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Comparison of Pb, Cd, Zn, and Cu chlorination during pyrolysis and incineration

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HIGHLIGHTS

- PVC can directly react with ZnO or CuO, while PbO or CdO reacts with HCl from PVC.
- PbO was more easily chloridized than other metal oxides during thermal treatment.
- NaCl alone can convert PbO to $PbCl_2$ via a liquid-solid reaction at >801 °C.

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ABSTRACT

The mechanisms of chlorination of PbO, CdO, ZnO, and CuO by poly(vinyl chloride) (PVC) and sodium chloride (NaCl), including their reaction temperatures, pathways, and products, were studied and compared. It was found that PVC can chloridize the four oxides via different mechanisms, producing corresponding chlorides. The heavy metal oxides in PVC–PbO and PVC–CdO were chloridized by gas–solid reaction with HCl, while direct chlorination by PVC occurred at 190 °C in PVC–ZnO and PVC–CuO, as their initial temperatures for weight loss were 35–44 °C lower than that of PVC decomposition. The relatively facile chlorination of PbO as compared with the other oxides might be a reason why Pb was more volatile than the other metals. NaCl had no chlorination effect on CdO, ZnO, or CuO in the absence of other media. It was found for the first time that NaCl alone could convert PbO to $PbCl_2$ via a liquid–solid reaction when the temperature was higher than the melting point of NaCl (801 °C), and oxygen was not involved. The chlorination effect of NaCl was markedly weaker than that of PVC. Since both PVC and NaCl are the most important chlorine sources in solid waste, their chlorination effects on heavy metals cannot be ignored.

1. Introduction

Waste-to-energy conversion has been an important technology for the treatment of mixed wastes such as municipal solid waste (MSW), medical waste, and hazardous waste. The migration of lead, cadmium, zinc, and copper in wastes during thermal treatments, including pyrolysis and incineration, can lead to secondary environmental pollution [1,2]. Chlorination reactions are crucial to the distribution of heavy metals into gas or solid phases. Chlorine in wastes is mainly from poly(vinyl chloride) (PVC) and sodium chloride (NaCl) respectively [3–6].

High temperature (650–850 °C) and the presence of PVC can enhance volatilization of Pb, Cd, Zn, and Cu [4]. In some cases, PVC can be used to remove heavy metals from fly ash (FA) produced by MSW incineration [7], sewage sludge ash (SSA) [8,9], electric arc furnace dust (EAFD) [10,11] and other wastes [12]. Thermal treatment (850 °C) using PVC (5% by weight) has been found to increase volatilization of the heavy metals Pb, Cd, and Zn by 10–15% [7] in FA; recovery ratios for the metals reached >97.0% at 1000 °C upon addition of PVC to EAFD [11]. Other researchers [8,9] have found that increasing the temperature and PVC content of the SSA could increase the ratios of Pb, Cd, Zn, and Cu removed.

An increased partitioning tendency of some heavy metals into FA or flue gas has also been found when NaCl was added to simulate MSW [4], co-combusted bituminous coal, and recovered solid fuel [12], FA [13], EAFD [14] or other system [15]. In Chiang's study, the effect of inorganic chloride on metal volatilization was less significant than that of organic chloride because Na has a stronger

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affinity for Cl [4] than heavy metals have. Two kinds of chemical reactions have been proposed, i.e., the formation of heavy metal chlorides by the reaction of heavy metal oxides with (1) HCl produced from the reaction of NaCl and H_2O or SO_2 [5,16] and mineral matrixes (e.g., SiO_2 and Al_2O_3) [14,16]; and with (2) gaseous Cl_2 from the reaction of NaCl with mineral matrixes (e.g., SiO_2 and Al_2O_3) [14].

The heavy metal chlorides formed can significantly influence the volatilization of heavy metals during thermal treatment and depend on the temperature and residence time. Studies on the treatment of mixed wastes have generally focused on the volatilization of heavy metals; the present study, however, paid attention to chlorination reactions, which are fundamental to volatilization. Thermal analysis and simulated thermal treatment were utilized to investigate the mechanism of chlorination of heavy metal oxides (PbO, CdO, ZnO, and CuO) by organic chloride (PVC) and inorganic chloride (NaCl). This work examined (1) the temperatures of chlorination and (2) stoichiometry and products of incineration and pyrolysis, and (3) a comparison of chlorination of heavy metal oxides during these processes.

2. Materials and methods

2.1. Materials

Oxides, carbonates, and acetates of the heavy metals Pb, Cd, Zn, and Cu, the most common heavy-metal compounds of concern in solid waste, usually decompose into oxides during heating. Therefore, PbO, CdO, ZnO, and CuO were used as representative heavy metal compounds in this study. Analytical reagent grade PVC (Sigma-Aldrich Corporation, Shanghai, China), NaCl, and metal oxides (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) with particle sizes below 150 μm were dried and blended at ratios indicated in Table 1.

