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Abstract

A hexabromobenzene (HBB, C_6Br_6) powder was subjected to co-grinding with excess CaO powder in air using a planetary ball mill to investigate mechanochemical debromination of the HBB sample. The reaction proceeds smoothly with an increase in both grinding time and molar ratio of CaO addition. The co-grinding enables us to debrominate HBB, forming $CaBr_2$, C and $CaCO_3$ besides excess CaO in the product. $CaBr_2$ in the product tends to absorb moisture from the atmosphere to form $CaBr_2 \cdot nH_2O$. The reaction yield is quantitatively evaluated by measuring the amount of water-soluble bromide through water washing and the amount of unreacted HBB through toluene washing. It is found that almost 100% of debromination is achieved by 6 h grinding with the molar ratio kept constant at 2:1. Radicals are detected in the ground products, possibly due to rupture in the covalent bonds of C–C and C–Br in HBB.

Keywords: HBB; Fire retardant; Mechanochemistry; Bromide; Radical

1. Introduction

Once polymers containing halogen are subjected to heating in air, halide hydrogen is normally generated, which acts effectively to dilute flammable gases and finally to cease the cascading radical reaction. These polymers are called, therefore, as fire retardant materials, which reduce the degree of flame spread over a surface and afford protection to an underlying substrate. They act also as a buffer between a flammable substrate and any source of ignition. Such property enables us to use in wide applications such as circuit boards in electric devices, commodities in heating devices and a like. They are generally categorized into two groups; one is chloride group and the other bromide one. Especially, the latter group is of superior effect as a fire retardant to the former one, due to lower dissociation energy for C–Br bond than that for C–Cl bond. A representative compound of the bromine group is hexabromobenzene (HBB, C_6Br_6), of which production amount has increased year by year. Accordingly, the amount of HBB wastes is in accordance with the production amount, leading to increment of the wastes. They have been normally subjected to combustion in waste treatment facilities, where toxic gases such as HBr and highly toxic compounds like polybrominated dioxins, although small amount, are generated (Bindra and Narang, 1995, 1996; Wanke et al., 1996; Weber and Greim, 1997), causing pollution and contamination of environment. In order to avoid such defects, various methods to debrominate the waste have been proposed, which involve the uses of chemicals agents with aid of specific treatments such

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as ultrasound, photolysis, catalysis et al. (Khurana and Sehgal, 1996; Mackenzie and Kopinke, 1996; Hall et al., 1997; Atobe et al., 1998; Bedard and Van Dort, 1998; Wei and Hor, 1998). These methods are unique and excellent, however, they are generally difficult to operate and require uses of specific expensive reagents and/or devices. The authors have proposed a novel simple method to decompose organic polymer wastes containing halogens such as F, Cl by means of mechanochemical (MC) treatment, namely co-grinding with inorganic additives (Zhang 1999, 2001a,b). The halogens in the polymers can be transformed into inorganic phases such as Sr/Ca fluoride or chloride through the MC solid reactions even at room temperature. The authors have applied this method to the debromination of bromine polymer waste of HBB, which has an aromatic structure, different from the above polymers.

The main purpose of this paper is to provide basic information on MC debromination of HBB by grinding with CaO in air. This work offers a novel process to debrominate flame retardants. It also allow us to investigate comparatively the mechanism of MC decomposition of aromatic structures, on which the authors have been working recently (Ikoma et al., 2001; Zhang et al., 2001c).

2. Experimental

2.1. Samples and experimental procedure

A HBB sample was supplied from Sumitomo Bakelite Co. Ltd., Japan. A CaO sample was prepared by heating $Ca(OH)_2$, which was obtained from Wako Pure Chemicals Ltd., Japan, at 1000 °C for 2 h in an oven. HBB and CaO samples were mixed at different molar ratio of Ca to Br in the mixtures, which were used as a starting sample. The starting sample was subjected to grinding in air, then the ground sample was washed with distilled water to separate soluble compounds formed mechanochemically during grinding by filtration. These operations as well as characterizations were described in detail below.

