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MECHANOCHEMICAL DESTRUCTION OF 4-BROMOCHLOROBENZENE WITH CaO. EFFICIENCY, KINETICS, AND MECHANISM

The degradation of 4-bromochlorobenzene (4-BCB) containing both chlorine and bromine by mechanochemical destruction (MCD) using CaO powder was investigated. The degradation efficiency of 4-BCB almost achieved 100% after 2 h milling. The debromination rate (0.41 h^{-1}) was higher than the dechlorination rate (0.31 h^{-1}) which can be ascribed to the lower dissociation energy of C–Br bond than that of C–Cl bond in 4-BCB. The kinetic analysis demonstrates that nucleation growth was the control step of dehalogenation reactions. Additionally, the dehalogenation efficiency increased with increasing rotate speed and milling ball weight. The XRD and FT-IR spectra analysis manifests that the CaO powder was transformed to CaCl_2 , CaBr_2 , $\text{Ca}(\text{OH})_2$, and CaCO_3 . The identification of intermediates and analysis of Raman spectra indicates that the 4-BCB degradation by MCD treatment using CaO powder may occur through three pathways: (a) breakup of the benzene ring to form small molecular halogenated hydrocarbons and mineralization to form CO_2 and H_2O in sequence, (b) dehalogenation reaction to form benzene and monohalogenobenzene and addition reaction of halogen radicals to form dihalogenobenzenes in sequence; (c) polymerization reaction to form biphenyl, halogenated biphenyl, and graphite.

1. INTRODUCTION

4-bromochlorobenzene (4-BCB) is used as raw material, solvent, and intermediate for organic synthesis in petroleum, chemical, pharmaceutical, and other industries [1]. Only about 60% of 4-BCB was transformed into downstream products, and the residual was released to environment medium like air, water, soil, and sediment. 4-BCB is harmful to humans and animals because of its carcinogenicity, mutagenicity, and teratogenicity through food intake, air inhalation, dust ingestion, or dermal absorption [2]. Due

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to its low water solubility, high chemical stability, and strong biological toxicity, 4-BCB is highly resistant to degradation in the natural environment. Therefore, it is necessary to develop a viable and effective method to remove 4-BCB. However, as we know, almost no literature is regarding the effective degradation of 4-BCB.

Until now, several techniques have been developed for the degradation of persistent halogenated organic pollutants (HOPs), such as thermal disposal, ultraviolet degradation, and bioremediation [3–8]. However, the application of these techniques is seriously restricted due to the inevitable disadvantages, such as low degradation efficiency, high energy consumption, and the production of toxic by-products. Recently, mechanochemical destruction (MCD) has been paid attention to as a promising technology that does not require heating or off-gas treatment for the effective degradation of solid waste containing persistent organic pollutants (POPs) [9]. Unlike thermal treatment, MCD can avoid the production and release of unintentionally POPs. The MCD method has many advantages such as low energy consumption and its possible implementation in mobile units [12–13].

So far, several metal oxides/hydrides have been applied to effectively degrade various HOPs, including chlorinated benzene, polyvinyl chloride, and polychlorinated biphenyls [14–16]. Zhang et al. [17] investigated the mechanochemical debromination of hexabromobenzene (HBB) with CaO powder in planetary ball mills and concluded that the reaction proceeded smoothly with the increasing grinding time and CaO dose. Wang et al. [16] studied the mechanochemical dechlorination of hexachlorobenzene (HCB) with CaO, SiO₂, and Fe powder, and found that the HCB destruction ratio followed the sequence: CaO > SiO₂ > Fe. Although calcium hydrides have been employed in the HCB destruction and achieved very high efficiency, its safety consideration could not be neglected in practical applications [18]. Overall, MCD treatment has been proved to be an effective method for the degradation of HOPs.

However, in the previous studies, the target HOPs by MCD treatment only contain one halogen species (either bromine or chlorine). This study aimed to elucidate the MCD treatment of 4-BCB (contain both bromine and chlorine) by its co-grinding with CaO powder. The degradation and dehalogenation efficiency of 4-BCB by MCD treatment were evaluated in detail. The transformation of CaO powder and pathways of 4-BCB were also investigated. The degradation mechanism and dehalogenation kinetics of 4-BCB were emphatically discussed. The study helps to better understand the degradation of aromatic organic compounds containing multiple halogen species with MCD adopted as a treatment technique.

2. MATERIALS AND METHODS

Reagents and materials. All chemicals used in this study were of ACS grade or higher. 4-BCB and CaO powder were purchased from the Aladdin Chemical Reagent

Company (Shanghai, China). *n*-Hexane was obtained from the Shanghai Topfine Chemical Company (China). CaO was heated at 800 °C for 4 h and stored in a desiccator before use.

