

A new catalytic system for the removal of chlorine compounds from PVC containing waste plastic derived oil

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Introduction

The disposal of waste plastics has been recognized as a major environmental problem. Waste plastics are undesirable components for landfilling, since they are not biodegradable. At the same time, waste plastics are regarded as a cheap and abundant source of chemicals and energy. The conversion of waste plastics into useful fuel oil has been considered as the most promising recycling method [1]. The main problem poses during the recycling of waste plastics are associated with PVC. The waste plastics contain all kinds of plastics including PVC. The pyrolysis of these PVC mixed waste plastics (PVMIX) leads to the production of chloroorganic compounds [2]. It is necessary to remove chloroorganic compounds before the refinement of PVMIX-derived oil.

We have been developing a catalyst system for dehydrochlorination (DHC) of PVMIX [2] using iron oxide carbon composite catalysts. In the present study, we are reporting a new $\text{FeCl}_2/\text{SiO}_2$ catalyst system for the DHC of chloro organic compounds from the PVMIX-derived oil. The DHC of model chloro alkanes like chlorocyclohexane and 1-chloroheptane was also carried over these catalysts to understand more about DHC reaction.

Experimental

The waste plastic derived oil was prepared by degrading the mixed plastics containing PE (33%), PP (33%), PS (33%) and PVC (1%) as a model sample. The oil derived from mixed plastic degradation contains 1152 ppm of organic chlorine compounds. The $\text{FeCl}_2/\text{SiO}_2$ catalysts are prepared by impregnation method using required amount of aqueous iron chloride solution.

After allowing the adsorption of iron chloride on silica for over night, the excess solution was evaporated and dried in air oven at 120 °C for 12 h. The catalysts are calcined in inert atmosphere at 350 °C for 3 h.

The dehydrochlorination reaction was carried out on a fixed bed micro reactor at atmospheric pressure with a reaction temperature of 350 °C. In the DHC of model chloro alkanes, the catalysts were pretreated in He flow at 300 °C for 1 h. The reactant (3 ml/h) was fed by a micro feeder along with the carrier gas He (40 ml/min) into the reactor in which the catalyst (about 0.5 ml) was suspended between two quartz wool beds. The same reactor set up was used for the dechlorination of plastic derived oil. In this case, a LHSV of 10 h⁻¹ was maintained. The chlorine content in the waste plastic derived oil was measured using a GC with atomic emission detector (GC-AED).

Results and Discussion

Firstly, the catalytic activity of $\text{FeCl}_2/\text{SiO}_2$ catalysts was tested in DHC of model chloro organic compounds. The chloro cyclohexane(CCH) and 1-chloroheptane(1-CH) are used as model chloro organic compounds. The effect of iron chloride content in the dechlorination of CCH and 1-CH is studied and the results are presented in Figure 1. The dechlorination of CCH and 1-CH over these catalysts lead to the formation of cyclohexane and 1-heptene as major products (about 98% selectivity) respectively.

The results from Fig. 1 suggests that the $\text{FeCl}_2/\text{SiO}_2$ catalysts are selectively dechlorinating the chloro alkanes and the dechlorination activity is found to be

highest at the FeCl_2 loading about 3~6 wt%. The main problem associated with the dechlorination reaction was the deactivation of the catalyst by HCl , produced during the reaction [3].

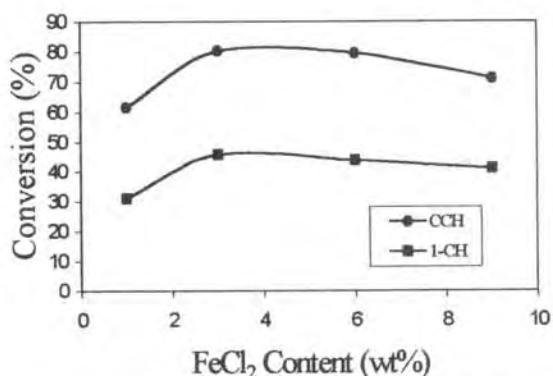


Fig. 1. DHC of CCH and 1-CH over $\text{FeCl}_2/\text{SiO}_2$ catalysts

The time on stream analysis over these catalysts was carried out to understand the stability of these catalysts. These results are presented in Figure 2. It is important to note that the catalysts showed high activity and stability except a slight initial deactivation.

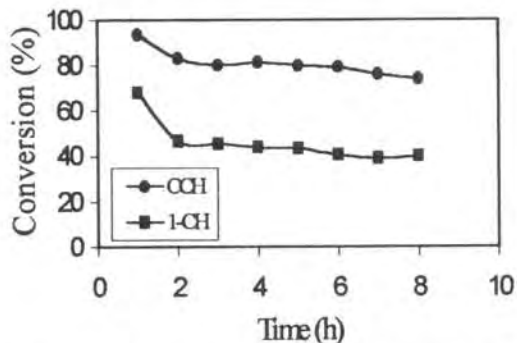


Fig 2. Time on stream analysis: DHC of chloro alkanes over 6wt% $\text{FeCl}_2/\text{SiO}_2$ catalyst.

After knowing these catalysts activity in dechlorination of model chloro alkanes further experiments were carried out on the dechlorination of PVMIX derived oil. The amounts of removal of chlorine content over different $\text{FeCl}_2/\text{SiO}_2$ catalysts at reaction temperature of 350 °C are presented in Figure 3. These results show that these catalysts effectively removed the chlorine content. The activity patters in the dechlorination of PVMIX-derived oil are

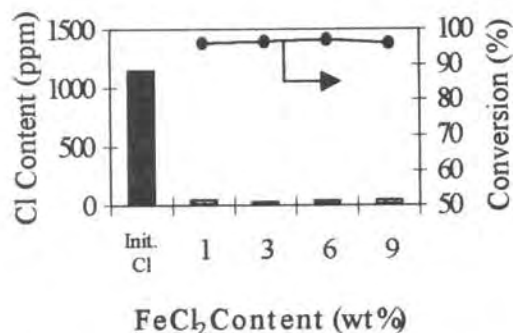


Fig 3. DHC of PVMIX over $\text{FeCl}_2/\text{SiO}_2$ catalysts.

similar to that of model chloro alkanes dechlorination. This result suggests that the $\text{FeCl}_2/\text{SiO}_2$ catalysts are very active in selectively removing the various chloro organic compounds from the PVMIX derived oil.

The time on stream analysis over 6wt% $\text{FeCl}_2/\text{SiO}_2$ catalyst was carried out to understand the stability of these catalysts. The results are presented in Figure 4. It is noteworthy that this catalyst is showing high stability with very high activity whereas catalyst deactivation in dechlorination reaction is very common due to the poisoning of catalyst surface by HCl that produced during the reaction.

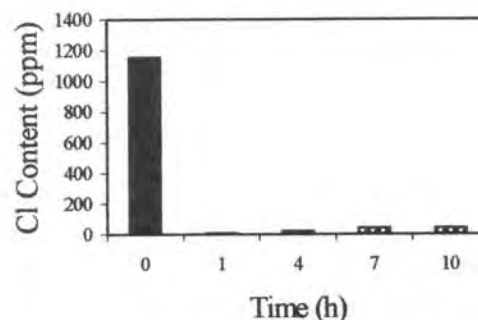


Fig 4. Time on stream analysis: DHC of PVMIX over 6wt% $\text{FeCl}_2/\text{SiO}_2$ catalyst.

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