2.2. Grinding and washing

A planetary mill (Pulverisette-7, Fritsch, Germany) was used for grinding the mixture. The mill consists of a pair of pots made of zirconia and a rotating disc. Two grams of the mixture was put in the zirconia pot (45 cm^3 inner volume) with seven zirconia balls of 15 mm diameter and subjected to grinding in air at 700 rpm speed for various periods of time.

2.3. Characterization

The ground mixtures were characterized as follows: X-ray diffraction (XRD) analysis was conducted by using a diffractometer (RAD-B, Rigaku, Japan) with Cu-Kα radiation to identify the phases formed in the ground products as well as the washed ones. Thermogravimetric analysis (TG) was performed for the samples by using a TG/DTA analyzer (TAS-200, Rigaku Denki, Japan) at 5 K/min of heating rate in air. FT-IR analysis was taken for the samples by means of Fourier transform infrared (FT-IR) spectroscopy using a KBr disc method. ESR spectrometer (X-band, 9.6 GHz, Bruker ESR-380E) was also used to detect radicals in the ground samples. The filtrate was characterized by an ion chromatography (LC10 series, Shimadzu, Japan) to determine the ion type and its concentration.

2.4. Confirmation of the formed compound and reaction yield

The ground mixtures were dispersed in distilled water to dissolve soluble compounds formed during grinding, then the filtrate was dried in an oven to form solid powder. In order to confirm a compound formed in the ground mixture, a chemical reagent, $CaBr_2 \cdot 2H_2O$ sample was used as a reference. Two methods for determining the reaction yield were employed: One is a toluene washing, where unreacted HBB sample remaining in the product dissolves. The amount of the remaining HBB after evaporating the toluene solvent was weighed. For comparison, water washing was conducted to dissolve $CaBr_2$ formed in the product. The concentrate of Br anion in the filtrate was measured by IC analysis. The degree to which the MC reaction proceeds were quantitatively evaluated by calculating the percentage of the reacted HBB and the soluble bromide, respectively.

3. Results and discussion

3.1. Effect of CaO amount in mechanochemical reaction

Fig. 1 shows XRD patterns of 4 h ground mixtures, which has been prepared by changing the amount of CaO from 1:2 to 2:1 in molar ratio of Ca to Br. The molecular ratio of 1:2 for Ca:Br in the mixture was set for stoichiometric generation of $CaBr_2$. Several small peaks corresponding to HBB are still observed in two patterns with Ca:Br addition ratios of 1:2 and 1:1, respectively. The peaks of HBB has disappeared when the addition ratio of Ca:Br is increased to 3:2 or more (2:1). These results indicate that HBB has been decomposed
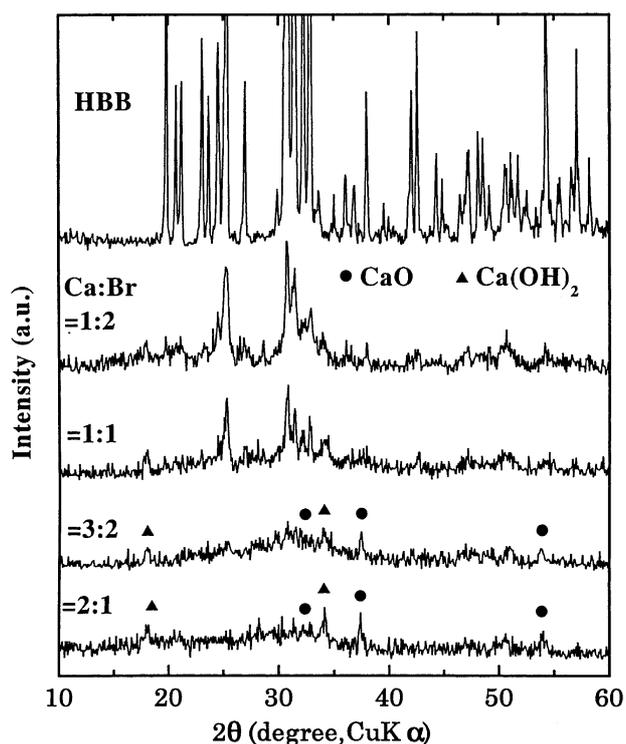
Fig. 1. XRD patterns of the original HBB and the 4 h ground samples with different molar ratios of Ca:Br.

