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Hydrolysis of Chlorobenzene over Cu-Promoted Hydroxyapatites

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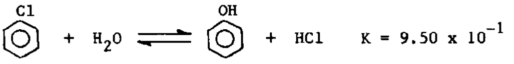
The chlorobenzene hydrolysis to phenol over Cu-promoted and -nonpromoted hydroxyapatites at different operational conditions was studied in a flow equipment under atmospheric pressure. The by-product was benzene. The different Ca to P ratios did not affect the catalyst activity and selectivity or the oxidation state of Cu. Catalyst deactivation was produced by the loss of Cu, which was associated with the temperature of operation. Correlations between the loss of Cu as a function of time at different temperatures and the decrease of activity with the loss of Cu were derived. Considerations about the reaction mechanism and about the reaction through which benzene was produced are made.

INTRODUCTION

Chlorobenzene hydrolysis produces phenol:



(1)

The reaction is catalized by different phosphate compounds (*1–6*), copper being an effective promoter in all cases. Hydroxyapatites of Ca and P, $Ca_{10x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, are widely used. In the formula presented, $x = 0$ for stoichiometric hydroxyapatites.

This paper refers to the influence of the operational conditions (temperature, space velocity, etc.) on phenol production, when hydroxyapatites of Ca and P promoted by Cu were used as catalysts. Catalyst deactivation was also studied, and equations which correlate the loss of Cu with temperature and time and the activity corresponding to each Cu concentration were derived.

EXPERIMENTAL

Catalyst preparation. Hydroxyapatites were prepared as previously described (*2*) following a modification of Hayek and Newesely technique (*7*): a $(NH_4)_2HPO_4$ solution was slowly added to a $Ca(NO_3)_2$ solution with vigorous agitation. The gel formed was filtered and washed in the filter with demineralized water. Then it was dried overnight at 120°C and finally it was calcined at 400°C for 2 h. Infrared analysis of the samples has shown a spectrum of hydroxyapatites similar to the ones of the literature (*8–10*).

The catalysts promoted with copper were prepared by dispersion of hydroxyapatites in $Cu(NO_3)_2$ solutions. Such concentrations were fixed according to the amount of copper desired. Ca^{2+} and Cu^{2+} are easily exchanged in hydroxyapatites (*2, 11*); according to Misra *et al.* (*12*) the exchange Ca^{2+}–Cu^{2+} occurs through two different mechanisms: an instantaneous one which is independent of the Cu concentration in the solution and another very slow one.

The concentrations of Ca, P, and Cu in the catalysts were analyzed by complexometry, photometry, and atomic adsorption spectrometry, respectively.

To prepare the catalysts and for their chemical analysis pure grade reagents were used.

Infrared analysis. They were performed with a Perkin Elmer 180 spectrometer, in the range 400–3800 cm^{-1} in KBr tablets.

Thermogravimetric analysis. They were done with an Aminco instrument from 20 to 700°C under a 70 cm^3/min N_2 stream.

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Determination of catalytic activity, selectivity, and stability. They were carried out in a conventional bench scale flow equipment previously described (*13*). Reactants were fed by means of two syringe pumps to a 1.2-cm-diameter and 8-cm-long glass reactor provided with an internal tube for a thermocouple. As coke was deposited on the catalyst during the reaction, a reactivation with air at 380°C for 45 min was performed after every 2 h of reaction. Steam was passed for 15 min before and after each air passage. The two phases in which the product was separated were independently analyzed by gas chromatography. Values of total conversion (X_T), conversion to phenol (X_F), and selectivity to phenol (S) were calculated from the analysis.

RESULTS

Effect of Thermal Pretreatment on Catalyst Activity

A promoted and a nonpromoted hydroxyapatite were heated at 800°C for 2 h. Afterward their surface area and catalytic activity and selectivity were measured. The results are presented in Table 1.

For both catalysts, the thermal pretreatment reduced the surface area drastically and in the same amount. The Cu-promoted catalyst did not lose the promoter after the pretreatment. The nonpromoted catalyst did not change activity and selectivity, although there were modifications of activity in the promoted one. As both catalysts had the same surface area modifications and Cu had not been lost, it is possible to infer that pretreatments at around 800°C promoted the migration of Cu to nonactive sites. Moreover, during experiments in which Cu was added to the thermally deactivated catalyst, the original activity may again be reached.

TABLE 1

Effect of Thermal Pretreatment of a Promoted and a Nonpromoted Hydroxyapatite on Surface Area, Catalytic Activity, and Selectivity[a]

Catalyst Cu (%)	Pretreatment at 800°C	Sg (m^2/g)	X_F (%)	S (%)
0	No	49.4	2.8	100
0	Yes	8.4	2.6	100
1.01	No	49.4	12.6	92
1.02	Yes	8.4	6.1	91

[a] Reaction conditions: $T = 380°C$, $H_2O : C_6H_5Cl = 4.7$ (molar), WHSV = 0.42 h^{-1}.