Analytical methods. 4-BCB was analyzed by a gas chromatograph (GC, Agilent 6890) equipped with a flame ionization detector (FID) and HP-Innowax separation column (30 m×0.32 mm, 0.5 μm). The instrumental conditions were set as follows: injection volume of 0.6×10^{-6} dm³, helium carrier gas flow rate of 1.0 cm³·min⁻¹, split ratio of 5:1, injector temperature 230 °C, detector temperature 250 °C, and initial oven temperature held at 70 °C for 3 min, ramped to 200 °C at 15 °C·min⁻¹ and held for 3 min. Chloride and bromide ions were quantified by an ion chromatograph (Dionex-ICS2000) equipped with an Ionpac AS19 column (250 mm×4.0 mm, 5.0 μm). KOH solution (20 mM/dm³) was used at a flow rate of 1.0 cm³·min⁻¹. The 4-BCB degradation intermediates were extracted by adding 10 cm³ of acetone into 0.05 g of a powder sample and identified using a gas chromatograph equipped with a mass spectrometer (GC/MS, Agilent 6890N/MS5975) and HP-Innowax separation column (60 m×0.32 mm, 0.5 μm). The instrumental conditions were set as follows: injection volume of 1.0×10^{-6} dm³, helium carrier gas flow rate 2.0 cm³·min⁻¹, injector temperature 300 °C, ion source temperature 230 °C, and initial oven temperature held at 36 °C for 2 min, ramped to 250 °C at 10 °C·min⁻¹ and held for 6 min. The total ion chromatogram (TIC) mode from *m/z* 50 to 700 was used to identify the intermediates.

The morphology of CaO powder before and after grinding was recorded using a scanning electron microscopy (SEM) (Hitachi 7500, Japan) with a voltage of 15.0 kV. The crystalline phase composition of powder samples was analyzed by X-ray diffraction (XRD) (D/max-rA, Rigaku, USA). The operation parameters of XRD spectrometer were as follows: CuK_α radiation at 40 kV and 100 mA, the 2θ ranging from 10° to 90° with a 0.02° step, and a count time of 0.15 s at each step. The molecular structure of powder samples was determined by Fourier transform infrared spectroscopy (FT-IR) spectrometer (Nicolet 6700, USA) using KBr disks in the frequency range of 400–4000 cm⁻¹. Raman spectra were recorded at room temperature using a microscopic confocal Raman spectrometer (Renishaw RM 2000, UK) with Ar-laser beam at the 514.5 nm line.

To calculate the bond dissociation energy (BDE) of the C–Cl and C–Br bonds in 4-BCB, density functional theory (DFT) calculations were carried out using Gaussian 09 program. All stationary point structures were optimized using (U)B3LYP functional with 6-311++G(d, p) basis set and the single point energy calculations were carried out with 6-311++G(2df, 2p) [19–20].

Reaction system. A planetary ball mill (Pulverisette-7, Fritch, Germany) was used for grinding the mixture. The mill consisted of a pair of jars made of stainless steel (80 cm³). The mass ratio of milling balls (37.2–55.8 g) to the initial mixture (3.1 g) was

12–18. The milling balls with a diameter of 8, 10, and 12 mm were mixed with a proportion of 1:1:1. The milling balls with a larger diameter were conducive to the spread of mechanical force, while those with a smaller diameter were beneficial to diminish the size of grinding powder. CaO powder (2.96 g) and 4-BCB (0.14 g) with a molar ratio of 102:1 was milled in the steel mill and the rotation speed of the jars was set at 500 and 600 rpm. 0.2 g of the milled mixture was extracted with 2 cm³ of *n*-hexane and then enriched by nitrogen blowing for the analysis of 4-BCB and intermediates. 0.5 g of the milled mixture was washed with 30 cm³ distilled water and then centrifuged for 10 min at a rotate speed of 8000 rpm. The supernatant was filtered through a 0.22- μ m (pore size) membrane for the analysis of Cl⁻ and Br⁻. 0.5 g of the milled mixture was sampled for the analysis of morphology, crystalline phase composition, and molecular structure. All experiments were conducted in duplicate, and the relative percent difference was calculated for the measurement data.

3. RESULTS AND DISCUSSION

3.1. DEGRADATION AND DEHALOGENATION EFFICIENCY

As shown in Fig. 1, 4-BCB was degraded rapidly by milling with CaO powder. After 1 and 2 h milling, the 4-BCB degradation efficiency reached 96.2% and 99.2%, respectively.

