MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5497–5501

Mechanochemical dechlorination of chlorinated compounds

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The mechanochemical decomposition of different chemicals such as 1,2,3-trichlorobenzene (TCB), monochlorobiphenyl (BP-Cl), and aromatic polyamide (aramid) was attempted by using a planetary mill with inorganic additives such as CaO. The ground products were characterized by different equipment, including ion chromatography (IC), gas chromatography (GC/MS), X-ray diffraction (XRD), Raman spectroscopy, and electron spin resonance (ESR). The dechlorination reaction reached almost 100% during prolonged grinding periods of time, and was accompanied by radicals, which play a significant role in the decomposition and its yield. One of the main components in the ground product was inorganic chloride, and its amount was found to increase with lengthier grinding time. Other components in the products were amorphous carbon and $CaCO_3$. These findings should be useful for practical applications in the detoxication of many organic toxic substances. © *2004 Kluwer Academic Publishers*

1. Introduction

It is said that more than 10 million different chemicals have been already produced, and this number is increasing annually [1, 2]. These man-made chemical compounds are used in agricultural chemicals, insecticides, medicines, and plastics. They cannot be disposed and decomposed easily, due to their toxic substances, thus making it necessary to detoxicate them before exposure to the environment. There have been several means developed for decomposing toxic organic chemicals: (1) A base catalyzed decomposition developed by US Environmental Protection Agency (UP-EPA). This can dechlorinate in a N_2 gas atmosphere at 300–350°C and atmospheric pressure by adding hydrogen donor and catalyst. (2) A chemical extraction method (ex. DMI/NaOH), that involves the use of NaOH under DMI aprotic polar solvent. The hydrogen source is insulation oil. The main products are biphenyl and NaCl. (3) An organic alkali metal method (ex. t-BuOK), that uses an organometallic compound such as t-BuOK to decompose PCBs at 200–250°C and atmospheric pressure. (4) A catalytic hydrogenise method (ex. Pd/C), that occurs in hydrogen gas in order to substitute chlorine under a catalyst such as palladium and carbon (Pd/C). PCBs can be decomposed and changed into biphenyl, phenylcyclohexane, bicyclohexyl, and HCl, etc. (5) A super critical water (SCW) oxidation method has been developed by Molder Co. US, and applied at high temperature and water pressures to decompose PCBs into carbon dioxide (CO_2), water, and finally HCl under SCW conditions. (6) Bioremediation, which uses selected microorganism to decompose PCBs or organic toxic chemicals. Among all of these, the currently most popular method to detoxicate the compounds is incineration; however, this raises concerns about the formation of toxic byproducts such as dioxins, i.e., polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), and polycyclic aromatic hydrocarbons (PHAs) [3–6]. This has created impetus to develop other safe and more reliable methods for disposing of such toxic substances. There is a growing interest and necessity to find efficient and economic methods to treat man-made pollutants, of which the chlorinated compounds, particularly the polychlorinated biphenyl (PCBs) class and dioxins, remain points of concern in regard to environmental protection.

Although the above reported processes are effective in dechlorinating organics, each exhibits certain technological and economical difficulties in their applications. Recently, much attention has been paid to the mechanochemical treatment of toxic substances, due to its easy operation and practicability regarding the vast amounts of contaminated samples at low concentrations and the toxic chemical itself [7–10]. It is known that grinding plays a significant role in causing mechanochemical effects on solid particles as well as being a simple operation to reduce particle size. One

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of the unique phenomena of this effect is the ability to dissociate the material by rupturing the bonds. In previous reports, cogrinding with oxides of alkaline earth metals has been found to be effective in the dechlorination of halogen-containing organic polymers such as poly (vinyl chloride) [11], and poly (tetrafluoroethylene) [12].

In this work, based on the experimental results of several other decomposition examples of trichlorobenzene (TCB), aromatic polyamide (aramid), and monochlorobiphenyl (BP-Cl), some important phenomena of mechanochemical decompositions are discussed to reveal further the inherent nature of the processes.

