



Influence of activated-carbon-supported transition metals on the decomposition of polychlorobiphenyls. Part I: Catalytic decomposition and kinetic analysis

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HIGHLIGHTS

- Up to 350 °C, all the catalysts could decompose PCB-153 with an efficiency >94%.
- Reactivities with respect to PCB decomposition of: Ni > Cu > Zn > Fe.
- PCBs decomposed by absorption-reaction-desorption using LaTM-C.
- PCBs decomposed by reaction-desorption using IRTM-C.
- For ion-exchange-type catalysts, the activation energy order was Ni < Cu < Zn < Fe.

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ABSTRACT

In this study, the synergism between activated carbon (AC) as a catalyst support and transition metals (TMs) is used to destroy low concentrations of PCBs. AC-supported TM catalysts were prepared according to two different methods: impregnation and ion exchange. Thermal reactions between 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153) and catalysts generated using AC-supported Ni or Cu ion exchange were conducted under a N₂ atmosphere and resulted in a decomposition efficiency > 99.0%. Decomposition efficiency of PCB-153, the residual PCB-153 distribution, and the fingerprint characteristics of the decomposition products are investigated. Important findings include: (i) establishing a ranking of TM reactivities with respect to PCB decomposition of: Ni > Cu > Zn > Fe, (ii) PCB degradation reactions proceed via adsorption, reaction, and desorption, (iii) for ion-exchange-type catalysts, the activation energy order was IRNi-C < IRCu-C < IRZn-C < IRFe-C, which matches the order of the catalytic effects of the catalyst.

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1. Introduction

Polychlorinated biphenyls (PCBs) are highly stable and exhibit excellent thermal properties, poor flammability and electrical conductivity and high capacitance which give them excellent electrical insulation property to be an ideal medium for heat transfer. Since their commercial production beginning in 1929, they

have been an important component in the insulation oil used in electrical transformers and capacitors due to the excellent electrical insulation property of PCBs (Wentz, 1989). Over a 50-year period from 1929 to the end of 1970s, approximately, 1.5 million tons of PCBs were produced worldwide (Hosomi, 2000). In China, 10,000 tons of PCBs were produced before 1980 (Chen et al., 2008). In 2004, China joined the “Stockholm Convention on Persistent Organic Pollutants,” which mandated the disposal of PCB wastes before 2028.

In many developed countries, PCBs are destroyed primarily by chemical disposal technologies or incineration, either of which

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results in a decomposition efficiency as high as 99.9999% (Rahuman et al., 2000). However, disposal is associated with the generation of large amounts of exhaust gas containing residual PCBs. Activated carbon (AC) has been used to adsorb low concentrations of PCBs in flue gas, after which it is disposed of by incineration. However, problems also arise during the incineration of contaminated AC, including the generation of dioxins in the incinerators, the high cost of the construction and maintenance of high-temperature equipment, and the risk of exposure to AC-adsorbed PCBs during their conveyance and pulverization prior to incineration. Accordingly, there is a great deal of interest in the development of an inexpensive and safe technology to treat flue gas containing low concentrations of PCBs.

In the 1980s, zero-valent metals were shown to act as reducers in the dechlorination of organic halogen compounds. This property has been widely exploited in environmental engineering (Fang and Al-Abed, 2008). Among zero-valent metals which can decompose organic compounds, mainly iron, tin, and zinc (Boronina et al., 1995; Su et al., 2014), are used for treating halogenated hydrocarbons.

In the treatment of PCB- and polyaromatic hydrocarbon (PAH)-contaminated sediment from Hunters Point Naval Shipyard (San Francisco Bay, CA), the sediment was exposed to coke (3.4 and 8.5 wt%) and AC (3.4 wt%) for 1 and 6 months, respectively. In the AC-treated sediment, 92% and 84% reductions in the aqueous equilibrium PCB and PAH concentrations and 77% and 83% reductions in PCB and PAH uptake by semipermeable membrane devices, respectively, were reported (Zimmerman et al., 2004). AC acts as a catalyst support in many reactions, including those reducing the concentrations of organic compounds (Derbyshire et al., 2001). Zero-valent metals were shown to act as reducers in the dechlorination of organic halogen compounds (Fang and Al-Abed, 2008). Cobo et al. (2009) reported the simple and efficient degradation of PCBs using an AC-supported palladium (Pd)/AC-catalyzed reaction carried out at room temperature. A Pd catalyst loaded on AC was used to decompose dioxin-like materials, with decomposition efficiencies reaching 98.8% under certain conditions (Cobo et al., 2009; Zhang et al., 2008). In addition, several catalysts supported on alumina or AC have been compared with respect to their reaction with *o*-dichlorobenzene (Frimmel and Zdrzil, 1997).

