

DESTRUCTION OF DECHLORANE PLUS BY MECHANOCHEMICAL METHOD

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Introduction

Dechlorane Plus (DP) has been commercialized as a chlorinated flame retardant since 1960s, with an annual world production of about 5,000 tons. In China, Jiangsu Anpon Electrochemical Co., Ltd has been known as the sole producer of DP currently, with the annual production capacity of 2000 t/a (<http://www.xfnj.cn/news/HTML/20060627091859.html>). Although it has been used for decades, DP has not received much attention until recently when it was found in air, sediment, and fish from the Great Lakes. In China, occurrence of DP in serum samples from electronics dismantling workers and air samples in China has been reported recently ^[1-2]. Compared to the increasing concerns about the monitoring of DP, very few attentions have been paid to the destruction or degradation of DP. As DP has been proven to be persistent, bio-accumulative and toxic, it might be included in the regulatory list of the international treaty, such as the Stockholm Convention.

In recent years, mechanochemical destruction (MCD) has been identified as a promising technology to destroy solid waste containing persistent organic pollutants ^[3-4]. It is a proven non-combustion technology and does not require heating or off-gas treatment ^[4]. Unlike combustion technology, MCD might avoid the production and release of unintentionally produced POPs like PCDD/PCDF. Furthermore, the MCD method has many advantages such as low-energy consumption, and suitability for installation in mobile units.

In the present study, the feasibility of MCD to be applied in the destruction of solid-state DP was investigated. In the experiments the ultimate fate of DP was elucidated. The results of this study could provide valuable information regarding CaO ratio and loading parameters for the pilot-scale applications of MCD in the destruction of DP and other organochlorine compounds.

Materials and methods

Dechlorane Plus 25 (C₁₈H₁₂Cl₁₂, 99% in purity) was purchased from Jiangsu Anpon Electrochemical Co., Ltd. CaO (98% in purity; BET surface area 7.3 m² g⁻¹; Beijing Modern Oriental Fine Chemicals Corporation) was heated at 800 °C for 2 h and stored in a dryer prior to use. A planetary ball mill (QM-3SP2, Nanjing University Instrument Corporation, China) was used for the experiments. A mixture of CaO and DP with different ratios was put into a stainless steel pot in a vacuum control system, and the pot was sealed subsequently. The planetary ball mill was operated at 550 rpm and the rotation direction of supporting disk changed automatically every 30 minutes. Ground products were identified by X-ray powder diffraction (XRD, Rigaku D/max-r B, Japan); Microscopic Confocal Raman Spectrometer (Renishaw RM 2000, UK); Fourier transform infrared (FTIR) spectrometer (NICOLET 6700 FTIR).

Results and discussion

Effect of CaO amount in mechanochemical reaction

The degradation of DP in the experiments with different CaO/DP weight ratio is shown in Fig.1. The results demonstrate that the degradation of DP consistently increased with extended grinding time. The increase in CaO/DP weight ratio from 10 to 25 leads to a significant increase in degradation rate. While at the experiment with a CaO/DP weight ratio of 25:1 a 100% destruction efficiency (DP not detected) has been achieved after 4 h grinding. The sample with a CaO/DP weight ratio of 10:1 has only reached a destruction efficiency of 45.6% for syn-DP and 47.9% for anti-DP degradation rate after 4 h grinding. This demonstrates that the content of calcium oxide is a key factor for the mechanochemical destruction. The weight ratio (25:1) showing the best degradation performance in our experiments is significantly higher than the mass stoichiometric ratio of 0.5:1. One study mentioned that excess CaO surface can absorb organic compound and avoid gas generation during the grinding [5].