Fig. 2. TG curves of the 4 h ground samples with different molar ratio of Ca:Br.

efficiently by adding CaO in molar ratio more than 1:1. Unfortunately, there are no new peaks observable in the patterns, suggesting the formed products in the ground sample are somehow amorphous in crystalline state. There exist some weak peaks of CaO, which is added in extra amount based on the stoichiometric molar ratio of $CaBr_2$, and of $Ca(OH)_2$, which is formed through the water absorption of unreacted CaO. Fig. 2 shows TG curves of the 4 h ground mixtures, which are the same ones as that shown in Fig. 1. Weight loss due to the combustion of HBB at around 250 °C is observed with Ca added in 1:2 to Br, confirming that HBB is still remaining after grinding, consistent with the result by XRD analysis shown in Fig. 1. However, the value of the weight loss tends to decrease with an increase in the molar ratio of Ca to Br in the mixtures and there is no weight loss observed in the case of 2:1 for Ca:Br. The results indicate clearly that the increase in molar ratio of CaO addition facilitates the decomposition of HBB by grinding and two times of Ca to Br is required to break HBB completely. On the other hand, the weight loss, which is attributed to thermal decomposition of reaction products, is observed in the temperature range from around 600 to 780 °C. The much higher temperature at which the reaction products decompose implies that they are more stable than HBB itself. These reaction products are inorganic rather than organic ones. Both C and Br in
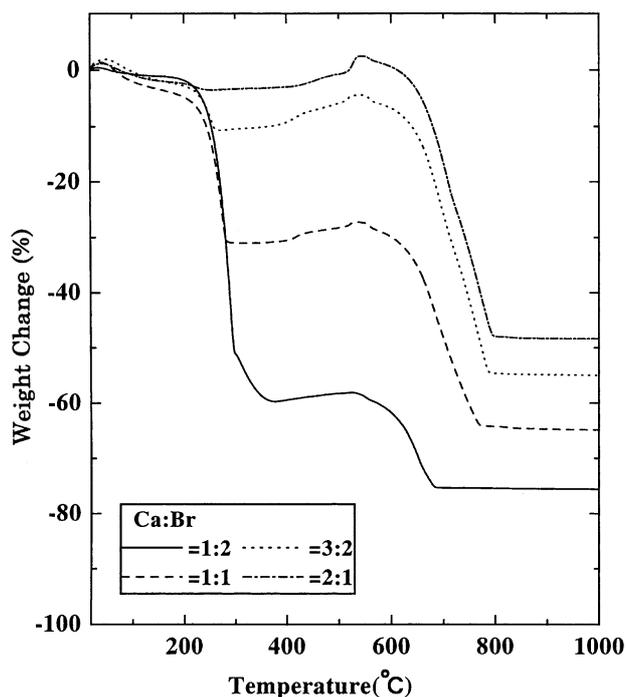
HBB have been transformed and fixed in inorganic phases, of which the composition will be discussed in later session. Value of weight loss increases with an increase in the amount ratio of Ca to Br in the samples. Taking the results by XRD analysis and TG analysis into account, the mixture having the molar ratio of 2:1 for Ca:Br would be suitable for the starting sample to facilitate the MC reaction. Therefore, it was fixed as 2:1 hereinafter experiment.

3.2. Effect of grinding time in the mechanochemical reaction

Fig. 3 shows XRD patterns of the mixture ground for different periods of time. The peak intensity of HBB is drastically lowered within 1 h grinding, suggesting that the MC reaction proceeds quickly by the co-grinding. However, some small peaks of HBB still exist in the pattern of the sample ground for 2 h. These peaks have disappeared for the sample ground for 3 h or more, indicating 3 h grinding is required to decomposing HBB completely, while results of the practical quantitative analysis are provided in the later session. Peaks of CaO sample remain in all the patterns because of the extra addition.

