Catalytic degradation of Polybrominated Diphenyl Ethers (PBDEs) in the effluent gas during a novel thermal desorption process

Feiyue Fan[1], Long Zhao[1*], Qi Zhang[2], Hong Hou[1]

[1]State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, PR China, 100012

[2]Department of Chemical Engineering, East China University of Science and Technology, Shanghai, PR China, 200237

Introduction

Over the past three decades, polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in various customer products, such as electronics, electronic appliances, furniture, and textile [1, 2]. Generally, PBDEs are simply blended with the materials, and thus are likely to leak out during the production, usage and disposal of the products [3]. Due to the high hydrophobicity, persistence and bioaccumulation, PBDEs released from the products have caused serious environmental problems and threats to human health.

Up to now, several methods such as photochemical method, biological method, reduction by zero-valent iron and thermal desorption have been applied to degrade PBDEs [4-6]. Among them, thermal desorption was the preferred remediation method for PBDEs-contaminated soils due to its high removal efficiency and stable reaction process. However, the high energy consumption and cost have prevented the thermal desorption technology widely used in the treatment process of PBDEs contaminated soils. Furthermore, the low-brominated PBDEs in the effluent gas were usually collected by activated carbon, which may cause secondary pollution. Therefore, it is urgent to develop an effective treatment method to deal with the former problems.

In this study, a novel thermal degradation process of decabromodiphenyl ether (BDE-209) in soils was firstly conducted. Then, the low-brominated PBDEs in the effluent gas were further degraded by an in-situ catalytic degradation technology. The effects of different catalysts and reaction time on catalytic degradation of PBDEs were extensively investigated.

Materials and methods

Materials

BDE-209 (99% purity) was purchased from J&K Scientific Ltd. (Beijing, China). A standard mixture of 14 PBDEs congeners (BDE-17, -28, -71, -47, -66, -100, -99, -85, -154, -153, -138, -183, -190, and -209) was purchased from J&K Scientific Ltd. (Beijing, China). Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99.0~102.0%), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, $\geq$ 98.0%) and ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, $\geq$ 98.5%) were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Catalyst preparation

The plate-type anodic alumina (γ-Al_2O_3/Al) support was prepared by anodization technology [7]. The pretreated plate was anodized in a 0.4 M oxalic acid solution for 12 h with a current density of 50 A/m^2 at 20 °C to form porous alumina layers. The plate was then washed, dried for 12 h and calcined in air at 350 °C for 1 h to remove the residual oxalic acid. Subsequently, a hot water treatment (HWT) in deionized water at 80 °C was conducted for 1 h. Finally, the resulting plate was calcined in air at 500 °C for 4 h to obtain the anodic γ-Al_2O_3.

With the anodic alumina support, a series of Cu/M/γ-Al_2O_3/Al (M=Ni or Fe) catalysts were prepared through impregnation method. The monolithic γ-Al_2O_3/Al support was impregnated in an aqueous solution of Cu (II) nitrate or M nitrate (M=Ni or Fe) under ambient conditions. The resulting catalyst was then dried by natural air, and calcined at 500 °C for 4 h.

Thermal degradation of PBDEs

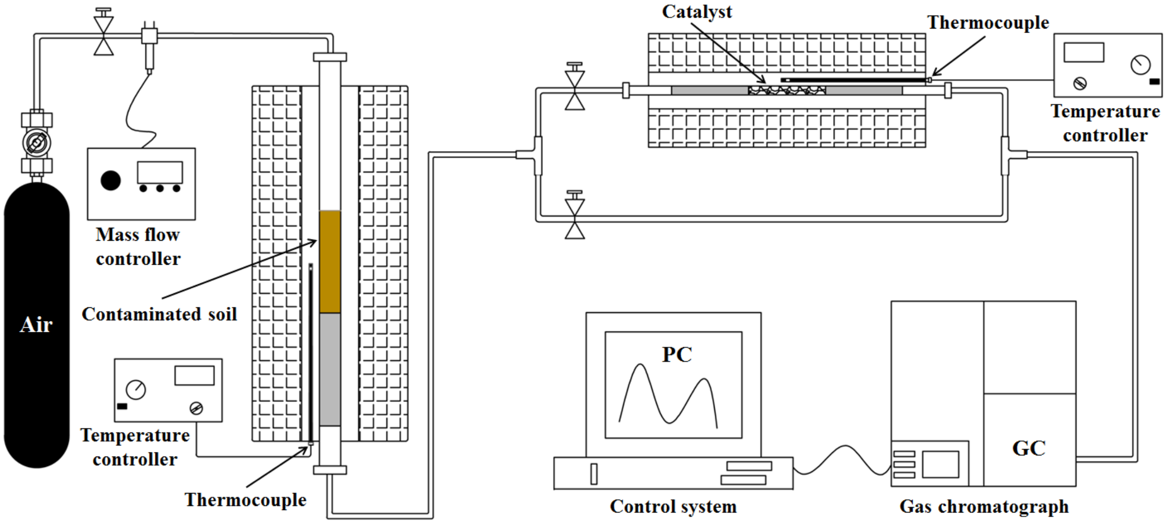

Fig.1 The flow chart of novel thermal desorption-catalytic degradation process

Fig. 1 shows the flow chart of novel thermal desorption-catalytic degradation process. The thermal desorption process was conducted in a fixed-bed reactor (I.D. 48 mm). The BDE-209 contaminated soils (100 g, 5000 μg/kg) were packed into the reactor. The treatment temperature (650 °C) was controlled by a thermocouple, which was placed in the center of the soil bed. The flow rate of carrier gas (Air) was fixed at 200 mL/min.

