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Kinetics and reaction pathway of Aroclor 1254 removal by novel bimetallic catalysts supported on activated carbon

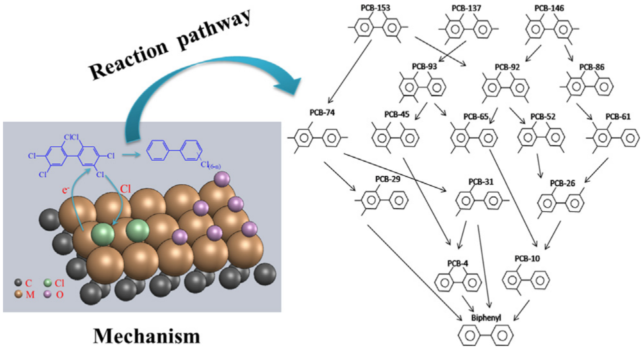
Jiani Xu [a,b], Yawen Liu [a,c], Fei Tao [a], Yifei Sun [a,*]

[a] *Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Space and Environment, Beihang University, Beijing 100191, China*
[b] *School of Chemistry, Beihang University, Beijing 100191, China*
[c] *School of Physics and Nuclear Energy Engineering, Beihang University, Beijing 100191, China*

HIGHLIGHTS

- AC-supported bimetallic catalysts were prepared using an ion-exchange method.
- Below 300 °C, Ni-Cu/C decomposed Aroclor 1254 more efficiently than Ni-Zn/C or Ni-Pd/C.
- Up to 300 °C, all the catalysts can decompose Aroclor 1254 with an efficiency >99%.
- PCBs are dechlorinated stepwise to form the final biphenyl product.

GRAPHICAL ABSTRACT



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ABSTRACT

Bimetallic catalysts supported on activated carbon (AC) with high metal loadings were prepared by an ion-exchange method. AC-supported Ni-Cu, Ni-Zn and Ni-Pd bimetallic catalysts were used to decompose Aroclor 1254, which is one of the most commonly used commercial mix of polychlorinated biphenyls. Characterization by scanning electron microscopy and energy-dispersive X-ray analysis showed that the metals were uniformly distributed on the surfaces and inside the catalysts. The efficiencies of Aroclor 1254 decomposition were measured at different reaction temperatures and times. With increasing temperature, the catalytic activities increased and the activation energies of the reactions decreased, resulting in higher decomposition efficiencies. At 300 °C in a nitrogen atmosphere, Aroclor 1254 decomposition efficiencies of 99.3%, 99.4% and 99.5% were achieved for reactions with Ni-Cu/C, Ni-Zn/C and Ni-Pd/C, respectively. The kinetics and pathway of the decomposition reaction were discussed, and we concluded that the reactivity of the chlorine atoms located on the benzene rings followed the order para-position > meta-position > ortho-position. The PCBs were dechlorinated stepwise to form the final biphenyl product. The design concept and synthetic strategy developed in this study are of great significance in the disposal of chlorinated organic compounds, for use with the existing adsorption technology of AC.

1. Introduction

Polychlorinated biphenyls (PCBs) are a group of persistent organic pollutants that were used worldwide before the 1970s. Commercial

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* Corresponding author.
E-mail address: sunif@buaa.edu.cn (Y. Sun).

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production of PCBs started in the United States in 1929. Owing to their high stability and excellent thermal properties, PCBs have been an ideal medium for heat transfer and as a component of insulating oil in electrical transformers and capacitors (Bennett, 1992). Approximately 1.5 million tons of PCBs were produced worldwide over a 50-year period, of which 10,000 tons originated from China (Chen et al., 2008; Cui et al., 2015; Gong et al., 2017). Although their production and usage have been banned, the substantial release of PCBs into the environment remains a global problem. The soil and water pollution caused by PCBs has become a serious concern due to PCB bioaccumulation, resistance to degradation, persistence, long-distance transport, and toxicity (Kannan et al., 1997; Lu et al., 2015). According to the Stockholm Convention on Persistent Organic Pollutants, PCB-containing waste must be disposed of properly by 2028, and therefore the removal of PCBs from the natural environment is a matter that requires urgent study.

Several technologies have been utilized for PCB decomposition with varying degrees of success (Balasubramani and Rifai, 2018; Gomes et al., 2013; Kamarehie et al., 2014; Nadarajan et al., 2017; Qin et al., 2018; Xu et al., 2010). In some developed countries, PCBs are destroyed primarily by incineration and chemical dechlorination, with a decomposition efficiency of up to 99.9999% for high PCB concentrations (Hosomi, 2000; Takata et al., 2015). However, large volumes of exhaust gas containing residual PCBs are generated in the disposal process. Aroclor 1254 is considered to be a representative component of residual PCB waste, which contains 22 PCB congeners comprising >1% of the weight. Low-concentration PCBs are adsorbed onto activated carbon (AC) and subsequently removed via incineration (Chi et al., 2006; Millward et al., 2005; Qi et al., 2014). However, many problems arise from this approach, such as the high costs involved in the construction and maintenance of high-temperature equipment, the generation of dioxins, and the risk of exposure to adsorbed PCBs during transport and incineration. Therefore, substantial efforts have been made to overcome these problems. AC is not only an excellent adsorbent but also a catalyst support because of its high surface area and pore volume. Zero-valent metals supported on AC have been employed as catalysts to reduce and dechlorinate organic halogen compounds and widely applied in the field of environmental engineering for decades (Choi et al., 2009; Choi et al., 2008). A catalyst consisting of palladium (Pd) loaded onto AC was synthesized for the decomposition of polychlorodibenzo p dioxins and polychlorodibenzofurans, with a decomposition efficiency of 98.8% achieved under certain conditions (Zhang et al., 2008). However, noble metals have high costs, which restrict the metal loading of the catalysts and thus limit their catalytic activity. In contrast to noble metals, transition metals, of which iron (Fe), nickel (Ni), copper (Cu) and zinc (Zn) are the most studied in their zero-valent forms, are abundant and inexpensive (Fang et al., 2017; Gryglewicz et al., 2006; Sun et al., 2015; Sun et al., 2016b; Tang et al., 2015; Xie et al., 2014; Zhu, 2011). Our previous work has shown that AC-supported monometallic (Ni, Cu, Zn, or Fe) catalysts effectively decompose low-concentration PCBs in a nitrogen atmosphere (Sun et al., 2013; Sun et al., 2016a). Although Fe is the most abundant metal, it is vulnerable to chemical oxidation. Therefore, we chose Ni, Cu, and Zn for preparation of bimetallic catalysts with the aim of enhancing the efficiency of PCB decomposition.

