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## Ball milling 2,4,6-trichlorophenol with calcium oxide: Dechlorination experiment and mechanism considerations

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### ABSTRACT

Mechanochemistry method is widely used for waste treatment and organic pollutant destruction. Previous research did not account for all phenomena in the mechanochemistry decomposition process. 2,4,6-trichlorophenol (2,4,6-TCP) with CaO and SiO<sub>2</sub> as additives was grinded using a ball milling equipment in present work. Content of the residual 2,4,6-TCP was measured by Gas chromatography coupled electron capture detector (GC-ECD) and found that the degradation rate is 99.0% after 6 h milling. Cl<sup>-</sup> content detected by ion chromatography (IC) show inconformity with the degradation rate. Products of Ca(OH)<sub>2</sub> and CaOHCl can be confirmed by crystal structure X-ray diffractometer (XRD). The residue samples were also examined using differential thermal analysis (DTA) and thermogravimetric analysis (TG and DTG) to see their thermal characterizations. Finally, a four-step pathway was proposed to describe the degradation process of 2,4,6-TCP during ball milling.

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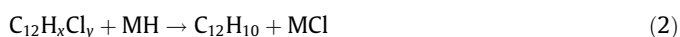
### 1. Introduction

Mechanochemistry is a branch of chemistry [1]; it draws on mechanical energy to induce chemical reactions. Mechanochemical reaction does not require harsh operating conditions, such as high temperature and pressure. It is applied in many areas such as extractive metallurgy, material synthesis, coal industry, powder surface modification, pharmacy and waste treatment [2–4]. For solid waste treatment, mechanochemistry is mainly used in the following fields: fly ash modification, rubber and plastic recycling, and attracted a lot of interests. The main advantages include [5]: simplified, ecological safe processes, excluding the use of solvents, intermediate fusion, etc.

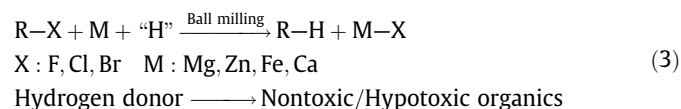
Previous studies by Rowlands et al. [6], Hall et al. [7], Zhang and Saito [8] and Birke et al. [9], show that chlorinated compounds like DDT, PCBs, dioxins can be degraded by milling with calcium oxide or metal sodium/magnesium and hydrogen donor species. A simplistic summary of these toxicant disposal reactions are:



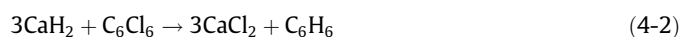
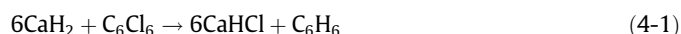
where C<sub>14</sub>H<sub>9</sub>Cl<sub>5</sub> is the equation for DDT, C<sub>28</sub>H<sub>8</sub> is a highly unsaturated hydrocarbon [7].



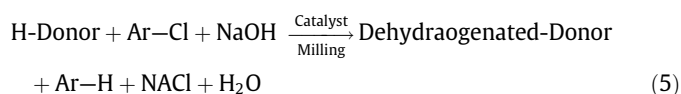
where C<sub>12</sub>H<sub>x</sub>Cl<sub>y</sub> represents polychlorobiphenyls or PCBs (with 0 < x < 8 and 2 < y < 10); MH is the hydride donor compound (NaBH<sub>4</sub>, LiAlH<sub>4</sub>); C<sub>12</sub>H<sub>10</sub> is biphenyl and MCl is the chloride salt formed in the reaction [8].



Eq. (3) summarized the reactions in some of Birke's researches. Toxic halogenated organics are dechlorinated by metal with appropriate hydrogen donors (alcohols, ethers, amines, and so forth) at room temperature yielding biphenyl and metal chloride [9].



Giorgio Cocco et al. used Eq. (4) to describe the Mechanochemical Self-Propagating Reaction between hexachlorobenzene and calcium hydride [10]. CaH<sub>2</sub> not only plays as the dechlorination agent and hydrogen donor, but also releases a large amount of reaction energy when reaction taking place.



Shown in Eq. (5), Pri-bar and other researchers conducted further study on the effects of palladium-based catalysts in the reductive

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dechlorination on the basis of the former researches on alkali base reductive hydrodechlorination using ball milling machine [11]. Peng et al. [12,13] milled fly ashes directly, proved that metal components in the ashes is effective on dioxin degradation.

