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Dechlorination of polychlorinated biphenyls by iron and its oxides

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HIGHLIGHTS

- N_2 was the optimum atmosphere for PCB decomposition using iron or iron compounds.
- No matter which PCB congener was tested, Fe_3O_4 showed the highest activity.
- More active sites for PCBs decomposition were provided with low O/Fe ratio of Fe_3O_4.
- Reactive characteristics of Cl atoms on benzene rings followed *para* > *meta* > *ortho*.

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ABSTRACT

The decomposition efficiency of polychlorinated biphenyls (PCBs) was determined using elemental iron (Fe) and three iron (hydr)oxides, i.e., α-Fe_2O_3, Fe_3O_4, and α-FeOOH, as catalysts. The experiments were performed using four distinct PCB congeners (PCB-209, PCB-153, and the coplanar PCB-167 and PCB-77) at temperatures ranging from 180 °C to 380 °C and under an inert, oxidizing or reducing atmosphere composed of N_2, $N_2 + O_2$, or $N_2 + H_2$. From these three options N_2 showed to provide the best reaction atmosphere. Among the iron compounds tested, Fe_3O_4 showed the highest activity for decomposing PCBs. The decomposition efficiencies of PCB-209, PCB-167, PCB-153, and PCB-77 by Fe_3O_4 in an N_2 atmosphere at 230 °C were 88.5%, 82.5%, 69.9%, and 66.4%, respectively. Other inorganic chlorine (Cl) products which were measured by the amount of inorganic Cl ions represented 82.5% and 76.1% of the reaction products, showing that ring cleavage of PCBs was the main elimination process. Moreover, the dechlorination did not require a particular hydrogen donor. We used X-ray photoelectron spectroscopy to analyze the elemental distribution at the catalyst's surface. The O/Fe ratio influenced upon the decomposition efficiency of PCBs: the lower this ratio, the higher the decomposition efficiency. X-ray absorption near edge structure spectra showed that α-Fe_2O_3 effectively worked as a catalyst, while Fe_3O_4 and α-FeOOH were consumed as reactants, as their final state is different from their initial state. Finally, a decomposition pathway was postulated in which the Cl atoms in *ortho*-positions were more difficult to eliminate than those in the *para*- or *meta*-positions.

1. Introduction

In the United States, polychlorinated biphenyls (PCBs) were first produced commercially in 1929 and used as a heat-transfer medium or insulation oil in electrical transformers and capacitors, due to their excellent stability and thermal properties (Wentz, 1995; Qi et al., 2014). Over a 50-year period, approximately 635 million tons of PCBs were produced worldwide (Buckley, 1982). In 1968, the Yusho event in Japan (Yoshimura, 2003), and in 1979 the Yucheng event in Taiwan (Rogan et al., 1988) greatly amplified the concerns over the safety of using PCBs. Because of their persistence and propensity to bio-accumulate in fatty tissues, the manufacturing of PCBs ceased in Japan in 1974 and in the USA in 1977, with the passing of the *Law Concerning the Examination and Regulation of Manufacture, Etc. of Chemical Substances* and the *Toxic Substances Control Act*, respectively. However, a large fraction of the PCBs that were produced are still present in the environment (Bert and Esteban, 2008; Lu et al., 2012). From 1930 through to 1970, the cumulative losses of PCBs to the environment were estimated at 354,000 tons (Ackerman et al., 1983).

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Prior to 1980, the whole amounts of PCBs produced in China were 10,000 tons (MEPPRC, 1991; Chen et al., 2008). Due to the poor storage methods applied to PCB-contaminated equipment in China, a great deal of soil became contaminated: approximately 50,000 tons with high concentrations (>500 ppm) and approximately 500,000 tons with low concentrations (50–500 ppm) of PCBs (MEPPRC, 1991; Chen et al., 2008). In 2004, China joined the Stockholm Convention on Persistent Organic Pollutants, which requires all PCB-contaminated waste to be eliminated before 2028.

In developed countries, including Europe, the United States, and Japan, a great deal of progress has been achieved in disposing of PCBs by incineration or other methods, such as chemical destruction using palladium/carbon (Pd/C) as a catalyst (Kume et al., 2008). Since the 1980s, zero-valent metals have been used to reduce and dechlorinate organic halogen compounds, and the technique has widely been used in the field of environmental engineering (Fang and Al-Abed, 2008). Zero-valent metals, mainly Fe, Sn, and Zn (Boronina et al., 1995; Su et al., 2014), allow the treatment of halogenated hydrocarbons. Zero-iron (Fe) can convert PCBs into biphenyl in 10 min at 400 °C (Chuang et al., 1995), and nano-sized Fe powder can be used as a catalyst to destroy 1,1′,2,2′-tetrachlor oethane (Chuang et al., 1995). Zero-valent Fe acts as an electron donor and thus becomes oxidized to Fe^{2+}, while C_2Cl_4 gains an electron and is dechlorinated (Li et al., 2006). The decomposition efficiency of 1,2,3,4-Tetrachlorodibenzodioxin (TCDD) attains 95% with Fe–Pd as a catalyst (Wang et al., 2010). Catalytic hydrodechlorination with noble-metal catalysts has been widely used for the dechlorination of a variety of chlorinated organic compounds under relatively mild conditions (Ukisu et al., 1996; Urbano and Marinas, 2001; Alonso et al., 2002; Ukisu and Miyadera, 2003). However, noble metals are very expensive, and it is essential to find cheaper substances to eliminate PCBs. Activated carbon supported iron showed high PCBs decomposition efficiencies with inert atmosphere (Sun et al., 2006, 2012). However, as the iron was easily oxidized, it was not sure what compounds of iron played a role to destroy PCBs.