Fig. 4 shows TG curves of the mixtures ground for different periods of time. Significant weight loss around 250–300 °C due to HBB combustion can be seen for the
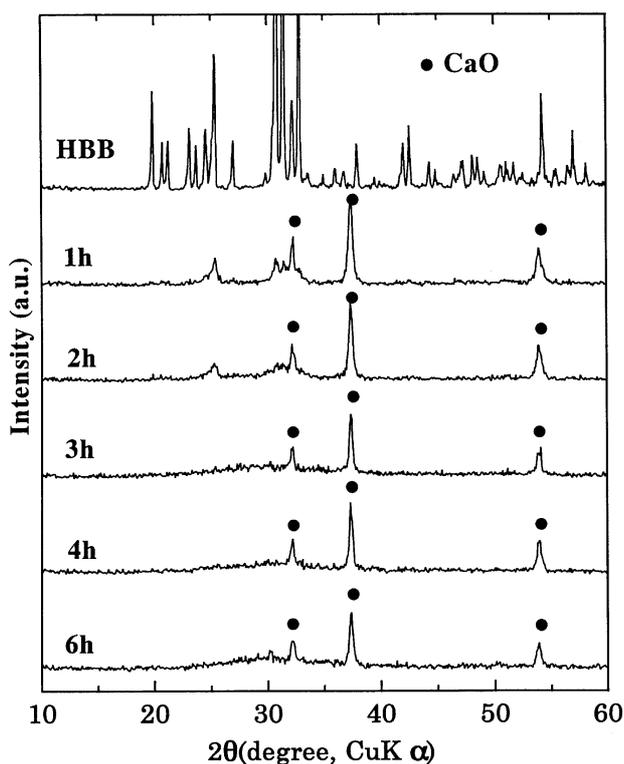
Fig. 3. XRD patterns of the original HBB and the mixed sample (Ca:Br=2:1) ground for different periods of time.
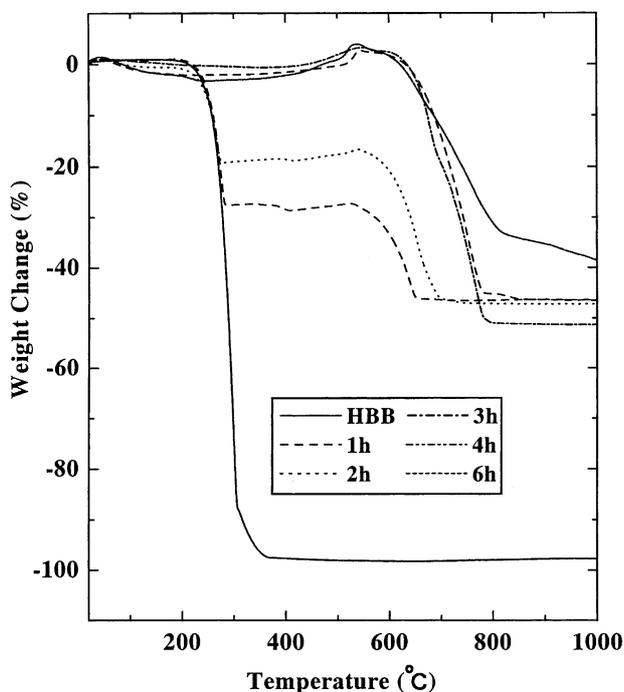

Fig. 4. TG curves of the original HBB and the mixed sample (Ca:Br=2:1) ground for different periods of time.

there is not any significant change in the curves of the mixtures ground for 3 h or more in the same temperature range as above up to 550 °C, indicating that the HBB sample is decomposed completely by grinding for 3 h or more, the results consistent with that by XRD analysis shown in Fig. 3. One the other hand, new weight loss is observed around temperature range from 600 to 780 °C, due to the products formed by the grinding, which is similar to that shown in Fig. 2. Its value increases correspondingly with an increase in grinding time, suggesting that the MC reaction proceeds with an increase in grinding time.

