

LOW-TEMPERATURE DEGRADATION OF POLYCHLORINATED BIPHENYLS USING ACTIVATED CARBON-SUPPORTED TRANSITION METALS

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Introduction

Commercial PCBs had been first produced in the United States since 1929¹, and have been used as dielectric fluids for transformers and capacitors because of their excellent stability and thermal properties². In a fifty-year period by the end of 1980, approximately 1.4 billion pounds of PCBs have been produced in U.S.A and the total world production of PCBs was guessed to be close to 2×10^9 kg (Ballschmitter and Zell, 1980). While, between the start of production in 1964 and end in 1974, approximately 10,000 tons of PCB were manufactured in China³. Whereas a part of the PCBs went into the environment by illegal dumping or accidental spill, remediation of PCB-contaminated soils, groundwater, and sediments has become a major environmental management problem. There are 50,000 tons of high concentration PCB wastes (PCBs concentration over 500 mg/kg) and 500,000 tons low concentration PCB wastes (PCBs concentration below 500 mg/kg) need to be disposal of³.

Presently, chemical decomposition methods were used to destroy most of the PCB wastes with high amount in the world; however, the processes generate exhaust gas with low concentration of PCBs in large quantities. The use of activated carbon (AC) to adsorb the residual PCBs has been developed at present. And then AC can be disposed of by incineration. However, this involves many problems, such as the high construction and maintenance costs of high temperature equipment, the generation of dioxins with facility, and the risk of PCB exposure during the conveyance and pulverization process of AC before incineration. Therefore, it is important to find an inexpensive, safe method to dispose of the low concentration of PCB waste derived from processing high amount. AC is not only a strong adsorbent; it can also be used as a catalyst support in many reactions⁴. On the other hand, transition metals are reported to dechlorinate PCDD and PCDF derivatives and other chlorinated compounds⁵. In this study, we tried to utilize the synergism between AC and transition metals, so AC-supported transition metals was made to decompose low concentrations of PCBs.

Materials and Methods

Two methods for producing AC-supported transition metals were proposed. LaNi-C or LaFe-C was produced by impregnating AC (20–48 mesh, Shirasagi C2C20/48; Takeda Pharmaceutical, Osaka, Japan) with nickel or iron ion solution. A novel method prepared AC with highly dispersed Ni or Fe by the carbonization of ion-exchange resins (Mitsubishi Chemical, WK-11). AC prepared by this method was called IRNi-C or IRFe-C. Inductively coupled plasma-atomic emission spectrometry (IRIS-Intrepid ICAP, Thermo Electron) was used to measure the metal concentration in catalyst after decomposed in a digestion apparatus MARS-3000 (CEM, Mathews, NC). Two kinds of IRNi-C (low or high Ni concentration loading) called IRNi-H-C or IRNi-L-C were made to compare the decomposition effect. The metal concentration in IRNi-H-C 543 mg/g-AC, which was more than that in LaFe-C (374 mg/g-AC). The metal concentration in IRNi-L-C was 316 mg/g-AC.

Characterization of BET, scanning electron microscopy (SEM) (S530, Hitachi, Japan) and energy dispersive spectroscopy (EDS) (Oxford, England), X-ray photoelectron spectra (XPS) (ESCA-3200, Shimadzu, Japan) and X-ray diffraction (XRD) (XRD-6000, Shimadzu, Japan) were obtained.

The decomposition system in this study was shown in Fig. 1. One milliliter of a PCB-153 solution (10 $\mu\text{g}/\text{ml}$ -hexane) was injected and vaporized at the inlet of the electrical furnace, IRNi-C (means IRNi-H-C without illustration), IRNi-L-C or LaNi-C was used as catalysts. The decomposition process was allowed to proceed for 600, 1200 or 3600 h^{-1} of space velocity (SV) under N_2 . The furnace temperature was set at 200, 250, 300 or 350. 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 catalyst 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 m \times 0.250 mm, respectively; film thickness, 0.25 μm ; Hewlett Packard, Palo Alto, CA, USA). The carrier gas was helium at a constant flow rate of 1 ml/min ⁶.

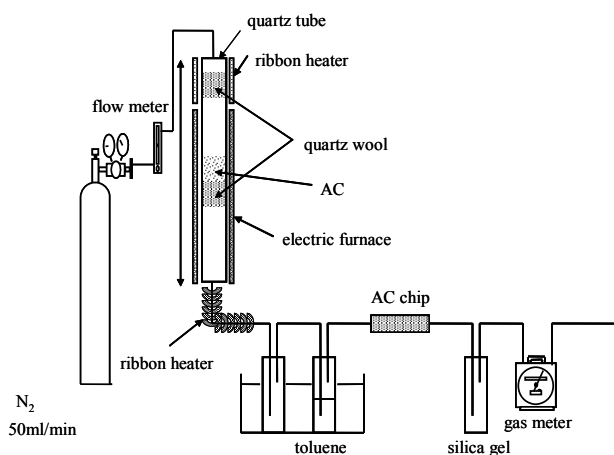


Fig.1 Schematic illustration of the system used to destroy PCB-153 catalyzed by catalyst.

