

PREPARATION OF VISIBLE-LIGHT RESPONSE PHOTOCATALYST BY MECHANOCHEMICAL DESTRUCTION OF DECA-BDE

Zhang KL¹, Wang HZ¹, Zhang QW², Huang J^{1*}, Yu G¹, Deng SB¹, Wang B¹, Kano J²

¹School of Environment, Tsinghua University, 1 Qinghuayuan, Haidian, Beijing, P.R. China; ²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Introduction

Over the last decades, polybrominated diphenyl ethers (PBDEs) have been widely used in polymers to improve their flame resistance and prevent fire. There were three main formulations of PBDEs in the market, i.e., penta-, octa- and deca-BDE. However, concerns about these kinds of chemicals have arisen because of their toxic, bioaccumulative and persistent properties¹. In 2009, the commercially used penta- and octa-BDE were listed in the annex A of the Stockholm Convention on Persistent Organic Pollutants. Meanwhile, the environmental soundness of deca-BDE is also doubted as it can be degraded into low brominated BDEs in the environment.

As a result, the sound disposal of PBDEs containing wastes is becoming a practical need. Instead of high temperature incineration, mechanochemical (MC) destruction has been recommended as a promising non-combustion technology for the disposal of solid waste containing halogenated POPs². In MC reactions, the pollutants are put into a ball mill machine with co-milling additives, in which the reactions between additives and pollutants are driven by mechanic force. The residues after ball milling are usually inorganic halide salts and carbon besides excess additives. CaO is a traditional co-milling additive that has been studied on the MC destruction of many chlorinated POPs such as DDT, PCBs and Dioxins³. Our previous study showed that zero valent iron is also an excellent additive⁴. Although these additives have a good performance for the MC destruction, excess additives are usually required to ensure high reaction speed and complete destruction. What's more, additional treatment is still needed for the residues containing excessive additives.

Therefore, it is necessary to look for new additives that are used only with the amount exactly needed to react with pollutants rather than excessive. And the products are expected to have proper utilization as well. Since ball mill can be used in both the destruction of POPs and the synthesis of catalyst, there should be the possibility to couple these two processes together, in which not only POPs were destroyed but also the final products can be useful. In the present study, Bi₂O₃ was applied as a new additive in the destruction of PBDEs (represented by decaBDE). With exactly the stoichiometric amount to react with decaBDE, Bi₂O₃ was completely turned into a visible light response photocatalyst BiOBr, and decaBDE was simultaneously destroyed.

Materials and methods

Bismuth (III) oxide (Bi₂O₃, 99% in purity), Calcium hydroxide (Ca(OH)₂, 99% in purity) were provided by Wako Pure Chemical Industries Ltd. Calcium oxide (CaO) was prepared by 1000 °C heating of Ca(OH)₂ for 2 hours. The MC experiments were carried out in a planetary ball mill (Pulverisette-7, Fritch, Germany) with two zirconia pots (45 cm³). Seven zirconia balls (15-mm diameter, approx. 10.5 g each) were employed in the pots. In each experiment, 2.125 g Bi₂O₃ was mixed with 0.875 g decaBDE, keeping the molar ratio Bi:Br=1:1, and then put in the ball mill pots. The rotary speed of machine disk was set as 700 rpm for 15-min intervals, after which there was a 15-min cooling period. The ground samples were collected and then preserved in a hermetic and dry apparatus for further use.

During quantification experiments, 0.05 g of each ground sample was taken and extracted with 50 mL hexane/acetone (1:1, v/v) with 10-min ultrasonic treatment. The solution was firstly filtered by 0.45 μm polytetrafluoroethylene (PTFE) membrance and then subjected to instrumental analysis. A Shimadzu 2010 GC-MS equipped with a DB-5HT column (15 m×0.25 mm i.d., 0.10 μm film thickness) was used and operated in negative ion chemical ionization (NCI) mode. For the characterization of the structural change in the solids, the ground samples was also analyzed by Fourier transform infrared (FTIR) and X ray diffraction (XRD). The thermo-gravimetric analysis (TG) was also performed for the samples using a TG/DTA analyzer.