Loiselle studied the mechanochemical reaction conditions of three different additives ( $\text{CaH}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ) [14], and found that  $\text{CaO}$  is an effective and low-cost reductive dechlorination agent considering factors of dechlorination efficiency, economy and safety. Wei et al. [15] disposed pentachlorophenol (PCP) with additives of  $\text{CaO}$  and  $\text{SiO}_2$ , they [16] also used egg shells as reductive dechlorination agent and proved that  $\text{Ca}$  compounds improve the reaction. Tanaka et al. [17] compared the effects of  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$ , and found  $\text{CaO}$  is more effective. In this paper,  $\text{CaO}$  is chosen as the reductive dechlorination agent.

In general, mechanochemical degradation is essentially a heterogeneous surface reaction. The reaction system is complicated, and the intermediate varies. In previous studies, more attention was paid to the dechlorination in mechanochemical degradation process, but very less description was known to the detailed decomposition pathways. In present study, 2,4,6-trichlorophenol (2,4,6-TCP) was degraded by ball milling with  $\text{CaO}$  as additive. The physical and chemical properties of the major reaction products and the decomposition efficiency were analyzed and calculated in the text. Finally, a more detailed decomposition pathways of 2,4,6-TCP are proposed and discussed.

## 2. Experimental apparatus and methods

### 2.1. Experimental materials

2,4,6-Trichlorophenol (2,4,6-TCP) was purchased from ACROS Organic, US,  $\text{CaO}$  (AR) was bought from Lianhua Chemical Reagent Co., Ltd, China and  $\text{SiO}_2$  (AR) is obtained from Sinopharm Chemical Reagent Co., Ltd, China.

2,4,6-TCP,  $\text{CaO}$  and  $\text{SiO}_2$  were mixed in a brown jar following the mass ratio of 2,4,6-TCP: $\text{CaO}$ : $\text{SiO}_2 = 158:717:125$ , equivalent to molar ratio:  $n_{\text{TCP}}:n_{\text{CaO}} = 1:16$ . The mixture was stirred for 10 min with a glass rod to make it mixed evenly. The addition of  $\text{SiO}_2$  can help to accelerate the breakdown of the agglomerates and therefore to improve the decomposing reaction.  $\text{SiO}_2$  plays a significant role of a grinding aid, not reactant. It is chemically stable against trichlorophenol under these grinding conditions [18,19]. Before preparation of the mixture, calcium oxide ( $\text{CaO}$ ) was dried in a muffle furnace at  $800\text{ }^\circ\text{C}$  for 2 h.

### 2.2. Experimental facility and procedure

The experiment was carried out on the planetary ball milling system. The bench experimental system is shown in Fig. 1. There

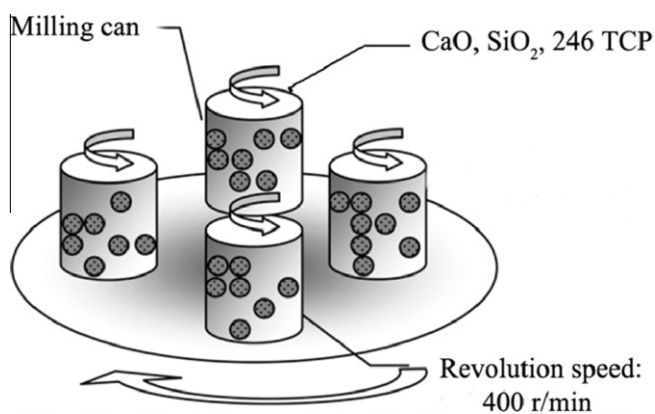


Fig. 1. Schematic diagram of a planetary ball milling machine.

are two or four milling cans in a single planetary disk. The milling cans move in a planetary movement. When the disk rotates, the cans move not only with the disk, but also rotate around their own axis. Revolution speed and cycle time of the planetary disk are controlled by the inverter controller. Revolution speed of the machine can range from 50 to 400 r/min. Two or four milling cans were symmetrically placed on the planetary disk in each experiment. The weight of the symmetrically placed cans were the same (weight difference  $<0.05\text{ g}$ ), or the equipment would be damaged by the centrifugal force.

