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Introduction

The disposal of halogenated waste plastics is a serious environmental problem. Conversion of halogenated waste plastics into a fuel oil was considered to be the suitable option for the recovery of energy and also chemical feedstock. During pyrolysis of poly (vinylchloride) (PVC- C_2H_3Cl) and poly (vinylidene chloride) (PVDC- $C_2H_2Cl_2$) containing mixed waste plastics, chlorine evolves mostly as hydrogen chloride (HCl), in the preliminary stages of pyrolysis process. Hydrogen chloride (HCl) is also emitted in significant quantities by utility and industrial coal-fired furnaces as well as municipal, medical, and hazardous waste incinerators. Removal of HCl is essential since it is harmful, corrosive and it may lead to formation of halogenated organic compounds during pyrolysis process of the chlorinated waste plastic [1]. In the present study, we have examined the calcium and iron based sorbents for the removal of hydrogen chloride gas and optimized the reaction conditions.

Experimental

Sorbents used in the present study: The carbon composites of calcium carbonate sorbent (Ca-Z), iron oxide sorbent (Fe_3O_4) (TR-00301) was cooperatively developed with the Toda Kogyo Corporation, Hiroshima, Japan.

The cylinder containing 2.01%(v/v) hydrogen chloride balance nitrogen was used in the present study.

Adsorption of HCl gas: Adsorption of hydrogen chloride was carried out using the fixed bed micro reactor (dia: 8 mm, length: 470 mm) at

atmospheric pressure. Briefly, about 2 g of sorbent was loaded into the reactor in between two quartz wool plugs and reactor temperature was increased linearly ($5^{\circ}C/min$) to $350^{\circ}C$ in nitrogen atmosphere (50 ml/min) and kept for hour for the pretreatment of the sorbent. The known concentration (2.01% v/v) of hydrogen chloride gas mixed with nitrogen was fed to the reactor and the outlet of reactor gases (HCl) were trapped using ion-exchanged water (600 ml). The quantitative analysis of hydrogen chloride gas was analyzed by Ion chromatograph (DIONEX: DX-120). The adsorption isotherms were plotted taking adsorption time (hour) on X-axis and the quantitatively estimated outlet HCl concentration (from Ion chromatograph) on Y-axis. The inlet HCl concentration (for a period of 1 h) fed into the reactor was estimated in a separate experiment.

Results and Discussion

The adsorption of hydrogen chloride gas on Ca-Z and TR-00301 was carried out using fixed bed micro reactor at $350^{\circ}C$ and adsorption isotherms were presented in Fig 1. The other experimental conditions for adsorption were Av. dia. of adsorbent (particle size) 1mm, total gases flow 535 ml/min, inlet HCl concentration 1820 ppm. Figure 1 shows that the calcium based sorbent was found to be effectively adsorbed the hydrogen chloride gas for a period of 7 h (breakthrough point) with zero ppm at the outlet and reached saturation level at around 14 h. However, the adsorption of HCl with TR-00301 showed that the HCl was leaking

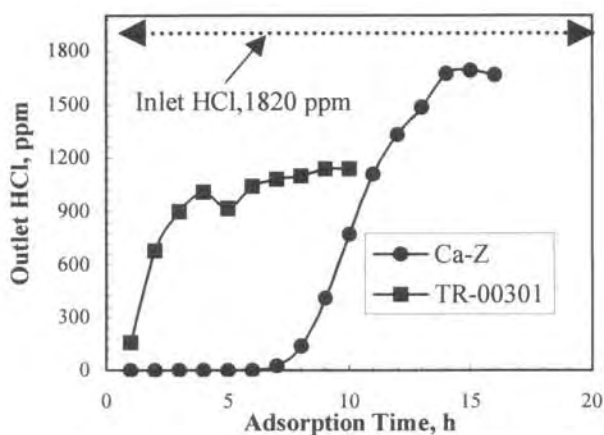


Fig 1. HCl gas adsorption on Ca-Z and TR-00301 sorbents at 350°C

from first hour onwards and reached saturation level at around 4 h. The carbon composite of calcium based sorbent (Ca-Z) was found to be suitable for the adsorption of hydrogen chloride (Figure 1). It is well known that the adsorption capacity of sorbent depends on various factors like sorbent particle size (Av.dia), inlet HCl concentration, total gas flow, adsorption temperature, porosity, and total surface area. The adsorption conditions optimized for the Ca-Z sorbent for the maximum utilization of sorbent capacity. The effect of temperature on the adsorption capacity