Results and discussion

In order to investigate the performance of Bi_2O_3 in MC destruction of decaBDE, the comparison experiment with CaO was carried out with the same weight ratio (2.125 g Bi_2O_3 or CaO with 0.875 g decaBDE, keeping Bi:Br=1:1). The destruction efficiency of decaBDE by Bi_2O_3 or CaO is shown in Fig.1.

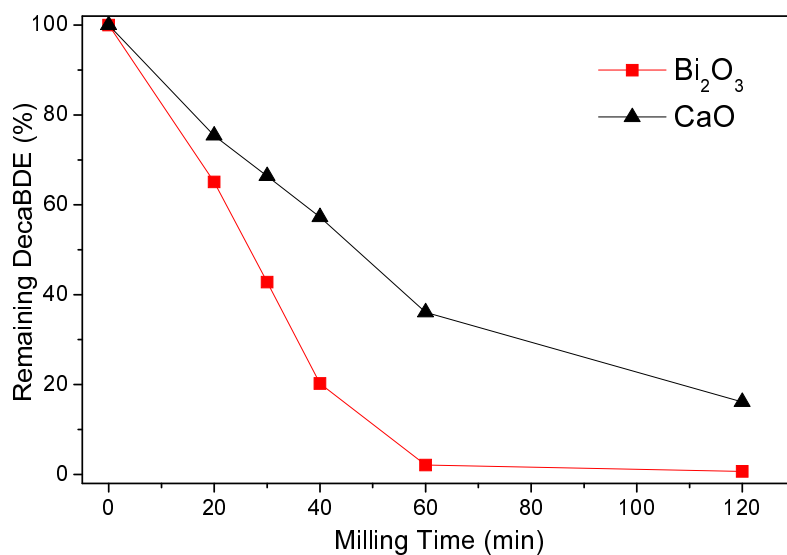


Fig.1. The comparison of Bi_2O_3 and CaO as additives in the MC destruction of decaBDE

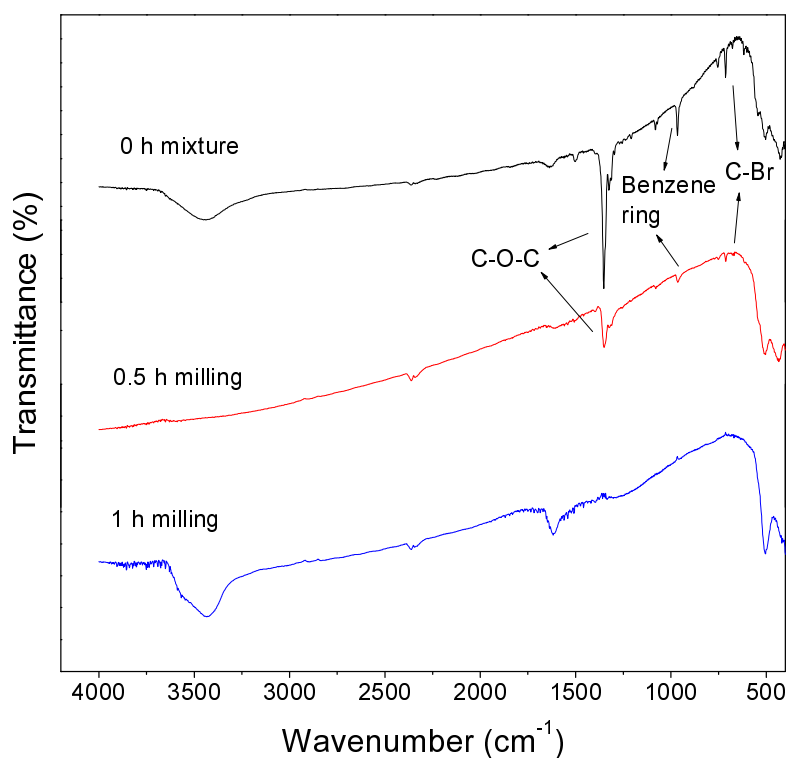


Fig.2. FTIR spectra of samples milled with Bi_2O_3 for different time

As shown in Fig.1, with the extension of milling time, the remaining decaBDE decreased quickly roughly following a linear declination trend. When using Bi_2O_3 as additive, nearly all the decaBDE was destroyed after 1 h ball milling. But when using CaO as additive, there was more than 15% decaBDE remained in the solid even after 2 h ball milling. Obviously, for the destruction of PBDEs, Bi_2O_3 showed better performance as co-milling additive than the traditionally used CaO. Therefore, the following experiments were performed using the Bi_2O_3 milling samples.

