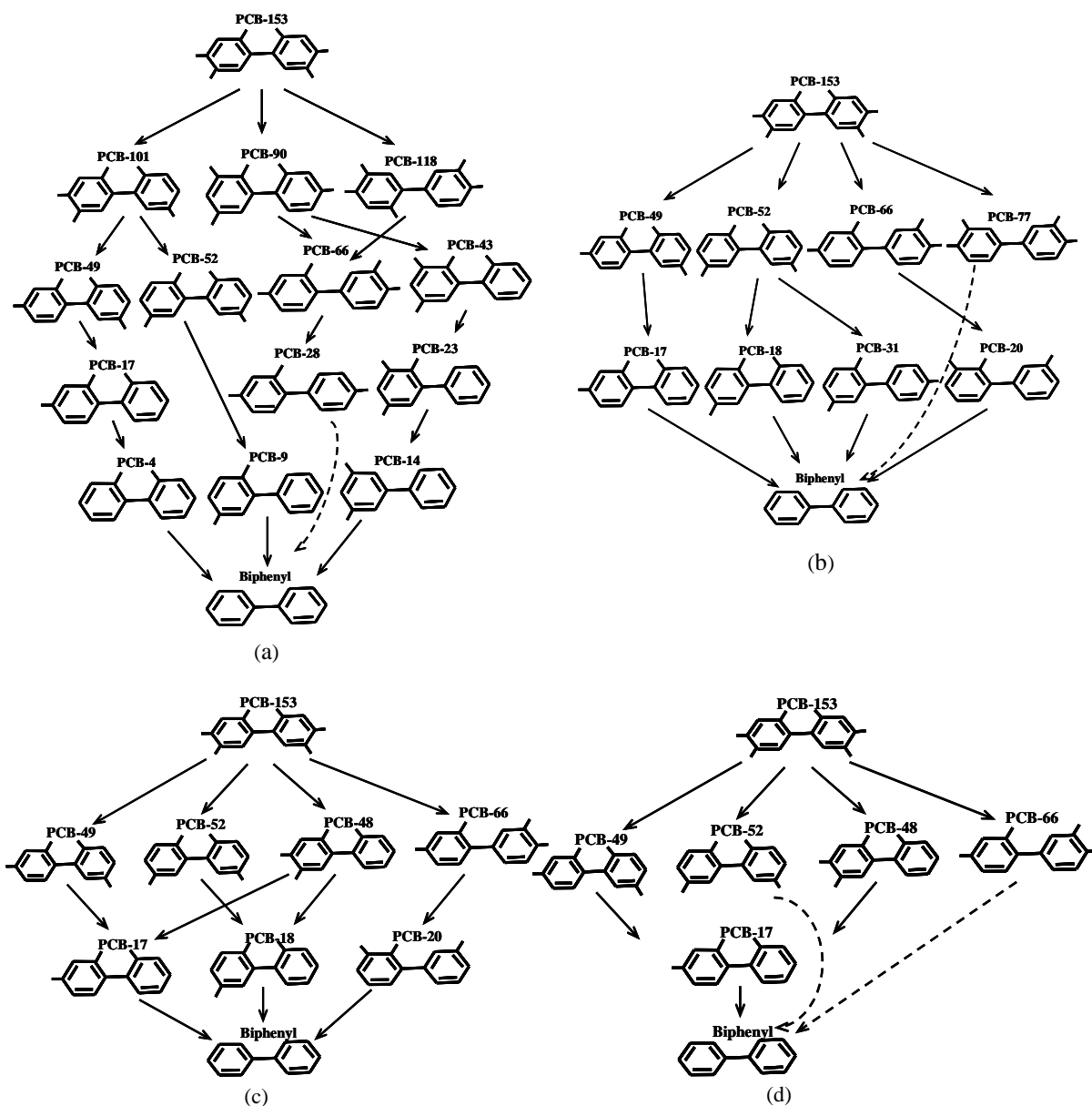


Fig.3 Decomposition pathway with LaFe-C under air (a) and N₂ (b) or with IRFe-C under air (c) and N₂ (d).

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