

DEBROMINATION OF DECABROMODIPHENYL ETHER BY MECHANOCHEMICAL TREATMENT

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Abstract

In order to develop a treatment technology for waste plastics with brominated flame retardants, we focus on Mechanochemical (MC) treatment that involved milling by use of a planetary ball mill. Decabromodiphenyl ether (DeBDE) powder, which is one of brominated flame retardants, was milled with excess calcium oxide (CaO). After 1 h milling, more than 99% of DeBDE was degraded, and bromine components were recovered as bromide ions in water.

Introduction

Brominated flame retardants, which have efficient fire retardant action, have been used for electric appliances and others. Polybromodiphenyl ethers (PBDEs) have been commonly used as brominated flame retardants since 1960s. PBDEs have been detected from the environment and lives, and their ecological effects are concerned^{1,2}. Recently, PBDEs were included in new persistent organic pollutants (POPs) candidate substances. Although presently waste of commercial products containing PBDEs have been treated by incineration and landfill disposal, off-gas and leachate containing toxic substances such as dioxins and heavy metals are concerned.

As one alternative technology for treating stockpiles of POPs and other organochlorine agrochemicals, the Ministry of Agriculture, Forestry, and Fisheries (MOAFF) selected MC treatment due to non-heating process and applicability of mobile treatment system. MC treatment has been demonstrated to efficiently degrade organochlorine compounds such as DDT³, PCB^{4,5}, chlorobenzenes^{4,6}, and dioxins⁷. Because MC reactions proceed in solid phases, it is expected that MC treatment is applicable to degrade PBDEs on solid. The essential information is how the PBDEs are degraded in MC treatment, but there is no information available.

Therefore, this research was carried out to elucidate the degradation mechanism of PBDEs in MC treatment by using model compounds. Here we selected DeBDE among PBDEs, and milled DeBDE with CaO.

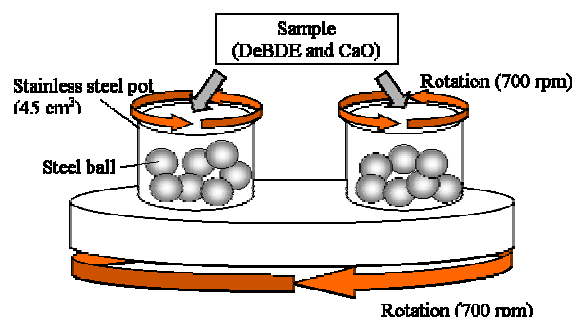


Fig.1 Schematic of MC treatment with a planetary ball mill

Materials and methods

The MC reactor used a planetary ball mill (Pulverisette-7, Fritch, Germany) with two stainless-steel pots (45 cm³) in which seven steel balls (15-mm diameter) were arranged. The pots were situated on a rotating disk that permitted the pots and disk to rotate in opposite directions. Figure 1 shows a schematic diagram of the MC treatment process.

Under atmospheric pressure, 200 mg of DeBDE and 4.0 g of CaO as activator were added to the pots. The planetary ball mill was operated at 700 rpm speed for 15-min intervals, with a 15-min cooling period after each interval.

A treated powder sample was collected from the pots and analyzed for organic bromides and bromide ions as follows: To confirm degradation of DeBDE by analyzing organic bromides, the treated powder sample was extracted with toluene. The solution was filtered, and the filtrate was analyzed by the high-resolution gas chromatography (HRGC/MS). To confirm mineralization of bromine components by analyzing bromide ions, the treated powder sample was extracted with ultra pure water (95 °C). The solution was filtered, and the filtrate was analyzed by the ion chromatography. As a control experiment, extracts of DeBDE and CaO mixture were also analyzed for bromide ions.

The treated powder sample was also analyzed by X-Ray Diffraction spectroscopy (XRD) to identify reaction products.

Results and Discussion

Table 1 shows the amount of PBDEs in the MC treated sample analyzed by HRGC/MS with the selective ion monitoring (SIM) mode for PBDEs. Figure 2 shows the time dependence of residual ratio (defined as the ratio of the amount of DeBDE after milling to the initial amount of DeBDE). Degradation of DeBDE was progressed with milling time, and more than 99% of DeBDE was degraded by 1 h milling. Although a small amount of Nonabromodiphenyl ethers (NBDEs), Octabromodiphenyl ethers (OBDEs), and Heptabromodiphenyl ethers (HpBDEs) was detected at the beginning of milling time (Table 1), it is not concluded that these productions by MC treatment were main intermediates, considering that NBDEs, OBDEs, and HpBDEs were equivalent to only about 2%, 0.1%, and 0.002% of initial DeBDE, respectively. The degradation fate of each congener indicates that the dissociation of several bromine compounds occurs simultaneously, not consecutively, suggesting that debromination progresses rapidly by radical reaction. Furthermore the toluene solutions of the MC treatment sample were also analyzed by HRGC/MS with scan mode to detect organobromine compounds other than PBDEs, however, no peaks were detected except for the peaks of PBDEs. From these results, it is suggested that cleavages of dipheyl ethers and bone structure of DeBDE were taken place during MC treatment.

Figure 3 shows the debromination ratio (defined as the ratio of the amount of bromide ions after milling to the amount of bromine included initial DeBDE). The debromination ratio was increased with time, and 100% of the

ratio had been achieved after 2 h milling. We demonstrated more than 100 % of debromination of the DeBDE by the MC treatment by measurement of bromide ions. These results confirmed the feasibilities of degrading brominated flame retardants as a safe method without by-production of organic bromine compounds.