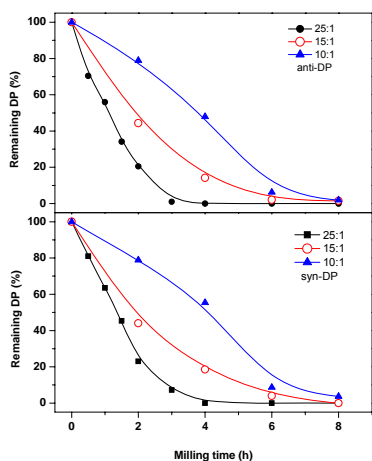


Fig.1 Change of the remaining DP with different weight ratio of CaO and DP

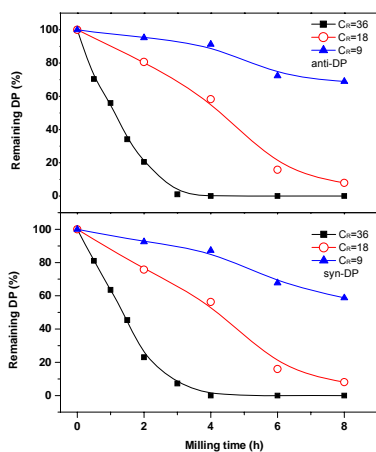


Fig.2 Change of the remaining DP with different Charge ratio, weight ratio (CaO/DP=25:1)

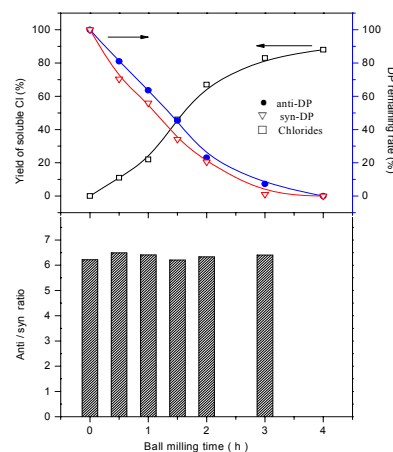


Fig.3 Anti/syn ratio and chlorides change with ball mill time, weight ratio (CaO/DP=25:1)

Effect of charge ratio in mechanochemical reaction

As second determining factor of destruction efficiency we evaluated the charge ratio C_R . $C_R = m_b/m_p$ is the charge ratio, where the m_b is the total mass of the balls and the m_p is the mass of the added reaction mixture (here mass of CaO and DP). The effects of the charge ratio on mechanochemical destruction has not been reported yet for persistent organic pollutants and other organochlorine compounds. However systematical investigation on mechanical alloying (metal binary mixtures) has shown that the highest transformation rate pertains to the milling trial performed at the highest C_R rate [6]. The destruction rate of DP with different charge ratio is shown in fig. 2. The degradation rates decrease with the increase in charge ratio. A destruction efficiency of 100% (DP not detected) within 4 h grinding was reached for the sample with a charge ratio of (36:1). While the sample with the lowest charge ratio tested (9:1) has only reached 41.3% syn-DP and 31.1% anti-DP even after 8 h grinding time. This demonstrate that the charge ratio is an important factor for destruction of organochlorine compounds and therefore relevant for the development of a successful practical application of mechanochemical destruction.

Effect of dechlorination and syn/anti change in mechanochemical reaction

An important evaluation parameter for verifying the degradation of organochlorine compounds in non-combustion technologies is the amount of chloride generated during destruction. The chloride generation and DP degradation is shown for one experimental series with a weight ratio of CaO/DP of 25:1 in Fig.3. The yield of soluble chloride ions increases with the increase of grinding time and decrease of DP and reaches 88.6% after 4 hours where a DP destruction rate of 100% have been reached. The generation of this high chloride yield verifies that dechlorination is the major degradation mechanism of DP. The chloride content could however only account for approximately 90% of chlorine contained in the degraded DP. A similar observation has also been described by Hall. His explanation was that the high molecular weight polymerized compounds still contain some organic bound chlorine [7].

The organic extracts have been screened with GC/MS for organic degradation products in SCAN mode (m/z 50 to 700). The products of dechlorination have not been detected in the screened samples. This demonstrates that the chlorine in DP is not substituted to a measurable extent by a hydrogen or hydroxy-group. This indicates that the main first reaction step is polymerization and finally carbonization (see below) during the dehalogenation reaction. These high molecular products can not be detected by GC/MS. In all experiments the anti-DP and syn-DP showed basically a similar degradation rate (e.g. the ratio of anti/syn was between 6.20-6.48 in experimental series in Figure 3) indicating a comparable stability of these two stereoisomers for mechanochemical treatment with CaO.

