

Dehydrochlorination of Organic Chlorine Compounds over Iron Oxide Carbon Composite Catalysts for the Refinement of Waste Plastic Derived Oil.

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The dechlorination of model chloro alkanes such as chloro cyclohexane and 1-chloroheptane was carried out over various iron oxide and iron oxide-carbon composite catalysts. The dechlorination of chloro organic compounds from the product oil derived from PVC containing waste plastics degradation was studied further. The iron oxide catalysts were found to be stable and selective for the dechlorination of chloro alkanes even in the presence of HCl produced during the reaction. In the dechlorination of waste plastic derived oil, it was observed that the catalytic activity was stable after the initial deactivation.

Introduction

Conversion of waste plastics into fuel oil by thermal or catalytic degradation have been considered for the recycling of waste plastics as an energy source [1]. The degradation of mixed waste plastics containing PVC leads to the formation of chlorine compounds [2]. When the plastic derived oil is used as fuel, the chlorine compounds corrode instruments and produce harmful substances. In order for the waste plastic derived oil to qualify as fuel, it is necessary to remove as much chlorine as possible. Many methods have been reported for the dechlorination of chloro organic compounds [3]. Catalytic dechlorination is of increasing interest because it excludes the formation of more toxic compounds such as dioxins and has a low reaction temperature [4].

In this work, we report the dechlorination of model chloro alkanes such as chlorocyclohexane and 1-chloroheptane over iron oxide-carbon composite catalysts. Further study carried out for the removal of chlorine compounds from the product oil derived from PVC containing mixed plastics in order to examine the possibility of the application of the catalyst in practical process.

Materials and Methods

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 plastics degradation contains 1894 ppm of organic chlorine compounds.

The iron oxides α -FeOOH, γ -Fe₂O₃ and TR97305 (Fe₃O₄- carbon composite) catalysts were supplied by Toda Kogyo Corporation, Japan. The TR97305 was prepared using 90 wt% α -FeOOH and 10 wt% phenol resin and treated at 530°C in nitrogen flow. This catalyst contained the crystalline phase of Fe₃O₄ and 6.7 wt% amorphous carbon.

The dechlorination reaction was carried out on a fixed bed micro reactor at atmospheric pressure with a reaction temperature of 300~400°C. In the dechlorination of model chloro alkanes, the catalysts were pretreated in He flow at 300°C for 1 h. The reactant (1.2 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 1 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 20 h^{-1} was maintained. The products were collected at the outlet of the reactor in a cold trap and analyzed by gas chromatography. The chlorine content in the waste plastic derived oil was measured using a GC with atomic emission detector (GC-AED).

Results and Discussion

The activity data of the vapour phase catalytic HDC of chlorocyclohexane and 1-chloroheptane over $\alpha\text{-FeOOH}$, $\gamma\text{-Fe}_2\text{O}_3$ and TR97305 are presented in Figure 1.