2. Experimental section

1,2,3-TCB sample (Wako Pure Chemicals Ltd.), BP-Cl sample (Lancaster, UK), and commercial aramid film were used. Each sample was mixed with the additives of CaO, MgO. The CaO or MgO sample was prepared by heating calcium hydroxide ($Ca(OH)_2$) at 800°C or magnesium hydroxide ($Mg(OH)_2$ (both from Wako Pure Chemicals Ltd.)) at 1000°C for 2 h in an air in an electric furnace. A few grams of each mixture of sample were ground by a planetary ball mill (Fritsch Pulverisette-7, Germany) in air at 700 rpm for various periods of time. The mill is composed of pair of pots made of zirconia; each pot has an inner volume of 45 cm^3. Seven zirconia balls of 15 mm in diameter were charged in the pot together with the mixture. To prevent excess heating, the milling was stopped for 15 min after every 15 min grinding operation.

The ground samples and gases in the pots were characterized using the following analytical methods: GC/MS (model 6890 and 5973, Hewlett-Packard), IC (LC10series, Shimadzu Co. Ltd.), X-ray diffraction (XRD) (RAD-B system, Rigaku) using Cu K_α radiation, Raman spectra (Labspec Raman Spectrograph, Horiba), and ESR spectrometer (Bruker ESP-380E).

3. Results and discussion

3.1. The case of TCB decomposition

Fig. 1 shows the yield of TCB remaining in the ground product and the yield of the chlorides determined by washing the ground product with water as a function of the grinding time. It is clearly shown that the yield decreases rapidly with an increase in grinding time and only 0.02% of TCB is detected in the sample ground for 6 h. This dissociation of TCB is due to the mechanochemical reaction between the TCB and CaO. The yield of water-solved chlorine was seen to increase rapidly with a correspondingly longer grinding time and reached 95% at 6 h grinding. The good correlation between the yields clearly confirms that the chlorine in the organic compound has been transformed mechanochemically into a water-soluble inorganic chloride.

Fig. 2 shows GC/MS spectra of the products extracted from the samples ground for 0, 1, and 6 h by using acetone. Weak peaks are observed in the spectrum of the sample ground for 1 h, besides a strong peak of TCB, corresponding to dichlorobenzene (DCB)

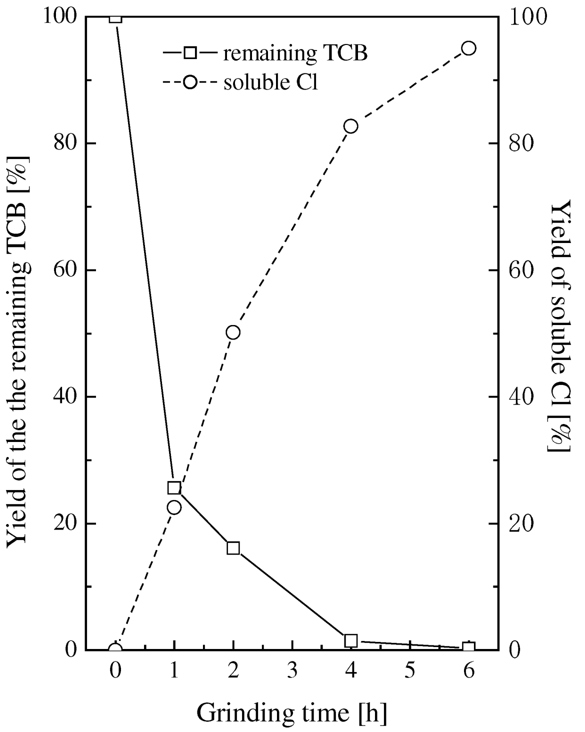

Figure 1 Change in the yield of the remaining TCB and water-soluble Cl with grinding time. Grinding condition is as follows: TCB:CaO = 1:12 molar ratio, 700 rpm.

