Catalytic decomposition of polychlorinated biphenyls by activated carbon-supported bimetallic catalysts

Yifei Sun[1], Yawen Liu[1,2], Fei Tao[1], Xungang Diao[2],

[1] School of Space and Environment, Beihang University, China
[2] School of Physics and Nuclear Energy Engineering, Beihang University, China

Introduction

Polychlorinated biphenyls (PCBs) have been widely used as insulating oil for transformers and condensers owing to their high stability and excellent thermal property. With the revelation that PCBs are harmful to the human body merely upon contact, their production and use have recently been prohibited. Up to this day, soil and water pollution caused by PCBs have become a serious concern due to their typical features of bioaccumulation, difficult degradability, persistence, long distance transport and toxicity. The disposal of PCBs by incineration generates large amounts of exhaust gas containing residual PCBs. Aroclor 1254 is supposed to be one of the industrial wastes with low-concentration PCBs.

Incineration and chemical disposal are used in the treatment of high-concentration PCBs-contaminated wastes, followed by treatment with activated carbon (AC) to absorb residual low-concentration PCBs. AC is well known to act as a catalyst carrier. Zero-valent metals have been used to reduce and dechlorinate organic halogen compounds since the 1980s, and the technique has been widely used in the field of environmental engineering [1]. In contrast to noble metals [2,3], transition metals, including nickel (Ni), copper (Cu), and zinc (Zn), are inexpensive but as zero-valent metals they are also vulnerable to chemical oxidation [4].

In the current study, we attempt to utilize the synergy between Ni and Cu, Zn or noble metal such as Pd by preparing AC-supported Ni/Cu, Ni/Zn and Ni/Pd to destroy low-concentration commercial PCBs mixture of Aroclor 1254 and evaluate the catalytic dechlorination efficiencies of PCBs by the AC-supported bimetallic catalysts. Furthermore, other factors contributing to PCBs reduction, such as time, temperature and catalyst type, were investigated. The decomposition pathway and kinetics of PCBs were also discussed.

Materials and methods

Three kinds of bimetallic catalysts, including AC-supported Ni/Cu, Ni/Zn and Ni/Pd with different metal ratios were synthesized by carbonizing an ion-exchange resin.

The PCBs decomposition experiments were conducted in a tubular furnace system, equipped with a silica tube of 500-mm length and 20-mm inner diameter, as shown in Fig.1. To insulate the thermal of system, ribbon heater was used to impel the gas to enter into the impingers. 1 g of Ni/Cu-C, Ni/Zn-C or Ni/Pd-C was loaded into the middle position of the furnace and 1 mL of hexane solution of Aroclor 1254 (10 $\mu g \cdot mL^{-1}$) was injected and vaporized at the inlet of electrical furnace. The decomposition experiments of Aroclor 1254 were performed under different temperatures to evaluate the activities of Ni/Cu-C, Ni/Zn-C and Ni/Pd-C. The corresponding temperatures were set at 200 °C, 250 °C and 300 °C, respectively. When the reaction was completed, the Ni/Cu-C, Ni/Zn-C or Ni/Pd-C catalyst was extracted for 20 h with 200 mL toluene using a Soxhlet apparatus. The extracts were then concentrated to 4 mL solutions in a rotary evaporator at 40 °C, followed by column clean-up with anhydrous sodium sulfate and silica gel. The volumes of the solutions were

further reduced to100 μL by evaporation with compress nitrogen gas. PCB homologs and biphenyl in the extracts and in the toluene solvents were analyzed by gas chromatography-mass spectrometry (GC-MS).

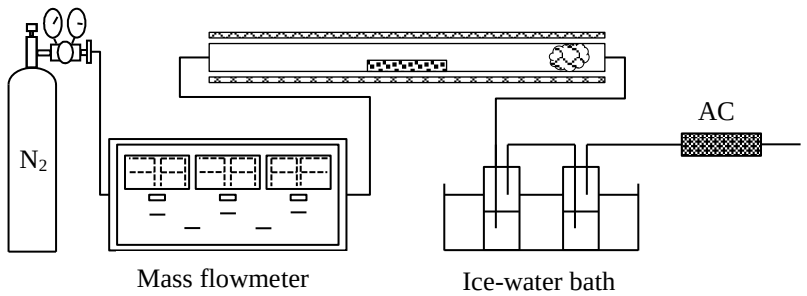

Fig. 1. The experimental setup for PCBs decomposition experiments

Results and discussion

1. Characterization of bimetallic materials

Table 1 shows that all the metal concentrations of bimetallic materials supported with AC exceed 394 $mg \cdot g^{-1}$. The characterization of scanning electron microscopy and energy dispersive X-ray exhibits higher density and dispersity of bimetallic materials, both at the surface and inside the catalysts.

Table 1: Metal concentrations of bimetallic materials supported with AC.

