Dechlorination of 2,2′,4,4′,5,5′-hexachlorobiphenyl by thermal reaction with activated carbon-supported copper or zinc

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Abstract  Activated carbon (AC)-supported copper or zinc made from ion exchange resin (IRCu-C and IRZn-C) have an increased metal load of 557.3 mg·g⁻¹ and 502.8 mg·g⁻¹ compared to those prepared by the traditional method involving impregnation with AC and copper (II) citrate or zinc citrate solution (LaCu-C and LaZn-C) of 12.9 mg·g⁻¹ and 46.0 mg·g⁻¹ respectively. When applied to decompose 2,2′,4,4′,5,5′-hexachlorobiphenyl at 250 °C, IRCu-C achieved higher activity of 99.0% decomposition efficiency than LaCu-C of 84.7%, IRZn-C of 90.5% and LaZn-C of 62.7%. When the reaction temperature rose to 350 °C, all the four kinds of reactants can decompose PCB-153 with efficiency above 90%. Further, X-ray photoelectron spectroscopy characterization of IRCu-C before and after the reaction indicated transformation of 19.1% of Cu atoms into Cu²⁺, illustrating that Cu is the active ingredient or electron donor promoting the decomposition of PCB-153. The mechanism underlying this process differs from a traditional H donor. However, there is no significant change on the surface of IRZn-C before and after the reaction, suggesting that Zn acts as catalyst during the process of PCB-153 decomposition.

Keywords  polychlorinated biphenyls, activated carbon-supported copper or zinc, dechlorination, electron donor

1 Introduction

Incineration and chemical disposal are used in the treatment of high-concentration polychlorinated biphenyls (PCBs)-contaminated wastes [1], followed by treatment with activated carbon (AC) to absorb residual low-concentration PCBs. In addition, AC is known to act as a catalyst carrier. Traditional AC supported by a noble metal catalyst is used to reduce dioxins [1,2]. A catalyst of Pd loaded on AC has been applied to decompose polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); the decomposition efficiency reached 98.8% under certain conditions [3–5]. Kume et al. reported the practical degradation of PCBs using Pd/C-catalyzed at room temperature [6]. Ukisu and Miyadera reported that when Pd or Rh supported AC was used as a catalyst, the decomposition efficiency of PCDD or PCDF was 99.96% [2]. However, this is expensive and has a reduced metal load that restricts catalytic activity. Fe or Fe compounds have been used as catalysts to decompose deca-PCBs with 99% decomposition efficiency [7]. Chuang et al. reported that zero-iron (Fe) destroys PCBs to biphenyl in 10 min at 400°C [8]. Cheng et al. found that chlorophenols (CPs) was dechlorinated by nanoscale Fe⁰ [9]. Commercial nickel-molybdenum (Ni–Mo) catalysts have been applied to dehalogenate PCB waste [10–12]. Hagenmaier et al. reported that copper dechlorinated PCDDs and PCDFs at low temperature by 99.99% decomposition efficiency [13]. CuO/zeolite can remove 92% gaseous toluene under optimal conditions [14]. 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 [15].

Of the most commonly transition metals, Cu and Zn are typical. As well, Cu and Zn are more difficult to be oxidized than Fe or Ni. In the present study, we attempted to utilize the synergy between AC and Cu or Zn by making AC-supported Cu or Zn then destroy low-concentration PCBs. Then, AC-supported Cu or Zn will replace simple AC for decomposition of PCBs, which can avoid AC contamination of waste. For this purpose,
the decomposition efficiency and mechanism of PCBs will be discussed.

2 Materials and methods

2.1 Materials

In order to prepare the AC-supported copper or zinc, chemicals of analytical grade were used, including CuSO$_4$·5H$_2$O, ZnSO$_4$·7H$_2$O, copper(II) citrate 2.5-hydrate, zinc citrate dehydrate and ammonia. Silica gel and anhydrous sodium sulfate were used for column cleanup. Hexane and toluene of HPLC grade were provided by J. T. Baker Co., USA. To simplify the investigation, 10 μg·mL$^{-1}$ of PCB-153 (AccuStandard, Inc., USA) dissolved in hexane was used as the target object, which is the main component of Kanechlor 600, a commercial mix of PCBs manufactured in Japan. PCB mixture standards in hexane and PCB internal standards labeled with $^{13}$C in hexane (Wellington Lab., Canada) were used in the gas chromatographic analysis.

