MECHANOCHEMICAL DECOMPOSITION OF HEXACHLOROBENZENE WITH CAO-AL ADDITIVES

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Introduction

Hexachlorobenzene (HCB), first introduced in 1945 to treat seeds, HCB kills fungi that affect food crops. It was widely used to control wheat bunt. It is also a byproduct of the manufacture of certain industrial chemicals and exists as an impurity in several pesticide formulations. It is enrolled as one of the 12 initial Persistent Organic Pollutants (POPs) under the Stockholm Convention [1], as well as one of the Environmental Endocrine Disruptors (EEDs). The health hazard of HCB has caused extensive attention.

At present, incineration [2] is the best available remediation technology for POPs with the required temperatures of 870-1200. However, widespread application of incineration technology in backward areas is limited within problems of harsh reaction conditions and dioxin (PCDD/Fs) formation during incineration. During the last two decades, several alternative non-combustion technologies have been proposed such as base catalyzed decomposition, bioremediation, UV photocatalytic degradation. [3] Recently, the mechanochemical (MC) methods have shown excellent decomposition performance for chlorinated, brominated and fluorinated persistent organic pollutants by using planetary or horizontal ball mills. [4-5]

Regular kinds of additives have been studied to attain high disposal efficiency in a short milling time, including pure metals (Mg, Na, K, Zn, Fe et al.), metal oxides (CaO, Al_2O_3, MgO et al.), metal hydroxides (NaOH, KOH, $Ca(OH)_2$ et al.), as well as assistant additive SiO_2. The joint additives of Fe and SiO_2 (Fe-SiO_2), applied in MC process, showed a strong destroy of HCB [2], rather than traditional additives of CaO-SiO_2 or pure iron (Fe). However, nitrogen atmosphere was required for Fe-SiO_2 process, which confined its industrial application of MC treatment. Atmosphere is one of the main factors that influence MC degradation efficiency.

Different kinds of additives were mixed with HCB, and milled in ambient air, except for Fe-SiO_2 in nitrogen. Thus, the aim of the paper is to point out an effective MC additive as CaO-Al, and then confirm the optimum content of Al in CaO-Al process.

Materials and methods

The experiment was performed using an all-dimensional planetary ball mill (QXQM-2L), equipped with four stainless steel grinding vials of 250ml. Vials rotate in a planetary movement on the disk, while the disk do a 360° flip in three-dimensional space. Problems of bottom-sinking and wall-sticking of milling samples, commonly happened in traditional ball milling, can be relieved in QXQM-2L. Stainless steel grinding balls within 215 gram are contained in each vial， grinding ball diameters are between 8-12 mm.

Hexachlorobenzene (purity AR) was purchased from Wuhan Jinnuo Chemical Engineering Co., Ltd., China. The CaO, quartz, Al_2O_3 and Fe (purity AR) and Al (100-200 mesh, purity 4N), purchased from Sinopharm Chemical Reagent Co., Ltd., China, were used as the additives in mechanochemical (MC) treatment. Organic solvents, acetone (purity 99.9%, Mreda Technology Inc., USA), hexanes (purity 99.9%, Avantor Performance Materials, Inc., USA) and isooctane (purity >99%, GC, Aladdin Industrial Inc., China) were used for extraction and detection of HCB. GC-ECD was used to analyze HCB, while the pretreatment of HCB preferred to the PHD thesis of Yan Mi [6]. Scanning Electron Microscope (SEM) was used to observe changes of sample microstructure during MC treatment.

Different dechlorination additives and combinations were proposed so as to effectively shorten the MC treatment time of persistent HCB, i.e. CaO, CaO-SiO_2, CaO-Al_2O_3, CaO-Al, Fe-SiO_2. The former four kinds of additives were operated in ambient air, while Fe-SiO_2 was in nitrogen (N_2) atmosphere, described in Table 1. Each additive within 13.5 gram was mixed with 0.9 gram of HCB, i.e. ratio of the additives and HCB equals 15: 1. The rotation speed of vials was 550rpm, ratio of rotation and revolution speed of disk equals 2: 1.The vials and disk rotate to the opposite direction alternately every 30min.

Table 1 Different dechlorination additives and combinations for MC treatment of HCB

Additives	Main (g)	Assistant (g)	HCB (g)	Total (g)	Ratio	Condition
CaO	CaO 13.5	/	0.9	14.4	15: 1	Air
CaO-SiO_2	CaO 9.0	SiO_2 4.5	0.9	14.4	15: 1	Air
CaO-Al_2O_3	CaO 9.0	Al_2O_3 4.5	0.9	14.4	15: 1	Air
CaO-Al	CaO 9.0	Al 4.5	0.9	14.4	15: 1	Air
Fe-SiO_2	Fe 9.0	SiO_2 4.5	0.9	14.4	15: 1	Nitrogen

According to the most effective process of CaO-Al, the influence of Al content was investigated so as to confirm the optimum condition. The MC reaction time was 4h, described in Table 2.

