Mechanochemical degradation of hexachlorobenzene using $\text{Mg}/\text{Al}_2\text{O}_3$ as additive

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Abstract In the present work, we investigate the destruction efficiency of hexachlorobenzene (HCB) by milling with various reagents in a planetary ball mill under different milling conditions. Under the same conditions of mill rotary rate and charge ratio, the mixture of magnesium powder and aluminum oxide ($\text{Mg}/\text{Al}_2\text{O}_3$) was found best in promoting the destruction of HCB, which can be completely destroyed after 90 min grinding at a charge ratio of 20:1 (reagent/HCB, m/m), a ball mass/reagent mass ratio of 30:1 and a mill rotation speed of 550 rpm. The ground samples were characterized and analyzed by X-ray fluorescence, gas chromatography (GC), X-ray diffraction and ion chromatography. The intermediate products, such as pentachlorobenzene, tetrachlorobenzene, trichlorobenzene isomers, dichlorobenzene and monochlorobenzene were detected by GC. Then the main dechlorination pathway for HCB was proposed. With a series of verification experiments, the final degradation products of HCB were amorphous carbon and inorganic chlorine. Based on this study, $\text{Mg}/\text{Al}_2\text{O}_3$ has the potential to complete the innocuous treatment of chlorinated compounds.

Keywords Mechanochemistry · Dechlorination · Hexachlorobenzene · Magnesium and aluminum oxide ($\text{Mg}/\text{Al}_2\text{O}_3$)

Introduction

Hexachlorobenzene (HCB) is listed as one of the 12 persistent organic pollutants (POPs) by Stockholm Convention in the first batch, aiming at to reduce and restrict the production and use of POPs [1]. HCB has been widely used as fungicide for seed treatment and an industrial chemical for wood preservation [2]. As HCB is persistent, bio-accumulative, semi-volatile and toxic, it can persist and disperse in the environment extensively and is also considered as a probable human carcinogen through all routes of exposure [3]. Although many countries have enacted bills to ban the production and use of HCB, there are large amounts of HCB in stockpile around the world, including the U.S. and Japan [4]. In China, it was estimated that the amount of HCB in stockpiles has reached 60 tons [5].

Incineration is the most commonly used treatment method for HCB, which can be almost completely destroyed; however, the by-products such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) pollutants may be generated and will increase the risk of cancer [6]. As an alternative method to combustion technologies, mechanochemistry destruction have received a lot of attention and has many advantages for the destruction of HCB, such as non-combustion and solvent-free, low energy consumption and its possible implementation process [7]. Mechanochemistry method is different from incineration, which can avoid the production of unintentionally products such as PCDDs and PCDFs [8].

Calcium oxide (CaO) has been widely employed as additive in mechanochemical destruction to destroy various halogenated organic compounds like POPs, including pentachloronitrobenzene (PCNB) [9], perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) [10], mirex [11], pentachlorophenol (PCP) [12], tetrabromobisphenol A

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(TBBPA) [13], polyvinyl chloride (PVC) [14], polychlorobiphenyls (PCBs) [15], and hexachlorobenzene [16]. Hall et al. [17] found that after 12 h of mechanochemical reaction of DDT with CaO, no organic materials was detected by GC–MS. Zhang et al. [18] demonstrated that over 99 % of 3-chlorobiphenyl was decomposed by co-grinding 3-chlorobiphenyl with CaO for 6 h. And Zhang et al. [19] also found that almost 100 % of debromination was achieved by grinding CaO with hexabromobenzene. Lu et al. [20] found that the degradation rate reached 99.0 % by grinding 2,4,6-trichlorophenol with the mixture of calcium oxide and SiO₂ for 6 h. However, when CaO was used as additive for mechanochemical degradation of POPs, the complete degradation of POPs taken a long time.

Moreover, calcium hydride (CaH₂) has been applied to the degradation of HCB too. Loisel et al. [21] utilized CaH₂ as a source of active hydrogen and chlorinated organic compounds can be dehalogenated by mechanochemical treatment, producing a much more specific reaction in less time compared with CaO and MgO substrates. Although CaH₂ is efficient in the destruction of HCB, more consideration should be paid on its high reactivity and lability in practical implementation [22]. And zero-valent iron combined with oxide drawn the attention of researchers due to its high destruction efficiency in shorter time. Researchers in Tsinghua University came up with the mixture of iron powder and SiO₂ to destruct HCB, with higher efficiency and lower volume of residue [22]. Considering the practical application of mechanochemistry destruction, zero-valent metal with different oxides may be a promising method to destruct HCB and other POPs.