2.2 Preparation of AC-supported copper or zinc

A novel ion exchange method [16] to prepare AC-supported Cu or Zn with a high metal load was presented. The author used raw resin (DIAION WK11; Mitsubishi Chemical, Tokyo, Japan) as preliminary supporter. Since it was a weak acid type, it had to be exchanged under an alkaline condition. Before, 5 g of ion-exchange resin was treated by deionized water to remove the soluble impurities. Then the treated cation resin was poured with solution of 10 g CuSO$_4$·5H$_2$O or ZnSO$_4$·7H$_2$O dissolved in 100 mL ammonia and 100 mL deionized water for 2 h directly. The exchanged resin was then rinsed by deionized water and dried at 70 °C for 24 hours to dehydrate. Then, the cooper or zinc ion-exchanged resin was heated to 500 °C and held for 20 min to carbonize them. The whole carbonization process was performed in a N$_2$ stream (300 mL·min$^{-1}$) to avoid catalysts oxidation in air. The AC-supported copper or zinc made by this method were called IRCu-C and IRZn-C respectively. The change of resin was shown as follows:

\[ \text{Biphenyl yield ratio}(\%) = \frac{c_t}{c_0} \times 100\%. \]  

where \( c_0 \) is the amount of PCB-153 before decomposition and is the total amount of biphenyl produced on AC and adsorbed in toluene after decomposition. All experiments were conducted twice under the same experimental conditions.

Simultaneously, traditional AC-supported copper or zinc were also prepared. 5 g of AC was added to 8.9×10$^{-2}$ M copper (II) citrate 2.5-hydrate or zinc citrate dehydrate solution at room temperature with vigorous stirring. The impregnated AC was dried at 70 °C for 24 hours, following the same carbonization process as described for IRCu-C and IRZn-C. AC-supported copper or zinc obtained by this method were called LaZn-C and LaZn-C respectively.

2.3 PCB-153 decomposition experiments

The PCB decomposition experiment was commanded in a tubular furnace system [17]. Before the reaction, 1 g AC-supported Cu or Zn was loaded in the middle position in the furnace, and then 1 mL PCB-153 solution (10 μg mL$^{-1}$ in Hexane) was injected and vaporized at the electrical furnace inlet. The furnace temperature was set at 250 °C, 300 °C, and 350 °C. Other conditions: reaction time was set to 30 min; the carrier gas nitrogen flow to 50 mL·min$^{-1}$. The exhaust gas was introduced into impingers filled with 100 mL of toluene to collect the decomposition products from the gas phase. After reaction, residual PCB-153 and its decomposition products distributed in both gas phase and AC phase were analyzed by gas chromatography-mass spectrometry (GC-MS) respectively, using a GCMS-QP2010 series gas chromatograph (Shimadzu, Kyoto, Japan) equipped with an HP-5MS column (60 m × 0.25 × 0.25 μm). Ultrahigh pure helium was used as the carrier gas at a constant flow rate of 1 mL·min$^{-1}$. The column temperature was programmed as follows: 150 °C, 20 °C·min$^{-1}$ to 185 °C, 2 °C·min$^{-1}$ to 245 °C, final 6 °C min$^{-1}$ to 290 °C.

The efficiency of PCB-153 decomposition and biphenyl yield ratio [18] after the reaction with AC-supported copper or zinc were calculated, as follows:

\[ \text{Biphenyl yield ratio}(\%) = \frac{c_t}{c_0} \times 100\%. \]  

where \( c_0 \) is the amount of PCB-153 before decomposition and is the total amount of biphenyl produced on AC and adsorbed in toluene after decomposition. All experiments were conducted twice under the same experimental conditions.