MECHANISTIC CHARACTERIZATION OF ACTIVATED CARBON-SUPPORTED METALS ON DECOMPOSITION OF POLYCHLORINATED BIPHENYLS

Yifei Sun, Xin Fu, Tianle Zhu

School of Chemistry and Environment, Beihang University, Beijing 100191, China

Introduction

Polychlorinated biphenyls (PCBs) were first produced commercially in the United States in 1929 [1], and have been used as dielectric fluids for transformers and capacitors because of their excellent stability and thermal properties [2]. 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 [2]. While, between the start of production in 1964 and end in 1974, approximately 10,000 tons of PCB were manufactured in China [3]. Furthermore, due to poor storage methods, a great deal of soil was contaminated. The contamination of soil with high-concentration PCBs (>500 ppm) was about 50,000 tons and that of low-concentration PCBs (50–500 ppm) was about 500,000 tons [3]. In 2004, China joined the "Stockholm Convention on Persistent Organic Pollutants," which mandated that PCB wastes must be disposed of before 2028. [3].

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. Fe or Fe compounds have been used as catalysts to decompose PCBs, and the decomposition efficiency of deca-PCBs was 99% [4]. AC, however, is not just a strong adsorbent; it can also be used as a catalyst support in many reactions, including those used to reduce the concentrations of organic compounds [5]. A catalyst of Pd loaded on AC has been applied to decompose dioxin-like materials, such as PCDDs, PCDFs and co-PCBs; the decomposition efficiency reached 98.8% under certain conditions [6]. Ukisu et al. reported that when Pd or Rh supported AC was used as a catalyst, the decomposition efficiency of PCDD or PCDF was 99.96% [7]. In addition, several catalysts supported on alumina or AC have been compared with respect to the reaction of o-dichlorobenzene [8]. On the other hand, transition metals are reported to dechlorinate PCDD and PCDF derivatives and other chlorinated compounds [9]. In this study, we tried to utilize the synergism between AC and transition metals, so AC-supported transition metals were made to decompose low concentrations of PCBs. Finally, the decomposition pathways were studied under different atmospheric conditions. A density functional theory (DFT) study was carried out to investigate the C-Cl bond energy of the ortho, meta and para positions in PCBs, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy. The information of C-Cl bond energy, the energy gap between HOMO and LUMO, was related to the dechlorination order of PCB isomers.

Materials and Methods

Two methods for producing AC-supported transition metals were proposed. LaCu, LaZn-C, LaFe or LaNi-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 Cu, Zn, Fe or Ni by the carbonization of ion-exchange resins (Mitsubishi Chemical, WK-11). AC prepared by this method was called IRCu, IRZn, IRFe-C or IRNi-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). The metal concentrations in LaCu, LaZn-C, LaFe or LaNi-C were 13, 46, 41 or 12 mg/g-C, while in IRCu, IRZn, IRFe-C or IRNi-C were 557, 502, 374 or 542 mg/g-C).

X-ray absorption fine structure spectroscopy (XAFS) measurement was carried out at a beam line BL01B1 in SPring-8, a synchrotron radiation facility in Japan. The spectra were collected in fluorescence mode using a 19-element Ge solid-state detector for the AC disks and in transmission mode using an ionization chamber for the model AC, with a Si(111) monochromator. The spectra of of X-ray absorption near edge structure (XANES) spectra with reference iron or nickel compounds were measured to be compared with iron compounds in AC. Species have also been distinguished using the linear combination fit (LCF) technique, in which spectra of known reference species Fe, Fe_2O_3, Fe_3O_4 and Ni, NiO are fitted to the spectrum of the unknown sample. The LCF of XANES spectra has been used to identify and quantify major species in AC-supported metal. The author conducted the LCF of XANES to determine the major species using the commercial software REX 2000 ver. 2.3 (Rigaku Co. Ltd., Japan). One free running parameter, partial concentration, was refined for each reference spectrum in the LCF of XANES. The residual value (R), calculated using Eq. 1, was used to evaluate the LCF for the experimental spectra.

$$R = \frac{\sum \left(XANES_{Measured} - XANES_{Calculated} \right)^2}{\sum \left(XANES_{Measured} \right)^2} \times 100\% \qquad (1)$$

One milliliter of a PCB-153 solution (10 µg/ml-hexane) was injected and vaporized at the inlet of the electrical furnace, 8 kingds of IRM-C or LaM-C was used as catalysts. 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 using a GCMS-QP2010 series gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a HP-5MS capillary column (Hewlett Packard, Palo Alto, CA, USA). The carrier gas was helium at a constant flow rate of 1 ml/min.

Results and Discussion

Decomposition Effects on Different Catalysts

For the eight kinds of catalysts, AC supported Ni shower the best effect on PCB decomposition. 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. When LaCu-C or IRCu-C used as catalysts, an increased temperature from 250 to 350°C increased decomposition efficiencies from 84.7 to 100.0%. However, when the decomposition time reached 300 °C, the decomposition efficiencies

reached 99.8%. LaFe-C showed the lowest decomposition efficiency of the eight kinds of catalysts. There were no obvious differences in decomposition efficiency at high temperature of 350°C, however IRNi-C showed the same decomposition capaciy at 250°C.