The catalytic degradation of PBDEs in the effluent gas was carried out in a fixed-bed reactor (I.D. 12 mm) under atmospheric pressure. The plate-type composition catalyst (2 g, the loaded quantity of alumina layers was about 0.7 g) was cut into small pieces (ca. 6 mm^2), and then packed into the reactor using Raschig ring (20-40 mesh) to dilute them. The temperature (250-400 °C) was controlled by a thermocouple, which was placed in the center of the catalyst bed.

Analysis of the degradation products

The analysis of effluent gas was conducted by an on-line gas chromatograph (GC 9860, Shanghai Qiyang Chromatography Analysis Co., Ltd.) equipped with an electron capture detector (ECD). A HP-5 column (15 m×0.32 mm×0.25 μm, Agilent, America) was used to separate the different PBDE congeners. The following temperature program was used during the treatment process: firstly, the temperature was held at 100 °C for 2 min; then, it increases from 100 °C to 200 °C at a rate of 10 °C/min; thirdly, the temperature increases from 200 °C to 290 °C at a rate of 20 °C/min; finally, it holds at 290 °C for 13 min.

Results and discussion

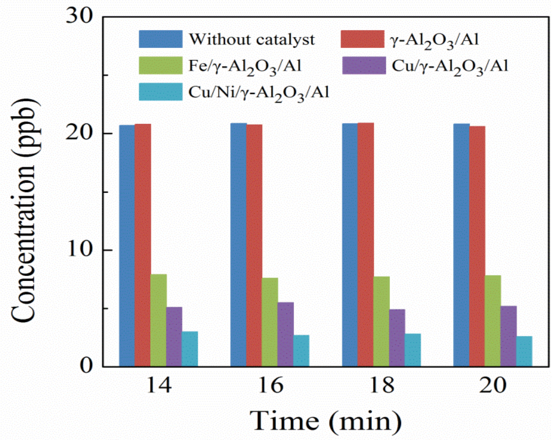

Fig. 2 Effects of different catalysts on the concentrations of tetra-BDE in the effluent gas

Fig. 2 shows the effects of different catalysts on the concentrations of tetra-BDE in the effluent gas. It can be seen from the figure that the concentrations of tetra-BDE maintained at 20 μg/kg after the thermal desorption (without catalyst). After the catalytic degradation process, the concentrations of tetra-BDE over γ-Al_2O_3/Al support were similar with those before catalytic degradation, indicating that the support could not catalyze the degradation of PBDEs in the effluent gas. However, the concentrations of tetra-BDE in the effluent gas were lowest over Cu/Ni/γ-Al_2O_3/Al catalyst, suggesting the highest degradation efficiency.

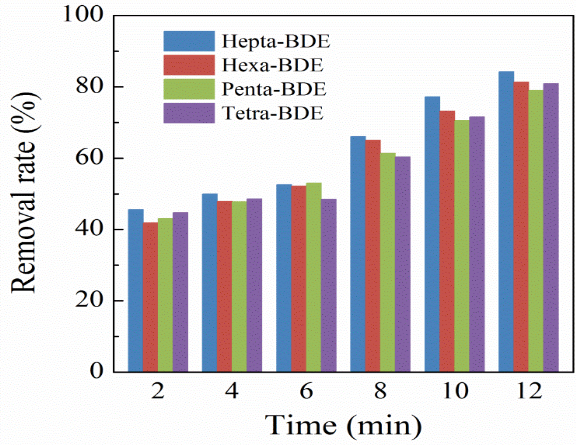

Fig. 3 Removal rate of PBDEs over Cu/Ni/γ-Al_2O_3/Al catalyst; Reaction conditions: T = 300 °C, GHSV = 90000 mL·g^{-1}·h^{-1}.

To further study the effects of Cu/Ni/γ-Al_2O_3/Al catalyst on the degradation of PBDEs in the effluent gas, the removal rate at different tine was compared and the results were shown in Fig. 3. It can be inferred that the removal rate of PBDEs increased with the reaction time. At 12 min, the removal rate of PBDEs in the effluent gas increased to ca. 80%. In the future, the catalytic degradation mechanisms will be studied using this novel thermal desorption technology.

Acknowledgements

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