Selective Catalytic Dechlorination of Chloro Alkanes over Iron-based Catalysts

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A selective vapour phase dehydrochlorination (DHC) of chloro alkanes was achieved over a simple iron oxide catalyst system. The chloro alkanes were selectively dehydrochlorinated to their corresponding alkenes. This catalyst was also found to be effective for the removal of chlorine from fuel oil derived from the degradation of PVC containing waste plastics.

Chlorinated organic compounds are the most prevalent contaminants in industrial organic waste pollutants and these compounds are potential threats to the environment.[1] Catalytic dechlorination method, that converts chlorinated compounds to less toxic dechlorinated ones have been developed as an alternative to incineration for the disposal of such compounds.[2] In general the catalytic dechlorination is achieved in presence of hydrogen over a noble metal catalyst.[3]

A large number of research papers reported on DHC of chloro alkanes.[4] Mochida et al studied extensively on the DHC of 1,2 dichloroethane and 1,1,2-trichloroethane.[5] There are also few reports on DHC of chlorocyclohexane, achieved in the presence of hydrogen over Ni/SiO_2 catalyst.[6] However, in that study, the DHC was carried in presence of hydrogen and the catalyst was readily deactivated within 2-4 h by the HCl produced during the reaction. In the present system the removal of chlorine is achieved in the absence of hydrogen over an iron oxide catalyst system with high stability, activity and selectivity. The dechlorination of aliphatic chlorine compounds is also very important in the removal of chlorine from the PVC containing waste plastics. In this communication, we report for first time the removal of chlorine from chloroalkanes selectively by vapour phase catalytic DHC using iron oxide based catalysts.

In this study chlorocyclohexane and 1-chloroheptane are used as model chlorine containing compounds. The iron oxide catalyst system used in this system was also extended to the practical removal of chlorine from fuel oil derived from PVC containing waste plastics.

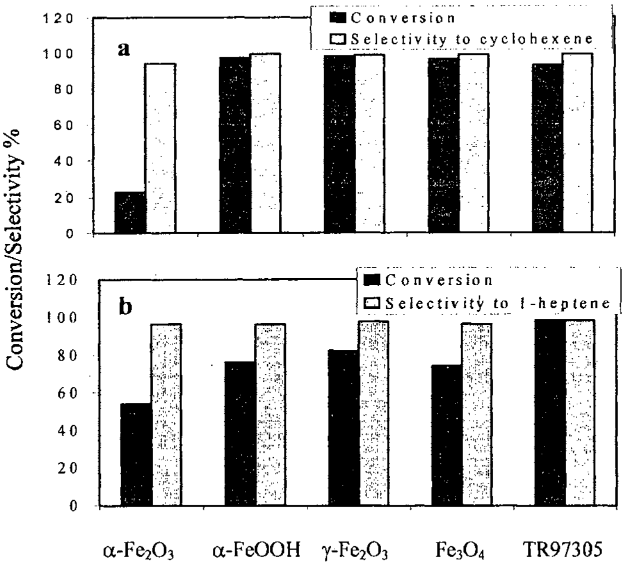

Figure 1. Conversion and selectivity data during the dehydrochlorination of (a) Chlorocyclohexane (b) 1-Chloroheptane over various iron oxide catalysts.

The iron oxides α-FeOOH, α- and γ-Fe_2O_3, Fe_3O_4, TR97305 (Fe_3O_4-carbon composite) catalysts used in this study were supplied by Toda Kogyo Corporation, Japan. The surface areas of these catalysts are 56, 4, 13, 5 and 74 m^2/g respectively. The TR97305 was prepared using 90 wt% α-FeOOH and 10 wt% phenol resin and treating at 530 °C in nitrogen flow. This