To classify the chemical change of decaBDE, Fourier transform infrared (FTIR) spectrometer was conducted on the samples milled with Bi_2O_3 . Fig.2 shows the FTIR spectra of Bi_2O_3 milling samples at different time. For the 0 h mixture of Bi_2O_3 and decaBDE, there is a strong peak centered at 1350 cm^{-1} , which comes from the vibration of the ether bond (C-O-C) and can be regarded as the indicator for decaBDE molecule. The peak band around $600\text{-}750\text{ cm}^{-1}$ is the C-Br stretching vibration and the peak around 1000 cm^{-1} may come from the benzene ring. For the 30 min milling sample, the three peaks quickly weakened, showing that the decaBDE was greatly destroyed. After 1 h ball milling, the peaks in FTIR spectra from decaBDE were totally disappeared, indicating that all the decaBDE in the sample was destroyed. These results are corresponding to the GC-MS results above.

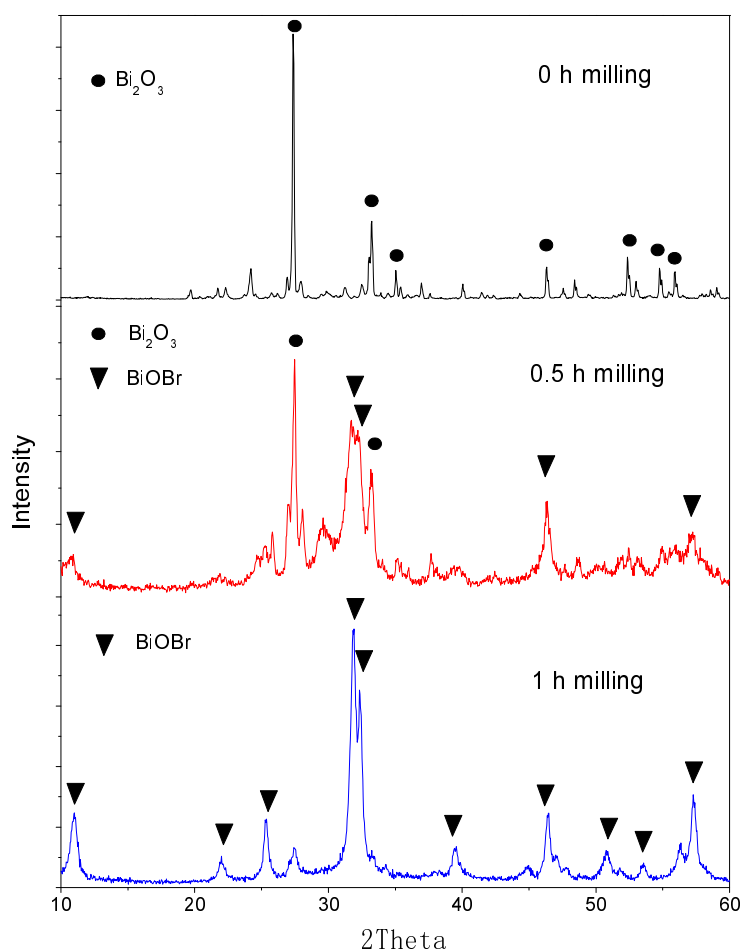


Fig.3. XRD spectra of the samples milled with Bi_2O_3 for different time

For the identification of the final products after MC treatment, XRD analysis of the samples was also carried out and the results are shown in Fig.3. In the spectra of 0 h mixture, only the diffraction peaks of Bi_2O_3 (labeled as ●)

were shown clearly. But after 30 min milling, the peaks of Bi_2O_3 became weak and another new group of diffraction peaks started to appear. According to the database of XRD patterns, the new peaks were proved to be the pattern of BiOBr (labeled as \blacktriangledown), which was a good visible light response photocatalyst as illustrated in our previous study⁵. After 1 h milling, the peaks of Bi_2O_3 were nearly disappeared, remaining only the pattern of BiOBr in the spectra, which means that all the Bi_2O_3 has just reacted with decaBDE together with the formation of BiOBr . And there was no excess additive or unreacted decaBDE remained as the amount of Bi_2O_3 was added exactly by the molar ratio $\text{Bi}:\text{Br}=1:1$, with the formation of a promising visible light response photocatalyst BiOBr that can be utilized.