Results and Discussion

Characterization of AC-supported iron

SEM images of IRNi-C are shown in Fig. 2. IRNi-C kept the sphericity of ion-exchange resin, the particle size was 100~200 μm . The size of particle were uniform and smooth on the surface, which shown the good carbonization method. As the IRNi-C made by ion-exchange resin, the nickle ion exchanged in the resin and then carbonized homogeneously. Therefore, the image and EDS results in Fig. 3 shows the high density and high distribution of Ni on both the surface and within IRNi-C. The concentration of Ni in IRNi-C at position No.1 ~ 4 was 67.3, 59.1, 59.7 and 57.0 %.

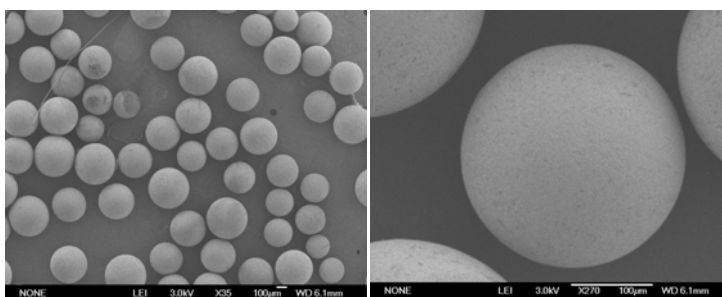


Fig. 2 SEM images of IRNi-C.

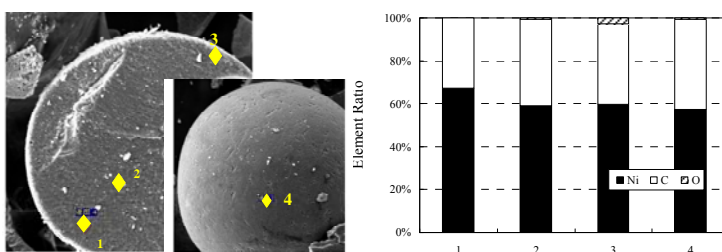


Fig. 3 EDS analysis and element ratio of IRNi-C.

Decomposition Effect on Different Catalysts under Multi-temperature

The effects of temperature on the decomposition of PCB-153 catalyzed by IRNi-C and LaNi-C under N₂ atmosphere are presented in Fig. 4. The decomposition efficiency also compared with Fe catalysts. According to the previous study, decomposition was allowed to proceed for 15 ~ 120 min using Fe catalysts. 30 min and 200~350 °C was conducted when Ni-catalysts used. With IRNi-C, an increase in temperature from 200 to 350°C increased decomposition efficiency from 67.0 to 99.8%, while the decomposition efficiency increased to 99.6% at 250°C. Decomposition efficiency improved from 66.9 to 99.8% from 250~350 °C using LaNi-C (Fig. 4). When

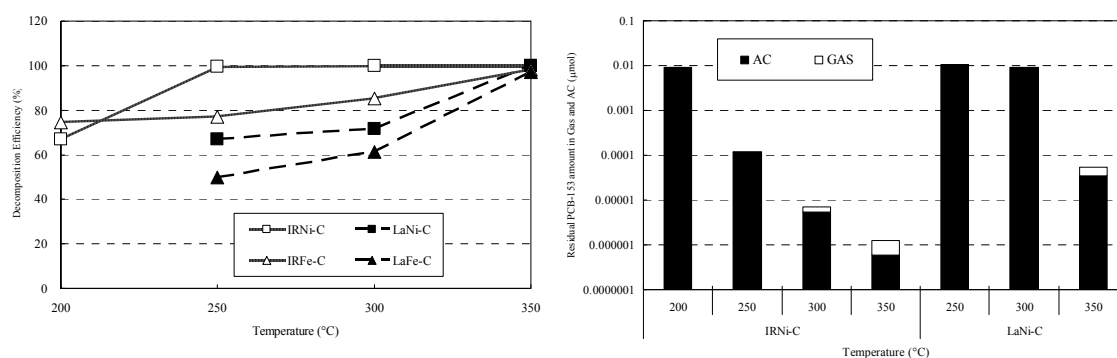


Fig. 4 Influence of reaction temperature on the efficiency of PCB-153 decomposition under N₂ with IRNi-C, LaNi-C, IRFe-C and LaFe-C. (a) Decomposition rate. (b) Residual PCB-153 ratio in the AC and gas phases. Decomposition time was 30 min.