The two cans were set symmetrically in the can base. Revolution speed was 400 rpm, and cycle length was set to 15 min, i.e. the machine stopped every 15 min for 1 min. Running direction alternated between clockwise and counterclockwise. The revolution direction of the disk and the rotation direction of the can were opposite. Sampling time was at total running time 0 h, 0.5 h, 1 h, 2 h, 4 h, 6 h, each sample is 1 g.

The mixture was grinded in the cans. The cans were of the same size. Each milling can (covered) weighted 965.00 g, the depth was 45 mm, diameter ( $\varphi$ ) is 50 mm, and effective volume was 85 mL. The can and the cover were sealed by a flexible gasket. Each of two cans was filled with 7 g mixture, 24 large balls and 99 small balls. Milling cans and balls were made of stainless steel. A large ball weighted 3.60 g, diameter is  $\varphi_L = 9.60\text{ mm}$ ; a small ball weighted 0.70 g, diameter was  $\varphi_S = 5.60\text{ mm}$ .

### 2.3. Sample analysis

The concentration of 2,4,6-TCP in residue was detected by a gas chromatography coupled electron capture detector (GC-ECD) (type: 6890 N, made by Agilent Company, United States). The detection was achieved by GC-ECD (electron capture detector chromatography) and the products are judged qualitatively by measuring the retention time. Extraction adopted the US EPA standard method 3550 and detection applied the US EPA standard method 8041A. The specific operation could be found on previous studies [9].

$\text{Cl}^-$  content in residue was detected by ion chromatography (IC) (type: 792-basic, made by Metrohm Company, Switzerland). Analyzing procedure was as follows: put 0.1 g sample into a 50 mL beaker, then add 30 mL ultrapure water, ultrasonically vibrate for 10 min to extract the  $\text{Cl}^-$  from the sample, filter through the fiber filter paper and pour filtrate into a 100 mL volumetric flask, repeat this three times; then set volume of the flask to 100 mL. Then the solution was analyzed by the equipment.

Crystal structure of the samples was tested by an X-ray diffractometer (XRD) (type: Rigaku D/max-2550pc, made by Rigaku Electric Co., Ltd., Japan). Micromorphology of the samples was analyzed by a field emission scanning electron microscopy (SEM) (type: SLR10N, produced by FEI Company, The Netherlands).

The milled samples were examined using differential thermal analysis (DTA) and thermogravimetric analysis (TG and DTG).

## 3. Results and discussion

### 3.1. Mechanochemical degradation

Fig. 2 shows that the residual 2,4,6-TCP gradually reduces with milling time. The residual 2,4,6-TCP reduced from 61.6% to 1.0% while the milling time prolonging from 0.5 h to 6 h. Dechlorination has been proved to be an important pathway of chlorinated aromatic decomposition during ball milling [20].  $\text{Cl}^-$  production ratio rapidly increased in the first 1 h and then increased slightly. After 6 h milling,  $\text{Cl}^-$  production ratio did not increase in the same proportion to the decrease ratio of 2,4,6-TCP: $\text{Cl}^-$  production ratio was

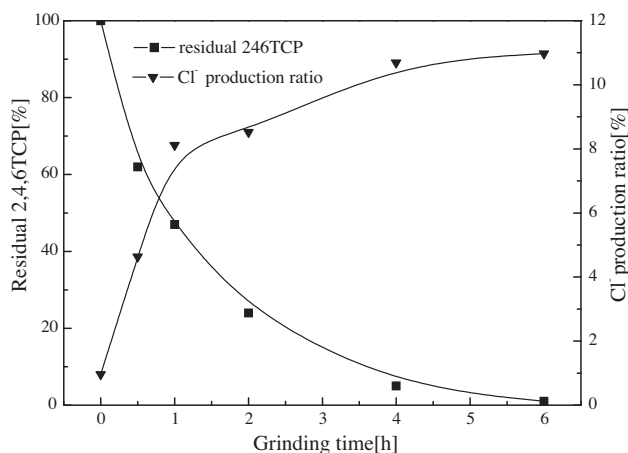


Fig. 2. Time trends for the change of 2,4,6-TCP and Cl<sup>-</sup>.

