Journal of Hazardous Materials 344 (2018) 64–72

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Sustainable superior function of the synthesized $Ni_xCo_{1-x}Fe_2O_z$ nanosphere on the destruction of chlorinated biphenyls in the effluent

Linyan Huang[a,b,c], Qianqian Li[a,b], Guijin Su[a,b,*], Minghui Zheng[a,b], Yalu Liu[a,b], Yangyang Gu[a,b], Lirong Gao[a,b], Guorui Liu[a,b], Wenbin Liu[a,b]

[a] *State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China*

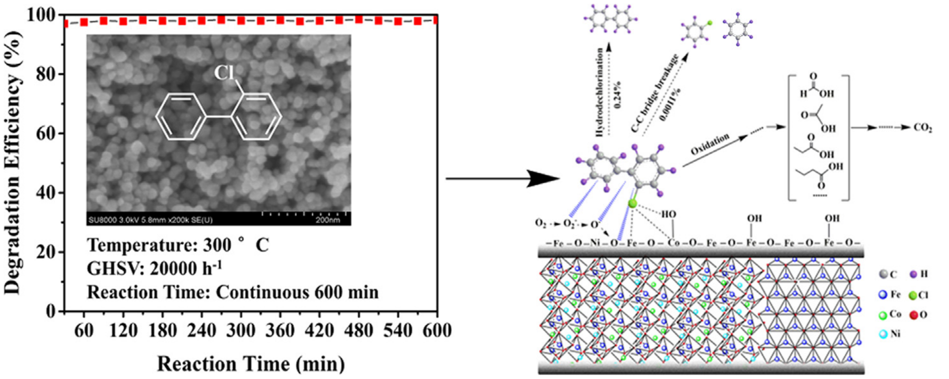
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

[c] *Institute for Environmental Reference Materials of Ministry of Environmental Protection, Beijing 100029, China*

HIGHLIGHTS

- Magnetic $Ni_xCo_{1-x}Fe_2O_z$ nanosphere was prepared by hydrothermal route.
- $Ni_xCo_{1-x}Fe_2O_z$ showed sustainable superior destruction activity of CB-1 in effluent.
- Excellent reactive performance may be due to the multicomponent structure property.
- Oxidative reaction majorly occurred with the consumed oxygen compensated rapidly.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 May 2017
Received in revised form 29 August 2017
Accepted 2 October 2017
Available online 6 October 2017

Keywords:
Composite oxides
Monochlorobiphenyly
Degradation
Oxidation
Nanosphere

ABSTRACT

$Ni_xCo_{1-x}Fe_2O_z$ composite oxide nanosphere was successfully prepared, to degrade 2-monochlorobiphenyly (CB-1) in continuous-flow fixed-bed microreactor at GHSV of 20000 h^{-1}. The five cycles of temperature-dependent run experiments between 150 and 350 °C showed its superior activity with a CB-1 conversion of more than 95% above 300 °C over $Ni_{0.5}Co_{0.5}Fe_2O_z$. Importantly, the sustainable higher reactivity could be observed over prolonged 600 min reaction times after the 5th run test. The degradation products detected as biphenyl and monochlorobenzene with yield ratio of 129, account for 0.24% and 0.0011% of initial CB-1 respectively. This indicated the weak occurrence of hydrodechlorination and breakage of C—C bridge bond during the degradation of CB-1. The possibly dominant occurrence of oxidative degradation probably follows Mars–van Krevelen mechanism, resulting in the generation of the formic, acetic, propanoic and butyric acids and so on. Due to the high oxygen mobility over $Ni_{0.5}Co_{0.5}Fe_2O_z$ nanosphere, the consumed oxygen species could be compensated rapidly by the gas phase oxygen via $O_2 \rightarrow O_2{}^{-} \rightarrow 2O^{-} \rightarrow 2O^{2-}$. The interaction among different elements in $Ni_{0.5}Co_{0.5}Fe_2O_z$ nanosphere confirmed by the derivation of the electron cloud, enhanced the mobility of the reactive oxygen species, which would be beneficial for the oxidation of chlorinated biphenyls.