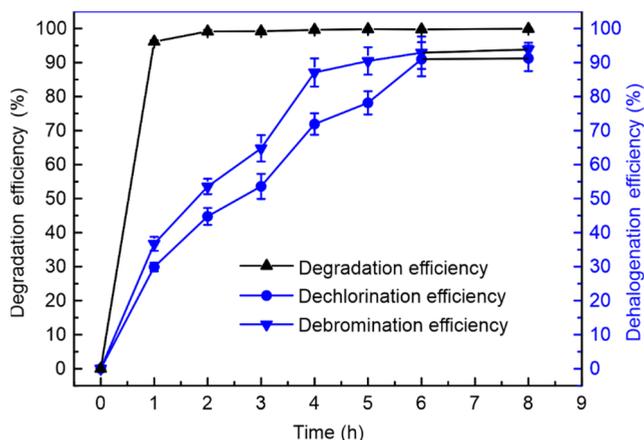


Fig. 1. The degradation and dehalogenation efficiencies of 4-bromochlorobenzene (4-BCB) by mechanochemical destruction (MCD) treatment; 4-BCB mass 0.14 g, CaO mass 2.96 g, milling ball mass 37.2 g, rotate speed 600 rpm

However, a gradual increase of dehalogenation efficiency was observed during 4-BCB degradation by MCD treatment. The dechlorination and debromination efficien-

cies only achieved 29.9% and 36.7% after 1 h milling, respectively. As the milling proceeding, the dechlorination and debromination efficiencies increased to 91.0% and 92.9% within 6 h, respectively. The dehalogenation efficiencies increased with the milling time. Tanaka et al. [21] studied the MCD treatment of trichlorobenzene on CaO surfaces and concluded that the decomposition of the target pollutant was on account of dechlorination reaction.

Table 1

The calculated dissociation energy of C–X bonds in 4-bromochlorobenzene (4-BCB) using (U)B3LYP/6-311++G(2df, 2p)/(U)B3LYP/6-311G(d, p) [kcal/mol]

Bond	(U)B3LYP/6-311++G(d, p)	(U)B3LYP/6-311++G(2df, 2p)	Experimental value
C–Br	79.0	80.2	82.6
C–Cl	91.0	92.8	97.6

Additionally, the debromination efficiency was higher than dechlorination efficiency during the MCD treatment of 4-BCB, indicating that the loss of bromine was easier to occur than that of chloride. It is well known that hydrogenolytic scission reactivity of C–X bond is dependent on its bond dissociation energy (BDE), following the order of C–I < C–Br < C–Cl < C–F. However, the thermal stability of C–X bond in hydrocarbons is not only subject to the property of halogen atom but also influenced by the halogenation degree and hydrocarbon structure. Table 1 shows the calculated BDE of the C–X bonds in 4-BCB were approximate to the experimental BDE of the C–X bonds in chlorinated and brominated benzene. Moreover, the BDE of the C–Br bond is lower than that of the C–Cl bond in 4-BCB. For example, the calculated BDE of C–Cl and C–Br bonds in 4-BCB under (U)B3LYP/6-311++G(d, p) level are 91.0 and 79.0 kcal·mol⁻¹, respectively. Therefore, the lower BDE of the C–Br bond can account for the higher debromination efficiency of 4-BCB.

3.2. DEHALOGENATION KINETICS

The dehalogenation kinetics (Fig. 2) was examined to further elucidate the dehalogenation reactions by MCD treatment. According to Lyachov [22], the rate of a mechanochemical reaction can be expressed as:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

$$F(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^t k dt = kt + C \quad (2)$$