TABLE 2

Cu Oxidation State of a Fresh Catalyst and of One Used for 2 h

	Fresh catalyst	Used catalyst
Cu^{2+}(%)	0.80	0.68
Cu^{+} (%)	0	0.08
Cu^{0} (%)	0	0.03

Oxidation State of Cu in Promoted Catalysts

The oxidation state of Cu in fresh and used catalysts was analyzed following the Podchainova method (*14*). The results for one of the catalysts are shown in Table 2.

During reaction, some of the Cu^{2+} was reduced to Cu^+ and also to Cu^0, but after reactivation with air, all the promoter went back to Cu^{2+}.

In order to study how the promoter oxidation state affected catalyst activity and selectivity between regenerations, experiments in which the catalyst was partially reduced following the method of Misono and Hall (*11*) before starting the runs were carried out. According to the results presented in Table 3 the partial reduction of the promoter did not affect catalytic activity and selectivity.

Influence of the Ca/P Ratio of Hydroxyapatites on Catalytic Activity

Catalysts with different Ca/P ratios were prepared to determine the influence of such ratio on catalytic activity and selectivity for chlorobenzene hydrolysis. The different Ca/P ratios were obtained changing the gel temperature or the period of time previous to its filtering. A similar procedure was fol-

TABLE 3

Influence of the Partial Reduction of the Promoter on Catalytic Activity and Selectivity[a]

Gas stream previous to the run	X_F (%)	S (%)
Air, 30 min	11.7	94.0
H_2, 30 min	12.0	92.9
H_2, 90 min	11.7	94.4
H_2, 210 min	11.3	93.7
H_2, 360 min	12.4	95.2
Air, 30 min	11.9	92.8

[a] $T = 380°C$; WHSV = $0.42\ h^{-1}$; $H_2O : C_6H_5Cl = 4.7$; FvH_2–air = $275\ cm^3/min$; catalyst with 0.6% Cu.

lowed by Eanes *et al.* (*15*) to obtain hydroxyapatites of different crystallinities. Thermogravimetric analysis of the hydroxyapatites with different Ca to P ratios was performed: the loss of water at 780°C was related to the Ca/P ratio, as found by Bett *et al.* (*16*).

Obtained Ca/P values and the activity and selectivity of the materials for chlorobenzene hydrolysis are shown in Table 4. Shorter times were necessary to obtain stoichiometric hydroxyapatites at higher temperatures. The Ca/P ratio did not affect the activity and the selectivity for chlorobenzene hydrolysis, whereas it is important for dehydrogenation and dehydration, as has been reported by Kibby and Hall (*17*) and Joris and Amberg (*18*).

Influence of Operational Conditions on Catalytic Activity

The influence of the operational conditions on the catalytic activity for chlorobenzene hydrolysis was studied with copper-promoted catalysts.

a. Water to chlorobenzene ratio. Molar values from 1.48 to 15.48 were used at 380°C and WHSV 0.42 h^{-1}. In Fig. 1 it is shown that activity increased with $H_2O : C_6H_5Cl$ values up to 5 and then it remained constant, whereas selectivity was not affected.

b. Addition of hydrogen to the feed. Experiments in which hydrogen was added to the feed were carried out with a nonpromoted and a 0.37% Cu-promoted catalyst; the results are shown in Table 5.

The addition of hydrogen to the feed decreased the selectivity of the promoted catalyst but did not affect it when the nonpromoted catalyst was used.

c. Weight hourly space velocity (*WHSV*). Values from 0.16 to 2.5 g chlorobenzene/h g-cat. were used, working at 380°C and $H_2O : C_6H_5Cl$ 4.7. As shown in Fig. 2, activity decreased continuously while selectivity remained practically constant.

d. Temperature. The influence of temperature on promoted and nonpromoted catalysts is shown in Fig. 3. In the range of temperature studied selectivity was not affected.

Catalyst Stability

Catalyst stability for chlorobenzene hydrolysis was studied with nonpromoted and Cu-promoted hydroxyapatites. Figure 4 shows the modifications of activity for a nonpromoted (curve a) and a 0.89% Cu-promoted hydroxyapatite (curve b) at

TABLE 4

Influence of Temperature of the Gel or Time before the Gel Is Filtered on Hydroxyapatite Stoichiometry and on Its Catalytic Activity for Chlorobenzene Hydrolysis

Temperature (°C)	20	20	20	20	20	20	30	30	30	30	30	80
Time (h)	0	6	12	18	24	30	6	12	18	24	30	2
Ca/P	1.46	1.47	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
X_T	2.9	3.1	3.3									
S	100	100	100									

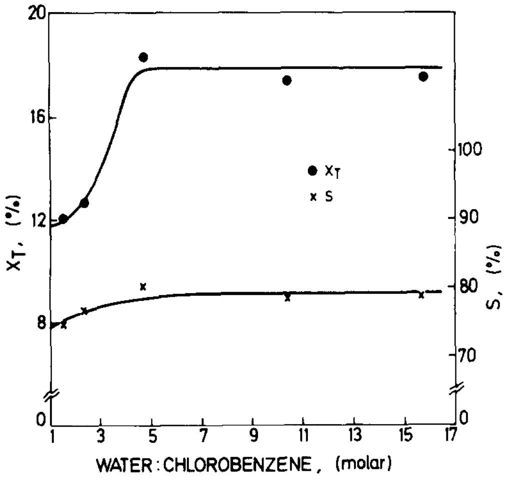


FIG. 1. Effect of water to chlorobenzene molar ratio on X_T and S. T = 380°C; WHSV = 0.42 h^{-1}; catalyst 1.3% Cu.