IRFe-C used as a catalyst, an increase in temperature from 200 to 350°C increased decomposition efficiency from 74.6 to 98.0% (Fig. 2). At the lowest temperature for each of the catalyst, the decomposition efficiency under N₂ was higher than that under air. While, the decomposition efficiencies at air atmosphere were higher than that at N₂ atmosphere as the temperature increased. LaFe-C showed the lowest decomposition efficiency of the four kinds of catalysts. There were no obvious differences in decomposition efficiency at high temperature of 350°C, however IRNi-C showed the same decomposition capacity at 250°C. The detected ratio of residual PCB-153 within the AC and gas phases following decomposition using Ni-catalysts were shown in Fig. 4. For both catalysts, the ratio of residual PCB-153 within the gas phase increased as temperature increased, however almost all of the residual PCB-153 was detected within the AC phase at low temperature, which showed a better adsorptive capacity for both types of Ni-catalysts at low temperature.

Decomposition Effect on Different Ni Loading Amounts

The effect of Ni loading amounts on the decomposition of PCB-153 catalyzed by AC-supported nickel is presented in Fig. 5. Decomposition was allowed to proceed for 30 min, 250°C. The decomposition efficiency of IRNi-H-C and IRNi-L-C were 99.6 and 98.7%, both have high decomposition capacity. Therefore, the decomposition efficiency of PCB-153 did not depend on the Ni concentration very much. However, the detected ratio of residual PCB-153 within the AC and gas phases following decomposition was different, IRNi-H-C showed high adsorptive capacity. The amount of residual PCB-153 within the gas phase increased as the Ni concentration decreased, suggesting that high concentrations of Ni-AC had high adsorption activity. The ratio of

biphenyl and inorganic substances in the by-products also increased as Ni concentration increased. The results revealed that PCB-153 was converted effectively to biphenyl and others using IRNi-H-C as catalyst.

Influence of BET Surface Area and Pore Volume

The BET surface area of IRNi-C before decomposition was $215.6 \text{ m}^2 \text{ g}^{-1}$, this value decreased to $118.2 \text{ m}^2 \text{ g}^{-1}$ after decomposition. After decomposition at 250°C for 30 min, the pore volume of micropores smaller than 20 \AA in diameter decreased from 0.11 to $0.071 \text{ cm}^3 \text{ g}^{-1}$ with IRNi-C. In addition, after decomposition under air, the pore volume of mesopores ($20\text{--}500 \text{ \AA}$ 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 IRNi-C. However, decomposition 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.

References

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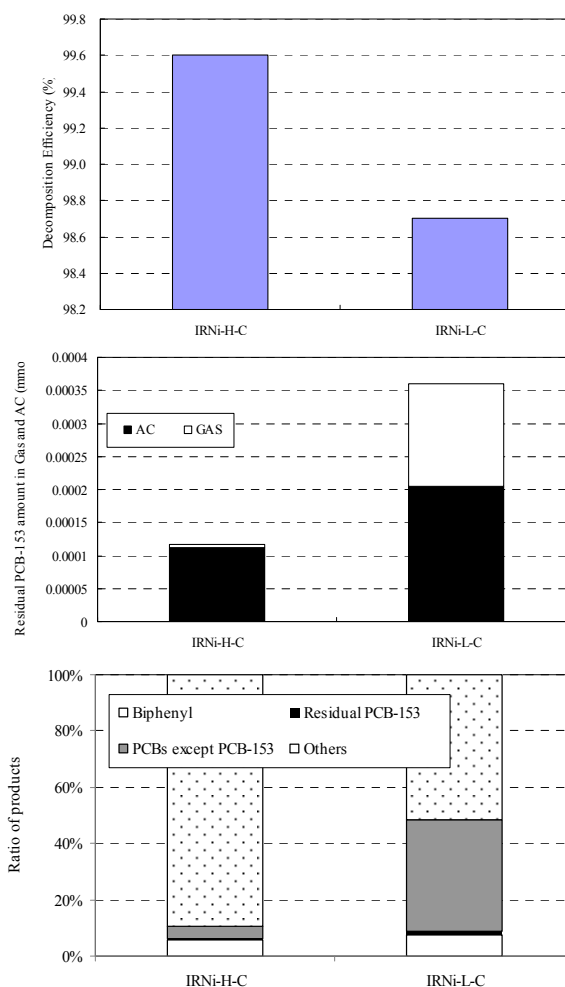


Fig. 5 Influence of Ni-loading amounts on the efficiency of PCB-153 decomposition with IRNi-H-C and IRNi-L-C. (a) Decomposition rate. (b) Residual PCB-153 ratio in the AC and gas phases. (c) Ratio of decomposition products.