Table 2 Content of Al in CaO-Al process

Al content (%)	Main CaO (g)	Assistant Al (g)	HCB (g)	Total (g)	Ratio
0	13.5	0	0.9	14.4	15: 1
3.7	13	0.5	0.9	14.4	15: 1
7.4	12.5	1	0.9	14.4	15: 1
11.1	12	1.5	0.9	14.4	15: 1
22.2	10.5	3	0.9	14.4	15: 1
33.3	9	4.5	0.9	14.4	15: 1
44.4	7.5	6	0.9	14.4	15: 1
66.6	4.5	9	0.9	14.4	15: 1
100	0	13.5	0.9	14.4	15: 1

Results and discussion

The initial HCB quantity was analyzed as 854mg in 900mg (0.9 gram) HCB sample. Results in Fig. 1 present the removal efficiency of HCB as a function of grinding time, it was calculated as:

$$\frac{HCB_{original}-HCB_t}{HCB_{original}}\times 100\% \qquad (1)$$

A very high degradation efficiency of 99.70% was attained by CaO-Al process after 8h grinding, while CaO-SiO_2 process showed 85.80% as the second effective. Nitrogen atmosphere was required to attain 98.50% degradation efficiency for the Fe-SiO_2 process, referred to PHD thesis of Zhang Wang. While the CaO-Al reaction simply exposed to ambient air, indicating that the CaO-Al process was easier to operate. Moreover, exposed micro iron would be easily oxidated and autoignited after milling, concerning security issues.

SiO_2 and Al_2O_3 showed parallel effect as a catalyzer in MC treatment of PVC.[7] However, lowest efficiency of 51.29% after 12h milling was attained by CaO-Al_2O_3, weaker than only CaO (87.25% after 12h) and CaO-SiO_2 (98.40% after 12h). Al_2O_3 did not act as an assistant agent in the CaO-Al_2O_3, differs from the catalytic effect of Al_2O_3.[7]

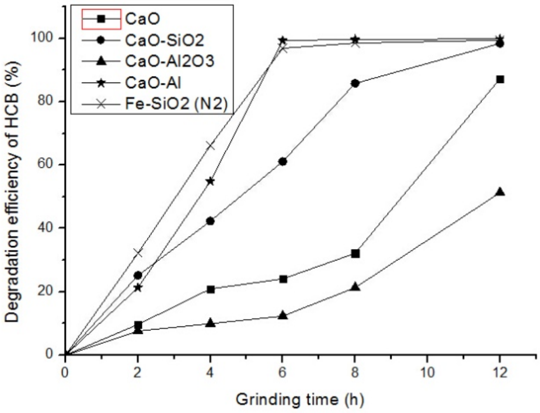

Figure 1

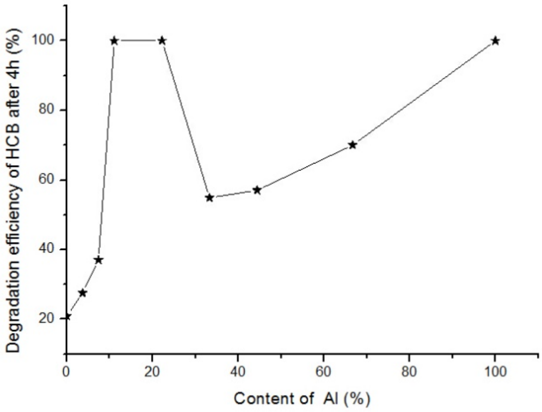

Figure 2

The content of Al in CaO-Al ranges from 0% to 100%, the degradation efficiency of HCB as a function of Al content after 4h grinding is presented in Fig. 2. The degradation efficiency of HCB increases from 20.91% to 99.99% as Al content ranges from 0% to 22.2%, then decreases to 57.06% as Al content increases to 44.4%, and then once again increases to 99.99% due to 100% of Al content. The CaO-Al process greatly reduces the required grinding time of MC treatment of HCB. The weight ratio of ball to sample equaled 15: 1 in our study, far less than 30:1 referred to the former research, which can significantly improve the disposal capacity of waste in MC industrial application.

According to the top four degradation of CaO-Al, Fig. 3 shows the degradation efficiency of HCB within 11.1%, 22.2%, 33.3% and 100% Al content as a function of grinding time. CaO-Al (22.2%) showed the highest efficiency of more than 99% after shortly 2h. Al is more expensive than CaO, thus CaO-Al (22.2%) costs less than pure Al with effective degradation.

