

## Reactivation of Cu-Promoted Hydroxyapatites during Chlorobenzene Hydrolysis

We have shown in a previous paper (1) that the deactivation of Cu-promoted hydroxyapatites during chlorobenzene hydrolysis is due to a temperature-dependent loss of copper and to coke deposition on the catalyst surface. The deactivation due to coke deposition may be avoided by periodic regenerations of the catalyst. Here, we present a method to maintain activity by a continuous incorporation of copper to the catalyst.

### EXPERIMENTAL

Catalysts were prepared and characterized as previously described (1). Determinations of catalyst activity and stability were carried out in flow equipment (1-3). In some experiments the catalyst bed was divided into two zones independently heated and controlled within  $\pm 0.5^\circ\text{C}$ . Conversion to phenol ( $X_F$ ) was taken as a measurement of the catalyst activity and was calculated by chromatographic analysis.

### RESULTS AND DISCUSSION

It was demonstrated (1) that permanent catalyst deactivation is only due to copper loss. The deactivation produced by coke deposition can be eliminated by periodic regenerations. To confirm these results a run without periodic regenerations was carried out in a 52 h period. After that time the coke was burnt with diluted air at reaction conditions; the catalyst recovered and kept the same activity it would have had if being operated since the beginning with periodic regenerations. The results are shown in Fig. 1. The sharp decrease in activity during the first 52 h of operation, when the catalyst was operated without periodic re-

generations, was mainly due to coke deposition. The direct relation between coke deposition and catalyst deactivation can be seen after comparing Fig. 1 with Fig. 10 of the previous paper (1), where the increment of coke deposited with time was shown. As a consequence, the accumulation of higher amounts of coke had no irreversible effect.

It is important to find a method to avoid catalyst deactivation produced by copper loss. A way to do this is by taking the catalyst from the reactor and dispersing it in a  $\text{Cu}(\text{NO}_3)_2$  solution of a concentration according to the desired increment of copper. In that way the reactivated catalyst behaves as a fresh one. Another and more important procedure is to keep the copper content of the catalyst without taking it from the reactor.

The finding of  $\text{CuCl}_2$  at the reactor outlet walls showed that copper is lost from the catalyst. We had done (1) experiments by dividing the catalyst bed in two layers, the upper one (through which reactants are introduced) contained a copper-promoted hydroxyapatite and the lower one had a nonpromoted catalyst. This procedure permitted us to discover that the lower layer retained part of the copper lost by the upper layer during reaction. Hence, at reaction conditions a hydroxyapatite may increase its copper content if it has a source of  $\text{CuCl}_2$ .

A way to provide a  $\text{CuCl}_2$  source is by placing a bed of copper metal chips prior to the catalyst bed. Even though very low conversions (around 4% at  $380^\circ\text{C}$ ) are achieved, Cu on kieselguhr catalyzes chlorobenzene hydrolysis. In the kieselguhr-

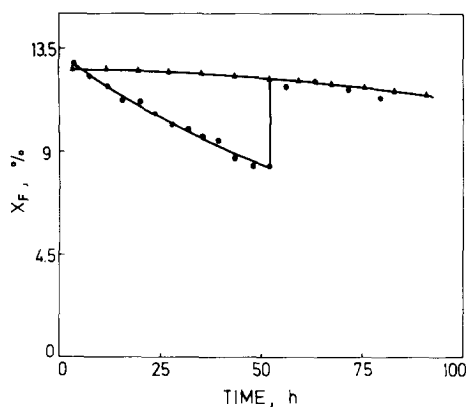


FIG. 1. Modifications of the conversion to phenol ( $X_F$ ) as a function of time for a hydroxyapatite containing initially 0.9% Cu. (▲) Run with regenerations each 2 h from the beginning. (●) Run without regenerations during the first 52 h, followed by regenerations every 2 h.  $T = 420^\circ\text{C}$ ;  $\text{WHSV} = 0.42 \text{ h}^{-1}$ ;  $\text{H}_2\text{O}$ : chlorobenzene molar ratio = 4.7.

supported catalyst, copper is present as CuO. The copper metal chips are partially CuO because air is passed over the catalyst before reaction and during regenerations. Hence, under reaction conditions, phenol and HCl are produced over the copper bed:



The HCl formed in the presence of CuO may produce  $\text{CuCl}_2$  according to the reaction:

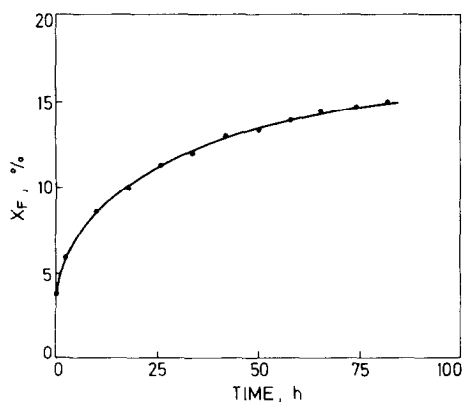


FIG. 2. Modifications of the conversion to phenol ( $X_F$ ) as a function of time for a nonpromoted hydroxyapatite when placing a bed of copper metal chips prior to the catalyst bed. Regenerations were performed every 2 h.