10.9%, namely only 10.9% organochlorine in 2,4,6-TCP changed to inorganic chloride (if the decomposition of 2,4,6-TCP was realized by cutting off Cl atom, the maximum decrease ratio of 2,4,6-TCP is 32.7%), while 99.0% 2,4,6-TCP had gone. Therefore, in this degradation only part of the organochlorine changed into inorganic chloride, the rest 2,4,6-TCP were degraded into other organic chlorinated substances, dechlorination only contributed a small part to the degradation (as shown in Eq. (6)):

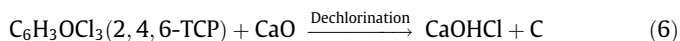


Fig. 3 provides the chromatogram of samples at different milling time. It can be found that 2,4,6-TCP reduced substantially in 1 h sample and the residual 2,4,6-TCP was hardly detectable in 6 h sample. There were monochlorophenols (2-MCP/4-MCP), dichlorophenols (24DCP/26DCP), Tetrachlorophenol (TeCP) and TCPs besides 2,4,6-TCP in the sample. The former two were lower chlorinated chlorophenols and phenols produced from 2,4,6-TCP during dechlorination; new TCPs produced from activated 2,4,6-TCP by exchanging chlorine atom positions on phenyl ring; TeCP was formed by active Cl atoms reacted with TCPs or other chlorophenols. The appearance of these intermediates suggests that dechlorination is important in the 2,4,6-TCP decomposition in ball milling process. After 6 h milling, chlorophenols in the products reduced significantly in comparison to that after 1 h milling, this proves that most 2,4,6-TCP had been decomposed into other substances.

### 3.2. Physical and chemical characteristic changes of TCP during milling process

As shown in Fig. 4, the 0 h sample (i.e. the prepared mixture of CaO, SiO<sub>2</sub> and 2,4,6-TCP) and the blank sample (i.e. mixture contains only CaO and SiO<sub>2</sub>) had the same crystal structure according to their XRD patterns. The main phase of the two samples was composed of CaO and SiO<sub>2</sub>. There were trace amount of Ca(OH)<sub>2</sub> in the samples due to the absorbing of moisture in the air during preparation. Trace carbon phase was detected in 0 h samples owing to the added 2,4,6-TCP.

As shown in Fig. 5, all spectral peaks of the sample broadened in the whole figure and the main crystal structure of CaO changed to amorphous phase with time extending. Peak height of CaO decreased gradually, and disappeared completely at time 4 h while peak height of Ca(OH)<sub>2</sub> gradually increased. SiO<sub>2</sub> is an inert ingredient without phase transition in the milling process. It can be used as referent to compare the phase changes of other substances. For the organic phase, XRD patterns qualitatively demonstrated that the form of carbon changed with the milling time. Saeki disposed

PVC mixed with CaO in a certain proportion [21] and found chlorine-containing inorganic phase CaOHCl peaks appeared in the milling sample of PVC after 5 h milling. In their study, signal of Ca(OH)<sub>2</sub> phase increased in 0–1 h, then weakened into amorphous. In present tests, CaOHCl peaks were not so obvious and hid in the broadening Ca(OH)<sub>2</sub> peaks, but still could be easily recognized. However, XRD analysis shows that the crystalline phase of the inorganic chlorine – CaOHCl, was not very intensive. In another study on pentachlorophenol (PCP) degradation carried out by Wei, unobservable formation of crystalline phase of CaOHCl suggests that the chloride formed is amorphous [14]. Thus it can be speculated that CaOHCl may be in a non-crystalline amorphous salt form in present experiment.

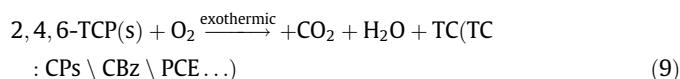
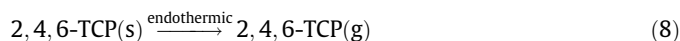
As shown in Fig. 6, in Raman spectrum of the sample, two peaks appeared at wavelength of 1582 and 1355 cm<sup>-1</sup> when milling time is 6 h. The peaks are characteristic peaks of graphite and amorphous carbon: the peak at wavelength of 1582 cm<sup>-1</sup> is the characteristic peak of G bond, corresponding to the typical Raman spectra of graphite, and broad peak at wavelength of 1355 cm<sup>-1</sup> is D bond characteristic peak, corresponding to the typical Raman peaks of amorphous carbon [6,8,22,23]. It can be determined that amorphous carbon and graphite are important products in the experiments; and the color of the sample turned black after milling. Tanaka et al. [24] milled the mixture of CaO and Aramid at revolution speed of 700 rpm. In their experiments, the amorphous carbon and graphite peak appeared in 1 h sample and intensified dramatically from 2 h with time extending. The carbonization peak appeared after 6 h milling in present experiment. This may attribute to the milling intensity of 400 rpm, which is weaker than Tanaka's experiment using 700 rpm; therefore, it tooks longer time for the appearance of carbonation peak.