In the present study, we used iron and its (hydro)oxides (α-Fe_2O_3, Fe_3O_4, and α-FeOOH) as catalysts to treat several PCB congeners (PCB-209, PCB-167, PCB-153, and PCB-77) under an N_2, $N_2 + O_2$, or $N_2 + H_2$ atmosphere. A decomposition pathway was postulated using PCB-209, and we investigated the influence of the position of chlorine (Cl) atoms on the ease of dechlorination. In addition, the dechlorination mechanism of PCBs was identified using coplanar PCBs, i.e. PCB-77, PCB-167 and PCB-153, which are non-ortho, mono-ortho and di-ortho coplanar PCBs, respectively. Coplanar PCBs such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly toxic (Sun et al., 2006), compared to non-coplanar PCBs, and the toxic effects of coplanar PCBs occur at relatively smaller concentrations than those of non-coplanar PCBs (Sun et al., 2012). The molecular structures and C–Cl bonds were different when the coplanar PCB species were different, which is important to decide the Cl position easy to dechlorinate. In order to select the most useful iron or iron compounds, X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) analyses were used to analyze the structural changes in the iron or iron compounds of the catalysts used during the reaction (Tanaka et al., 1988).

2. Experimental section

2.1. Materials and reagents

Four kinds of catalysts were used: Fe powder of 177 μm (Nakalai Tesque Inc., Kyoto, Japan), α-Fe_2O_3 (1 μm) of 99.9% purity (Soekawa Chemical Co. Ltd, Tokyo, Japan), Fe_3O_4 (1 μ) of 99% purity (Soekawa), and α-FeOOH powder of 99% purity (Soekawa).

Four congeners of PCBs (PCB-209, PCB-167, PCB-153, and PCB-77) were selected to investigate the influence of the *ortho*-position on dechlorination; using PCB-209, the entire dechlorination pathway could be established. The other three types of PCBs are major components of Kanechlor, a commercial Japanese PCB mixture.

2.2. Apparatus

The test decomposition system was designed and operated on the basis of a pulse reactor. The length of the silica reactor tube used was 700 mm, and the inner diameter was 20 mm. A total of 0.5 g of Fe or Fe compounds was placed in the middle of the furnace, and then 1 mL PCB solution (10 μg/mL hexane) was injected at the inlet of the reactor, using a JP-S-W.6 microfeeder (Furue Science Co. Ltd, Japan) and decomposition was continued for 30 min under an N_2, $N_2 + O_2$, or $N_2 + H_2$ flow at a rate of 50 mL/min. The electric furnace temperature was controlled at 230 °C, 330 °C, or 380 °C for the different reaction atmospheres, respectively. After the decomposition time had elapsed, the reaction atmosphere was still maintained and the decomposition equipment was allowed to cool down to room temperature. The exhaust gas was sent to impingers filled with 100 mL toluene to collect the decomposition products. Following PCB-decomposition, the catalyst was extracted using Soxhlet extraction to quantify the residual products remaining in the catalyst zone. Finally, the PCB homologs and biphenyl were quantified in the toluene solution and in the extract, using gas chromatography and/or mass spectrometry.

The analysis was performed using an HP6890 series gas chromatograph (Hewlett Packard, Palo Alto, CA), which was connected to an HP 5973 mass-selective detector (electron impact, 70 eV) operated under the selected ion-monitoring (SIM) mode, using the molecular ion of each compound at 1.5–2 scan/s. The capillary column was an HP-5MS (Hewlett Packard, Palo Alto, CA), of 60 m in length and an inside diameter of 0.250 mm, with a film thickness of 0.25 μm. The carrier gas was helium at a constant flow-rate of 1 mL/min.

XPS (ESCA-3200, Shimadzu, Japan) using Mg Kα (1253.6 eV) radiation and a retarding potential analyzer, was used to characterize the different catalysts. The sample chamber vacuum pressure was 10^{-5}–10^{-6} Pa. The catalysts were analyzed before and after reaction under atmospheres of N_2 and $N_2 + O_2$ at 330 °C. X-ray absorption fine structure spectroscopy (XAFS) measurements were carried out at a synchrotron radiation facility in Japan, used a beamline BL01B1 in SPring8 (Aritani et al., 2002). The spectra were collected in the fluorescence mode using a 19-element Ge solid-state detector for the Fe or Fe compound disks, and in the transmission the mode using an ionization chamber for the model AC. K edge XANES spectra of α-Fe_2O_3, Fe_3O_4, α-FeOOH before and after decomposition were compared.

3. Results and discussion

The decomposition efficiency and the biphenyl yield were calculated as follows:

$$\text{Decomposition efficiency } (\%) = (1 - c/c_0) \times 100\% \tag{1}$$

$$\text{Biphenyl yield} (\%) = c_b/c_0 \times 100\% \tag{2}$$

where c_0 is the original amount of PCBs injected into the system, and c and c_b are the total amounts of PCBs and biphenyl remaining on the catalyst and absorbed in toluene, respectively. All