Fig. 5 shows FT-IR spectra of the mixture ground for different periods of time together with that of the pure HBB sample. Peaks positioned around $1400 \ cm^{-1}$ due to benzene mode and peak around $600 \ cm^{-1}$ due to C–Br stretching vibration appear in the spectrum of HBB sample, and these peaks have been still observed in the spectrum of the mixture ground for 2 h. However, the peaks have disappeared from the spectra of the mixtures ground for 4 h or more. These results indicate that grinding over 4 h has cut the C–Br bonding and broken the benzene ring completely. A sharp peak appears in the ground mixtures at around $900 \ cm^{-1}$, which is attributed to the C–O stretching vibration. In addition, new peaks due to the C–O binding can be seen in the all spectra of the ground mixtures at around $1500 \ cm^{-1}$,
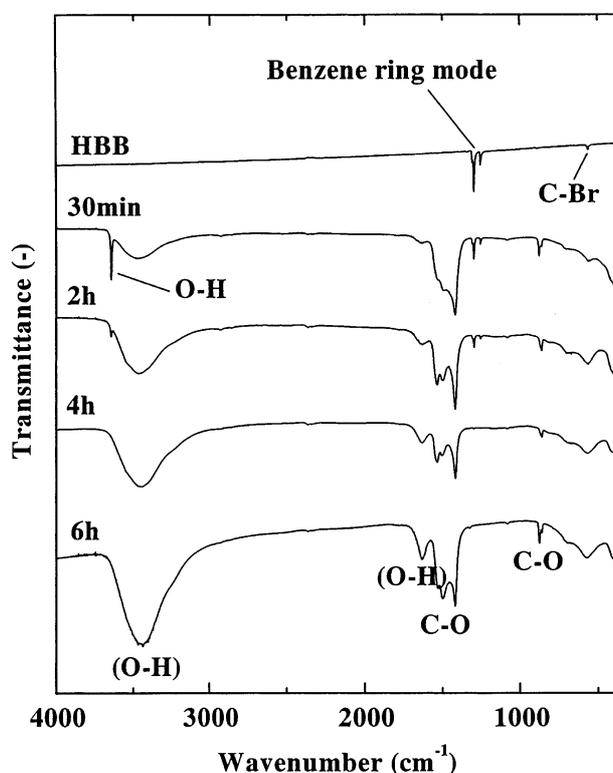

Fig. 5. FT-IR spectra of the original HBB and the mixed sample (Ca:Br=2:1) ground for different periods of time.
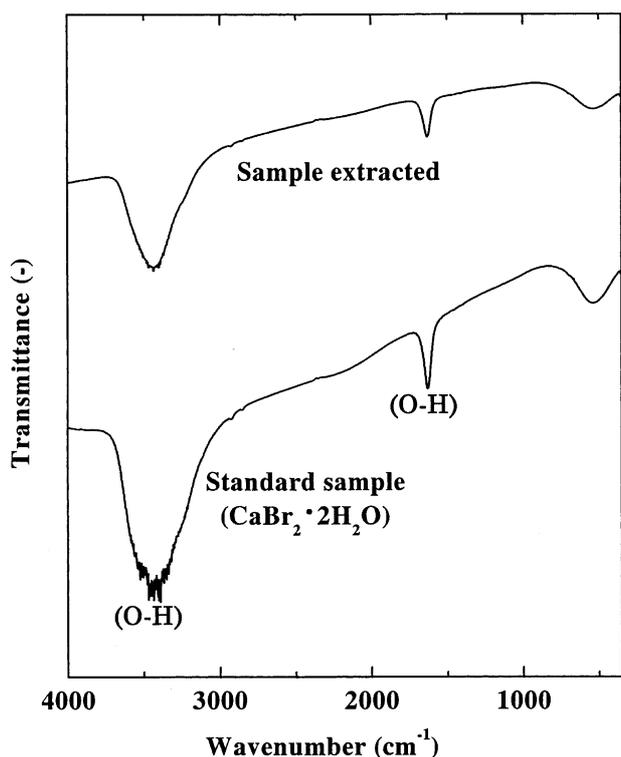
mixtures ground for 1 and 2 h, and their values are measured as 30 and 20 wt.%, respectively. However,