The  $\text{CuCl}_2$  may be transferred to the catalyst during the reaction.

To confirm such assumptions some experiments were carried out with a nonpromoted hydroxyapatite. Prior to the catalyst bed, a bed of 0.5 g of copper metal chips was placed and kept at  $440^\circ\text{C}$ . The run was performed at  $420^\circ\text{C}$ ,  $\text{WHSV} = 0.42 \text{ h}^{-1}$  with a water to chlorobenzene molar ratio of 4.7 and the coke was burnt every 2 h of operation. Figure 2 shows how activity increased with time. After the experiment the hydroxyapatite contained 0.4% Cu, the value to which the final activity corresponds, as shown in Fig. 8 of our previous paper (1). The results indicate that Cu was transferred to the hydroxyapatite.

The increment of copper with time follows the expression:

$$\text{Cu} (\%) = at^b,$$

where  $a = 2.5 \times 10^{-2} (\text{h}^{-1})$ ,  $b = 6.68 \times 10^{-1}$ , and  $t = \text{time (h)}$ .

As a consequence it should take 213.2 h to reach a copper content of 0.9%.

A hydroxyapatite initially containing 0.9% Cu was used in other experiments. Runs were performed at  $420^\circ\text{C}$  to increase

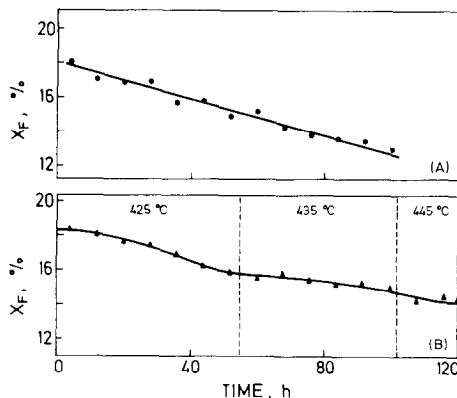


FIG. 3. (A) Modifications of the conversion to phenol ( $X_F$ ) as a function of time for a hydroxyapatite containing initially 0.9% Cu. (B) The same catalyst but placing before the catalyst bed, a bed of copper metal chips (0.5 × 5 mm) at different temperatures. Regenerations were performed every 2 h in both cases.

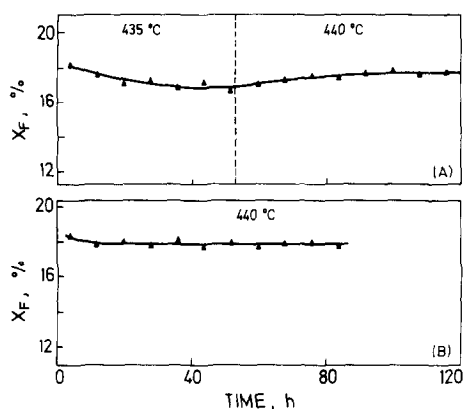


FIG. 4. Modifications of the conversion to phenol ( $X_F$ ) as a function of time for a 0.9% Cu hydroxyapatite, placing before the catalyst bed a bed of copper metal chips ( $0.5 \times 2.5$  mm) at different temperatures. Regenerations were performed every 2 h.

copper loss and to produce a quicker deactivation. Regenerations with air were done every 2 h. The decrease in activity during chlorobenzene hydrolysis is shown in Fig. 3A. The same catalyst was used at the same temperature, but placing 0.5 g of copper metal chips of 5 mm length and 0.5 mm diameter prior to the catalyst bed. Copper was first kept at 425°C and, as deactivation continued, temperature was increased to 435 and then to 445°C. Modifications of the conversion to phenol ( $X_F$ ) as a function of time are shown in Fig. 3B.

In another experiment the size of the copper metal chips was decreased to 2.5 mm length  $\times$  0.5 mm diameter and kept at 435°C during the 52 h. Since a decrease in  $X_F$  was still observed, the copper temperature was increased to 440°C, and at this temperature the  $X_F$  remained constant, as shown in Fig. 4A. To confirm that 440°C was the proper temperature to keep con-

stant the activity of a hydroxyapatite containing 0.9% Cu and operated at 420°C, a run was performed placing before the hydroxyapatite 0.5 g of copper metal chips in the size last mentioned whose temperature was kept at 440°C. Figure 4B shows that  $X_F$  remained constant for almost 90 h.

Consequently, Cu-promoted hydroxyapatites can be operated during chlorobenzene hydrolysis without a decrease in conversion if coke is periodically burnt and a source of  $\text{CuCl}_2$ , as a copper metal chip layer, is placed prior to the catalyst bed. The copper metal chip particle size and the temperature at which the copper must be kept are related to the initial copper content of the hydroxyapatite and to the reaction operational conditions. The copper lost by the hydroxyapatites is related to their initial copper content and operating temperature.

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