### 3.3. Thermal characteristics of the samples at different milling time

Fig. 7 shows weight loss curve of the mixtures sampled at different milling time. There're three main weight loss steps. The first weight loss step (100–450 °C) is volatilization of bound moisture and remaining 2,4,6-TCP. The second step (550–700 °C) is oxidation of organics in the samples and decomposition of Ca(OH)<sub>2</sub>. The third step (700–1000 °C) is CaCO<sub>3</sub> pyrolysis. The total weight loss of the samples decreases with milling time, the weight loss for samples at 1 h, 5 h and 6 h are 30.2%, 28.7% and 26.6%, respectively.

The weight loss curve of the first step becomes less steep with milling time. The weight loss in the region of 343–400 °C attributes to the vaporization and oxidation of TCP is observed in the curves of the sample ground with in 1 h. In the region of 100–400 °C, sample in the air has a lower weight loss than in the N<sub>2</sub>, that is because of the CaO and the CO<sub>2</sub> combine to form calcium carbonate. During the milling process, organochlorine in 2,4,6-TCP turns to inorganic chloride, as shown in Eq. (6), chloride content increases with milling time, shown in Fig. 2, the organics are broken into low-molecular matters, and vaporizes into the air, that is why the total loss of the milling product decreases with milling time. The final weight loss at over 700 °C can be attributed to the decompose of calcium carbonate.

The first step (100–450 °C):