For the sake of engineering application of mechanochemistry destruction, the milling time should be shortened and the degradation intermediate products as well as the degradation pathways or the mechanism should be studied. In the present study, a series of additive systems differing from CaO were investigated and the effect of milling conditions on the destruction of HCB using Mg/Al₂O₃ as additive was also researched. The chemical properties of the milled residue were analyzed and the intermediates and the final products were determined. Finally, based on the experimental data, a degradation pathway of HCB was proposed.

Materials and methods

Materials

Hexachlorobenzene (HCB, 99 %) was purchased from HWRK Chem, China. The CBs standards contained HCB and low chlorinated benzenes. Among them 1,2,3,5-tetrachlorobenzene (1,2,3,5-TeCB) and chlorobenzene (MCB)

were obtained from Accu Standard, Inc. Others including 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene (1,2-DCB, 1,3-DCB, 1,4-DCB), 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene (1,2,3-TrCB, 1,2,4-TrCB, 1,3,5-TrCB), 1,2,3,4-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene (1,2,3,4-TeCB, 1,2,4,5-TeCB), pentachlorobenzene (PCB) and hexachlorobenzene were purchased from National Institute of Metrology, China. Anhydrous sodium sulfate (GR, dried in a muffle furnace at 400 °C for 4 h before using), magnesium powder (Mg, purity 99 %, 30 µm) was bought from Sinopharm Chemical Reagent Co., Ltd, China. And aluminum oxide (Al₂O₃, particle size 60 mesh) was obtained from Acfa Aesar. Hexane (HPLC Grade) and acetone (HPLC Grade) were purchased from Fisher Scientific.

Milling experiment

The destruction of HCB was carried out by mechanochemical method in a planetary ball milling (QM-3SP2J, Nanjing University Instrument Corporation, China). The mixture of additives and HCB was placed into a 250 mL steel pot with stainless balls. The size of the stainless steel balls were Φ 5.6 mm.

Firstly, five different kinds of additives were examined for comparison purposes: magnesium powder (Mg), quartz sand (SiO₂), aluminum oxide (Al₂O₃), a mixture of magnesium powder and aluminum oxide (Mg/Al₂O₃), a mixture of magnesium powder and quartz sand (Mg/SiO₂). Secondly, the mixture of Mg and Al₂O₃ and HCB was milled under different mill conditions to study the effects of milling time, the ratio of magnesium powder mass to aluminum oxide mass, the ratio of ball mass to reactant mass and the ratio of additive mass to HCB mass.

After milled at different conditions, all samples were collected and preserved in a closed dryer for further use.

Analytical procedures

0.05 g of each milling sample was extracted with 5 mL hexane in an ultrasonic instrument for 15 min. Then, the extract was centrifugalized at 2862g for 3 min to separate the solids and the extraction. This procedure was repeated three times and the water in extraction was removed by anhydrous sodium sulfate to protect column of gas chromatography (GC). HCB and possible degradation chlorinated intermediates were analyzed with gas chromatography–mass spectrometry (GC–MS). The GC–MS analysis conditions are given in Table 1.

The HCB destruction rate for samples after milling was calculated based on the remaining HCB in residue. The equation below can be used to assess the treatment efficiency for destruction in the milling process [22].

Table 1 Analytical GC–MS conditions

Gas chromatography	Conditions
Column	HP5-MS (agilent, 30 m × 0.25 mm × 0.25 μm)
Carrier gas	He (99.9999 %), 1.5 ml min ⁻¹
Injection mode	Split less
Injection volume	1.0 μl
Injection temperature	250 °C
Mass spectrometry	Agilent 5975C
Ionization mode	Electron ionization (EI)
Oven temperature	50 °C (5 min)–3 °C/min–80 °C–5 °C/min–130 °C–20 °C/min–230 °C (2 min)
Electron impact energy	70 eV
Ion source temperature	230 °C
Injector temperature	280 °C
Detector temperature	300 °C
GC/MS transfer line temperature	280 °C

$$D_R(\%) = \left(1 - \frac{q_t}{q_0}\right) \times 100\%, \quad (1)$$

where D_R is the destruction efficiency of HCB; q_0 (mg kg⁻¹) is the initial leaching quantity without milling, q_t is the leaching quantity of the sample after milling treatment.