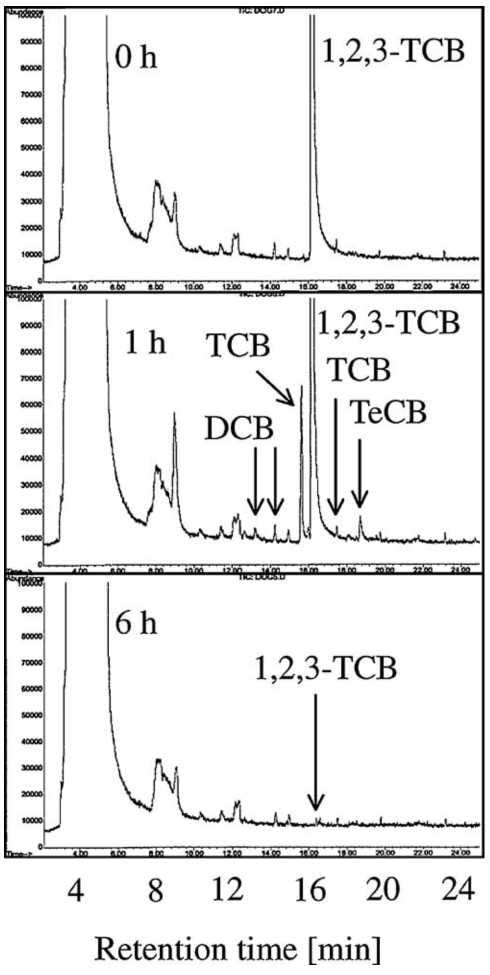

Figure 2 GC/MS spectra of the products extracted by acetone from the ground samples.

and tetrachlorobenzene (TeCB). These disappear in the spectrum of the sample ground for 6 h, and the peak of TCB can no longer be observable. According to the analysis of the extraction of ground samples by toluene, ethanol, ethyl acetate, and hexane, no other intermediates have been detected from the ground samples. The formation of DCB and TeCB suggests that the reaction between TCB and CaO is not dehydrochlorination, but dechlorination. It is considered that the dechlorination occurs in the grinding of TCB with CaO, substituting Cl by O in the structure by changing its form. The structure may not be more than TCB at this stage, and the product is composed of several different compounds such as CB, DCB, TeCB, and others as intermediates, besides TCB and CaO. Further grinding with CaO causes the dissociation of DCB and/or TeCB, forming inorganic chlorides, which would be $CaCl_2$ or $CaCl_2{\cdot}H_2O$ and C.

Fig. 3 shows the GC/MS spectra of the gases collected from the pot immediately after 1 h grinding. Compared with the results of solid samples, similar ones such as TCB, DCB, and CB have been observed. Furthermore, benzene, and light molecular weight hydrocarbon and other gases such as C_2H_6, C_2H_4, CO_2, CH_4, and H_2O are observed, even in small quantities. Chlorinated aromatic compounds are absorbed, then to occur as the intermediate phases when the sample is ground for 1 h, and these phases disappear when the grinding time is extended to 6 h except for light gases such as C_2H_6, CO_2, CH_4, and H_2O (not shown here).

While not shown here, some radical peaks are observed on ESR spectra. This is highly consistent with the results in a previous report on the ground mixture of CaO and chlorobiphenyl [13]. Farther research will be necessary for a detailed discussion of the radical generation of mechanochemical grinding operation.

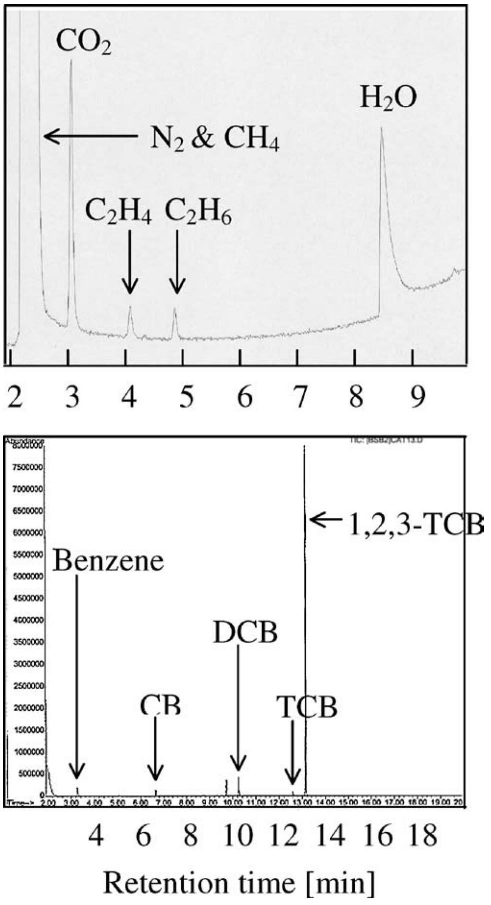

Figure 3 GC/MS spectra of gases collected from mill pot headspace after 1 h grinding.