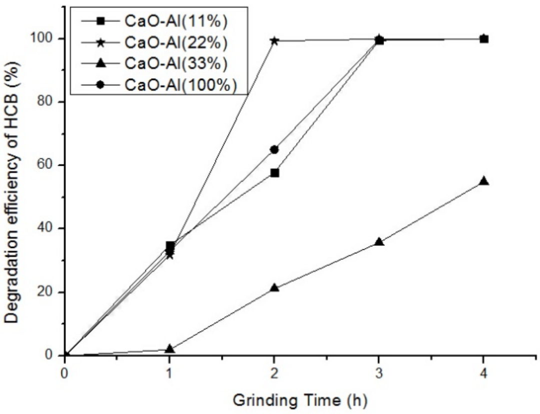

Figure 3

Microstructures of CaO-Al (33.3%) and HCB milled samples were presented in Fig. 4, spiculate HCB sample and aggregated aluminum powder can be easily recognized in the original sample (0h), shown in the labeled circles (Fig. 4). Sample particles distributed loosely before grinding as unrefined, and became finer since grinding for a while (4h). Finer powders agglomerated after a certain period of time (8h), and finally levigated to equally mini spheres within diameters under 1 um (12h). Mechanical forces, such as fiction, collision and shear, yielded during ball milling. Instantaneous high temperature and pressure triggered in certain localities (micro- or nano-scale), thus induced effective MC reactions, defined as triboplasma. Distributed micro-scaled spheres resulted from triboplasma.

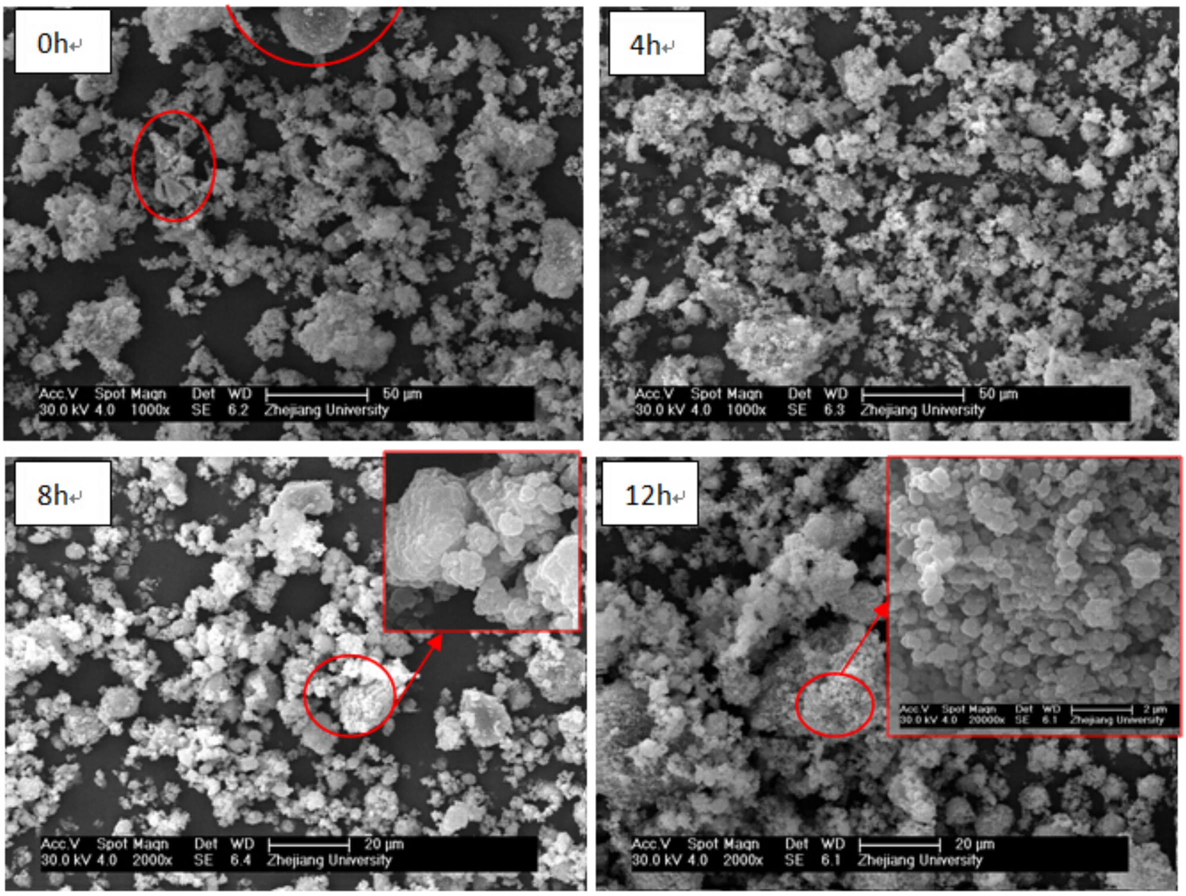

Figure 4

Effective degradation of HCB resulted after MC treatment by applying CaO-Al process and using all-dimensional planetary ball mill, rather than traditional CaO-SiO_2 or novel Fe-SiO_2 (N_2) technique. Degradation efficiency of more than 99% was attained after shortly 2h grinding by mixing 22.2% of Al content to CaO-Al, regarded as the optimum condition of CaO-Al process. Instantaneous intensive reactions were triggered in Micro- or nano-scale because of triboplasma, thus resulted effective treatment of POPs.

Acknowledgements

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