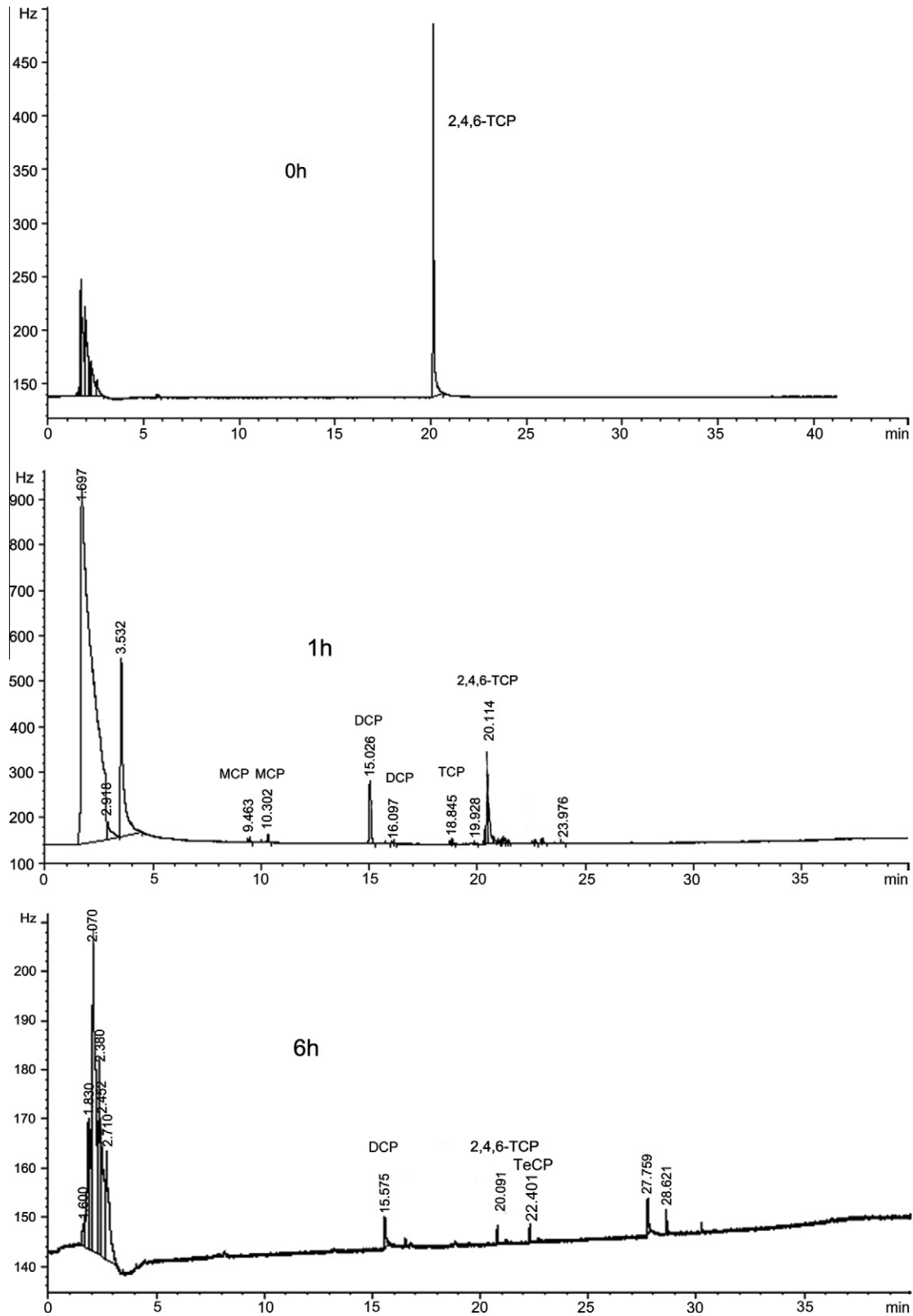


Fig. 3. Chromatogram of the products with the with milling time (MCP: monochlorphenol, DCP: dichlorophenol, TCP: trichlorophenol).

The second step (550–700 °C):



The third step (700–1000 °C):





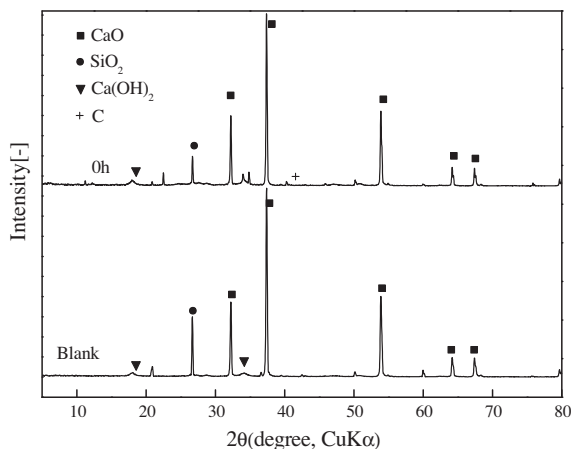


Fig. 4. XRD spectra of mixture sample at 0 h and blank sample.

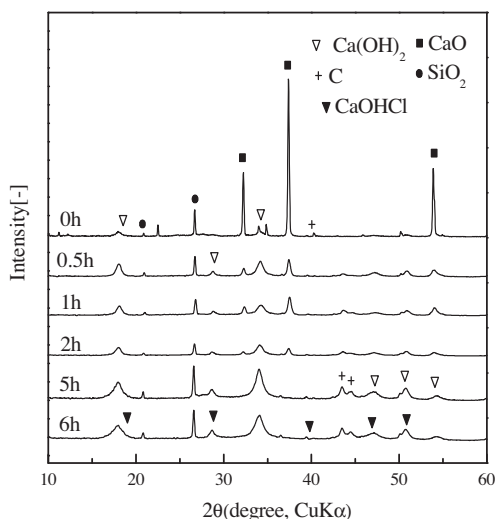


Fig. 5. Crystal changes of products at different milling time.

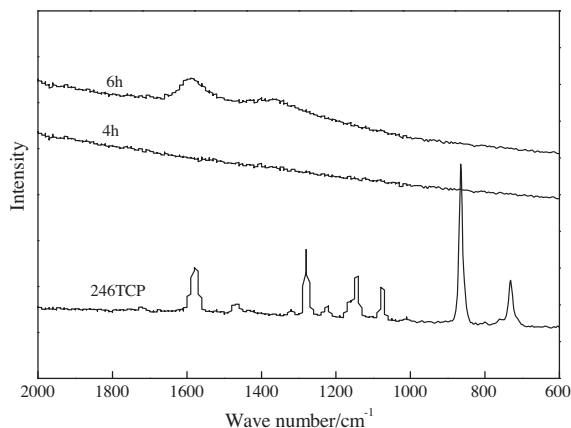


Fig. 6. Raman spectrum of milled mixture samples.