Chloride (Cl⁻) released during the destruction process was determined by ion chromatography (ICS 2000, Thermo Scientific, USA). Extraction procedure was as follows: put 0.1 g milled powders into a 50 ml beaker, then add 20 ml dilute nitric acid (0.01 mol·L⁻¹), ultrasonically vibrate for 60 min at 60 °C to extract the Cl⁻ from the residue and then centrifugalized at 2862g for 5 min. Then, the solution was analyzed for chloride ions by IC. Before sample injection, the solution was filtered with needle filters.

Characterization of the milled samples

The milled mixture was sampled for crystal structure analysis. Crystal structure of the samples was tested by an X-ray diffractometer (XRD, X'Pert PROMPD, PANalytical, Netherlands) using the Ni-filtered Cu radiation over an angle of 10° < 2θ < 90°. The analysis of XRD data were carried out by MDI Jade 6.0 software.

Results and discussion

Comparison of destruction rate for different additives

In this section, HCB was co-grinded with five different additives: Mg, SiO₂, Al₂O₃, Mg/Al₂O₃ and Mg/SiO₂. And

other milling conditions were: milling time 60 min, rotation speed 450 r min⁻¹, ball to reactant mass ratio 30:1 and additive to HCB mass ratio 20:1. The mass ratios of Mg/Al₂O₃ and Mg/SiO₂ was 1:1 and the ball mass was 180 g. The mass of each additive was summarized in Table 2. Figure 1 showed the results of HCB destruction rates for the different reagents examined and the efficiencies differed for each reagent used.

In all cases, HCB contents in milled mixture were lower than that in the initial mixtures. After 60 min of milling, nearly 100 % removal was achieved for HCB with Mg/Al₂O₃. The destruction of HCB using Al₂O₃ powder only was poor, with 88.2 % of HCB leaving after 60 min milling. When using Mg alone, a degradation rate of 83.4 % was obtained over the same milling time. The degradation rates of HCB followed the sequence Mg/Al₂O₃ > Mg/SiO₂ > Mg > SiO₂ > Al₂O₃. Obviously, the use of Mg/Al₂O₃ accelerated the destruction of HCB.

Effect of ball milling conditions

For the mechanochemical destruction of HCB, the processing parameters and experimental conditions had effect on the destruction rate of HCB. In this section, the effects of milling time, the ratio of magnesium powder mass to

Table 2 Mass of each additives

Additives	Mass (g)	HCB (g)
Mg	6.0	0.3
SiO ₂	6.0	0.3
Al ₂ O ₃	6.0	0.3
Mg/Al ₂ O ₃	2.4 + 3.6	0.3
Mg/SiO ₂	2.4 + 3.6	0.3

Fig. 1 HCB destruction rate of samples obtained by milling HCB with Mg/Al₂O₃, Mg/SiO₂, Mg, SiO₂ and Al₂O₃, respectively. Milling conditions: milling time 60 min, rotation speed 450 rpm, ball to reactant mass ratio 30:1 and additive to HCB mass ratio 20:1

aluminum oxide mass, the ratio of ball mass to reactant mass and the ratio of additive mass to HCB mass were studied.

Effect of the ratio of magnesium powder mass to aluminum oxide mass

In the Mg and Al₂O₃ system, the mixture was grinded at the Mg mass fraction of 10, 20, 30, 40, 60, 80 and 100 %. And other conditions were: milling time 45 min, rotation speed 550 r min⁻¹, ball to reactant mass ratio 30:1 and additive to HCB mass ratio 20:1. The result of HCB destruction rate was presented in Fig. 2.

The result showed that Mg and Al₂O₃ had synergistic effect on the degradation of HCB. When the Mg mass fraction was lower than 40 %, the destruction rate of HCB increased rapidly as the mass ratio of Mg increased. At the Mg mass fraction of 40, 99.65 % of HCB was destroyed in 45 min milling. As the Mg content increased from 40 to 80 %, the destruction rate of HCB had little change. When the Mg was used alone, a destruction rate of 96.2 % was achieved. Compared with the optimum efficiency of 99.6 %, the destruction rate declined slightly more than 3 %. Based on these results, the following experiment was carried out at the Mg mass fraction of 40 %.