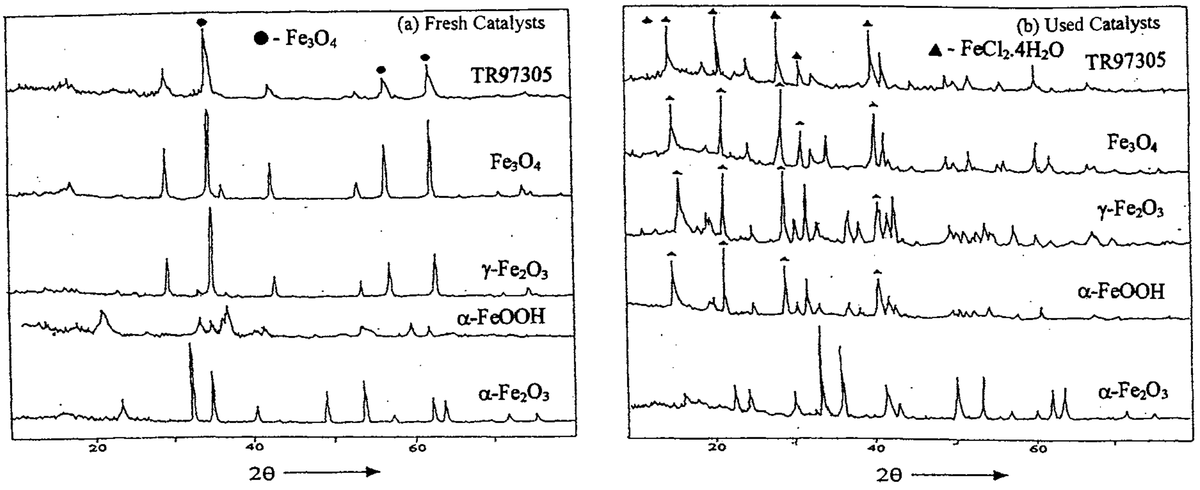

Figure 2. X-Ray diffraction patterns of the fresh and used iron oxide catalyst.

iron oxide-carbon composite contains the crystalline phase of Fe_3O_4 and 6.7 wt% amorphous carbon. The iron oxide-carbon composite catalyst was prepared in order to increase the mechanical strength of the iron oxide catalyst particle.

The DHC reaction was carried out on a fixed bed micro reactor at atmospheric pressure with a reaction temperature of 300°C. About 1 ml of catalyst was loaded in the reactor and pretreated in He flow (60 ml/min) at 300 °C for 1 h. The reactant was fed in to the reactor by means of micro feeder at a flow rate of 1.2 ml/h along with He as carrier gas (30 ml/min). The products were analyzed by gas chromatography.

The gas phase catalytic DHC of chlorocyclohexane over iron oxide catalyst leads to the formation of cyclohexene as the major product with selectivities of over 98%. The other products (<2%) were identified as methylcyclopentene and chlorocyclohexene. The 1-chlorohepatane also yields the DHC product 1-heptene with a selectively of about 97%.

The conversions and main product selectivities for DHC of chlorocyclohexane and 1-chloroheptane over various iron oxide catalysts are presented in Figure1 (a) and (b) respectively. The iron oxides γ-Fe_2O_3, Fe_3O_4, α-FeOOH, TR97305 (Fe_3O_4-carbon composite) showed a high activity and selectivity in the DHC of both chlorocyclohexane and 1-chloroheptane, where as the α-Fe_2O_3 showed a lower activity. The reaction carried out in the absence of a catalyst chlorocyclohexane conversion was only about 1.6%, implying that the reaction is catalytic. In order to elucidate the different behaviour of α-Fe_2O_3 in contrast with the other iron oxides, the catalysts were characterized by XRD after the reaction. The XRD patterns of the fresh and used catalysts are presented in Figure 2. The XRD of used catalysts shows the patterns relative to the $FeCl_2.nH_2O$ (n=2,4). The used α-Fe_2O_3 catalyst did not show major $FeCl_2$ patterns. It is possible that the HCl produced during the reaction reacts with the oxide and converts it to chloride phase. The α-Fe_2O_3 may not able to convert to the chloride phase during the reaction causing the HCl to be adsorbed physically on the active sites of the catalyst leading to a decrease in activity. Another reason for lower activity of α-Fe_2O_3 might be due to its lower surface area (4 m^2/g). However, the surface area may not be directly related to the activity since Fe_3O_4 also possessing lower surface area but shows good activity.