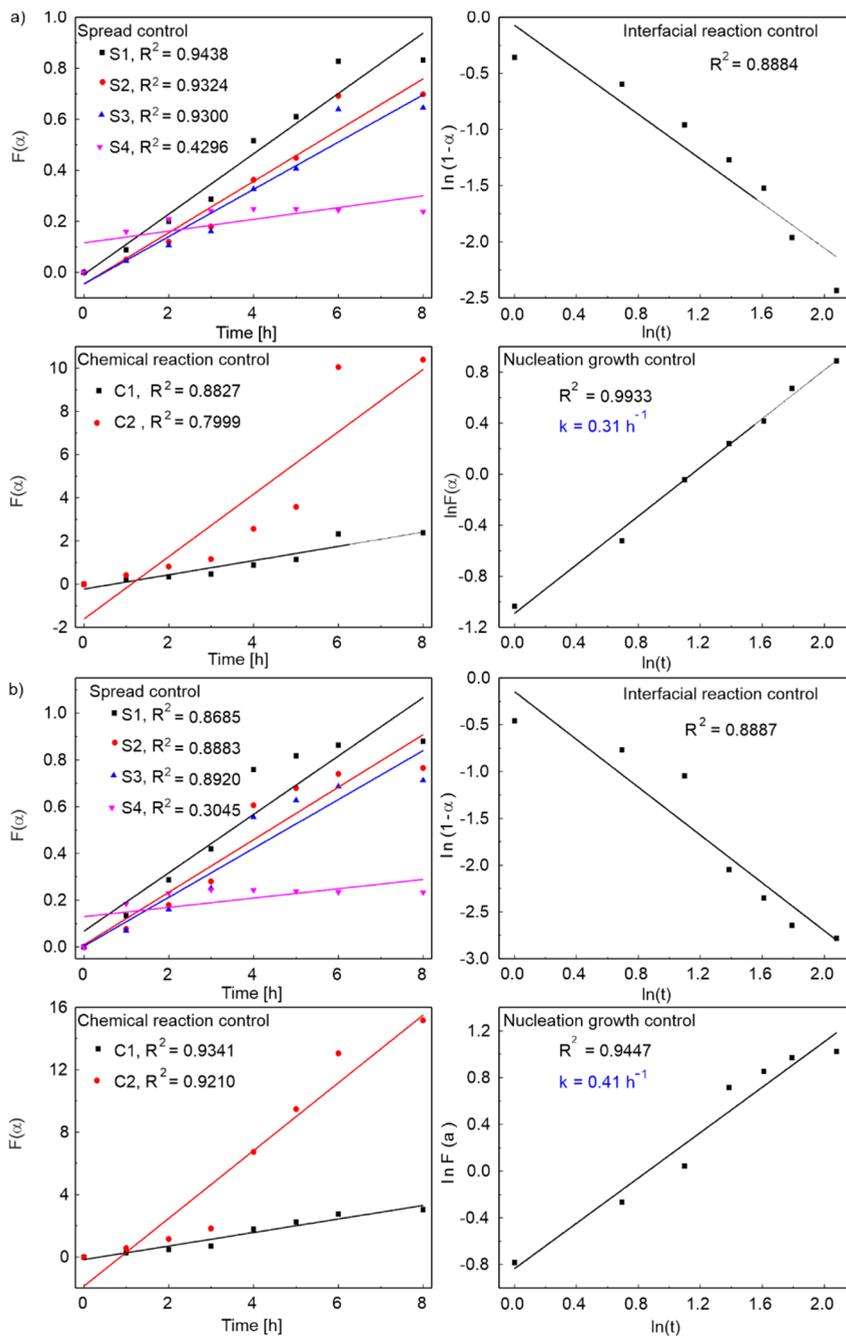


Fig. 2. The kinetics of the dechlorination (a) and debromination (b) reaction during 4-BCB degradation by MCD treatment; 4-BCB mass 0.14 g, CaO mass 2.96 g, milling ball mass 37.2 g, rotate speed 600 rpm

where α is the dehalogenation efficiency, %, t is the milling time, h , k is the dehalogenation rate constant, h^{-1} , $f(\alpha)$ and $F(\alpha)$ are functions of α , %. The degradation of 4-BCB by MCD treatment with CaO powder is a solid-phase reaction, which involves four control steps, i.e., spread control, interfacial chemical reaction control, chemical reaction control or nucleation growth control. The kinetic model of each control step was shown in Table 2.

Table 2

The kinetic models for the four control steps in the solid-phase reaction

Control step	Model	$F(\alpha)^a$
One-dimensional spread	parabola (S1)	α^2
Two-dimensional spread	Valensi (S2)	$\alpha + (1 - \alpha)\ln(1 - \alpha)$
Three-dimensional spread	Jander (S3)	$(1 - (1 - \alpha)^{2/3})^2$
	Ginstling–Brounshtein (S4)	$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$
Interfacial chemical reaction		$1 - (1 - \alpha)^{1/n}, 1 < n < 3$
Chemical reaction	1.5 order (C1)	$(1 - \alpha)^{-1/2} - 1$
	2 order (C2)	$(1 - \alpha)^{-1} - 1$
Nucleation growth	Avrami–Erofeev	$(-\ln(1 - \alpha))^{1/m}, 0.5 < m < 4$

^a α is the dehalogenation efficiency, %.

As shown in Fig. 2, the experimental data fitted well with Avrami–Erofeev (eq. (3)), indicating that the nucleation growth was the control step of dehalogenation reactions. The result indicate that the agglomeration of the CaO powder inhibited the dehalogenation of 4-BCB. Corresponding to degradation efficiency, the k value of debromination was higher than that of dechlorination, with values of 0.41 and 0.31 h^{-1} , respectively.

$$F(\alpha) = (-\ln(1 - \alpha))^{1/m}, \quad 0.5 < m < 4 \quad (3)$$

where α is the dehalogenation efficiency, %, $F(\alpha)$ is a function of α , %.

3.3. EFFECT OF ROTATE SPEED AND MILLING BALL WEIGHT

Figure 3 shows the dehalogenation efficiency under various rotation speeds of the jars and mass ratios of milling balls to the initial mixture (MB/IM). The dehalogenation efficiency increased with increasing rotate speed. For example, with an MB/IM value of 12, within 8 h milling, the dechlorination efficiency increased from 68.3% to 91.2% as the rotation speed of the jars increased from 500 to 600 rpm, and the k value for

dechlorination increased from 0.16 to 0.31 h⁻¹, correspondingly. Meanwhile, the dehalogenation efficiency increased with increasing the MB/IM value. For example, at a rotate speed of the jars of 600 rpm, within 8 h milling, the debromination efficiency increased from 93.8%, 95.6% to 98.9% as the MB/IM value increased from 12, 15 to 18, and the k value for debromination increased from 0.41, 0.49 to 0.57 h⁻¹, correspondingly. Faster rotation speeds produce higher destruction percentages due to the accumulation of the energy dose in a quicker manner [23].