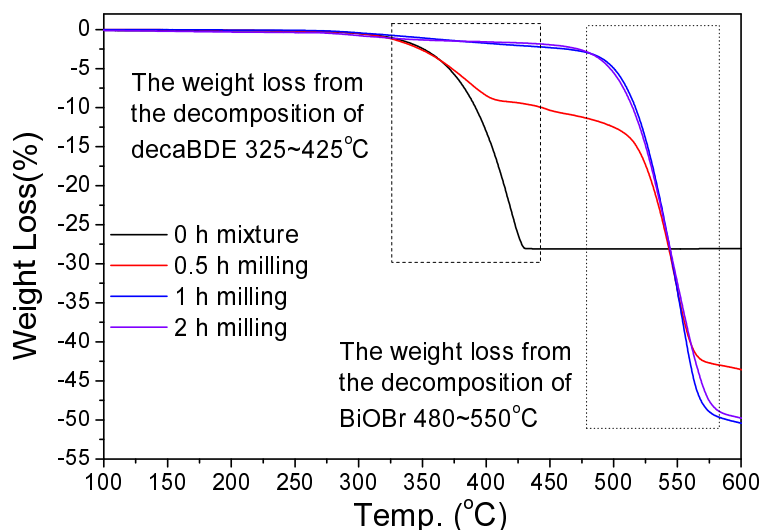


Fig.4. TG/DTA analysis of the samples milled with Bi_2O_3 for different time

To ensure the destruction of decaBDE and the formation of BiOBr during MC treatment, the samples were also analyzed by TG/DTA. For the 0 h mixture, a nearly 30% weight loss during heating can be clearly observed at the range of 325~425°C, which can be attributed to the decomposition of decaBDE in the sample. After 30 min ball milling, this 325~425°C weight loss became smaller and there was another weight loss at the range of 480~550°C. The new weight loss should come from the decomposition of the final product BiOBr ($3\text{BiOBr} \xrightarrow{500-550^\circ\text{C}} \text{Bi}_2\text{O}_3 + \text{BiBr}_3 \uparrow$). For the samples after 1 h and 2 h ball milling, there was no weight loss at 325~425°C at all, indicating that decaBDE was completely destroyed. And there was a nearly 50% weight loss at 480~550°C, which was exactly the percentage of the evaporated BiBr_3 from the decomposition of BiOBr . This result again shows that the Bi_2O_3 has just reacted with decaBDE and all the decaBDE was destroyed with the formation of BiOBr during ball milling. Therefore, by using Bi_2O_3 as co-milling additive in MC destruction of PBDE, not only a good performance was achieved, but also the final products can be utilized as visible light response photocatalyst.

Acknowledgements

This work was supported by the High-tech Research and Development Program of China (No. 2013AA06A305), the National Natural Science Funds (No. 51278270; 51078212), and the National Special Science & Technology Program for Non-profit Industry, Ministry of Environmental Protection of China (No. 201009026).

References

1. Viberg H, Eriksson P. (2011) *Toxicology*. 289(1): 59-65
2. Rowlands SA, Hall AK, McCormick PG, et al. (1994) *Nature* 367(6460): 223-223
3. Guo X, Xiang D, Duan G, Mou P. (2010) *Waste Manage.* 30 (1): 4-10
4. Zhang K, Huang J, Zhang W, Yu Y, Deng S, Yu G. (2012) *J Hazard Mater.* 243: 278-285
5. Chang X., Huang J, Cheng C, Sui Q, Sha W, Ji G, Deng S, Yu G. (2010) *Catal Comm.* 11(5): 460-464