

Cl₂ Gas Recovery from Waste PVC

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Hydrogen chloride, evolved from polyvinyl chloride by heating at 533 K, was fixed by metal oxides at 533-673 K to form corresponding metal chlorides. The metal chlorides thus formed were calcined at 623-723 K under an oxygen flow in order to recover chlorine gas and to regenerate the metal oxides. Among the metal oxides employed, cobalt oxide was the most effective both for the fixation and release of chloride ions. With the iterative use of cobalt oxide for HCl fixation at 573 K and subsequent Cl₂ release at 673 K, the amount of chloride ions fixed by cobalt oxide powder decreased to one-fifth of those fixed by the fresh cobalt oxide. This is due to the decrease in the BET surface area of cobalt oxide caused by the iterative use.

Introduction

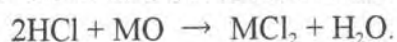
Plastic wastes available to commercial plants are strictly limited to polyethylene, polypropylene and polystyrene, but polyvinyl chloride (PVC) waste is excluded because of the evolution of corrosive gases containing chlorine and because of the resultant contamination of the fuel oils with chloride ions. In order to overcome these problems, dehydrochlorination of PVC has been studied. However, most of the investigations have been concerned with the kinetics or mechanisms of dehydrochlorination of PVC resin during thermal degradation. A key technique for the conversion of mixed plastic waste (MPW), including PVC, into fuel oils is the elimination of hydrogen chloride (HCl) from PVC and the subsequent fixation of the HCl gas evolved. Preheating MPW at temperatures lower than 573 K is the conventional way for HCl evolution from PVC; more than 99.9 % of chloride ions in PVC were evolved from MPW, containing around 15 wt % PVC, by heating at 573 K [1]. Kaminsky et al. used lime for HCl fixation [2] and Saitou employed an aqueous solution of NaOH as a HCl trap [3]. Though these two methods will be used commercially, chloride ions in the PVC are lost when disposed in the form of CaCl₂ or NaCl. In the present work, the development of techniques to recover chlorine gas from PVC waste has been attempted using metal oxides for the fixation of HCl evolved from PVC and subsequent Cl₂ release from resultant metal chlorides.

Experimental

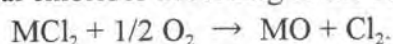
Fixation of chloride ions and release of chlorine gas

Fig. 1 shows the apparatus used for HCl fixation by metal oxides and Cl₂ release from the resultant metal chlorides. Apparatus consists of two reactors; one is for the evolution of HCl from 1 g of pure PVC resin by heating at 533 K. Hydrogen chloride evolved was introduced

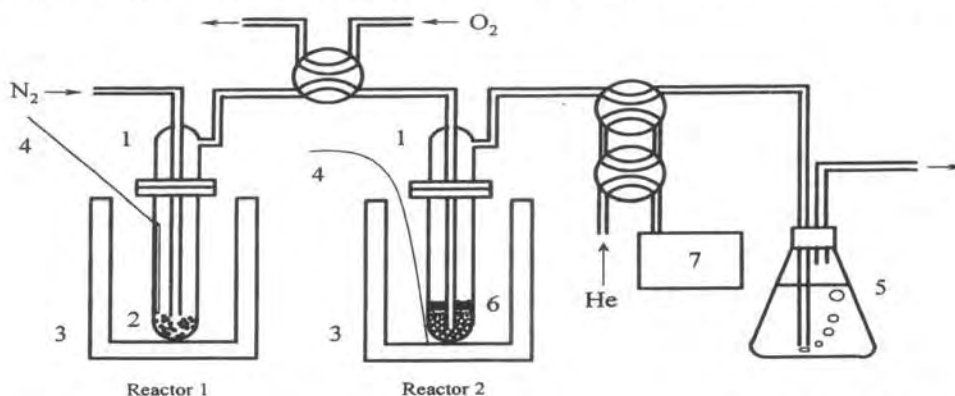
from 1 g of pure PVC resin by heating at 533 K. Hydrogen chloride evolved was introduced into the second reactor with N₂ flowing (50 ml/min), where metal oxide powders were placed and heated at 523-673 K in order to fix or react with HCl gas as follows;



Since the amount of HCl gas evolved from 1 g of pure PVC is calculated to be 0.583 g, the amount of metal oxides to react with 0.583 g of HCl gas can be estimated. Hydrogen chloride passed through the second reactor was directly measured by gas chromatography at 30 min intervals during the reaction, or was collected in a reservoir, filled with distilled water, to be measured by an ion analyzer. When no more HCl gas was evolved from the PVC, the gas introduced into the second reactor was changed from N₂ to O₂ (50 ml/min) using a four-way valve. The second reactor was then heated up to 623-723 K in order to release Cl₂ gas from the resultant metal chlorides according to the following reaction;



Amount of Cl₂ gas released was directly measured by gas chromatography at 15 min intervals during the reaction, and the total amount of Cl₂ released was calculated by integration of the observed curve (Cl₂ gas released vs reaction time). For iterative tests of cyclic HCl fixation and Cl₂ release, dehydrochlorinated PVC in the first reactor was replaced with another 1 g of the pure PVC resin while the oxidization of chlorinated metal oxides was carried out.



