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Thermal degradation of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) over synthesized Fe–Al composite oxide

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HIGHLIGHTS

- Fe–Al composite oxide materials for BDE-47 degradation were successfully synthesized.
- Component and morphology of material were controlled by concentration of urea.
- Distribution of hydrodebromination products are analyzed over different material.
- Morphology and component might affect degradation pathway.

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ABSTRACT

A series of Fe–Al composite oxides were synthesized by the hydrothermal method using different urea dosages and examined towards the degradation of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) at 300 °C. The as-prepared oxides were characterized by field-emission scanning electron microscopy, X-ray diffraction and energy-dispersive X-ray spectroscopy. The morphology and composition of the prepared materials could be regulated by controlling the urea concentration. Interestingly, these properties influenced the nature and amount of the hydrodebromination products generated during the degradation of BDE-47. The degradation of BDE-47 over the composite oxide prepared at a urea dosage of 3 mmol generated BDE-17 as the major isomer product, followed by BDE-28/33, -30, and -32, among the tri-bromodiphenyl ethers (tri-BDEs). Regarding the dibromodiphenyl ethers (di-BDEs) produced, the amount of the isomers decreased in the order of BDE-8/11 > BDE-7 > BDE-15 > BDE-10. And the BDE-1 among monobromodiphenyl was determined. In contrast, over the composite oxides prepared at urea dosages greater than 3 mmol, BDE-28/33 gradually become the major isomer product instead of BDE-17 among tri-BDEs. The amount of the other di-BDEs isomer such as BDE-15 and -10 approach to be comparable to that BDE-8/11. However, regardless of the urea dosage, BDE-47 converted into BDE-75 via an isomerization reaction. Based on these intermediate products identification, a possible hydrodebromination mechanism of BDE-47 over Fe–Al composite oxide was comprehensively traced.

1. Introduction

Polybrominated diphenyl ether (PBDEs) are a class of polyhalogenated aromatic compounds, commercially used as fire retardants in consumer products (Roberts et al., 2011; Stapleton et al., 2009). As a kind of additive flame retardants, PBDEs are widely used in electronics, electrical appliances, transportation, building materials, textile, oil, and mining industries. Spillage and emissions during production and disposal of end-of-life consumer products have led to increased environmental levels of PBDEs. Since PBDEs are polymer additives not chemically bound to materials, they are known to leach into the surrounding environment (Lacorte and Ikonomou, 2009; Moss et al., 2009; Zhang et al., 2010). PBDEs are recognized as a type of persistent organic pollutant that can bioaccumulate and amplify. Upon reaching a certain level of accumulation, PBDEs can interfere with the balance of thyroid hormone in animals or humans, potentially exerting carcinogenic effects. Among the 209 types of PBDEs homologs, 2,2′,4,4′-

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tetrabromodiphenyl ether (BDE-47) is distributed most widely, and has the higher level of toxicity to organisms and humans (Hites, 2004; Schecter et al., 2004).

Degradation of PBDEs is a significant challenge owing to their extreme persistence and recalcitrance nature. Because of their wide distribution in environment, high toxicity and resistivity to degradation, many methods have been investigated to degrade PBDEs, such as biological method (Gerecke et al., 2005; Robrock et al., 2008), photochemical method (Bezares-Cruz et al., 2004; Schenker et al., 2008), reduction by zero-valent iron (ZVI) (Kim et al., 2012) and electrochemical method (Yang et al., 2006). However, these methods have many disadvantages, such as harsh reaction conditions, high equipment costs, and poor efficiencies. Alternatively, the application of various metal oxide catalyst into the degradation of persistent organic pollutants at relatively low temperatures caused much attention due to their high catalytic activity, thermal stability, low costs, and ease of preparation (Jia et al., 2010; Ma et al., 2014; Pitkäaho et al., 2013). Furthermore, the studies have revealed that the composite iron oxide catalysts exhibited better catalytic activity than single iron oxide, for the decomposition of halogenated compounds (Ma et al., 2005, 2013). Nevertheless, to our knowledge, studies investigating the decomposition of PBDEs especially by composite metal oxides are rare, and the influence of material preparation conditions on the degradation pathway is unclear.

In this study, environmentally friendly Fe–Al composite oxides were successfully prepared by the hydrothermal method. The morphology and composition of the hybrid oxides prepared at different concentrations of urea were characterized. Subsequently, the performance of the composite oxides in the degradation of BDE-47 was examined. The possible degradation pathways of BDE-47 over the prepared composite oxide materials were determined based on the identification of the intermediates generated during degradation. Additionally, the relationship between the degradation pathway and structure characteristics of the prepared materials was investigated.