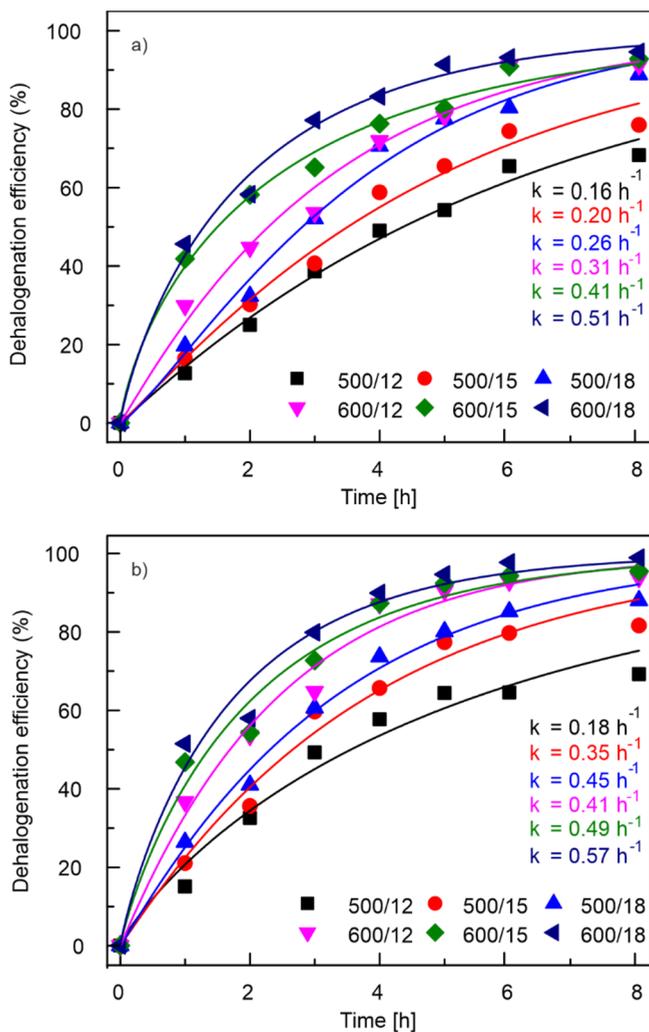


Fig. 3. Effect of rotate speed and milling ball weight on the dechlorination (a) and debromination (b) reactions during 4-BCB degradation by MCD treatment; 4-BCB mass 0.14 g, CaO mass 2.96 g

3.4. PHYSICOCHEMICAL CHARACTERISTICS OF GROUND MIXTURE

Figure 4 shows the microstructure of CaO powder, 4-BCB particles, and the mixture after 4 h milling. The initial CaO powder exhibited a smooth surface and lamellar crystal structure, while the initial 4-BCB particle presented a rough surface and amorphous structure. The mixture after 4 h milling was in a state of agglomeration and contained both lamellar crystals and amorphous substances. The observation of tiny particles at the nanometer level may be attributed to the mechanochemical grinding of CaO powder and formation of calcium compounds, such as CaCl_2 , CaBr_2 and $\text{Ca}(\text{OH})_2$.