Fig. 6. FT-IR spectra of the standard $CaBr_2 \cdot 2H_2O$ and the reaction product extracted by water from the ground sample.

suggesting the existence of $CaCO_3$ in the product. Peaks due to O–H binding can also be seen in the all spectra of the ground mixtures at around 1650 and 3500 cm^{-1}, and their peak intensities tend to increase as grinding progresses. This suggests the presence of water in the product. Fig. 6 shows FT-IR spectrum of the standard $CaBr_2 \cdot 2H_2O$ sample together with that of a solid powder sample, which was prepared from the 6 h ground mixture by the extraction with distilled water followed by drying procedure. As can be seen in the figure, the spectrum of the solid powder sample is quite similar to that of the standard $CaBr_2 \cdot 2H_2O$ sample, implying that the solid should be Ca bromide hydrated ($CaBr_2 \cdot nH_2O$). Therefore, the co-grinding of the mixture allows transformation of bromine from HBB into inorganic $CaBr_2$, which adsorbs moisture from the environment to form $CaBr_2 \cdot nH_2O$. Accompanied by the Ca–Br bonding, the carbon in HBB might be bound to oxygen in CaO to form CO gas (Zhang et al., 2001a). However, the extra addition of CaO has led to different products. Formation of Ca carbonate is observed. Another is free carbon, which is confirmed indirectly from the color change. The white color of the starting powders has changed gradually into black with an increase in grinding time and samples ground over 3 h are found to be in deep black. Both Ca carbonate and bromide will decompose around 600–800 °C, consistent

with the results by TG analysis shown in Figs. 2 and 4. The reaction induced by grinding may be described as follows:

$$C_6Br_6 + 12CaO + 3nH_2O$$
$$\rightarrow 3CaBr_2 \cdot nH_2O + (3/2)CaCO_3$$
$$+ (15/2)CaO + (9/2)C \qquad (1)$$
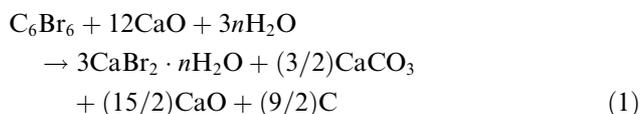
3.3. Quantitative measurement of mechanochemical reaction yield

Fig. 7 shows the reaction yield determined by the two methods described in the experimental section as a function of grinding time. It is worth mentioning that the two curves are well consistent, and the reaction proceeds smoothly in the early stage of grinding, and subsequently the reaction rate levels off. Its yield reaches about 90% at 3 h and almost 100% at 6 h grinding. This means that the HBB sample tends to degrade gradually with an increase in grinding time and almost finishes up to 6 h grinding. Fig. 8 shows ESR spectra of the mixtures ground for different periods of time. It is clearly indicated that radical signal is detected in all ground mixtures at around 3420 G, its intensity tends to increase generally as the grinding operation progresses. However, the intensity for the 6 h ground mixture is slightly
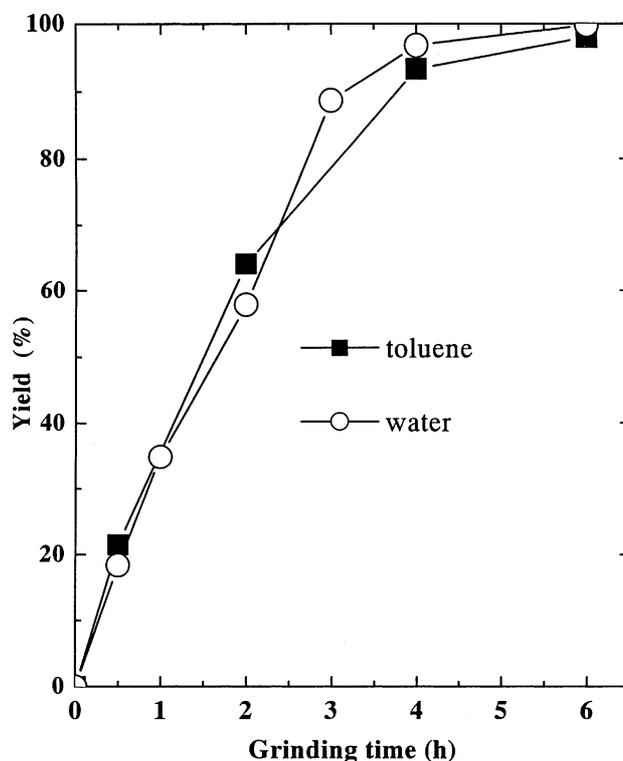