Effect of surface change in mechanochemical reaction

The Raman spectra of samples after MCD are shown in Fig. 4. Since some peaks in the sample of low content DP will not appear by Raman spectra, the weight ratio (CaO/DP=5:1) has been chosen in order to reveal the product. Compared with the solid surface obtained from the untreated sample, the difference of the samples' color can be observed. The color of the untreated sample was white (the color of CaO and DP powder are both white), while the color of the samples after 6 h and 10 h MCD were black. The most probable explanation is that carbon has been formed during the treatment which then is verified by the Raman spectra: There were two specific absorption peaks (at 1582 cm^{-1}) corresponding to the typical Raman spectra of graphite and (1335 cm^{-1}) corresponding to the typical Raman peaks of amorphous carbon [8]. The 1582 cm^{-1} peak is associated with the optically allowed E_{2g} zone center of crystalline graphite structures and involves bond-stretching motion of pairs of C-sp² atoms. The 1335 cm^{-1} peak is a breathing mode of A_{1g} symmetry involving phonons near the K zone boundary, which becomes active in the presence of disorder in graphitic structures. After grinding for 6 h, the graphite peak (1582 cm^{-1}) emerged (Fig.4). When prolonging the grinding to 10 h, the carbon peak at 1335 cm^{-1} associated with amorphous carbon emerged. One conclusion we can draw is that the first carbon structure formed in mechanochemical reactions of DP is graphite, while the second is amorphous carbon.

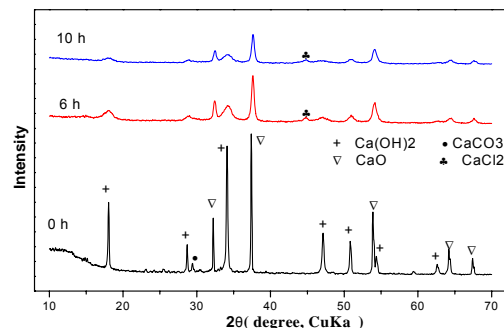
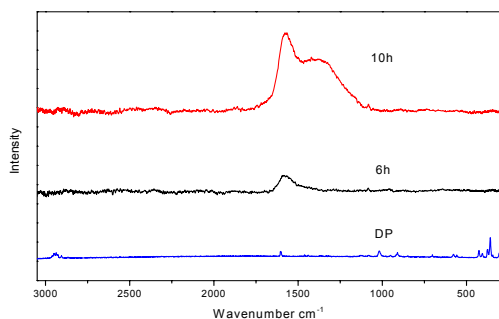


Fig.4 Raman spectra of CaO and DP (weight ratio 5:1) Fig.5 XRD patterns of ground samples with time, (CaO/DP)=5:1
 Fig. 5 shows the XRD patterns of the mixture ground for different periods of time with the weight ratio (CaO/DP=5:1). The peak intensity of CaO becomes smaller with a longer grinding operation. Although the CaO powder has been heated at 800 °C for 2 h before grinding, the peak intensity of Ca(OH)₂ is still present. However, its peaks become weaker and disappear with prolonged grinding time. During mechanochemical treatment of the particles, defects in the crystal structure are generated and accumulate. A valuable method employed for the investigation of crystal structure defects is the observation of line broadening in the X-ray diffraction spectra. The half-widths of the X-ray lines in different grinding time can reflect the amorphous degree and the lattice distortion of the powders. The peaks of CaCl₂ formed from dechlorination from DP can be observed after grinding (Figure 5). The DP is absorbed in the surfaces of calcium oxide, and the grinding induces excitations in metal oxide particles and a subsequent charge transfer to DP molecules and Ca-Cl bonding forms. This phenomenon has not been reported before. In other experiments, the formation of CaCO₃ was identified after 12 h grinding [5], but in our study, the CaCO₃ exists only in original sample because the calcium oxide has been heated at 800°C for 2 h and CaCO₃ has formed. Maybe reason is that the amount of CaCO₃ formed is small and its peak has been concealed behind the broadening line of Ca(OH)₂.

Acknowledgement

This research was supported by the National High-Tech Research and Development Program (No. 2009AA064001) and the National Key Project of Scientific and Technical Supporting Programs (No. 2007BAC03A09).

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