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Efficient destruction of hexachlorobenzene by calcium carbide through mechanochemical reaction in a planetary ball mill

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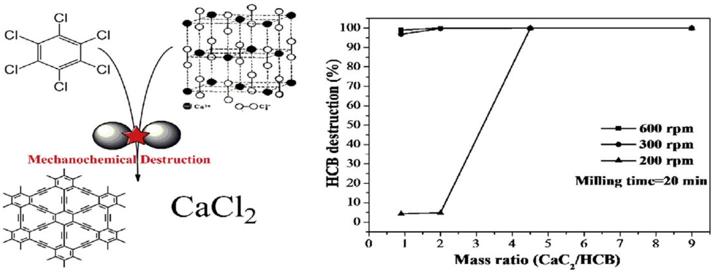
HIGHLIGHTS

- HCB is completely destroyed by CaC_2 within 20 min via mechanochemical treatment.
- CaC_2 shows much higher reactivity than traditional alkaline co-milling regents.
- HCB is converted to nonhazardous $CaCl_2$ and carbon materials.
- HCB is destroyed via nucleophilic substitutions of C-Cl by alkynyl in CaC_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Mechanochemical destruction (MCD) is a good alternative to traditional incineration for the destruction of persistent organic pollutants (POPs), like hexachlorobenzene (HCB), and the key is to find an efficient co-milling reagent. Toward this aim, HCB was milled with various reagents in a planetary ball mill at room temperature, and CaC_2 was found to be the best one. HCB can be destroyed completely within 20 min at a mass ratio of $CaC_2/HCB = 0.9$ and a rotation speed of 300 rpm. The ground samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The results show that the destruction products are nonhazardous $CaCl_2$ and carbon material with both crystalline and amorphous structures. On these bases, possible reaction pathways were proposed. Considering its excellent efficiency and safety, CaC_2 may be the most feasible co-milling regent for MCD treatment of HCB. Further, the results are instructive for the destruction of other POPs.

1. Introduction

Hexachlorobenzene (HCB) has been widely used as a pesticide in the past decades. It can cause tremendous hazards to the ecological environment due to its persistence, bio-accumulation, semi-volatility and toxicity. HCB is considered as a probable human carcinogen and also toxic by all routes of exposures (Randi et al., 2006). Aimed to reduce and restrict the production and use of HCB, it has been listed as one of the 12 POPs by Stockholm Convention in the first batch. Although the dedicate production of HCB has been prohibited, its emission is still enormous through combustion and by-produced HCB wastes in chemical industry (Bailey, 2001). Besides the increasing HCB wastes, there are also large amounts of HCB stockpiles around the world, including the US and Japan, and the HCB stockpile is about 70 tons in China (China's,

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For the destruction of HCB, high-temperature incineration is a conventional method due to its high efficiency and universality for all kinds of POPs. However, it has become increasingly unpopular due to its high capital cost, intensive energy consumption, and coinstantaneous by-products of new POPs, such as polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-p-furans (PCDF) (Rowlands et al., 1994; Kaštánek and Kaštánek, 2005). Recently, numerous techniques have been explored, such as catalytic hydrodechlorination (de Lucas Consuegra et al., 2006; Jujjuri, 2006; Jujjuri et al., 2014), chemical reduction (Kümmling et al., 2001; Liu et al., 2014), base-catalyzed decomposition (Ye et al., 2011; Hai et al., 2014), supercritical water oxidation (Lee et al., 2006) and mechanochemical destruction (MCD). Among them, MCD is considered as a mild and environment-friendly process (Tong and Yuan, 2012). Compared with incineration, MCD has many advantages, such as non-combustion, no fuel requirement, low energy consumption, and possible implementation in mobile units (Guo et al., 2010). Furthermore, MCD can avoid the production and release of any unintentionally produced POPs(Nomura et al., 2005). Successful MCD has been reported for different kinds of POPs, *e.g.*, pentachloronitrobenzene (Zhang et al., 2013b), perfluorooctanesulfonate and perfluorooctanoic acid (Zhang et al., 2013a), PCDDs and PCDFs (Mitoma et al., 2011), mirex (Yu et al., 2013), polyhalogenated phenol (Lu et al., 2012; Zhang et al., 2012; Di Leo et al., 2013), dechlorane plus (Wang et al., 2016), polychlorobiphenyls (Nah et al., 2008), and HCB (Mulas et al., 1997).

For the MCD treatment of POPs, calcium oxide (CaO) is widely used as a co-milling regent. However, its reactivity is relatively low, and harsh conditions are needed for the complete degradation, namely, high molar ratio, long milling time, and high rotation speed (Nomura et al., 2005; Mitoma et al., 2011; Lu et al., 2012; Yu et al., 2013). In contrast, calcium hydride (CaH_2) is very efficient for the destruction of HCB. However, its safety is problematic for practical uses because of the sudden temperature surging in the reaction process (Loiselle et al., 1996; Mulas et al., 1997). Recently, the mixture of zero-valent metal powder and assistant, such as Fe/SiO_2 and Mg/Al_2O_3 (Zhang et al., 2014; Ren et al., 2015), are used as co-milling regents to destroy HCB. However, these reagents also require severe MCD operation conditions. Thus, it is necessary to find an efficient and safe co-milling reagent for the MCD treatment of HCB.