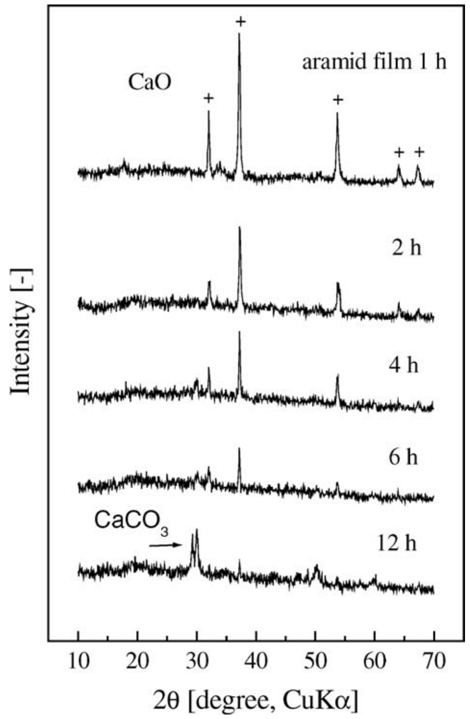

Figure 4 XRD patterns of the mixed samples (Ca:Cl = 8:1) ground for different periods of time.

3.2. Decomposition of aromatic polyamide film with the change in NH group

Fig. 4 shows XRD patterns of the mixture ground for different periods of time. The peak intensity of CaO becomes smaller with a longer grinding operation. When the grinding is prolonged to 12 h, the peak existence in the pattern virtually disappears. In contrast, the main peaks of calcium carbonate ($CaCO_3$) and zirconia (ZrO_2) can be observed from the pattern. It is clear that the appearance of ZrO_2 comes from the abrasion wear of the zirconia pot and balls. Although the grinding was conducted in air, the pots were sealed during grinding so that there is no concluding that the CaO sample absorbs CO_2 gas from the outside to form $CaCO_3$. The formation of $CaCO_3$ comes from the mechanochemical reaction between CaO and aramid samples. A possible reason for this will be discussed in another paper. Since there are no other peaks observed in the patterns of the ground sample, the chlorine-containing products should be amorphous.

Fig. 5 shows the Raman spectra of original aramid film and ground samples following different grinding times. The original sample shows a clear aromatic polyamide pattern. However, it is difficult to observe any clear peaks even with the 1 h grinding sample, compared with the original sample. Raman shifts at 1570 and 1320 cm^{-1} bands are observed and the peak intensity rises with the increase in grinding time. Although a little lower than others reported, the two peaks are typical of amorphous carbon. The sharp peak (1570 cm^{-1})

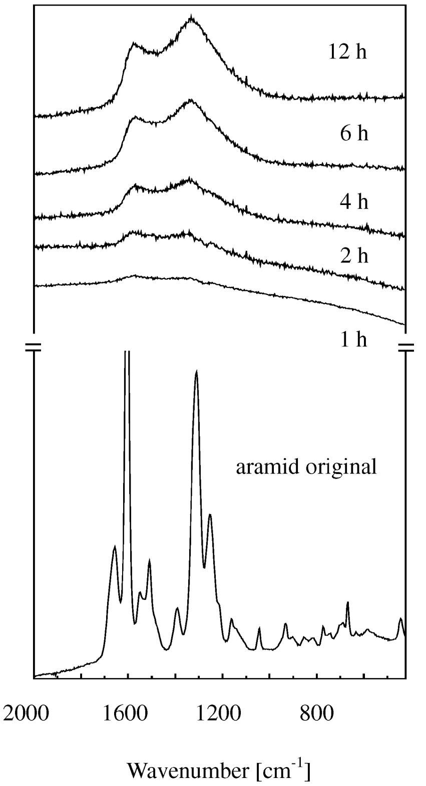

Figure 5 Raman spectra of the original aromatic amide film and samples with different grinding time.

