MECHANICAL DESTRUCTION OF BFRs WITH IRON AND QUARTZ IN A PLANETARY BALL MILL

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Introduction

Over the last four decades, various brominated flame retardants (BFRs) have been widely used in polymers to improve their flame resistance. Tetrabromobisphenol A (TBBPA), polybromodiphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are the three most widely used BFRs[1]. However, concern for these emerging chemicals has risen because of their occurrence in the environment and human biota that could adversely affect human health and wildlife in various aspects[2]. Considering the disposal of BFRs containing solid wastes, high temperature incineration (HTI) is the most widely applied disposal method[3]. However, recent studies have revealed the generation and release of toxic PBDD/Fs from the combustion of BFRs containing waste printed circuit board[4]. Compared with HIT, mechanochemical (MC) reaction has been identified as a promising non-combustion technology for the disposal of solid waste containing persistent organic pollutants[5,6]. Most previous MC studies focused on the chlorinated pollutants but few paid attention to the brominated compounds especially BFRs, except hexabromobenzene by Zhang Qiwu[7] and decaBDE by Hosomi[8]. In the present study, two widely used BFRs (HBCD and TBBPA representatively) were co-ground with calcium oxide (CaO) or the newly developed mixture of iron powder and quartz sand (Fe+SiO$_2$) in a planetary ball mill at room temperature. The decomposition efficiency was evaluated and compared, the reaction intermediates and final degradation products of TBBPA were investigated, and the degradation pathway and reaction mechanism were proposed.

Materials and methods

1,2,5,6,9,10-hexabromocyclododecane (HBCD, C$_{12}$H$_{18}$Br$_6$, 99% in purity) was purchased from TCI (Japan). Tetrabromobisphenol A (TBBPA, C$_{15}$H$_{12}$Br$_4$O$_2$, 98% in purity) was purchased from Sigma-Aldrich, USA. Reactive iron powder (Fe, ≥98% in purity) and quartz sand (SiO$_2$, 99.8% in purity) were obtained from Sinopharm Chemical Reagent Co., Ltd, China. Calcium oxide (CaO, ≥98% in purity, Beijing Modern Eastern Fine-Chemical，China) was heated at 800 °C for 2 h before use. All solvents (methanol, hexane and acetone) used in the study were of HPLC grade (J.T. Baker Inc., USA).

A planetary ball mill machine (QM-3SP2, Nanjing University Instrument Corporation, China) and stainless steel pots were used for the ball milling experiments, with the pots volume of 60 mL and balls diameter of 5.50 mm. Fe+SiO$_2$ (weight ratio 10:1) and CaO were used as reactive chemicals during ball milling. They were mixed with BFRs by a weight ratio of 11:1 (5.5 g Fe+SiO$_2$ or CaO and 0.5 g BFR, totally 6.0 g) and put into the stainless steel pots with 180 g balls (balls to materials weight ratio 30:1). The planetary ball mill was operated at a speed of 550 rpm and the rotation direction changed automatically every 30 min.

The extractions of ground samples were analyzed by high-performance liquid chromatography (HPLC, Ultimate 3000, DIONEX Co., USA) with a C$_{18}$ reversed phase column (2.1×50 mm, 3.5 μm particles, XBridge, Waters, USA), followed by a tandem mass spectrometer equipped with electro-spray ionization (ESI-MS-MS, API3200, AB Sciex, USA). The soluble bromide ion was determined by ion chromatography (IC, DX-2000, DIONEX Co., USA). The ground samples were also characterized by a Microscopic Confocal Raman Spectrometer (RM 2000, Renishaw Co., UK) and a Fourier transform infrared (FTIR) spectrometer (NICOLET 6700 FTIR).

Results and discussion

Destruction efficiency

The MC treatment of HBCD and TBBPA using CaO or Fe+SiO$_2$ was performed by the planetary ball mill machine, during which the remaining BFR and the amount of bromide ions were measured. The change of residual BFR and yield of bromide are shown in Fig.1. As a new reactive chemical, Fe+SiO$_2$ showed a much better MC performance than the traditional used CaO in both the destruction rate of BFRs and the