Effect of the mass ratio of ball to reactant

The ratio of ball mass to reactant mass was one of the important processing parameters which had great impact on the destruction of HCB. To explore the effect of mass ratio, the reactant was milled at the grinding ball mass/

Fig. 2 Effect of the ratio of magnesium powder mass to aluminum oxide mass on the destruction rate of HCB for samples milled at the Mg mass ratio of 10, 20, 30, 40, 60, 80 and 100 % respectively. Milling conditions: milling time 45 min, rotation speed 550 rpm, ball to reactant mass ratio 30:1 and additive to HCB mass ratio 20:1

reactant mass ratio of 10, 15, 20, 25 and 30. And other conditions were: milling time 45 min, rotation speed 550 r min⁻¹, Mg mass fraction 40 % and additive to HCB mass ratio 20:1. The result was showed in Fig. 3.

When the mass ratio of ball to reactant increased from 10 to 15, the HCB destruction rate increased slightly from 26.7 to 36.2 %. However, as the ratio increased from 15 to 20, the HCB destruction efficiency increased significantly reaching 86.3 %. At the ratio of 30, the destruction rate of HCB reached 99.1 %. According to the study of Delogu et al. [23], when the mass ratio of ball to reactant reached certain value, the effective impact among mill balls increased. The energy produced by the impact can destruct the structure of HCB. Based on the result, the HCB degradation rate increased with the increase of the mass ratio of ball to reactant. The greater mass ratio needs more energy, bigger milling pot and more milling ball for the disposal of a certain amount of HCB. When mechanochemical method is used for the degradation of HCB on a large scale, optimal mass ratio of ball to reactant should be the first to consider.

Effect of the charge ratio of additive mass to HCB mass

In this section, the effect of the charge ratio of additive to HCB was studied and the mass ratio was set at 1, 5, 10 and 20. And other conditions were: milling time 45 min, rotation speed 550 r min⁻¹, Mg mass fraction 40 % and ball to reactant mass ratio 30:1. The result was showed in Fig. 4.

The result indicated that: with the increasing of the mass ratio, the HCB destruction efficiency increased evidently and linear relationship was not presented. At the charge

Fig. 3 Effect of the ratio of ball mass to reactant mass on the destruction rate of HCB for samples milled at the grinding ball mass/reactant mass ratio of 10, 15, 20, 25 and 30, respectively. Milling conditions: milling time 45 min, rotation speed 550 rpm, ball to reactant mass ratio 30:1, Mg mass fraction 40 % and additive to HCB mass ratio 20:1

ratio of 1, the HCB degradation rate was lower than 30 % after 45 min milling. Because of the deficiency of magnesium and aluminum oxide, the additive was covered with HCB sufficiently and the activation of impact was weak. As the charge ratio increased to 5, HCB destruction efficiency increased rapidly reaching 56.5 %. When the charge ratio was 20, HCB degradation rate was more than 99 %. The higher charge ratio, the faster rate of HCB degradation. However, high charge ratio would generate more residue and lead to the increase of the cost of additive. Therefore,

Fig. 4 Effect of the ratio of additive mass to HCB mass on the destruction rate of HCB for samples milled at the mass ratio of 1, 5, 10 and 20, respectively. Milling conditions: milling time 45 min, rotation speed 550 rpm, Mg mass fraction 40 %, additive to HCB mass ratio 20:1 and ball to reactant mass ratio 30:1

the appropriate charge ratio of additive to HCB was important for the mechanochemical method.

Effect of milling time

To explore the effect of milling time on the destruction of HCB, the mixtures of HCB and Mg/Al₂O₃ were grinded for 15, 30, 45, 60 and 90 min. And other conditions were: ball to reactant mass ratio 30:1, rotation speed 550 r min⁻¹, Mg mass fraction 40 % and additive to HCB mass ratio 20:1. Figure 5 shows the change of HCB in residue with milling time for the Mg/Al₂O₃ and the change of Cl⁻ with time was shown in Fig. 6.

In the first 15 min, the yield of residual rate decreased rapidly from 100 to 31.7 %. After 30 min milling, the residual rate was only 2.5 %, meaning that most of the HCB was destructed. When the milling time prolonged to 60 min, the HCB residual rate of HCB was only 0.094 %. In article of Zhang et al. [24], the removal efficiency of the HCB reached 94.2 % after 60 min thermal disposal with γ -Al₂O₃ at 300 °C.