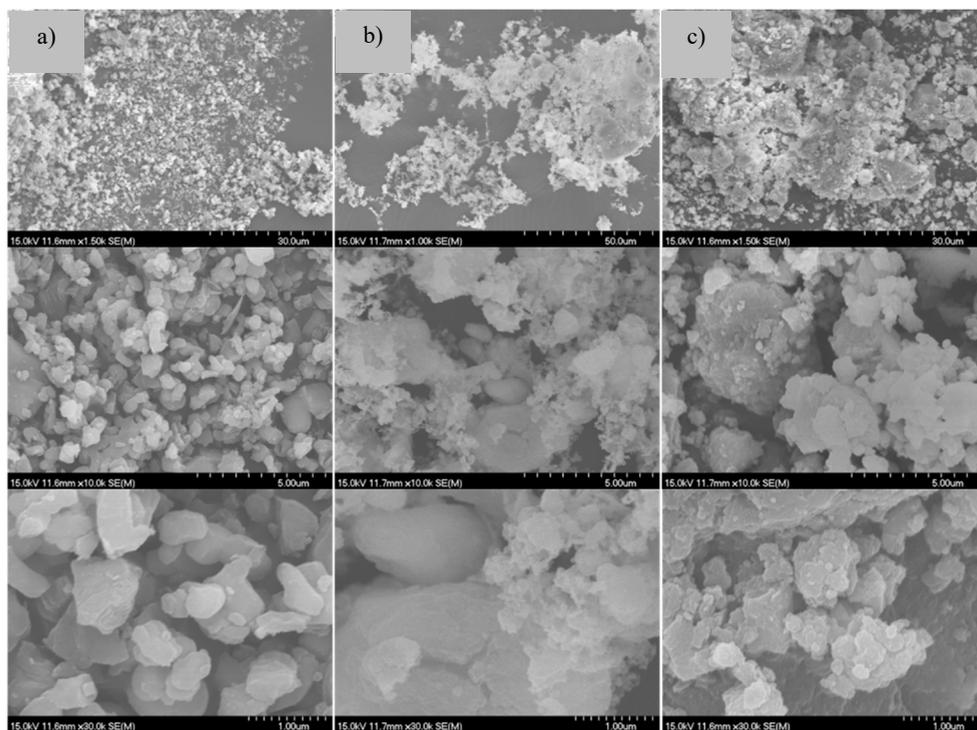


Fig. 4. SEM images of CaO powder (a), 4-BCB sample (b), and the mixture after 2 h milling (c)

To further reveal the composition evolution of the ground mixture by MCD treatment, five samples were collected regularly for XRD analysis (Fig. 5a). The peaks of CaO powder became weaker and weaker gradually, which can be explained by the destruction of crystal structure and transformation of the materials. The peaks corresponding to CaCl_2 and CaBr_2 appeared obviously after 2 h milling. It suggests that the organic halogen in 4-BCB (i.e., Cl and Br) was transformed to inorganic halide ions (i.e., Cl^- and Br^-) and then reacted with CaO during MCD treatment. Additionally, the peaks of $\text{Ca}(\text{OH})_2$ became stronger and stronger gradually. Lu et al. [24] found that CaCl_2 ,

Ca(OH)_2 , and CaOHCl were formed during the degradation of 2,4,6-trichlorophenol by MCD treatment. However, the formation of CaOHCl was not detected in this study.

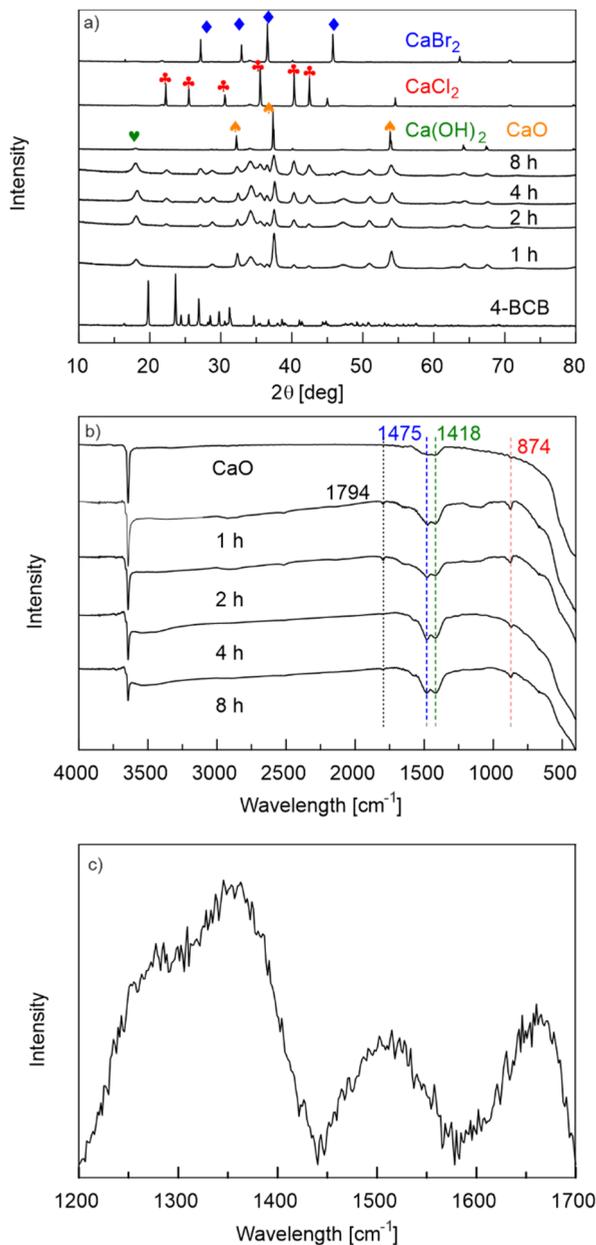


Fig. 5. The XRD (a), FT-IR (b) and Raman (c) spectra of the ground mixture during MCD treatment; 4-BCB mass 0.14 g, CaO mass 2.96 g, milling ball mass 37.2 g, rotate speed 600 rpm

Wei et al. [25] disposed pentachlorophenol using CaO and SiO₂ powder as additives and reported an unobservable formation of the crystalline phase of CaOHCl, which explained as the generated CaOHCl may be in a non-crystalline amorphous salt form.