---

[*] Corresponding author at: State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China.

E-mail address: gjsu@rcees.ac.cn (G. Su).

https://doi.org/10.1016/j.jhazmat.2017.10.005
0304-3894/

1. Introduction

The release of dioxin-like chlorinated aromatic compounds has attracted much attention because of their hazardous effects on the environment and human health. Polychlorinated biphenyls (PCBs), structurally similar with polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), are chemically inert and feature exceptional dielectric characteristics. Because of their bioaccumulation and high toxicity on living individuals, PCBs together with PCDD/Fs, have been classified as prior controlled persistent organic pollutants (POPs) in the Stockholm Convention. Although the production and usage of PCBs have been banned since the mid-1970s, unintentional emissions of PCBs (UP-PCBs) from industrial thermal processes such as the coking industry, secondary nonferrous metallurgical facilities, and municipal solid waste incinerators (MSWIs), are increasingly expected to become the important source of PCBs [1–4]. The emission level of 0.0003–0.126 ng WHO-TEQ N m^{-3} was determined from secondary copper metallurgy (toxic equivalent; TEQ) [5]. Nie et al. [6] reported the TEQ concentrations of UP-PCBs in flue gas and residual ash released from thermal wire reclamation to be 0.4–2.1 ng Nm^{-3} and 0.008–0.2 ng g^{-1}, respectively. Therefore, the stringent emission control of PCBs is the matter of public concern.

To eliminate PCBs in effluents of thermal industries, several technologies have been examined such as activated carbon adsorption and catalytic destruction. Even though activated carbon injection technology can efficiently remove PCBs in flue gas, it just enriches and transfers the contaminants into the solid phase but not destroys them. Furthermore, disposal of the used activated carbon needs to be considered.

The catalytic technique is progressively thought to be promising owing to its lower reaction temperature requirements and higher destruction efficiencies. Recent decades have witnessed the fast development of the application of transition metal oxides into the degradation of chlorinated aromatic compounds owing to their low cost and high thermal stability [7–11]. Especially, the considerable efforts have been made to develop multicomponent materials for the decomposition of organic pollutants because of the remarkable multifunctionality that they can offer over single metal oxides [12,13]. Fan et al. [14] reported the higher activity of $Cu_xMg_{1-x}Al_2O_4$ spinel-type catalysts over that of $MgAl_2O_4$ toward the dechlorination of HCB. Su [15] reported the excellent catalytic effect of $Ce_{0.2}TiAl_\alpha O_x$ toward 1,2,4-trichlorobenzene oxidation, and the degradation efficiencies were higher than that achieved by $Ce_{0.2}TiO_x$. Ma et al. [16] synthesized Ca-doped FeO_x hollow catalyst, which showed excellent activity toward the oxidation of 1,2-dichlorobenzene. However, these results only displayed the superior function of the multicomponent materials toward the pollutants within one cycle experiment. The iron-based spinel composite oxides are inexpensive, resistant to poisoning, and environmental friendly, and feature magnetic properties. Unfortunately, the potential of iron-based spinel composite oxides has been unlocked toward the fast decomposition of PCBs in effluents.

The catalytic degradation rate is considerably related to the number of surface active sites of the catalyst, which depends basically on its surface area, particle size and phase composition. Nanomaterials can feature a large exposed surface area for interaction and surface catalytic reaction due to their abundance of reactive and coordinatively unsaturated sites [17,18]. By controlling its composition, it becomes possible to endow the nanomaterials with more superior function. Therefore, an important research direction in nanoparticles synthesis is the expansion from single component nanoparticles to multicomponent hybrid nanostructures. A wealth of methods has been developed for controlled synthesis of the multiple nanostructured nanomaterials [19–23]. The hydrothermal route could be convenient, low-cost, and suitable for large-scale production [23,24]. Although many single metal oxides with nanostructures have been successfully synthesized by this method, there have been few reports on the synthesis of multicomponent metal oxide nanomaterials. The synthesis of the multicomponent composite oxide nanomaterial by such simple hydrothermal route is therefore of great interest for the development of nanomaterial technique.