1:reactor, 2:PVC resin, 3:heater, 4:thermocouple, 5:water trap, 6:metal oxide, 7:GC

Fig.1 Apparatus for HCl fixation and Cl₂ release on metal oxides

Measurement of hydrogen chloride and chlorine gas

Amount of HCl evolved from the PVC resin was measured by two methods; in the first method, gas chromatography (GC-390B, GL Science) was employed using a column packed with Daifl oil (#10) dispersed on Flusin T60/80. All tubes and valves in the GC machine were coated with teflon to protect against corrosion caused by hydrogen chloride and chlorine gas. In the second method, liquid chromatography (Ion Analyzer- PIA-1000, Shimadzu) was used, where HCl was trapped in distilled water to be submitted to the analyzer. Amount of Cl₂ gas recovered from resultant metal chlorides was directly measured by GC.

Preparation and characterization of metal oxides

Metal oxides employed were MgO, BaO, CaO, TiO₂, Cr₂O₃, Fe₂O₃, Co₃O₄, CuO, and ZnO. Among them, BaO and CaO were prepared from the corresponding carbonates by firing

isopropoxide, followed by firing at 823 K for 4h. Other oxides were prepared from aqueous solutions of corresponding metal nitrates using ammonium hydroxide as a precipitant. Since it was found that Co_3O_4 was the most effective for the fixation and release of chloride ions, Co_3O_4 was used for iterative tests of HCl fixation and Cl_2 recovery. Changes in the BET surface area of the regenerated Co_3O_4 were measured after HCl fixation/ Cl_2 release cycle.

Results and Discussion

Activities of various metal oxides at 573 K for the fixation of 0.583 g of HCl evolved from 1 g of PVC resin are listed in Table 1, together with the X-ray crystallographic structures after HCl fixation. Amount of metal oxides used is the amount needed for the reaction with 0.583 g of HCl (stoichiometric amount).

Table 1 HCl fixation on various metal oxides at 573 K and XRD crystallographic structure

Metal oxide	Amount of HCl fixed (g)	X-ray structure after HCl fixation
Non	0.525 ^a	—
MgO	0.317	MgO, $\text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$
BaO	0.15	BaO, BaCl_2
CaO	0.139	CaO, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$
TiO_2	0.017	TiO_2
Cr_2O_3	0.02	Cr_2O_3
Fe_2O_3	0.047	Fe_2O_3
Co_3O_4	0.361	Co_3O_4 , $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$
CuO	0.358	$\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, CuCl, Cu_2OCl_2
ZnO	0.191	ZnO, unknown

^a Amount of HCl evolved from 1 g of PVC at 533 K for 3 h.

Fig. 2 shows the activity of Co_3O_4 for HCl fixation at various temperatures, where 0.642 g of Co_3O_4 (stoichiometric amount) was employed for the fixation of HCl from 1 g of PVC. Fig.2 also shows the change in the amount of HCl fixed at 573 K with the amount of Co_3O_4 used, indicating that more than 90 % of HCl from 1 g of PVC was fixed when 1.12 g (1.75 times of the stoichiometric amount) of Co_3O_4 was used.