In this study, we attempted to take advantage of the synergies between Ni and the co-metals of AC-supported Ni-Cu and Ni-Zn bimetallic catalysts during degradation of the low-concentration commercial PCB mixture Aroclor 1254, and evaluated the efficiencies of catalytic PCB decomposition at low temperatures. An AC-supported Ni-Pd bimetallic catalyst was prepared for comparison purposes. In addition, the decomposition pathway and kinetics of Aroclor 1254 removal were analyzed carefully. Noble metal catalysts are expected to be replaced by transition metal catalysts in future industrial PCB decomposition processes. Most importantly, this work is of universal significance for the development of highly efficient noble metal-free catalysts for the decomposition of chlorinated organic compounds.

2. Materials and methods

2.1. Materials

Analytical-grade powders of $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $PdCl_2 \cdot 2H_2O$, and ammonia solution were purchased from Guangdong Guanghua Sci-Tech Corporation. Raw resin (DIAION WK11) was purchased from Mitsubishi Chemical Corporation. Silica gel and anhydrous sodium sulfate were used for column chromatographic purification of decomposition products (described in detail below). Pesticide-grade hexane and toluene were purchased from J. T. Baker Corporation. Aroclor 1254 was chosen to investigate the process of PCB decomposition in this study. Native PCB standards, as well as internal PCB standards labeled with $^{13}C_{12}$ (both in hexane; Wellington Lab.), were used for gas chromatography analysis. All chemicals were used as received, without additional purification.

2.2. Preparation of AC-supported bimetallic catalysts

AC-supported bimetallic catalysts were prepared using an ion-exchange method. Raw resin was used as the initial support and then treated under alkaline conditions due to its weak acidity. The treated cation resin was then immersed for 2 h in mixed solutions (100 mL ammonia and 100 mL deionized water) of $NiSO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$ or $PdCl_2 \cdot 2H_2O$. The cations (MNH_3^{2+}) were trapped by the resin, accompanied by the release of protons. The bimetallic ion-exchange resin was rinsed with deionized water and vacuum dried at 70 °C for 24 h. Finally, the ion-exchange resin was heated to 500 °C at a rate of 10 $°C \cdot min^{-1}$ and then held at 500 °C for 20 min under a flow of nitrogen (300 $mL \cdot min^{-1}$) for carbonization. The transformation of the raw resin during the ion-exchange process is presented in Fig. 1. Hereafter, we refer to the catalysts obtained (i.e., AC-supported Ni and Cu or Zn) as Ni-Cu/C, Ni-Zn/C and Ni-Pd/C, respectively.

2.3. Aroclor 1254 decomposition experiments

PCB decomposition experiments were conducted in a tubular furnace system equipped with a silica tube of 500 mm length and 20 mm inner diameter (Fig. 2). A ribbon heater was used to maintain the temperature of the system and drive the gas flow onto the impingers. The bimetallic catalyst (1 g) was loaded onto the middle position of the furnace, and 1 mL Aroclor 1254 solution (10 $\mu g \cdot mL^{-1}$ in hexane) was injected and vaporized at the inlet of the electric furnace. Before reaction, nitrogen (50 $mL \cdot min^{-1}$) was first pumped into the system for approximately 30 min to displace the air in the tube. After the decomposition experiments were complete, the nitrogen flow was maintained for another 30 min to cool the furnace down to room temperature. The gas hourly space velocity (GHSV) was maintained at 1400 h^{-1} during the decomposition reaction. The gas-phase decomposition products were dissolved in toluene (100 mL), filled in the impingers. The catalysts were extracted in toluene (200 mL) for 20 h using a Soxhlet apparatus. The extracts were then concentrated to 4 mL volumes in a rotary evaporator at 40 °C, followed by column chromatography purification using anhydrous sodium sulfate and silica gel. The volumes of the solutions were further reduced to 100 μL by evaporation under a flow of nitrogen.

The Aroclor 1254 decomposition reactions were conducted for 10, 15, 20, 25, 30, 35, and 40 min at a constant temperature of 250 °C and nitrogen flow rate of 50 $mL \cdot min^{-1}$. To evaluate the activities of Ni-Cu/C, Ni-Zn/C, and Ni-Pd/C, the decomposition was also performed at different temperatures: 200, 250, and 300 °C. For these temperature-dependent experiments, the reaction time was 30 min, and the nitrogen flow rate was maintained at 50 $mL \cdot min^{-1}$.