Table 2 shows the recovery ratio of bromine components converted using amount of PBDEs and bromide ions. Organobromine components were degraded, and mineralization of bromine made progress with milling time. Although there were some bromine components which were not identified for milling time with 15 min and 30 min, all of bromine components were mineralized after more than 1 h-milling time.

Figure 4 shows the changes of XRD spectra of the original DeBDE and the MC treated samples during milling. The peaks of CaO have become small gradually. No peaks of bromine compounds were detected. The report about MC treatment of 1,2,3-trichlorobenzene (TCB) with CaO describes that calcium chloride (hydrate) ($\text{CaCl}_2 \cdot (n\text{H}_2\text{O})$) was detected by XRD analysis⁸. Here the production of calcium bromide (CaBr_2) was estimated in a similar way. We speculated that in this study no peaks except for CaO were observed because of excess CaO to DeBDE.

In conclusion, 99% of DeBDE was degraded by MC treatment, and 100% of bromine components were recovered in hot-water.

Table 1 Time dependence of PBDEs in the MC reactor pot analyzed by HRGC/MS during ball milling (initial PBDEs: 200 mg in the MC reactor pot)

Milling time	15 min	30 min	60 min
MBDEs [μg]	<10	<10	<10
DiBDEs [μg]	<10	<10	<10
TrBDEs [μg]	<10	<10	<10
TeBDEs [μg]	<10	<10	<10
PeBDEs [μg]	<10	<10	<10
HxBDEs [μg]	<10	<10	<10
HpBDEs [μg]	1.9	3.2	(0.54)
OBDEs [μg]	180	60	4.8
NBDEs [μg]	3,900	890	47
DeBDE [μg]	65,000	12,000	510
Total PBDEs [μg]	69,000	13,000	560

Table 2 Recovery rate of bromine components

Milling time	15 min	30 min	1h	2h	4h
Organic bromine components (Bromines in PBDEs) [%]	34.32	6.425	0.278	—	—
Inorganic bromine components (Bromide ions) [%]	24.3	48.5	92.9	101	100
Recovery rate of bromine components [%]	58.6	54.9	93.2	101	100

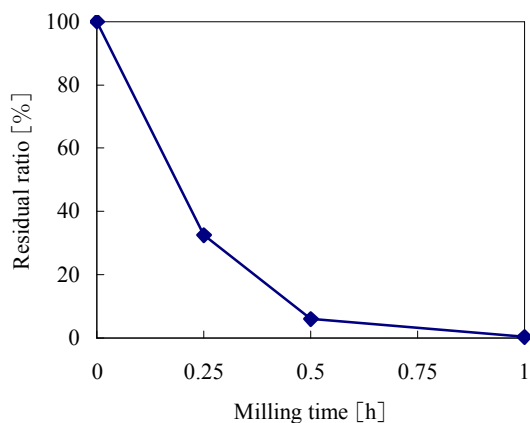


Fig. 2 Time dependence of residual ratio by MC treatment of DeBDE with CaO

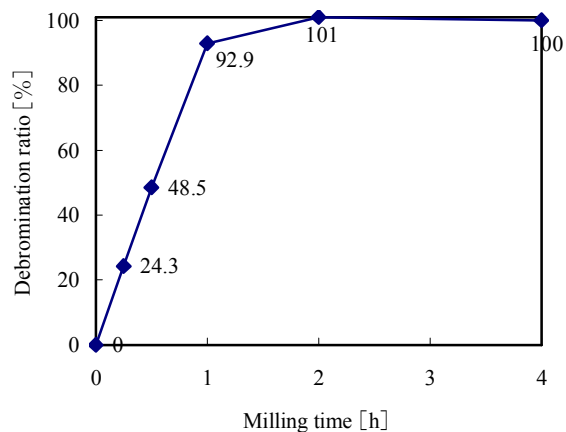


Fig. 3 Time dependence of debromination ratio by MC treatment of DeBDE with CaO

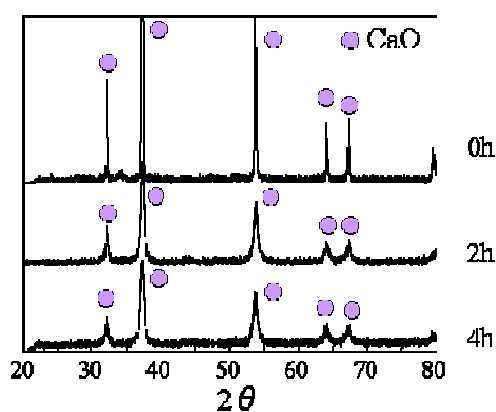


Fig. 4 Changes of XRD spectra of the original DBDE and the MC treated samples during ball milling

References

1. Noren K, Meironyte D. *Chemosphere* 2000; 40:1111
2. Watanabe I, Takahashi K, Ryo T. *Chemosphere* 1987; 16:2389
3. Hall A. K, Harrowfield J. M, Hart R. J, Maccormick P. G. *Environ. Sci. Technol.* 1996; 30:3401
4. Birke V, Mattik J, Runne D. *J. Material Sci* 2004; 39:5111
5. Nomura Y, Nakai S, Lee B-D, Hosomi M. *Kagaku Kougaku Ronbunshu* 2002; 28:565
6. Loiselle S, Branca M, Mulas G, Cocco G. *Environ. Sci. Technol.* 1997; 31:261
7. Nomura Y, Nakai S, Hosomi M. *Environ. Sci. Technol.* 2005; 39:3799
8. Tanaka Y, Zhang Q, Saito F. *Journal of Material Science* 2004; 39:5497