Fig. 7. Change in the yields of soluble bromide and reacted HBB with grinding time.
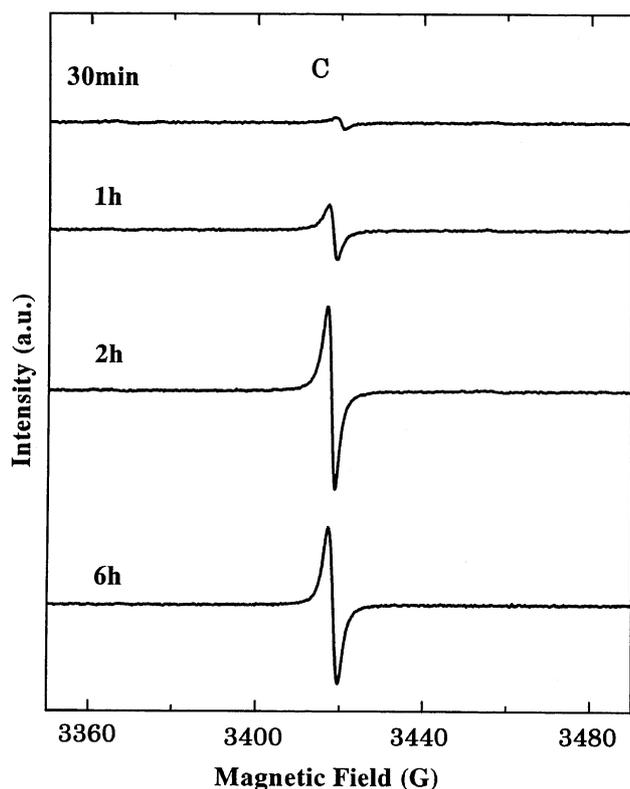
Fig. 8. ESR spectra of the sample ground for different periods of time.

weaker than that of the 2 h one. The radical generation could be attributed to the free carbon formation (Ikoma et al., 1998a,b; Raffi et al., submitted for publication) due to the breakage phenomenon in HBB structure. Further investigation about the characterization of the carbon composition and the relation of its formation with radical occurrence is under consideration.

4. Conclusion

HBB powder sample was mixed with a chemical re-agent, CaO powder at different molar ratio, then the mixture was subjected to grinding in air using the planetary ball mill to investigate the MC reaction to debrominate HBB sample. The experimental results are summarized as follows:

(1) Excess CaO sample plays a significant role to facili-tate the solid reaction and to avoid gas generation during the grinding.
(2) The reaction between HBB and CaO proceeds smoothly when the CaO sample is added to the HBB at molar ratio of 2:1 for Ca:Br. The co-grind-ing enables us to debrominate HBB, forming $CaBr_2$, C and $CaCO_3$ besides excess CaO in the product.

(3) $CaBr_2$ in the product tends to adsorb moisture from the atmosphere to form $CaBr_2 \cdot nH_2O$. The reaction yield is increased with an increase in grinding time, reaching almost 100% by about 6 h when the molar ratio of Ca to Br is kept constant at 2.
(4) Radicals are detected in the ground products, due to rupture in the covalent bonds of C–C and C–Br in HBB.

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