In the present study, CaC_2 was first used as a co-milling regent for the treatment of HCB, and identified as the best one for its high efficiency, safety, cheapness, and free of toxic by-products. The products from the MCD were investigated, and the chemical change of C-Cl bonds was characterized, whereby a possible reaction pathway was proposed.

2. Materials and methods

2.1. Materials

HCB (purity 99%) was purchased from Beijing HWRK Chemical Company (China). CaC_2 (wt% ≈ 75%) was purchased from Alfa Aesar Chemical Company (China) and shattered into 100 mesh particles before use. CaO and NaOH were purchased from Tianjin Yongda Chemical Reagent Company Limited (China). CaH_2 was purchased from Aladdin Industrial Corporation (China).

2.2. Ball milling experiment

A planetary ball mill (QXQM-2, Tianchuang, China) was used for the MCD experiments. To a stainless steel pot (250 mL) with 250 g of four different diameters (15, 12, 10, and 8 mm) stainless steel balls, a mixture of HCB and CaC_2 with specific mass ratio (CaC_2/HCB, g/g) was added, and the pot was subsequently sealed air tight by using a vacuum controlled system. The planetary ball mill was operated at specific rotation speeds under vacuum condition and room temperature, with a 15-min cooling interval after every 30 min to avoid excess temperature increases.

2.3. Sample treatment and analysis

For the analysis of the residue organic components in the milled mixture, 0.1 g of powder was taken out and extracted by toluene under ultrasonic treatment for 30 min. The resulting solution was centrifugalized at 7000 rpm for 5 min, and the supernatant was analyzed using a gas chromatography (Shimadzu GC-2010, Kyoto, Japan), equipped with a HP-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). Nitrogen (99.999% in purity) was used as carrier gas at a constant flow rate of 12.3 mL/min. GC oven temperature was programmed from 160 °C (held for 1 min) to 300 °C (held for 2 min) at 20 °C/min. 1 μL of the sample was injected in the split mode, and the injector temperature was set at 350 °C.

For the analysis of the final solid products, 1 g of the milled mixture was taken out and treated with dilute nitric acid for 1 h with a magnetic stirrer at room temperature, and then filtered with a microfiltration membrane and washed twice with distilled water. The chloride ion content in the filtrate was analyzed by ion chromatography (ICS-900, DIONEX, China). The dechlorination degree was expressed by the mass ratio of Cl^- in the filtrate with respect to the initial chlorine in the starting materials. As a control experiment, a physical mixture of HCB and CaC_2 was also treated and analyzed following the same procedure.

2.4. Characterization of the solid materials

The instant changes of the solid mixture during the milling process were characterized using multiple approaches. X-ray diffractions (XRD) was conducted using BRUKER D8 ADVANCE (BRUKER, Germany) with Cu Kα radiation at a speed of $6^\circ\ min^{-1}$ in the range of $2\theta = 10^\circ - 70^\circ$. Fourier transform infrared (FT-IR) was conducted using Nicolet 6700 (Thermo-Scientific, US) with the KBr disk method from 400 cm^{-1} to 4000 cm^{-1}. X-ray photoelectron spectra (XPS) was conducted using Thermo Escalab 250Xi (Thermo Electron, US), in which the binding energy scale was calibrated by C1s peak of 284.8 eV.

The solid mixture after 12 h milling was immersed in dilute nitric acid and washed with distilled water, whereby the resulting carbon materials were obtained by vacuum drying at 100 °C for 5 h. Raman spectra were recorded for the carbon materials at room temperature using Renishaw inVia (Renishaw, UK) with He-Ne-laser beam at the 632.8 nm line.

3. Results and discussion

3.1. The comparison of different co-milling reagents

To choose a suitable co-milling reagent, MCD experiments were conducted for different reagents, *i.e.*, CaO, NaOH, CaH_2 and CaC_2 at the same operation conditions, *viz.* co-milled 12 h at the mass ratio of reagent/HCB = 4.5 and rotation speed of 600 rpm.

As shown in Fig. 1, CaO and NaOH show negligible MCD capability for HCB with their dechlorination degree being only about 3.8% and 6.9%, respectively, after 12 h milling. In contrast, CaH_2 and CaC_2 show excellent dechlorination performance with their dechlorination degree being about 83.9% and 92.5%, respectively. The dechlorination performance of the co-milling reagents follows the order of $CaC_2 > CaH_2 \gg NaOH > CaO$. Further, for the CaC_2, the