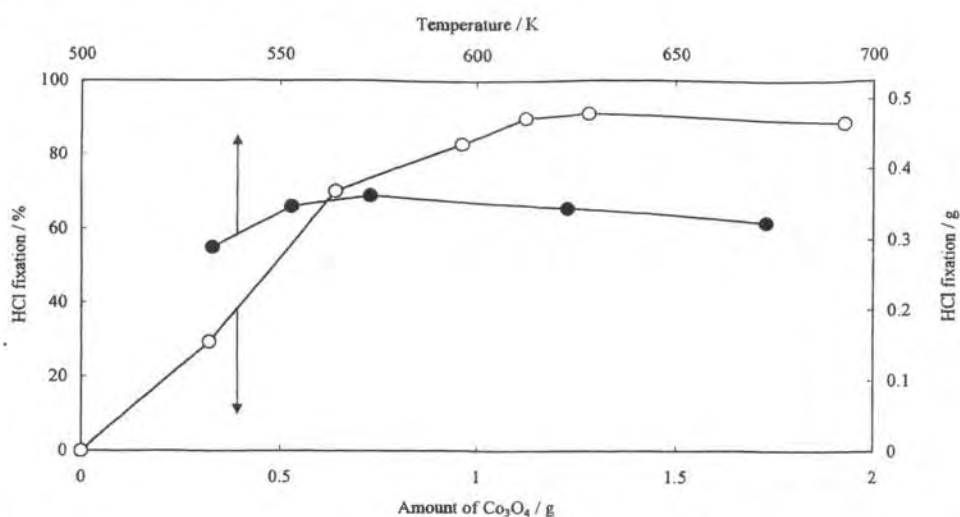


Fig.2 Effects of temperatures and amounts of Co_3O_4 used upon HCl fixation

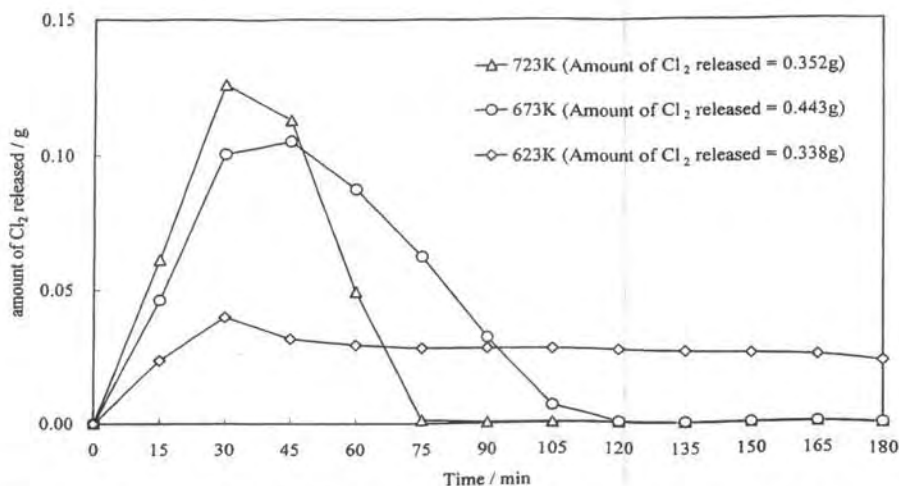


Fig.3 Cl₂ recovery from chlorinated Co₃O₄ at various temperatures

Fig. 3 shows the amount of Cl₂ recovered from the resultant CoCl₂ by following reaction at various temperatures; $3\text{CoCl}_2 + 2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + 3\text{Cl}_2$. From these results, it was found that Co₃O₄ worked well at 573 K for HCl fixation and that the resultant CoCl₂ released Cl₂ well at 673 K, respectively. Hence, the iterative tests for HCl fixation at 573 K and subsequent Cl₂ release at 673 K were carried out using 1.12 g of Co₃O₄, and the results are illustrated in Fig.4. Amounts of HCl fixed and Cl₂ recovered decreased monotonously with the iteration number. At the 5th cycle, amounts of HCl fixed and Cl₂ released were down to about one-fifth of those observed for the fresh Co₃O₄. The activity decrease is attributed to the significant decrease in the BET surface area of Co₃O₄ regenerated after Cl₂ gas release at 673 K.

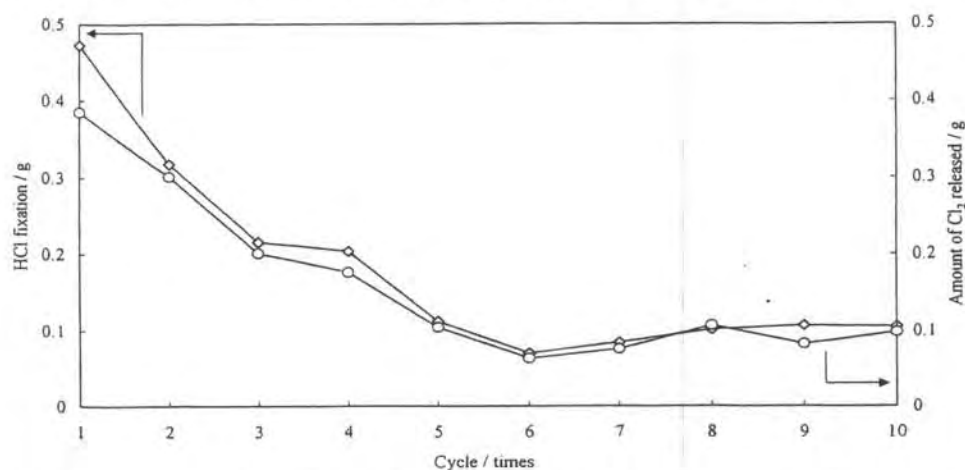


Fig.4 Iterative test for HCl fixation at 573 K and Cl₂ release at 673 K on Co₃O₄

References

- 1) Saitou, K. Kagaku-to-Kougyou (Chemical Industry), 66 (1992) 438 (in Japanese).
- 2) Kaminsky, W.; Schlesselmann, B.; Simon, C. Polym. Degrad. Stab., 53 (1996) 189.
- 3) Saitou, K. Annual Report of Agency for Industrial Science and Technology, Ministry of International Trade and Industry, Japan, 1990, p.37 (in Japanese).