In this study, the magnetic ternary iron-based composite oxide nanosphere was synthesized by a hydrothermal route. The catalytic activities of the prepared nanosphere toward the degradation of 2-monochlorobiphenly (2-MoCB, CB-1) model compound were investigated with a continuous-flow fixed-bed microreactor at the varied temperatures. Moreover, the sustainable stability of the catalyst activity was explored over prolonged reaction times. The degradation products were identified by gas chromatography mass spectrometry (GC–MS) and ion chromatography (IC). Based on these determined products, the related degradation mechanism was explored in combination of the as-prepared composite oxide nanosphre nature.

2. Experimental

2.1. Preparation of the ternary iron-based composite oxide nanomaterial

$Ni_xCo_{1-x}Fe_2O_z$ nanomaterials with different molar ratios of Ni:Co:Fe were synthesized by a hydrothermal method. In a typical procedure, 20 mmol urea was added to 40 mL aqueous solution containing $Ni(NO_3)_2$, $Co(NO_3)_2$, and $Fe(NO_3)_3$ at a Ni^{2+}:Co^{2+}:Fe^{3+} molar ratio of 0.2:0.8:2, 0.5:0.5:2, and 0.8:0.2:2, respectively. After vigorous magnetic stirring for 30 min, the solution was transferred to a Teflon-lined autoclave. The hydrothermal reaction was conducted at 180 °C for 10 h in an electric oven. After the reaction, the product was recovered by centrifugation and thorough washings with deionized water, then dried at 85 °C for 10 h. The ternary iron-based composite oxide was obtained by calcination at 350 °C for 3 h in air, and the final prepared catalysts were denoted as $Ni_{0.2}Co_{0.8}Fe_2O_z$, $Ni_{0.5}Co_{0.5}Fe_2O_z$ and $Ni_{0.8}Co_{0.2}Fe_2O_z$, respectively.

2.2. Material characterization

The synthesized catalysts were characterized by field-emission scanning electron microscopy (Hitachi S-3000N; accelerating voltage of 3 kV), transmission electron microscopy (TEM; Hitachi-7500), energy disperse X-ray spectroscopy (EDX) (IXRF system, Model 550i) coupled with SEM (Hitachi, SU8020), X-ray powder diffraction (XRD; Rigaku D/max 2500 diffractometer; Cu Kα radiation, $\lambda = 0.154056$ nm, 40 kV, 200 mA), vibrating sample magnetometry (730T), N_2 adsorption–desorption analysis (ASAP 2400, static measurement mode, 77 K), X-ray photoelectron spectroscopy (XPS; 250 XI, monochromated Al Kα), and in situ diffuse reflectance Fourier transform infrared spectroscopy of NH_3 adsorption (in situ DRFTIS; Varian 3100 equipped with an MCT detector cooled by liquid nitrogen).

2.3. Catalytic activity measurements

The catalytic activity of the composite oxide was evaluated at atmospheric pressure in a continuous-flow fixed-bed microreactor, as shown in Scheme 1. For each run, 50 mg catalyst was used. Nitrogen gas was used as the balance gas and to transport the CB-1 vapor by flowing through a saturator containing CB-1 liquid. Pure oxygen was also used. The three gas flows were introduced into the mixing chamber to obtain a reaction gas mixture consisting of 40 ppm CB-1 and 10 vol.% O_2/N_2. Then, the gas mixture was introduced into the catalyst bed at a total flow rate of 100 mL min^{-1}. A typical gas