XAFS study on AC-supported transition metals

The XANES spectrums of reference iron compounds such as Fe, Fe_2O_3, Fe_3O_4 and Ni, NiO were shown on the upper part of Fig. 1, while the XANES spectrums of LaFe-C, IRFe-C, LaNi-C and IRNi-C were shown in the nether part of Fig. 1. According to the results of pattern fitting, iron compounds in LaFe-C was Fe_3O_4, and in IRFe-C was a mixture of 31% of Fe and 68% of Fe_3O_4; nickel compounds in LaNi-C was a mixture of 82% of Ni and 18% of NiO, IRNi-C was a mixture of 86% of Ni and 14% of NiO. The catalysts contain more elementary substance of metals showed a higher decomposition effiencies.

Fig. 1 Fe and Ni K edge XANES spectra in reference Fe or Ni compounds and AC-supported metals.

Decomposition pathway

Decomposition pathway of PCB-153 at 350°C was investigateds. PCB-153 was dechlorinated to tetraCBs, and then dechlorinated to triCBs and diCBs. MonoCBs were not detected by GC-MS. Finally, PCBs were dechlorinated to biphenyl. PentaCBs were not detected for two possible reasons: either the reaction occurred too quickly or the decomposition did not pass the pathway to pentaCBs. The pathway showed that chlorine in the para position could be dechlorinated more easily. Due to steric hindrance, the chlorine atom located at the para position in PCB-153 was more reactive than the one at the ortho or meta position. We postulate the reactive characteristics of chlorine atoms located on the benzene rings as *para > meta > ortho*. The LUMO and HOMO energies of 2-MonoCB, 3-MonoCB, and 4-MonoCB were calculated based on DFT, which was performed with the Gaussian 03 package using the B3LYP exchange correlation function. The base set was 6-311+G**. The optimized structures of PCB-153 were calculated. The Energy gap between HOMO and LUMO of MonoCBs, energy of 2-MonoCB, 3-MonoCB, 4-MonoCB with biphenyl were separately optimized by the B3LYP/6-311+G (D,P) method shown in Table 1. The C-Cl bond energy, EB, of 2-MonoCB, 3-MonoCB, and 4-MonoCB was calculated as follows:

$$E_B = E_{B-monoCB} + E_H - E_{Biphenyl} - E_{Cl} \,, \tag{2}$$

where E_B is C-Cl bond energy, $E_{B-monoCB}$ is the molecular energy of monoCB, E_H is the H atom energy, $E_{Biphenyl}$ is the molecular energy of biphenyl, and E_{Cl} is the Cl atom energy. The E_B values of the *ortho*, *meta* and *para* positions were 0.0461, 0.0419 and 0.0418 a.u.; a higher E_B value indicates a more difficult dechlorination. The energy gap between the HOMO and LUMO predicated the molecular stability, i.e., the resistance to electron transfer. The energy gaps between the HOMO and LUMO for the *ortho*, *meta* and *para* positions were 0.2035, 0.1893 and 0.2035 a.u., revealing that the most stable position was ortho. The dechlorination order of different Cl positions was in good agreement with the calculated values of the characteristic bond energy and energy gap between the HOMO and LUMO.
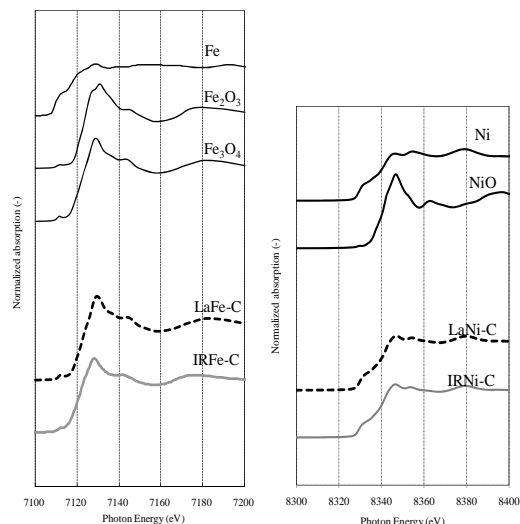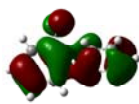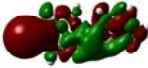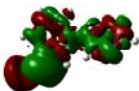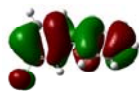
Table 1 Illustration of the HOMO and LUMO of MonoCB molecular and bond energies.

...omer	LUMO	HOMO	Energy gap between HOMO and LUMO (a.u.)	Molecular energy (a.u.)	C-Cl bond energy (a.u.)
	Energy (a.u.)				
...noCB	−0.0419	−0.2454	0.2035	-923.0413	0.0461
...noCB	−0.0493	−0.2386	0.1893	-923.0456	0.0418
...noCB	−0.0505	−0.2439	0.1934	-923.0456	0.0419

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