is the graphite band and the broadened one can be assigned to the finite in-plane domain size [14, 15], with other interpretations of the simple D band [16]. XRD analysis does not offer evidence on the carbon sample, suggesting that the small domains with limited quantity are below the limits of X-ray detection. Their presence is detected through the 1320 cm^{-1} peak of the Raman spectra. Also, the widely broadened pattern implies a wide distribution of the formed domain sizes. The results from Raman spectra clearly show the carbonization of the organic phases with the progress of decomposition reaction. In fact, the color of the ground samples becomes black with an increase in grinding time, physically confirming the formation of carbon.

While not shown here, water-soluble nitrite ion was detected by IC analysis although the yield was about 4%. This indicates that the nitrogen in the aramid sample can be oxidized into a nitrite state during the mechanochemical reaction induced by intense grinding.

3.3. Correlation of the decomposition yield of monochlorobiphenyl and generation of radicals

It is interesting to note cases in which the decomposition of chlorinated compounds has been carried out by means of radiation or photocatalysis [17, 18]. The generation of radicals has been reported to be involved in the dechlorination reaction. Our investigation revealed that the results from electron spin resonance (ESR) analysis were most reasonable for relating the function of radical formation to the mechanochemical induced decomposition of BP-Cl.

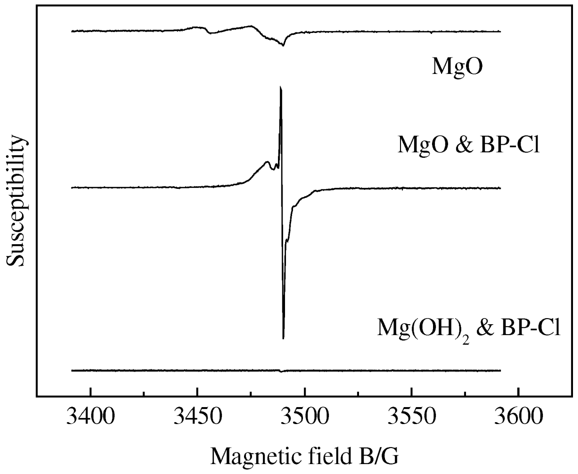

Figure 6 ESR spectra of the 6 h ground samples of MgO and Mg(OH)$_2$ with 5% BP-Cl mixture and MgO 6 h ground sample.

Fig. 6 shows the ESR spectra of the ground samples with MgO and Mg(OH)$_2$ respectively. The absence of BP-Cl caused the ground MgO to give two very weak and broadened peaks, suggesting that unpaired electrons arose from the intense grinding. Two peaks corresponding to the radical generation can be clearly observed from the cogrinding sample, namely MgO/BP-Cl. Similar phenomena occurring in the case of CaO have been reported [13]. On the other hand, no formation of radical was observed from the ground sample with Mg(OH)$_2$. Charge separation did not happen in grinding with the Mg(OH)$_2$. Without the charge transfer from Mg(OH)$_2$ to the absorbed BP-Cl molecule, therefore, the dechlorination on the surface of the Mg(OH)$_2$ would not occur effectively. From this result, it can be concluded that a metal oxide such as MgO can decompose BP-Cl with 100% effectiveness, but metal hydroxide such as Mg (OH)$_2$ can not be decompose BP-Cl.

4. Conclusions

Some specific features of the mechanochemical decomposition of organic polymers can be summarized as follows. The yield of remaining organic compound exhibits a good correlation with that of soluble chloride, suggesting the smooth transformation of chlorine from an organic state to inorganic chloride. On the other hand, various intermediate phases from the decomposition occur, indicating the complexity of the decomposition pathway. The charge separation and subsequent charge transfer induced mechanochemically play an important role in dissociating the Cl—C bonding to achieve dechlorination. The formations of calcium carbonate from organic carbon and nitrite from the NH group after the mechanochemical reactions imply that CaO exhibits a high oxidizing ability toward the organics. It is expected that final products after decomposition can be regulated by choosing oxides with different oxidizing abilities.

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*Received 11 September 2003
and accepted 27 February 2004*