Figure 5b shows the FT-IR spectra of the ground mixture together with that of CaO powder. The peak around 1475 cm⁻¹ was assigned to the C–H stretching vibration in the benzene ring and still observed after 8 h milling, suggesting that 4-BCB was incompletely mineralized. The peak around 1418 and 874 cm⁻¹ was assigned to the C–O asymmetric stretching vibration and C=O plane bending vibration in CaCO₃, respectively. The two vibration peaks appeared obviously, demonstrating the existence of CaCO₃ in the products. Zhang et al. [17] also reported the formation of CaCO₃ during the HBB degradation by MCD treatment. Nevertheless, the formation of CaCO₃ indicates the generation of CO₂ from 4-BCB. During MCD treatment, the benzene ring was cut off due to the electron transfer and transformed into small molecule organics (e.g., acetylene, ethylene, methane, and ethane) and inorganics (e.g., CO₂, and H₂O) [21]. Additionally, a small peak around 1794 cm⁻¹ assigned to halogenated carbonyl (–COCl) appeared after 1 h milling and disappeared after 4 h milling. Therefore, halogenated hydrocarbons are supposed to be the degradation intermediates of 4-BCB, which accounts for the phenomenon that dehalogenation efficiency did not increase in the same proportion to the degradation efficiency of 4-BCB.

3.5. 4-BCB DEGRADATION PATHWAYS

Degradation intermediates were analyzed to further elucidate the mechanisms of 4-BCB degradation using GC/MS. Seven intermediates, including 3-bromochlorobenzene, 1,4-dibromobenzene, diphenyl, 3-chloro-1,1'-biphenyl, 4,4'-dichloro-1,1'-biphenyl, 3,4'-dichloro-1,1'-biphenyl and 3,3'-dichloro-1,1'-biphenyl, were identified during 4-BCB degradation by MCD treatment (Fig. 6a).

The presence of the seven intermediates was confirmed by the comparison between their mass spectrum patterns with the patterns in the NIST database. The generation of 3-bromochlorobenzene and 1,4-dibromobenzene may be attributed to the formation of halogen radicals in dehalogenation reactions via the abstraction of halogen and substitution of hydrogen, which has been reported as a putative mechanism for the degradation of chlorinated organic compounds by MCD treatment [21]. The hydrogen atom in 4-BCB and the water formed during MCD treatment could act as the sources for hydrogen substitution. Additionally, during the MCD treatment of octa-chlorinated naphthalene, chlorine radical produced and then attacked the C–Cl bonds continuously as a chain reaction, generating more chlorine radicals [13]. Therefore, in this study, it can be speculated that the formed chlorine and bromine radicals reacted with dehalogenated 4-BCB to form 3-bromochlorobenzene, 1,4-dibromobenzene or their isomers. The detection of 3-chloro-1,1'-biphenyl, 4,4'-dichloro-1,1'-biphenyl, 3,4'-dichloro-1,1'-bi-

phenyl, 3,3'-dichloro-1,1'-biphenyl and diphenyl indicated that polymerization reactions with biphenyl structure formation (dipolymerization) occurred during 4-BCB degradation.

