

Supplementary Materials

Effect of NiFe₂O₄ on PCDF byproducts formation during thermal degradation of decachlorobiphenyl

Linyan Huang, Guijin Su*, Yexuan Liu, Liewu Li, Sha Liu, Huijie Lu, Minghui Zheng

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

*Corresponding author: Tel.: +86 10 62849356; Fax: + 86 10 62923563

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

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Content 1. The detailed instrumental information on the analysis of PCDD/Fs.

PCDD/F analysis was performed using an Agilent 6890 high-resolution gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) fitted with a DB-5 MS column (60 m long, 0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies) and a Waters Autospec Ultima high-resolution mass spectrometer (Waters Corp., Milford, MA, USA). The gas chromatograph was operated in splitless mode, and 1 μL of each sample extract was injected using a CTC PAL auto-sampler (CTC Analytics, Zwingen, Switzerland). The temperature program of oven is as follows: 160 $^{\circ}\text{C}$ hold 2 min, then increased to 330 $^{\circ}\text{C}$ with 5 $^{\circ}\text{C min}^{-1}$ and hold 1 min. The mass spectrometer was operated in positive electron impact ionization (EI^+) mode and selective ion monitoring mode, with an electron impact energy of 35 eV and a resolution of 10 000.

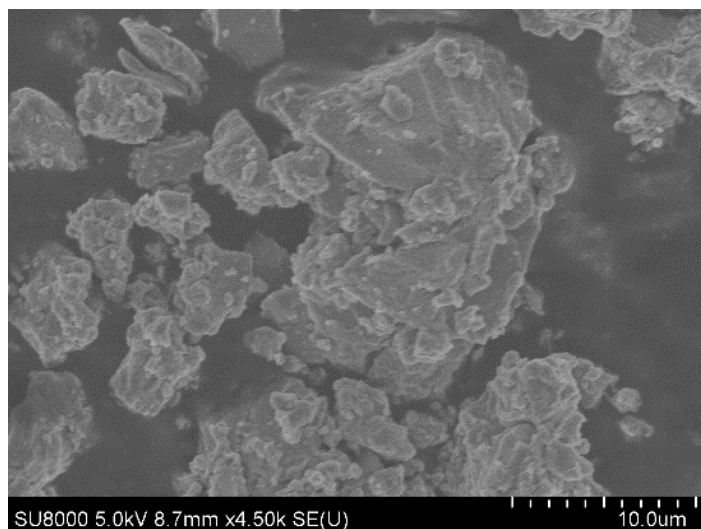


Fig. S1. SEM image of the prepared NiFe₂O₄.

Supplementary explanation for Fig. S1

The SEM image of the as-prepared NiFe₂O₄ is shown in Fig. S1 (measured on Hitachi S-3000N, Hitachi High-Technologies Corporation, Japan). The result exhibited that the NiFe₂O₄ particles agglomerated into coarser ones with irregular morphology.

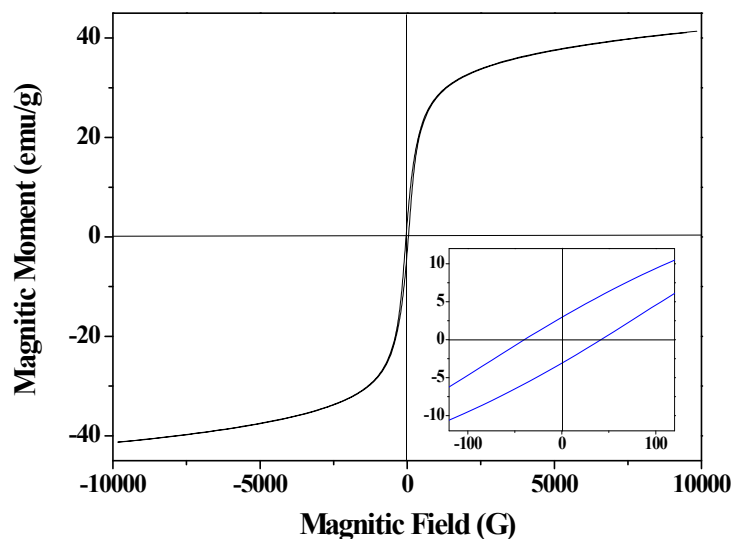


Fig. S2. The magnetic hysteresis loop of the as-prepared NiFe₂O₄.

Supplementary explanation for Fig. S2

The magnetic hysteresis loop of the prepared NiFe₂O₄ was measured by vibrating sample magnetometer of 730T, as shown in Fig. S2. The saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) were 41.3 emu/g, 2.95 emu/g and 39.9 G, respectively. It indicated the as-prepared NiFe₂O₄ is a magnetic material, which makes its recovery much easier.

Table S1

Chlorine atom distribution in the degraded products after reaction with 50 mg of NiFe₂O₄ at 300 °C for 60 min.

Products	PCBs	CBzs	2378-PCDD/Fs	Cl ⁻ (inorganic)	Other chlorinated products
Cl percentage (%)	5.69	5.07	7.80e-5	74.0	15.2

Supplementary explanation for Table S1

The mass balance of CB-209 during the thermal degradation was analyzed by calculation of chlorine atom distribution in the degraded products. The inorganic Cl⁻ in degradation products was measured by ion chromatograph (ICS-1500). After the thermal reaction, the ampoule was cooled to room temperature and crushed. The fragments were extracted by ultrasonic with 9 mmol L⁻¹ Na₂CO₃ aqueous solution three times.

Taken NiFe₂O₄ reaction system for example, the chlorine atom distribution percentage after degradation of 1 mg CB-209 using 50 mg NiFe₂O₄ at 300 °C for 60 min is showed in Table S2. The percentages of chlorine atoms in the detected PCBs containing the residual CB-209 and newly formed lower chlorinated biphenyls were 5.69%, while that for the formed chlorobenzenes (CBzs) was 5.07%. The inorganic Cl⁻ took the most of chlorine contribution with 74.0%. However, the chlorine percentage in 2,3,7,8-PCDD/Fs was only 7.80×10⁻⁵ % due to the inhibition of PCDF formation by NiFe₂O₄. The above sources of chlorine atoms combined account for only 84.8% of the initial chlorine atoms, leaving 15.2% of the chlorine atoms unaccounted for. A similar mass discrepancy was reported for the degradation of 1,2,4-trichlorobenzene over Co₃O₄ [1] and HCB over CaO/Fe₂O₃ [2].

References:

- [1] S. Lin, G. Su, M. Zheng, M Jia, Ch. Qi and W Li, *J. Hazard. Mater.*, 2011, **192**, 1697.
- [2] X. Ma, M. Zheng, W. Liu, Y. Qian, B. Zhang and W. Liu, *J. Hazard. Mater.*, 2005, **127**, 1.