2.2. Thermal analysis experiments

Experiments using simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Q600 SDT; TA Instrument Corporation, USA) were conducted on PVC and NaCl, as well as PVC–PbO, PVC–CdO, PVC–ZnO, PVC–CuO, NaCl–PbO, NaCl–CdO, NaCl–ZnO, and NaCl–CuO mixtures (<40 mg). The heating temperatures for TGA were increased from 50 to 190, 350, 450, 600, 850, or 900 °C at a rate of 10 °C min^{-1}. Gases used for simulating incineration and for pyrolysis, air and N_2 respectively, were introduced at a flow rate of 100 mL min^{-1}. TGA (STA6000; Perkin Elmer Corporation, USA) integrated with Fourier transform infrared (FTIR) spectroscopy (Frontier; Perkin Elmer Corporation, USA) was also used to analyze the gaseous products. In this case, the TGA temperature program for PVC–ZnO and PVC–CuO mixtures consisted of heating from 50 to 190 °C, holding at 190 °C for 30 min, and final heating from 190 to 900 °C. Two TGA instruments were used in the study, and both were calibrated with standard compounds. The FTIR spectral region was scanned at 4000–800 cm^{-1} at a rate of 0.6329 cm s^{-1} and a resolution of 8 cm^{-1}. The temperature of the gas line was set at 220 °C.

2.3. Simulated thermal treatment experiments

A horizontal tube furnace system was used for the simulated thermal treatment experiments. Each sample (1.0–2.0 g) was transferred to a corundum or platinum crucible to prevent interference by Al_2O_3 in the chlorination reactions for NaCl–PbO, NaCl–CdO, NaCl–ZnO, and NaCl–CuO mixtures. It was then heated from 50 to 190, 350, 450, 600, 780, 850, or 900 °C at a rate of 10 °C min^{-1}; residence times were 30–180 min. The residues in the crucibles and the condensates on the surface of the glass rings placed at the end of the quartz tube were collected and analyzed by X-ray diffraction (XRD) measurements (D8 Advance diffractometer, 40 mA and 40 kV; Bruker Corporation, Germany) using Cu Kα radiation. The step size was 0.02° and the scanning time was 0.1 s.

3. Results

3.1. Thermal analysis of PVC

All characteristic temperatures in the TGA, DSC, and DTG curves are summarized in Table 2. According to Fig. 3a and b, PVC decomposition during incineration and pyrolysis can be divided into two stages. During the first stage (225–350 °C), PVC loses 62–64% of its weight, resulting in endothermic peaks at 277 °C (incineration) or 289 °C (pyrolysis) on the DSC curves. The main products of PVC decomposition are HCl and benzene from polycondensation of carbon chains during both incineration and pyrolysis, similar to products observed in other investigations [17,18]. As shown in Fig. 1, HCl started to form at 229 or 250 °C, reaching maximum levels at 285 °C during incineration and 290 °C during pyrolysis. During the second stage of incineration (350–554 °C), PVC loses 36% of its weight (Fig. 3a) because of carbon oxidation and CO_2 volatilization (Fig. 1a). During pyrolysis, the weight loss reached 26% (Fig. 3b), and the main gaseous products were alkanes and alkenes (Fig. 1c), which were also observed by Ma et al. and Yannick et al. [19,20].

3.2. Thermal analysis of PVC and the heavy metal oxide mixtures

The thermal analysis results for the PVC–PbO, PVC–CdO, PVC–ZnO, and PVC–CuO mixtures are summarized in Fig. 3 and Table 2. The relative weight losses of all mixtures in the first stage were less than that of PVC of the same mass. The aforementioned endothermic peak for PVC decomposition during the first stage was replaced by an exothermic peak or was diminished in the presence of heavy metal oxides. In contrast to the TGA curves of PVC, those of the four

Table 1
Mass and molar fractions of PVC, NaCl, and metal oxides in the samples.

Sample	PVC		NaCl		PbO		CdO		ZnO		CuO	
	wt.%	mol%	wt.%	mol%	wt.%	mol%	wt.%	mol%	wt.%	mol%	wt.%	mol%
PVC-PbO	45.5	75.0	–	–	54.5	25.0	–	–	–	–	–	–
PVC-CdO	59.4	75.0	–	–	–	–	40.6	25.0	–	–	–	–
PVC-ZnO	69.7	75.0	–	–	–	–	–	–	30.3	25.0	–	–
PVC-CuO	70.1	75.0	–	–	–	–	–	–	–	–	29.9	25.0
NaCl-PbO	–	–	34.4	66.7	65.6	33.3	–	–	–	–	–	–
NaCl-CdO	–	–	47.7	66.7	–	–	52.3	33.3	–	–	–	–
NaCl-ZnO	–	–	59.0	66.7	–	–	–	–	41.0	33.3	–	–
NaCl-CuO	–	–	60.0	66.7	–	–	–	–	–	–	40.0	33.3