The conversion of iron oxide to $FeCl_2$ phase during the reaction gives rise to the doubt that the iron oxide is actually acting as a catalyst or an adsorbent. In order to elucidate this, a separate experiment was carried first by treating the iron oxide catalyst (TR97305) with HCl gas at 400 °C for 4 h. During this treatment the oxide converted to chloride phase and the reaction was carried out using this catalyst. The activity data of this catalyst is shown in Figure 3. Interestingly, the HCl treated catalyst showed an activity and selectivity with high stability similar to those of iron oxide catalysts. This result suggest that the iron oxide acts as a catalyst initially and under the reaction conditions it converted to $FeCl_2$ by interacting with the produced HCl, $FeCl_2$ is also catalytically active for this reaction.

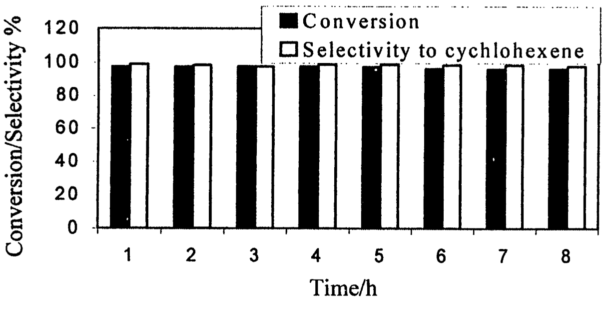

Figure 3. Activity and selectivity during dehydrochlorination of Chlorocyclohexane over HCl treated TR97305 catalyst.

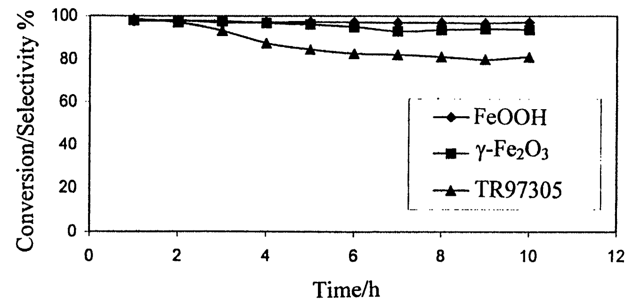

Figure 4. Time on stream analysis: Dehydrochlorination of chlorocyclohexane over iron oxide catalysts.

The time on stream analysis of the catalysts γ-Fe_2O_3, α-FeOOH, TR97305 are presented in Figure 4. It is worth mentioning that the catalysts have showed high stability with good activity and selectivity whereas catalyst deactivation in a variety of dechlorination process on Pd, Pt, Rh and nickel catalysts has been ascribed to a poisoning of the surface metal by HCl produced in the reaction that formed a stable surface chloride species.[7,8] The advantage of this catalyst system is that it can be used continuously for long time and later the spent catalyst can be reused by using it as a precursor for iron oxide catalyst.

The higher yields and selective formation of cyclohexene as the dechlorination product from chlorocyclohexane can be utilized as an alternative method of preparation for cyclohexene where the commercial process has a cyclohexene yield of only 60%.[9]

The dechlorination of fuel oil derived from PVC containing (PP/PVC, 8:2) waste plastics was performed using TR97305 catalyst in order to elucidate the practical use of this catalyst. The experimental procedure has been described elsewhere.[10] Initially the fuel oil derived from thermal degradation of plastics at 380 °C contains 12000 ppm organic chlorine. When this fuel oil treated with TR97305 catalyst at the same temperature, the chlorine content reduced to 200 ppm. Thus, this catalyst system shows promise for commercial use.

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