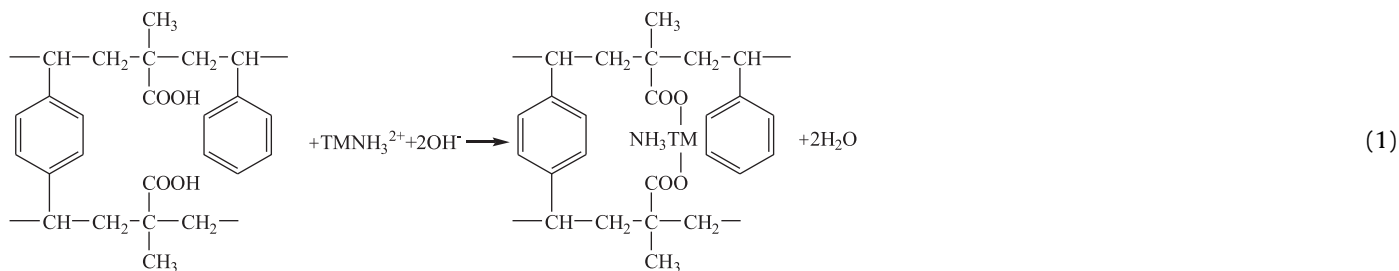
In contrast to noble metals, transition metals (TMs), including Fe, nickel (Ni), copper (Cu), and zinc (Zn), are inexpensive but as zero-valent metals they are also vulnerable to chemical oxidation. In this study, we developed AC-supported TMs to destroy the low concentrations of PCBs found in flue gas. The decomposition effects of Fe, Ni, Cu, and Zn at temperatures ranging from 200 to 350 °C were analyzed, together with the by-products of the decomposition process.

2. Materials and methods

The catalysts were prepared using chemicals of analytical grade, including $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, iron(II) lactate trihydrate, nickel(II) lactate tetrahydrate, zinc citrate dehydrate, copper(II) citrate 2.5-hydrate, and ammonia. Silica gel and anhydrous sodium sulfate were used for column clean-up. Hexane and toluene of pesticide grade were purchased from J. T. Baker. Congener PCB-153 was selected for studying the decomposition mechanism of PCBs in this study. Since PCB-153 is the main component of Kanechlor 600 (a commercial mix of PCBs manufactured in Japan) and Aroclor 1254 (a most widely used commercial mix of PCBs in America). It is also one of the most prevalent PCB congeners of environmental exposure (Longnecker et al., 2003) both in the environment and in human biological samples (e.g., serum and breast milk) and will disturb the hormone level in the life exposed in it. Also, PCB-153 will bring about less harm to the testers since it is a di-ortho congener thought to mediate its neurotoxicity via non-dioxin-like mechanisms. To simplify the investigation, 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153; AccuStandard, USA) dissolved in hexane (10 $\mu\text{g}/\text{mL}$) were used as the target compound. PCB native standards in hexane and PCB internal standards labeled with $^{13}\text{C}_{12}$ in hexane (Wellington Lab., Canada) were used in the gas chromatographic analysis.

2.1. Preparation of AC-supported TM catalysts

AC-supported TMs can be prepared by two methods: ion exchange and impregnation. In the ion-exchange method, raw resin (DIAION WK11; Mitsubishi Chemical, Tokyo, Japan) is used as the preliminary catalyst supporter. Since this resin is a weak acid type, it must be exchanged under an alkaline aqueous solution. To remove soluble impurities, the ion-exchange resin (5 g) was washed with deionized water prior to its direct interaction for 2 h with a solution containing 10 g of TM-sulfate dissolved in 100 mL of ammonia (3 mol/L) and 100 mL of deionized water. The exchanged resin was then rinsed with deionized water and dried at 70 °C for 24 h. Next, the dehydrated resin was heated to 500 °C (Cu, Ni, and Zn) or 700 °C (Fe) at a rate of 10 °C/min and held for 20 min at this temperature to allow carbonization. To avoid oxidation of the catalysts in air, carbonization was performed under a N_2 stream (300 mL min^{-1}). AC-supported TMs prepared according to this ion-exchange method are referred to in the following as IRTM-C, specifically, IRTM-C, IRNi-C, IRCu-C, and IRZn-C. The reactions are shown in Eqs. (1) and (2):



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