Correspondingly, Cl⁻ production rate increased rapidly in the first 30 min. Between 0 and 30 min, water-soluble Cl⁻ was corresponding to the degradation of HCB. However, during 30 and 45 min, HCB decreased slightly while Cl⁻ increased obviously. After 90 min milling, Cl⁻ production ratio was 70.1 %, while 99.9 % HCB had been destructed. Meanwhile, GC-MS result (see Fig. 5) demonstrated that no chlorinated intermediates were detected after 90 min milling except trace amount of HCB. The water soluble chlorines in solid phase were lower than the theoretical values of chlorine in HCB. According to the

Fig. 5 Effect of milling time on HCB residual ratio in the residue for samples milled at the milling time of 15, 30, 45, 60 and 90 min, respectively. Milling conditions were: ball to reactant mass ratio 30:1, rotation speed 550 r min⁻¹, Mg mass fraction 40 % and additive to HCB mass ratio 20:1

Fig. 6 Change of production rate of water soluble chlorine with milling time for samples grinded at the milling time of 15, 30, 45, 60 and 90 min, respectively. Milling conditions were: ball to reactant mass ratio 30:1, rotation speed 550 r min^{-1} , Mg mass fraction 40 % and additive to HCB mass ratio 20:1

related research of mechanochemical treatment of POPs, these research results were similar to the result of this study. Although there were no chlorinated degradation products found in the solid residual after mechanochemical reaction, the water soluble chlorines in solid phase are lower than the theoretical values in mechanochemical treatment of chlorinated POPs. Lu et al. [20] used the mixture of CaO and SiO₂ to destruct 2,4,6-trichlorophenol through mechanochemical treatment and the degradation rate is over 99.0 % after 6-h milling. However, Cl⁻ content detected by ion chromatography is only 10.9 %. In Zhang et al.'s [22] work, using Fe/SiO₂ the mechanochemical dechlorination of HCB, the yield of water-soluble chlorine was 91.5 % and no organic compounds were detected after 8 h of grinding. This means that most of chlorine was transformed into soluble inorganic Cl⁻. And some of the remaining chlorine still bounded to carbon atoms, or trapped between layers [11]. It is believed that some of the inorganic mineralization products are insoluble in water after the mechanochemical reactions. In our research, it was found that the water-soluble amount of chlorine reached 70 % when the HCB was decomposed after 90-min grinding, without any chlorinated organic compounds detected in the solid phase. Thus, in this HCB degradation process, organo-chlorine has been changed into inorganic chlorine, and most inorganic chlorine existed as water soluble state.

And the results presented in other articles demonstrated that HCB degradation methods, including thermal catalytic [25], photo degradation [26], thermal decomposition [27], catalytic oxidation [28] and based-catalyzed destruction [29], conducted in solvents or in gas phase and the end

products were low chlorinated benzenes and other organics. By comparison, the MCD is an efficient technology for thoroughly decomposition of HCB, and HCB can be mineralized to inorganic matters rather than organic intermediates. Therefore, the MCD technology may be an efficient alternative for the treatment of highly contaminated soil and industrial waste.

Characterization of sample

Elemental analysis of milled samples

The elemental analysis was carried out for the milled and non-milled samples by XRF and the result was presented in Table 3. For the original sample and the sample milled for 90 min, the elemental contents of C and Cl were listed in Table 3. 3.56 % of Cl existed in the original sample and 2.58 % of Cl was still remained in the solid after 90 min milling. For the content of C, it changed slightly during the reaction. Most of the carbon-containing compound was transformed from organic carbon compound to inorganic compound.

X-ray diffraction patterns of samples

The XRD patterns of HCB and grinding sample obtained by milling HCB with Mg and Al₂O₃ for 90 min were shown in Fig. 7. Compared with the XRD pattern of HCB, there were no peaks of HCB for the sample milled for 90 min, which demonstrated that HCB was destroyed sufficiently. Along with the degradation of HCB, carbon formed in the milling process. Because of amorphous feature of Al₂O₃ used in this experiment, peaks related to Al₂O₃ were also not presented. Peaks of Mg and MgO were found in the milling sample and the reaction of between Mg and O₂ during milling process might lead the formation of MgO. There were no peaks related to inorganic chlorine products because the chlorine products formed after the milling operation were amorphous species.

