



Degradation of polychlorinated biphenyls using mesoporous iron-based spinels

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HIGHLIGHTS

- The NiFe_2O_4 had the highest activity in degradation of CB-209, followed by Fe_3O_4 .
- Hydroxyl species, organic acids, PCBs and chlorobenzenes were identified as products.
- Three degradation reactions and one combination reaction competitively occurred.
- Hydrodechlorination of CB-209 was more favored over Fe_3O_4 than NiFe_2O_4 .
- Oxidation reaction of CB-209 was more favored over NiFe_2O_4 than Fe_3O_4 .

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ABSTRACT

A series of mesoporous iron-based spinel materials were synthesized to degrade polychlorinated biphenyls (PCBs), with CB-209 being used as a model compound. The materials were characterized by X-ray powder diffraction (XRD), pore structure analysis, and X-ray photoelectron spectroscopy (XPS). A comparison of the dechlorination efficiencies (DEs) of the materials revealed that NiFe_2O_4 had the highest DE, followed by Fe_3O_4 . Newly produced polychlorinated biphenyls, chlorinated benzenes, hydroxyl species and organic acids were detected by gas chromatography–mass spectrometry, high performance liquid chromatography–mass spectrometry and ion chromatograph. Identification of the intermediate products indicates that three degradation pathways, hydrodechlorination, the breakage of C–C bridge bond and oxidative reaction, accompanied by one combination reaction, are competitively occurring over the iron-based spinels. The relative amounts of produced three NoCB isomers were illustrated by the C–Cl BDEs of CB-209 at *meta*-, *para*- and *ortho*-positions, and their energy gap between HOMO and LUMO. The consumption of the reactive oxygen species caused by the transformation of Fe_3O_4 into Fe_2O_3 in the Fe_3O_4 reaction system, and the existence of the highly reactive $\text{O}_2^{\cdot-}$ species in the NiFe_2O_4 reaction system, could provide a reason why the oxidation reaction was more favored over NiFe_2O_4 than Fe_3O_4 .

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1. Introduction

Polychlorinated biphenyls (PCBs) are a group of chlorinated aromatic compounds, with the group itself containing 209 congeners, and determined as prior controlled persistent organic pollutants (POPs) in the Stockholm Convention because of their high levels of toxicity and bioaccumulation. They have been widely used as dielectric fluids in electrical transformers and capacitors, plasticizers in paint, and dye carriers in carbonless copy paper [1]. Although the production of PCBs has been banned since the mid 1970s, large amounts of PCBs were released into the environment because of

their historical widespread use. Accidental exposure to PCBs still occurs due to their presence in old transformers and capacitors. The control of PCBs is therefore a matter of public concern in the context of environmental protection.

High-temperature incineration is currently the principle method used for the destruction of PCBs [2]. However, considerable problems associated with this approach include high cost and possible generation of more toxic polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/Fs) [3]. Catalytic degradation technique has attracted considerable attention as a safe alternative. The use of metal oxides as catalysts for the degradation of PCBs showed the increasing attraction because of their relatively low costs and high levels of activity. A variety of different metal oxides have been tested for reaction activity in the dechlorination of PCBs, including Cr_2O_3 , Co_3O_4 , CuO , Al_2O_3 , La_2O_3 , and MgO [4,5]. Subbanna

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et al. [4] reported that the use of 10% CuO supported on α - Al_2O_3 showed better activity in the decomposition of Aroclor 1254 than the supported 4% Cr_2O_3 and 6% Co_3O_4 , with a destruction efficiency of 97.3% at 600 °C. Tanaka et al. [5] reported that Al_2O_3 , La_2O_3 and MgO efficiently dechlorinated monochlorinated biphenyls. In these reaction systems, less chlorinated PCBs were often identified as the degradation products, leading to an agreement about the presence of a hydrodechlorination pathway. However, little work has been done to determine the effect of the position of the chloride substituents on the performance of the different metal oxides to the hydrodechlorination reactions of PCBs. Although the C–C bond between two phenyls is separate in π -conjugated system, few work reported whether PCBs could degrade via the breakage of this bridge bond. Active oxygen species present on the surfaces of metal oxides may also participate in the oxidation reactions of PCBs. Thus far, however, the reports to identify the oxidation products and the associated mechanisms remain particularly scarce.