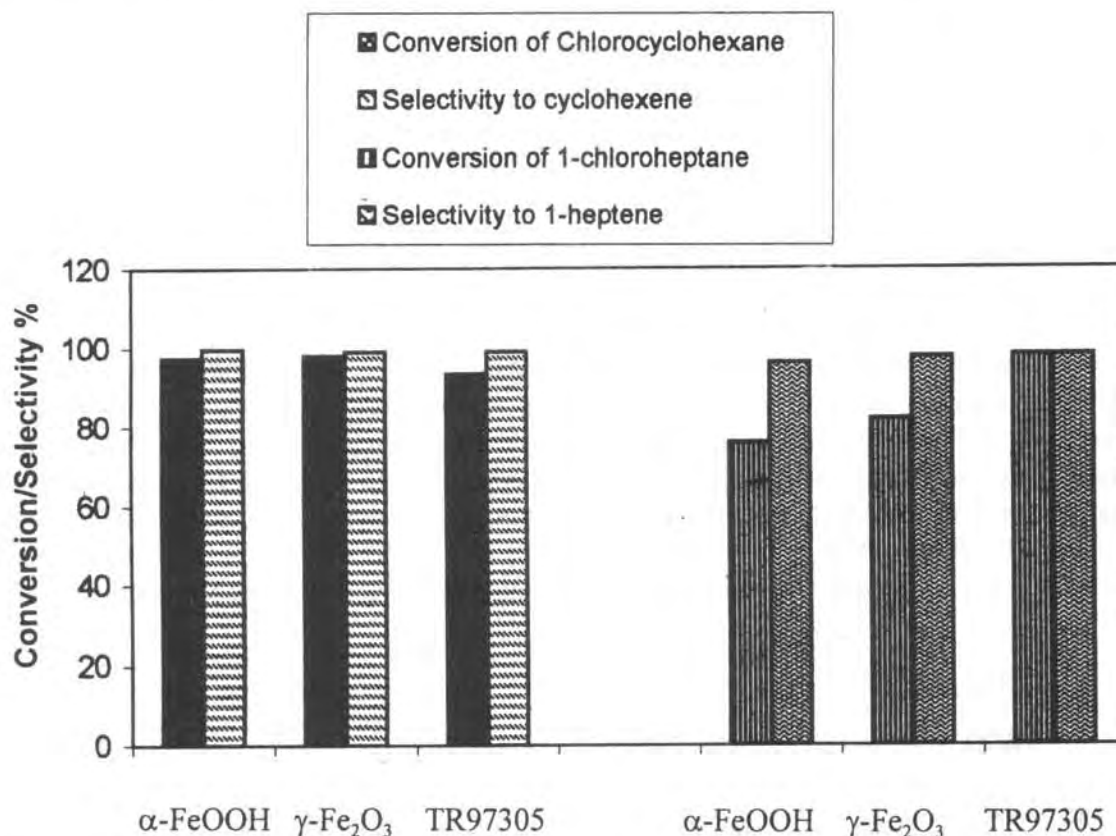


Figure 1. Conversion and selectivity data during the dechlorination of chlorocyclohexane and 1-chloroheptane over various iron oxide catalysts.

The HDC of chlorocyclohexane and 1-chloroheptane over these catalysts leads to the formation of cyclohexene and 1-heptene as major products (about 98% selectivity) respectively. In the absence of a catalyst, the conversion of chloro alkanes was about 1.6 %, implying that the reaction was catalytic. These results suggest that the dechlorination of chloro alkanes occur over iron oxide catalyst to produce hydrocarbon and HCl. The main problem associated with the dechlorination reaction was the initial deactivation of the catalyst by HCl, produced during the reaction [5].

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 whereas catalyst deactivation in dechlorination process has been ascribed to a poisoning of the surface by HCl produced in the reaction by forming metal chloride [6, 7].

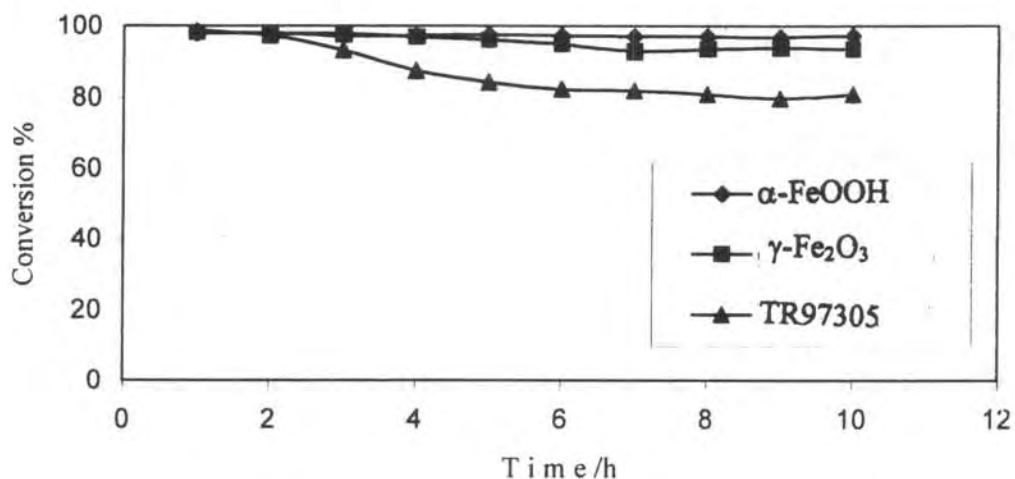


Figure 2. Time on stream analysis: Dehydrochlorination of chlorocyclohexane over iron oxide catalysts.

Dechlorination of product oil derived from PVC containing waste plastics over TR97305 catalyst was carried out at a reaction temperature of 350 °C and the results were presented in Figure 3. The initial chlorine content in the product oil was 1894 ppm. From figure it can be noted that catalyst removed a considerable amount of chlorine. Initially the catalytic activity was very high and reduced with time and eventually became stable for a long period. The deactivation of the catalyst might be due to the adsorption of HCl on the catalyst surface or due to the deposition of coke on the catalyst surface. The deactivation of catalyst by