yield of bromide. With Fe+SiO$_2$ in ball milling, the destruction rate of HBCD reached as high as 99.4% after 2 h grinding, and the yield of bromide attained 97% correspondingly. And the destruction rate of TBBPA reached as high as 99.6% after 5 h grinding with a nearly 95% yield of bromide. The complete destruction of BFRs and the generation of this high bromide verify that the organic bromine contained in BFRs could be largely transformed into soluble inorganic bromide mechanochemically. Actually no peaks could be found in LC-MS-MS spectra for the final grinding samples, which implies a complete destruction of BFRs and no organic products remain at the final reaction time.
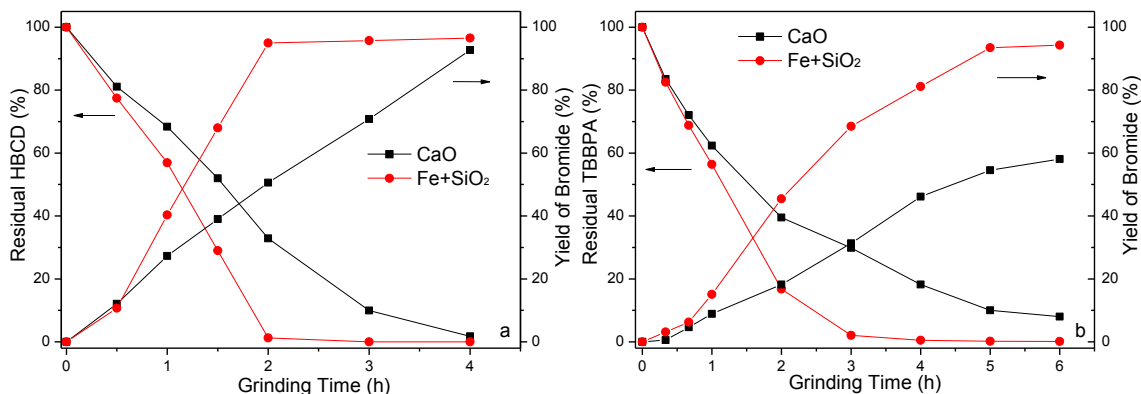

Fig.1. Change in residual BFRs and water-soluble Br with grinding time (a: HBCD, b: TBBPA)

Therefore, as a newly developed reactive chemical in ball milling process, Fe+SiO$_2$ achieved a better result of destruction and debromination data with a shorter grinding time, which made the ball milling consume less energy and reach higher efficiency.

Intermediates determination of TBBPA

It's noteworthy that the destruction of HBCD was faster than TBBPA during MC treatment, which might be a result of the higher reactivity of HBCD than TBBPA. Moreover, the destruction and debromination of HBCD were nearly synchronized, which means there was seldom obvious intermediate during the process (also testified by LC-MS-MS). While what was different for TBBPA, there was a time interval between destruction and the yield of bromide, which implies the formation of intermediates from TBBPA which still contain large fraction of bromine. As a result, further experiments on TBBPA were carried out to determine the intermediates and final products, find out the variations, and then propose the reaction pathway during ball milling with Fe+SiO$_2$.
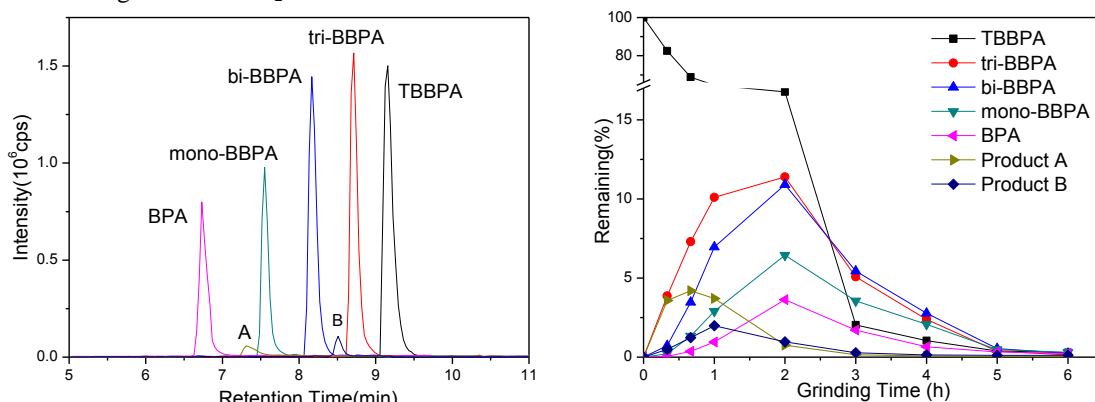

Fig.2. The intermediates of TBBPA ball milling with Fe+SiO$_2$ determined by LC-MS-MS (a). Formation and degradation of intermediates of TBBPA (b)

Fig.2a shows the species of intermediates of TBBPA ball milling with Fe+SiO$_2$ and Fig.2b performs the formation and degradation of them. There were 6 main species of intermediates found in the spectra of LC-MS-MS of the ground samples, including tri-BBPA, bi-BBPA, mono-BBPA, BPA, product A and product B (structure formula see below). During the milling process, TBBPA decreased and tri-, bi-, mono-BBPA and BPA were formed at concentration of 5% to 12% of the original TBBPA. With increasing reaction time

these intermediates decreased and disappeared after 5 h grinding (with a bromine recovery rate of more than 95%). And BPA, one of the TBBPA degradation products, was also finally destroyed with extended time, proving that the concern about the generation of BPA can be overcome by the chosen MC conditions.