2. Experimental

2.1. Materials

BDE-47, employed in the degradation tests, was purchased from Dr. Ehrenstorfer (Augsburg, Germany). For analysis of the degradation products, standard solution BDE-AAP-A15X, which was purchased from AccuStandard (New Haven, CT, USA), was used as the reference. The standard solution contained monobromodiphenyl ethers (mono-BDEs) BDE-1, -2, and -3, dibromodiphenyl ethers (di-BDEs) BDE-7, -8, -10, -11, -12, -13, and -15, tribromodiphenyl ethers (tri-BDEs) BDE-17, -25, -28, -30, -32, -33, -35, and -37, and tetrabromodiphenyl ethers (tetra-BDEs) BDE-47, -49, -66, -71, -75, and -77. Pesticide grade hexane was purchased from Dika Technologies (Lake Forest, CA, USA).

The Fe–Al composite oxide materials were synthesized by the hydrothermal method. In a typical synthesis, $Al(NO_3)_3 \cdot 6H_2O$ (3 mmol), ammonium ferric oxalate (3 mmol), and urea at a known concentration (i.e., 3, 9, 21, or 36 mmol) were added to deionized water (40 mL). Then, the system was mixed and stirred for 30 min, and subjected to hydrothermal treatment at 180 °C for 12 h. The obtained products were washed with deionized water and then three times with alcohol. Finally, the samples were dried at 60 °C.

The prepared materials were characterized by field-emission scanning electron microscopy (JEOL JSM-7500FE), energy-dispersive X-ray spectroscopy (EDX; IXRF 550i), and X-ray diffraction using Cu Kα irradiation (XRD; Philips XPERT-PRO).

2.2. Degradation of BDE-47

The catalytic activity of the prepared composite oxides was determined using sealed glass ampoules as reactor vessels. Typically, an aliquot (0.5 mL) of hexane solution containing BDE-47 (1028.8 nmol) was introduced into an ampoule and allowed to evaporate to dryness at ambient temperature. Then, the Fe–Al composite oxide material (50 mg) was introduced into the ampoule that was sealed and heated to 300 °C for 1 h. As reported by Tanabe (2004), low-bromine congeners, such as BDE-47, easily volatilize into the atmosphere from the matrixes in which they reside. Additionally, Guo et al. (2015) found that lower brominated PBDE congeners with higher vapor pressures migrate more easily from the matrix during heating at higher temperatures (~200–300 °C) than at ambient temperatures (25–35 °C). Under the present experimental conditions, BDE-47 could completely vaporize from the base of the ampoule, resulting in sufficient and homogeneous contact with the catalyst. After the heating process, the sealed ampoules were cooled to room temperature and thereafter crushed to extract the products with hexane for subsequent analysis. All experiments were performed in triplicate to ensure repeatability of the results.

2.3. Analysis of the degradation products

The unreacted BDE-47 and newly formed PBDEs (following degradation of BDE-47) were identified using an Agilent 6890 N gas chromatography (GC) instrument equipped with a DB-5 MS capillary column (15 m × 250 μm i.d., 0.25 μm film thickness), and an Agilent 5973 mass selective detector (MSD). The mass spectrometry instrument used a negative chemical ionization source in selected ion monitoring mode. The ion source temperature and interface temperatures were set at 150 and 290 °C, respectively. The ions at m/z 79 and 81 were monitored for identification of PBDEs examined herein in combination with their standards. High-purity helium carrier gas was used at a flow rate of 1.5 mL/min. For analysis, an aliquot (1 μL) of sample was injected into GC instrument inlet, which was used in splitless mode at 265 °C. The temperature program employed was as follows: the initial temperature was set at 80 °C, which was held for 1 min, increased at 10 °C/min to 220 °C, and further increased at 20 °C/min to 300 °C, and held for 15 min.

The degradation efficiency (DgE) was calculated as follows:

$$DgE = (1 - R_{BDE-47}/I_{BDE-47}) \times 100\%$$

where $I_{BDE\text{-}47}$ and $R_{BDE\text{-}47}$ are the initial and residual amounts of BDE-47.

3. Results and discussion

3.1. Characterization of Fe–Al composite oxides

Fe–Al composite oxides were obtained via a precipitation route upon heating of an aqueous solution containing $Al(NO_3)_3 \cdot 6H_2O$, $(NH_4)_3 \cdot Fe \cdot (C_2O_4)_3 \cdot 3(H_2O)$, and urea. Furthermore, the dosage of urea was varied, while keeping other process parameters constant as described in Section 2.1, in an attempt to prepare Fe–Al composite oxides with different morphologies and compositions. The related SEM and EDX results are presented in Fig. 1. As observed in Fig. 1a, a sphere-like product with a diameter approximately at 1.5 μm was obtained when the concentration of urea was 3 mmol. Its surface was covered with a number of non-uniform particles. As observed from the associated EDX spectrum in Fig. 1b, the product essentially comprised aluminum, iron, and oxygen, thereby