As Fig. 8 shows, an exothermic peak appears first at 100–450 °C due to the reaction of the remaining 2,4,6-TCP and the low-molecular organics produced during the milling process in the sample, as Eq. (9) shows. The oxidation reaction is exothermic. The peak decreases with the milling time prolonging, it can be concluded that

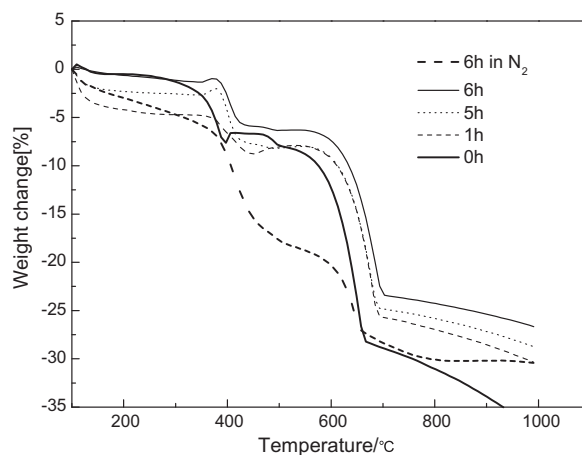


Fig. 7. TG curves of reaction products after different ball milling time.

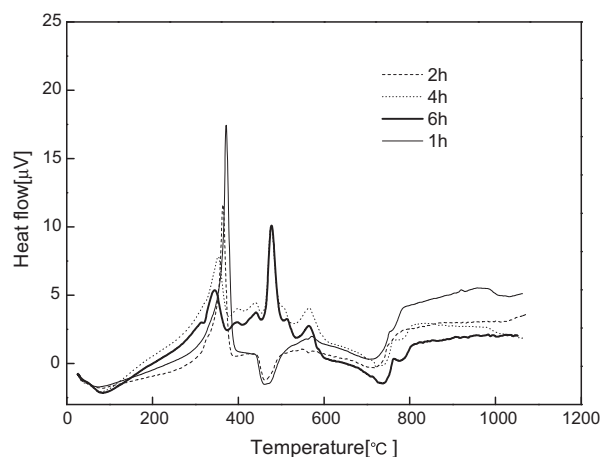


Fig. 8. DTA curves of mixture samples after different milling time.

it's because of the decrease of 2,4,6-TCP with milling time. In the region of 550–700 °C, the samples of 4 h and 6 h show an exothermic peak because of the heat release oxidation of amorphous carbon (R), as Eq. (11) shows. In the region of 700–1000 °C, all the milling samples show an endothermic peak due to the reaction showed by Eq. (12) and the trend enhances with milling time, in this step the main reaction is  $\text{CaCO}_3$  decomposition, the trend tells that  $\text{CaCO}_3$  content increases with milling time.

### 3.4. The mechanism and process of TCP degradations during mechanical milling

Zhang et al. respectively degraded trichlorobenzene (TCB) and s-hexabromobenzene (HBB) with mechanochemical method [20,25]. They found that at revolution speed of 700 rpm, both halogenated aromatic organic compounds can be completely degraded by adding calcium oxide. The similar method was adopted in present experiment except that the revolution was chosen at 400 rpm.

In the mechanochemical decomposition research of 2,4,6-TCP– $\text{CaO}$ – $\text{SiO}_2$  powder, 2,4,6-TCP was degraded by  $\text{CaO}$  in the ball milling process, after 6 h milling, only 1.0% of the initial 2,4,6-TCP was left. In this reaction process, we infer that the decomposition is realized in four reaction pathways: dechlorination, degradation, carbonation and carbonization, as shown in Fig. 9.