Mechanistic interpretation

For stepwise dechlorination process, the degradation pathways showed in Fig. 8a were in detail discussed as follows based on the detected intermediate dechlorination

Table 3 Carbon and chlorine content of non-milled sample and sample milled for 90 min, which were analyzed by XRF

	C (%)	Cl (%)
Original sample	1.20	3.56
Sample milled for 90 min	1.18	2.58

Fig. 7 XRD patterns of **a** HCB, **b** sample obtained by milling HCB with Mg/Al₂O₃ for 90 min

products. And the GC–MS spectra of the intermediates were presented in Fig. 9. PCB was formed after HCB molecules lost one chloride atom. Among the three isomers of TeCBs measured during the MCD, 1,2,3,4-TeCB was found in the largest amount. 1,2,3,4-TeCB can be transformed to 1,2,3-TrCB and 1,2,4-TrCB. The three isomers of TrCBs decreased in amount in the order of 1,2,3-TrCB > 1,2,4-TrCB > 1,3,5-TrCB. The products of 1,2,3-TrCB were 1,2-DCB, 1,3-DCB and 1,4-DCB, and 1,2-DCB was in the largest amount. MCB was also formed, and because of its high detection threshold, it could not be

quantified. In general, the main mechanochemical dechlorination pathway for HCB, showed in Fig. 8a, was HCB → PCB → 1,2,3,4-TeCB → 1,2,3-TrCB → 1,2-DCB → MCB. Since there were no effective methods for determination of benzene, it is unclear whether MCB can be transformed to benzene. This process needs to be further researched in the future.

After 90 min milling, the main existence state of chlorine in HCB was water-extractable inorganic chlorine (Cl[−]). In the milling process, a carbonization process taken place, which produced amorphous carbon and a portion of carbon was in the form of alkane. The GC spectra (Fig. 10) of the extract from milling solid samples indicated that the main products were alkane with different number of carbon atoms. The number of carbon atom ranged from 8 to 24. Analysis result showed that the relative strong peak was C₁₂H₂₆, *n*-dodecane. These alkane were end products after 90 min milling when almost all of HCB was destructed. Other study also presented similar results. Yasumitsu et al. [30] used calcium oxide as additive to destruct 1,2,3-Trichlorobenzene (TCB) by ball milling, and found that the final products contained some minor methane and ethane except carbon after 360 min milling. Loisel et al. [21] also detect methane and ethane in the end products during the process of mechanochemical treatment of chlorobenzenes. The alkane formed during milling process indicated that in the process of degradation of POPs a ring-open reaction was conducted. In general, the degradation process of HCB using Mg/Al₂O₃ as additive include three pathways: (1) dechlorination process generating low

Fig. 8 The proposed degradation pathway of HCB during the milling with Mg/Al₂O₃: **a** dechlorination: *bold arrows* show the main dechlorination pathway of HCB; **b** polymerization; **c** ring opening

Fig. 9 Distribution of low chlorinated benzenes at different milling time sample obtained by milling HCB with Mg/Al₂O₃. **a** 1,2,3,4-Tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene (1,2,3,4-TeCB, 1,2,4,5-TeCB, 1,2,3,5-TeCB); **b** 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene (1,2,3-TrCB, 1,2,4-TrCB, 1,3,5-TrCB); **c** 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene (1,2-DCB, 1,3-DCB, 1,4-DCB)

Fig. 10 GC spectra of the fluid extracting from milling sample

chlorinated benzene compounds; (2) dechlorination polymerization process forming graphite and amorphous carbon; (3) ring opening process producing alkane.

Conclusions

This work screened a better additive for the destruction of HCB by comparing five different additives. And HCB destruction rate using different reagents followed the following sequence: Mg/Al₂O₃ > Mg/SiO₂ > Mg > SiO₂ > Al₂O₃. Moreover, Mg/Al₂O₃ system is superior to the methods involving the use of CaO or Fe/SiO₂. Optimal milling condition was found by comparing the HCB destruction rate under different grinding conditions. Then the present study using Mg/Al₂O₃ as additive gave insight into the dechlorination of HCB via planetary ball milling and a degradation pathway of HCB was put forward. HCB was almost completely destroyed after 90 min of milling with Mg/Al₂O₃. When compared to CaO, Fe/SiO₂ in mechanochemical destruction and zero-valent iron based on base-catalyzed destruction of HCB, Mg/Al₂O₃ system saved over 3 h of the complete degradation time. The chlorinated intermediates and products contained PeCB, TeCB, TCB, DCB, and MCB. The dechlorination of HCB was a stepwise dechlorination process and the destruction pathway was put forward as: HCB → PCB → 1,2,3,4-TeCB → 1,2,3-TrCB → 1,2-DCB → MCB; Then, the following steps were ring cracking, carbonization and polymerization in the degradation reaction. The main final mechanochemical destruction products of HCB were amorphous carbon and inorganic chlorine compounds. Based on this study, Mg/Al₂O₃ has the potential to be applied in the disposal of waste containing HCB and other POPs.

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