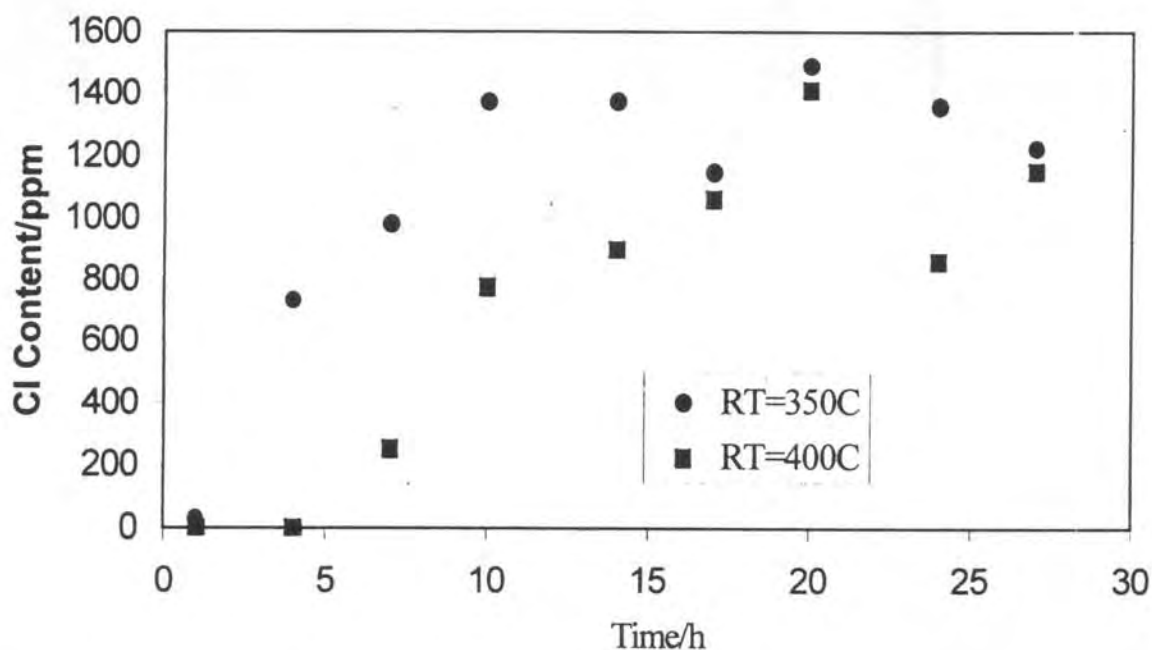


Figure 3. Removal of chlorine from PVC containing waste plastic derived oil with time at different temperatures over TR97305 catalyst

selective adsorption of HCl on catalyst active centers is well known in the dechlorination reaction [5]. However, in the model reaction no deactivation was observed due to HCl. The deactivation during dechlorination of waste plastic derived oil may be due to coke deposition.

The effect of space velocity on the dechlorination of waste plastic degradation oil over TR97305 is presented in Figure 4. The result shows that with increasing space velocity the activity for chlorine removal decreased as it is generally observed in catalytic reactions.

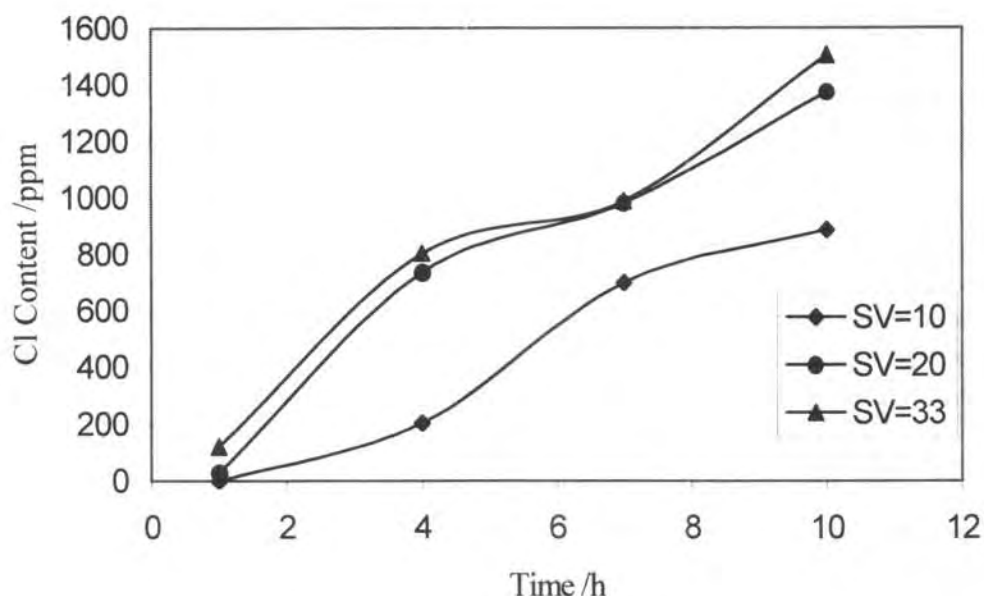


Figure 4. Effect of space velocity in the dechlorination of waste plastic derived oil over TR97305 at reaction temperature of 350°C.

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