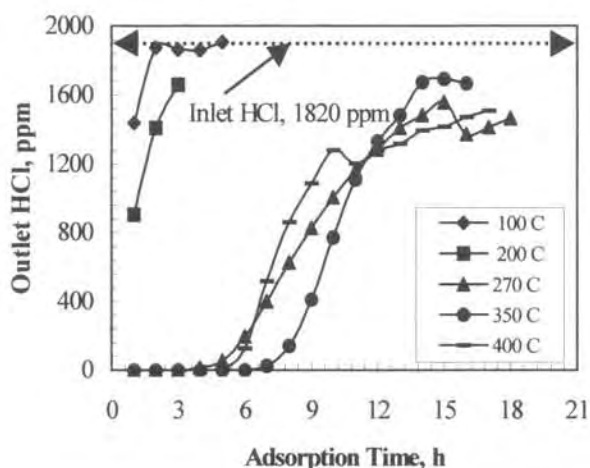


Fig 2. Effect of adsorption temperature on adsorption capacity of Ca-Z (2g)

of Ca-Z was studied and the adsorption isotherms were presented in Fig 2. The adsorption capacity of Ca-Z was found to

be maximum at 350°C with the 7h-breakthrough time. The effect of sorbent

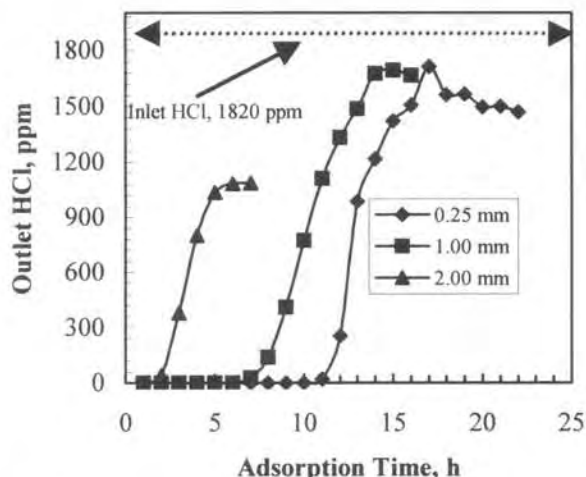


Fig 3. Effect of adsorbent particle size (Av. dia) on adsorption capacity of Ca-Z (2g) at 350°C

particle size on the adsorption capacity of Ca-Z was studied and the results were presented in Fig. 3. The amount of HCl adsorbed before breakthrough was increased with the decrease of particle size. For 0.25 mm particles, the amount of HCl adsorbed was maximum and it was 63% of the theoretical adsorption capacity of Ca-Z based on the solid gas reaction:



The other adsorption parameters like effect of total gas flow, effect of inlet HCl concentration was also studied on Ca-Z and suggested that total gas flow of 535 ml/min and 1820 ppm of inlet HCl was found to be optimum. The Ca-Z sorbent was used for the complete adsorption of HCl from waste plastic pyrolysis [2].

The Powder X-ray diffraction patterns of Ca-Z and TR-00301 sorbents show the presence of CaCO_3 and Fe_3O_4 phases respectively. After the adsorption of hydrogen chloride the XRD results suggests the formation of $\text{CaCl}_2 \cdot n\text{H}_2\text{O}$ for Ca-Z and $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ for TR-00301.

References

- [1] M.A. Uddin, Y. Sakata, Y. Shiraga, A.Muto, and K. Murata, *Ind. Eng. Chem. Res.* 1999, **38**, 1406.
- [2] Kaneko et al, *Proc. of Annual meeting of FSRJ2001*, 1-6, Fukuoka, Nov. 29-30, 2001.