In recent years, considerable efforts have been made to develop multicomponent materials for the decomposition of organic pollutants because of the remarkable reaction properties such as high surface areas, high melting points and multifunctionality that single metal oxides cannot realize [6–13]. Spinel oxides are a class of complex oxides with chemical formula AB_2O_4 , containing the normal and inverse structures. In normal spinels, A is generally a divalent cation occupying tetrahedral sites, while B is a trivalent cation occupying octahedral sites. In inverse spinels, half of B cations occupy the tetrahedral sites. Spinel oxides have high thermostability and high hardness, and some of them exhibit extraordinary electric and magnetic properties [14–17]. Recently, spinel oxides are increasingly being investigated as catalysts to remove environmental pollutants. Several studies have reported that spinels as multicomponent materials exhibited high level of activities toward degradation of chlorinated aromatics [18–21]. Cesteros et al. [18] found that the hydrodechlorination of 1,2,4-trichlorobenzene to benzene proceeded at a much greater rate in the presence of a spinel-supported nickel material ($\text{Ni}/\text{NiAl}_2\text{O}_4$) than it did in the presence of an aluminum-supported nickel materials ($\text{Ni}/\text{Al}_2\text{O}_3$) at 150–250 °C. Furthermore, Fan et al. [19] reported 85% dechlorination efficiency (DE) of hexachlorobenzene (HCBz) and 99% decomposition efficiency of polychlorinated dibenzodioxin (PCDD) were achieved over CuAl_2O_4 material at 250 °C, which was more effective than the corresponding metallic copper and copper oxide materials. In the further studies, they synthesized $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ spinel oxides for the hydrodechlorination of HCBz, and found that $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ provided a higher level of reaction activity than CuO , Al_2O_3 , and the other $\text{Cu}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$, as well as a lower level of activity toward the formation of toxic PCDD/Fs than CuO [20]. However, to the best of our knowledge, no studies have been reported in the literatures concerning the reaction activity of spinels, especially iron-based spinels, toward the decomposition of PCBs.

In the present work, mesoporous iron-based spinels were synthesized and characterized by X-ray powder diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis, and X-ray photoelectron spectroscopy (XPS). The activities of materials were investigated according to the dechlorination efficiency of CB-209 with fully substituted chlorines. To develop a deeper understanding of the degradation mechanism, the degradation products were comprehensively identified by gas chromatograph–mass spectrometry (GC–MS), high performance liquid chromatography–mass spectrometry (HPLC–MS), and ion chromatograph (IC). Electron spin resonance (ESR) experiments, in combination with the results of XPS analyses, were used to study the role of reactive oxygen species in the degradation of CB-209. Possible degradation pathways of CB-209 over the as-prepared spinels were elucidated based on the intermediates detected in the analysis process, in combination with the density functional theory (DFT). The impact of the substitution

of Fe with Ni in the spinel oxide on the degradation mechanism has also been discussed. The achieved results, hopefully, provide applications for eliminating PCB-concentrated wastes.

2. Experimental

2.1. Preparation of iron-based spinels

The NiFe samples and Fe_3O_4 were prepared by coprecipitation and ethylene glycol mediated reaction [22,23], respectively. The NiFe precipitate was calcined at 400 °C, 500 °C and 600 °C, which were marked as NiFe-400, NiFe-500 and NiFe-600, respectively. The preparation details could be seen in Supplementary Material.

2.2. Material characterization of iron-based spinels

XRD patterns of the samples were scanned on a Rigaku D/max 2500 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056$ nm, 40 kV, 200 mA). The nitrogen adsorption and desorption isotherms were measured at 77 K on an ASAP 2400 system in the static measurement mode. The specific surface areas of the materials were calculated using the BET model. XPS analyses were taken on an ESCALAB 250 instrument using monochromatized $\text{Al K}\alpha$ radiation (200 W, 200 eV) as the X-ray source.

2.3. Activity measurement

The reaction activities of the materials were tested in sealed glass ampoules (volume about 1.5 mL). Prior to the reaction, a 0.4 mL hexane solution of CB-209 (573 nmol) was injected into an ampoule and subsequently evaporated to dryness at room temperature, and then mixed with later added 25 mg of the materials. Then the ampoule was sealed in atmosphere and increased to 300 °C over an appropriate time period. After the heating reaction, the sealed ampoule was cooled down to room temperature, and was crushed and extracted for the product analysis. All experiments were performed in triplicate to ensure the repeatability of the results, and the average values were used.

2.4. Products analysis

After the decomposition reaction, the ampoule was cooled to room temperature. Then the ampoule was crushed and extracted with sample together.

Analysis of PCBs and chlorinated benzenes (CBz) by GC–MS. The samples were extracted with hexane and then anhydrous with anhydrous sodium sulfate. Then it was analyzed for unreacted CB-209, and newly formed CBz and PCBs, using an Agilent 6890 gas chromatograph equipped with a DB-5MS capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness) and coupled to an Agilent 5973N mass selective detector (MSD). The qualitative and quantitative determinations of PCBs were conducted according to EPA method 1668B. The qualitative determinations of produced PCBs were based on the m/z information, the retention time of $^{13}\text{C}_{12}$ -labeled PCBs and the relative retention time intervals between adjacent congeners. The quantitative determination were performed in selected ion monitoring mode using the two most abundant ions of the molecular ion clusters combined with those of the corresponding or the adjacent $^{13}\text{C}_{12}$ -labeled PCB standards. The qualitative and quantitative determinations of CBz were performed using external standard method.

Analysis of hydroxyl species of PCBs and CBz by HPLC–MS. The samples were extracted with HPLC grade methanol and then filtered through a 0.45 μm mesh membrane and concentrated to approximately 100 μL . Samples were analyzed using an HPLC apparatus

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