ICP	Ni/Cu-C			Ni/Zn-C			Ni/Pd-C
Metal Concentration (mg/g)	Ni/Cu(5/1)	Ni/Cu(1/1)	Ni/Cu(1/5)	Ni/Zn(5/1)	Ni/Zn(1/1)	Ni/Zn(1/5)	Ni/Pd(5/1)
	395	515	575	501	450	448	440

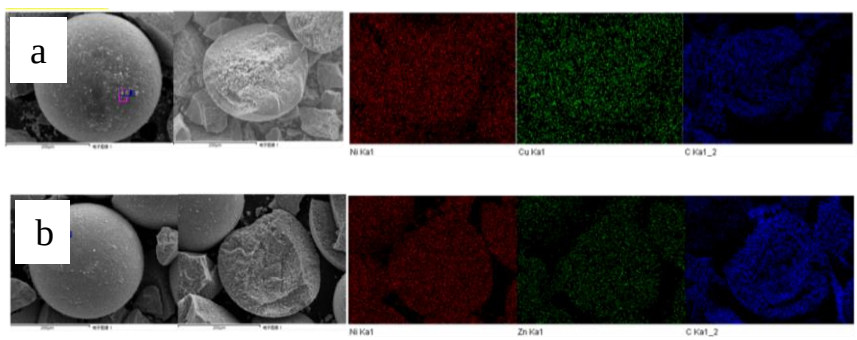

Fig. 2. SEM images and EDS analyses of catalysts Ni/Cu-C (a) and Ni/Zn-C (b).

2. Influence of decomposition times on the decomposition efficiency

The decomposition time was varied from 10 to 40 min to investigate the influence of time on the decomposition rate in the pulse injection system. The decomposition process was allowed to proceed for 40 min and Ni/Cu(1/1)-C catalyst was used. At the beginning of the 10-min decomposition period, Tetra-CBs, Penta-CBs and Hexa-CBs in Aroclor 1254 are decomposing rapidly, as presented in Fig. 3.

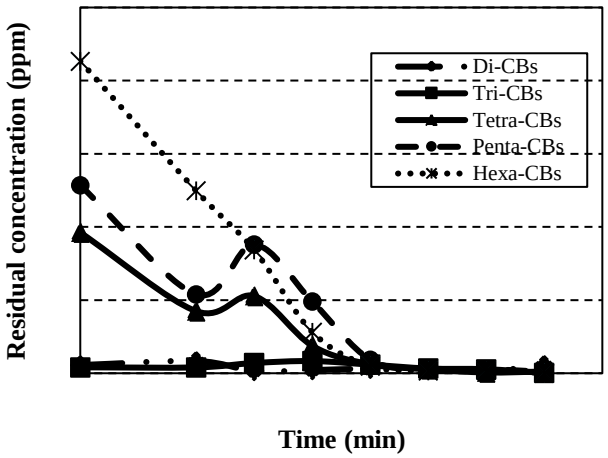

Fig. 3. Decomposition efficiency of Aroclor 1254 by Ni/Cu(1/1)-C at different decomposition reaction times: (a) temporal variation of Di-CBs (◆), Tri-CBs (■) Tetra-CBs (▲), Penta-CBs (●) and Hexa-CBs (※) in Aroclor 1254 at 523K.

3. Influence of reaction temperature on the decomposition efficiency

With rising temperature, the decomposition efficiency of Tetra-CBs, Penta-CBs and Hexa-CBs by bimetallic catalysts gradually increases. The activation energy reduces and the catalytic activity intensifies, resulting in higher decomposition efficiency at high temperature than at low temperature. At 200 °C, these efficiencies remain fairly low, with no significant differences between the three catalysts. Decomposition by Ni/Pd(5/1)-C, Ni/Cu(5/1)-C and Ni/Zn(5/1)-C at 300 °C is achieved within 30 min under N_2 atmosphere and the efficiency of Hexa-CBs in Aroclor 1254 attains 99.5 %, 99.3 % and 99.8 %, respectively. The quite high efficiencies could be the result of synergy between the metals and AC. It can be also concluded that precious metals can be replaced by cheap metals to effectively decompose PCBs.

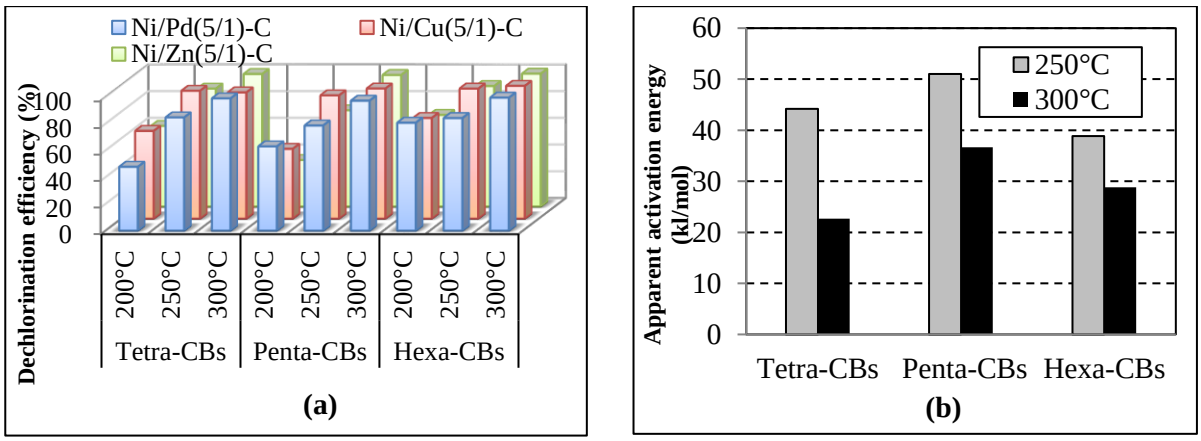

Fig. 4. Influence of reaction temperature on the decomposition efficiency of Aroclor 1254: (a) decomposition rate by Ni/Cu(5/1)-C, Ni/Zn(5/1)-C and Ni/Pd(5/1)-C. (b) apparent activation energy of the catalytic decomposition of Aroclor 1254 by Ni/Cu(5/1)-C at 250 °C and 300 °C.

Acknowledgements

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