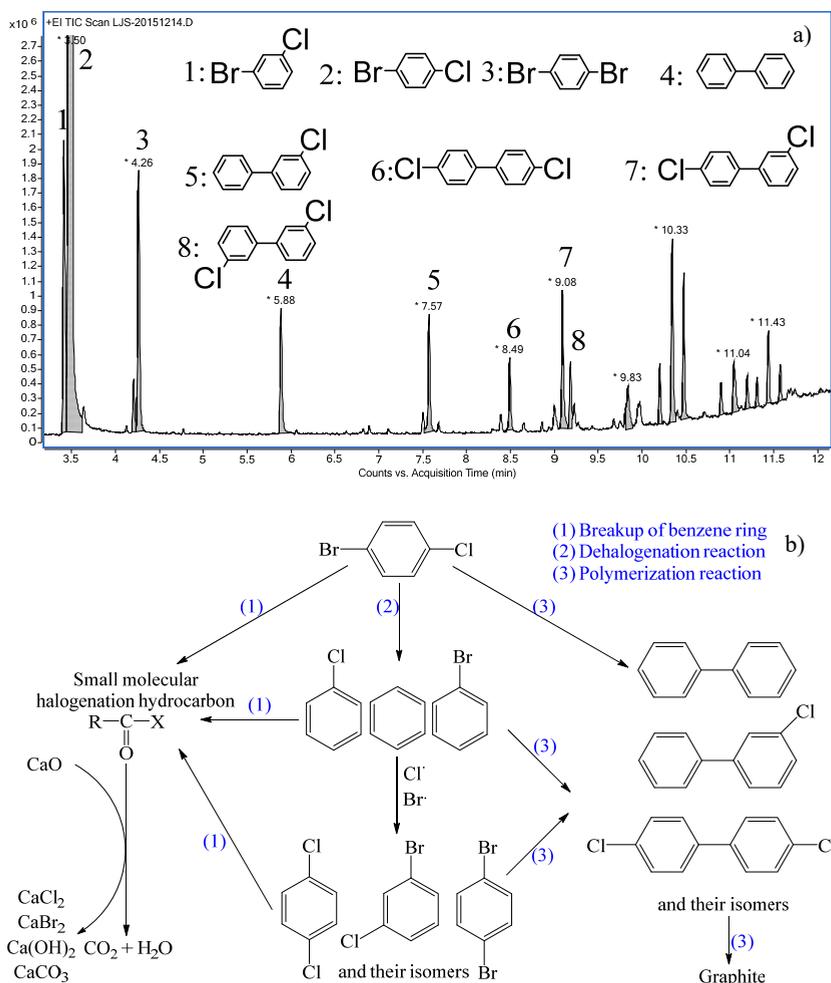


Fig. 6. Proposed 4-BCB transformation pathways by MCD treatment; 4-BCB mass 0.14 g, CaO mass 2.96 g, milling ball mass 37.2 g, rotate speed 600 rpm

Several previous studies demonstrated that polymerization reactions took place during MCD treatment, especially during the degradation of chlorinated organic compounds such as DDT [26]. It was reported that radicals were produced by electron transfer on the benzene ring during MCD treatment [27]. Therefore, it is reasonable to hypothesize that benzene radicals were produced as intermediates utilizing halogen ab-

straction from 4-BCB, and the subsequent polymerization reaction of two benzene radicals generated biphenyl. Similarly, the halogenated benzene radicals were formed via the abstraction of one halogen atom in 4-BCB. The generation of 4,4'-dichloro-1,1'-biphenyl, 3,4'-dichloro-1,1'-biphenyl and 3,3'-dichloro-1,1'-biphenyl was through the dipolymerization reactions of halogenated benzene radicals, while that of 3-chloro-1,1'-biphenyl was via the polymerization reactions between one benzene and halogenated benzene radical. Nomura et al. [11] investigated dioxins degradation by MCD treatment and found that two formed biphenyl radicals through halogen abstraction occurred the polymerization reactions to generate *p*-quaterphenyl and the cleavage reaction of the bond between the diphenyl groups to produce benzene radicals. Additionally, the polymerization reaction of biphenyl and benzene radicals could generate terphenyl.

Figure 5c shows the Raman spectra of the ground mixture during 4-BCB degradation by MCD treatment. Two peaks around 1525 and 1346 cm^{-1} appeared obviously. The Raman spectra for single graphite crystals exhibited a single line at 1575 cm^{-1} , other amorphous graphite materials like stress-annealed pyrolytic graphite, commercial graphite, activated charcoal, lampblack, and vitreous carbon displayed a band at 1355 cm^{-1} [28]. The slight shift of the two peaks may be ascribed to the high-temperature effect during MCD treatment, which altered the spectral characteristics of the formed crystal and amorphous graphite [21]. Therefore, it can be speculated that graphite crystals and amorphous carbon are the important products of 4-BCB degradation by MCD treatment. The formation of crystal and amorphous graphite may be ascribed to the polymerization reaction of benzene or halogenation benzene radicals. Tanaka et al. [21] ground the mixture of aramid and CaO powder at a rotate speed of 700 rpm and found the peaks of graphite crystals and amorphous carbon appeared after 1 h milling and intensified dramatically in 2 h milling sample. However, the carbonization peaks appeared after 4 h milling in this study, which may be on account of the lower rotate speed.

Overall, 4-BCB degradation by MCD treatment can probably be ascribed to three pathways (Fig. 6b): (a) breakup of the benzene ring to form small molecular halogenated hydrocarbons and mineralization to form CO_2 and H_2O in sequence; (b) dehalogenation reaction to form benzene and monohalogenobenzene, and addition reaction of halogen radicals to form dihalogenobenzenes in sequence; (c) polymerization reaction to form biphenyl, halogenated biphenyl, and graphite.

4. CONCLUSIONS

This study investigated the mechanochemical destruction treatment of 4-bromochlorobenzene by its co-grinding with CaO powder. The rate constant k of debromination was higher than that of dechlorination during the mechanochemical destruction treatment of 4-bromochlorobenzene, with values of 0.41 and 0.31 h^{-1} , respectively. The nucleation growth was the control step of dehalogenation reactions during the mechanochemical destruction treatment of 4-bromochlorobenzene. Higher rotation speed and

mass ratios of milling balls to initial mixture are beneficial to the mechanochemical destruction treatment of 4-bromochlorobenzene. The mechanochemical destruction treatment of 4-bromochlorobenzene can be ascribed to the breakup of the benzene ring, dehalogenation reaction, and polymerization reaction. These results show that mechanochemical destruction is promising for application due to its high dehalogenation efficiency without secondary pollution. In practical application, the treatment capacity of mechanochemical destruction can be improved significantly by the continuous recycling of CaO, which benefits to the cost reduction of mechanochemical destruction.

ACKNOWLEDGMENTS

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