Structural characterization of TBBPA sample

Fig.3 (a) shows the FTIR spectra of solid samples from the grinding of TBBPA with Fe+SiO$_2$. In FTIR, the peak band around 500-700 cm^{-1} in the spectra stems from the C–Br stretching vibration in TBBPA molecule, and the band around 1500-1625cm^{-1} is the vibration of C=C bond in the aromatic ring of TBBPA. The rapid disappearance of C–Br bond in the spectra indicates that the C–Br bonds in TBBPA were destroyed though the MC reaction and the bromine atom had been removed from the molecule. And the disappearance of aromatic ring and other functional groups in TBBPA implies the destruction of TBBPA molecule besides the debromination process.

Fig.3 (b) shows the Raman spectra of ground samples with different milling time. In Raman spectra, the peak band around 1460 cm^{-1} is the typical stretching vibration of the TBBPA molecule, which can be used to monitor the presence of unreacted TBBPA. The peak around 1312 cm^{-1} and 1582 cm^{-1} are usually identified as so called "D-band" (1330-1380 cm^{-1}) and "G-band" (1540-1580 cm^{-1}), which are characteristic for disordered carbon and graphite carbon. The disappearance of the peak of TBBPA and the generation in the peak of disordered and graphite carbon indicate that the carbonization and debromination are two important processes during the ball milling of TBBPA with Fe+SiO$_2$, via which TBBPA was transformed into inorganic carbon and bromide.
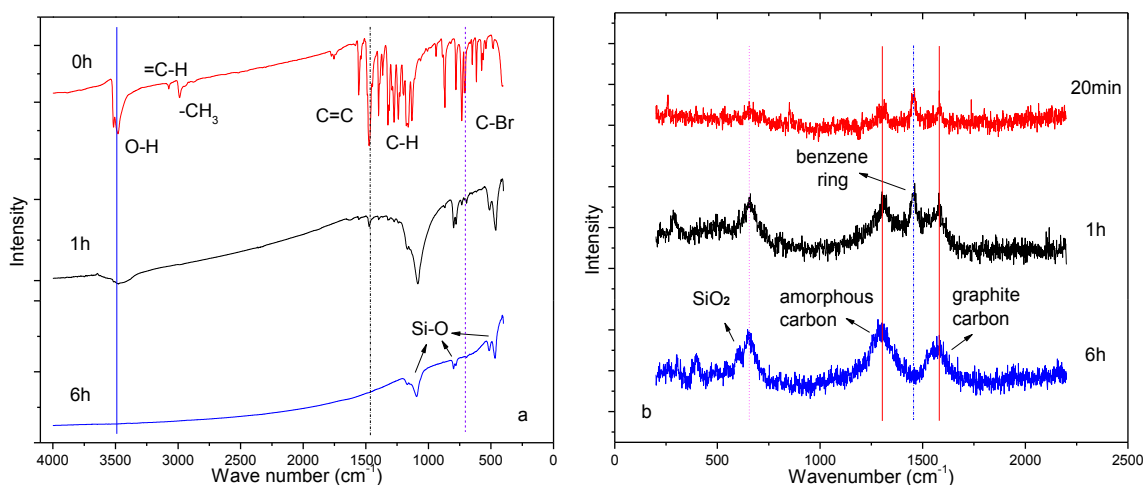

Fig.3. FTIR (a) and Raman (b) spectra of Fe+SiO$_2$ ground samples with different grinding time

Both the FTIR and Raman spectra demonstrate that TBBPA was destroyed through debromination and carbonization when ball milling with Fe+SiO$_2$, and the final products of TBBPA are inorganic carbon and soluble bromide ion, correspondingly with the results in Fig.1.

Degradation pathway of TBBPA

During the MC process with Fe+SiO$_2$ as reactive chemical, the particle size of iron powder became smaller and smaller and got activated. Such fine iron particles have high surface energy and activity, which can function as electron donor. The electron transfer can induce the breakage of the C-Br and other bonds. On the other hand, the crush of quartz was reported to generate surface radicals such as $\equiv$Si-O• and $\equiv$Si• in the MC treatment[8], which could also induce degradation reactions. Furthermore, quartz could also accelerate the refining and activation process of the iron powder due to its high hardness number.