As discussed before (Section 3.1), dechlorination contributed part to the degradation. Free radicals were induced by grinding

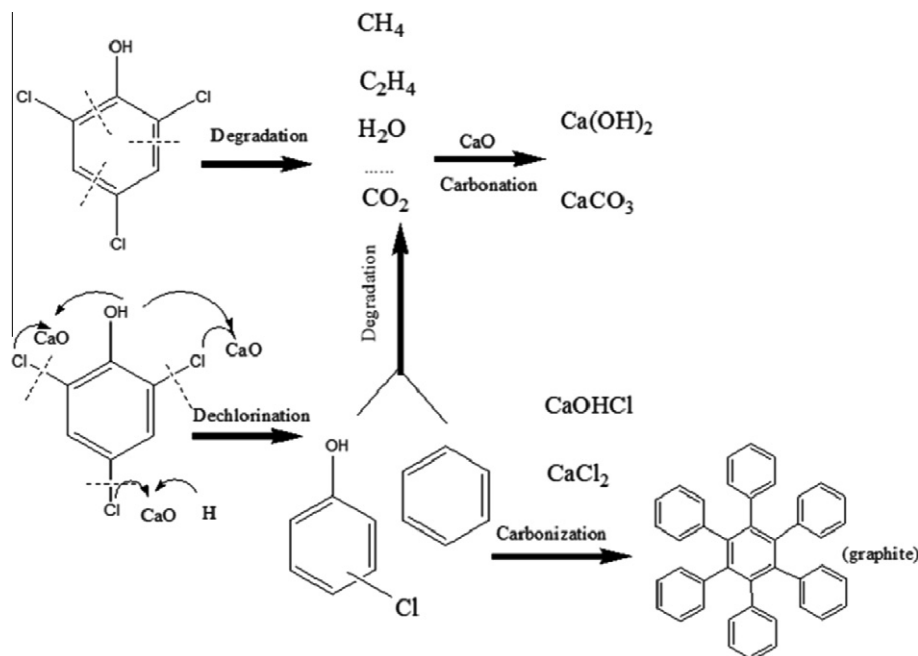


Fig. 9. Degradation ways of 2,4,6-TCP in the mechanochemical reaction.

on CaO surface; subsequently the charge transfer occurred on the organic TCP. C–Cl bondings in TCP were cut off to produce some intermediates; Cl atoms were split off from TCP. Generally, the radical Cl formed by dechlorination from TCP is trapped by CaO to form CaOHCl, which can be found in Fig. 5. It is still possible for some Cl radicals to have a chance to contact other TCP molecules and to replace H to form tetrachlorophenol, accompanied by the formation of dichlorophenol and monochlorophenol through the uptake of the substituted H.

Dechlorination can only do part of the decomposition and such degradation is another important way to break down TCP. Here degradation means fracture of the benzene ring. During grinding, charge transfer occurred on the organic, benzene ring of TCP or other organic was cut off and turns to small molecule organics, such as acetylene, ethylene, methane, ethane, and inorganic such as CO<sub>2</sub>, and H<sub>2</sub>O [20]. Chlorohydrocarbon is supposed to be the product in this process, which accounts for the phenomenon that Cl<sup>−</sup> production rate did not increase in the same proportion to the reduction rate of 2,4,6-TCP.

Then, carbonation took place: CaO reacted with CO<sub>2</sub> and H<sub>2</sub>O, turned to be CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>. Raman spectrum in Fig. 6 tells that amorphous carbon and graphite carbon emerged in the sample due to carbonization: benzene molecules formed in the dechlorination process were induced to combine together by ball grinding and form graphite like structures. Thus, color of the samples turned black in the end because of production of graphite carbon. In the dechlorination process, the C–Cl bond was cut off, the C atom on the benzene ring became an active site, and it is easy to combine with other benzene rings with active C atom. The active benzene rings finally formed amorphous carbon and graphite like structure as shown in Fig. 9.

#### 4. Conclusions

The mixture of 2,4,6-TCP and CaO or SiO<sub>2</sub> was subjected to grinding using a planetary ball mill in this paper. Ball milling is found very effective for 2,4,6-TCP treatment and decomposition rate could be over 99.0% after 6 h milling. The maximum production of 10.9%

Cl<sup>−</sup> proves that the dechlorination accounts for only part of the decomposition. A four-step mechanism for 2,4,6-TCP decomposition in ball milling system is proposed: reductive dechlorination, complete degradation, carbonation and carbonization.

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