According to the data and analysis above, the degradation pathway are proposed in Fig.4. In the MC process, either the electron from the activated iron powder or the radicals generated by the crushing of quartz could attack the TBBPA molecule. Either the bromine could get abstracted to soluble bromide, in which way tri-BBPA, bi-BBPA, mono-BBPA and BPA can be formed. On the other hand, these electron transfer and the radicals could also break down the TBBPA molecule into the radical M (labeled in Fig.4)

which was possibly the precursor of product A and B, resulting from its dehydrogenation or reaction with methanol during the extraction. All the intermediates were finally mineralized into inorganic carbon and soluble bromide during extended ball milling.
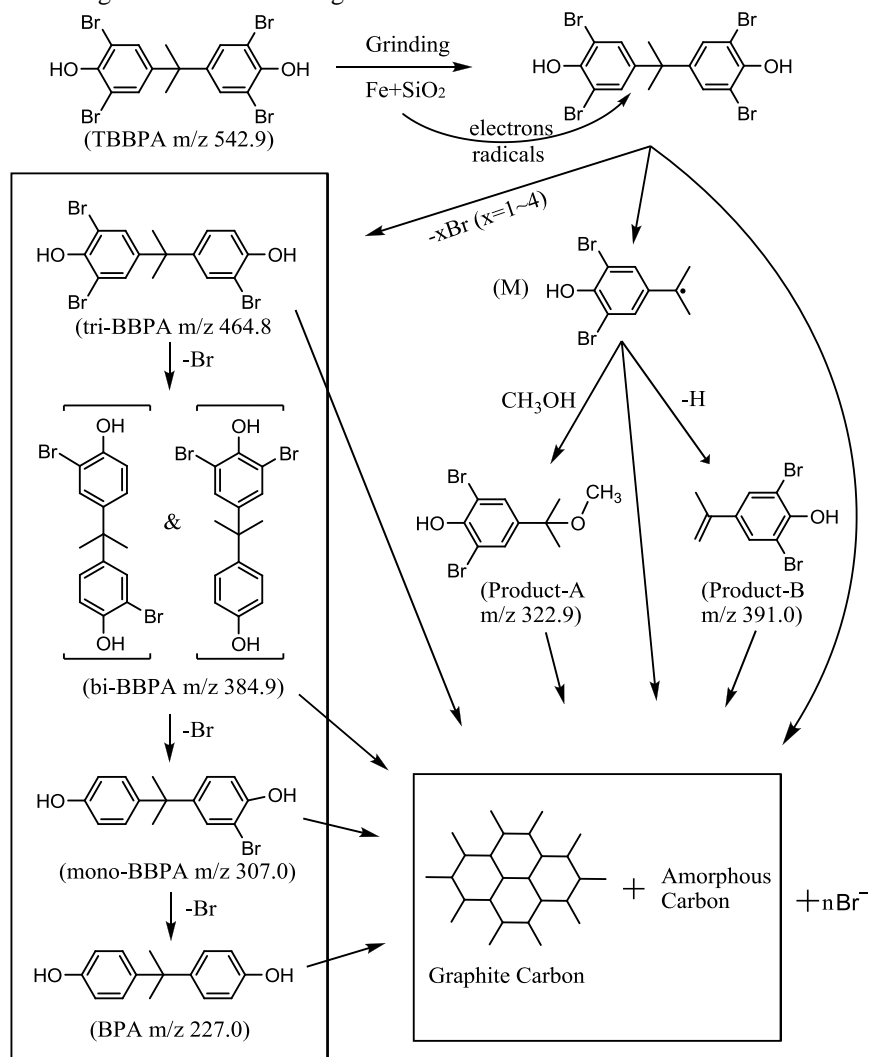

Fig.4. Proposed degradation pathway of TBBPA co-ground with Fe+SiO$_2$

References
1. Birnbaum L S, Staskal D F. (2004) *Environ Health Perspect.* 112(1): 9-17
2. Viberg H, Eriksson P. (2011) *Toxicology*. 289(1): 59-65
3. Grabda M, Oleszek-Kudlak S, Shibata E, Nakamura T. (2011) *J Hazard Mater.* 187(1-3): 473-479
4. Duan H, Li J, Liu Y, Yamazaki N, Jiang W. (2011) *Environ Sci Technol*. 45(15): 6322-6328
5. Rowlands S A, Hall A K, McCormick P G, Street R, Hart R J, Ebell G F, Donecker P. (1994) *Nature* 367(6460): 223-223
6. Nomura Y, Nakai S, Hosomi M. (2005) *Environ Sci Technol.* 39(10): 3799-3804
7. Zhang Q, Matsumoto H, Saito F, Baron M. (2002) *Chemosphere*, 48(8):787-793
8. Shintani M, Nomura Y, Nakashimada Y, Hosomi M. (2007) *Organohalogen Compounds*, 69(409): 2677-2680

9. Delogu F. (2011) *J Phys Chem C*. 115(43): 21230-21235