TABLE 5

Influence of the Addition of Hydrogen to the Feed on Promoted and Nonpromoted Hydroxyapatite[a]

Cu (%)	Feed	X_F (%)	S (%)
0	With H_2	2.9	100.0
0	Without H_2	3.0	100.0
0.37	With H_2	8.1	68.8
0.37	Without H_2	9.5	95.9

[a] T = 380°C; WHSV = 0.42 h^{-1}; $H_2O : C_6H_5Cl$ = 4.7 (molar); FvC_6H_5Cl = 1 ml/h; FvH_2 = 275 cm^3/min.

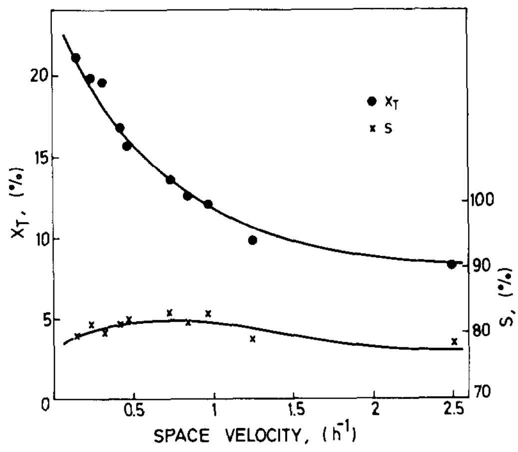


FIG. 2. Effect of space velocity on X_T and S. T = 380°C; $H_2O : C_6H_5Cl$ = 4.7; catalyst 1.3% Cu.

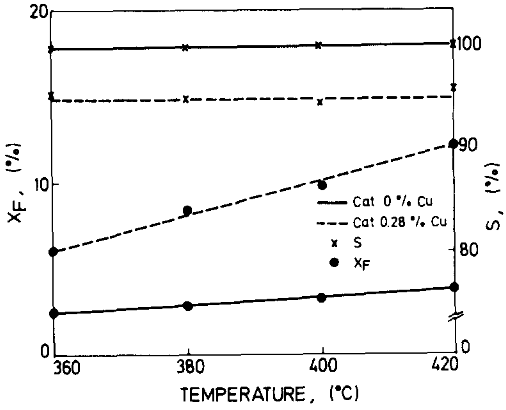


FIG. 3. Effect of temperature on X_T and S. WHSV = 0.42 h^{-1}; $H_2O : C_6H_5Cl$ = 4.7.

380°C for 100 h. It must be taken into account that every 2 h of reaction the catalyst was reactivated with air, so the deactivation due to coke deposition was eliminated. The activity of the nonpromoted catalyst was not affected, whereas the activity of the promoted one decreased with time. Several runs of different length up to 100 h were carried out with the promoted catalyst to determine why was it deactivated, measuring the specific surface area (Sg) and the Cu remaining on the catalyst after each experiment. These values are shown in Fig. 4

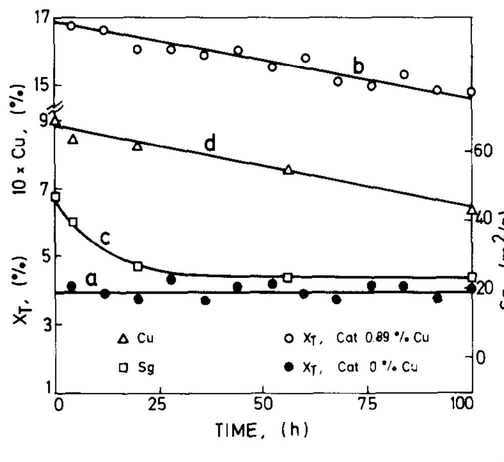


FIG. 4. Modifications of X_T, Sg, and Cu content of a catalyst containing initially 0.89% Cu and of X_T of a nonpromoted catalyst as a function of the time on stream. T = 380°C; WHSV = 0.42 h^{-1}; $H_2O : C_6H_5Cl$ = 4.7.

(curves c and d, respectively). The same Sg variations were noticed when runs of several lengths were made with the nonpromoted catalyst.

To study how temperature affects catalyst deactivation, runs at temperatures from 360 to 420°C for 100 h were carried out with catalysts containing initially between 0 and 0.89% Cu. In order to abbreviate, only some of the results appear in Fig. 5 where it is possible to observe that the catalyst deactivation was faster for higher temperatures and for catalysts with higher Cu contents.

It is possible to deduce from the results shown in Figs. 4 and 5 that the catalyst stability is ruled by the loss of Cu. As the loss of copper is related to the temperature of operation, for the same temperature, a fresh catalyst or a used one with the same Cu content should have the same activity. The previous statement is true as shown in Fig. 6, where X_F for fresh and used catalysts follows the same curve for each temperature.

Experiments in which a promoted catalyst was kept at different temperatures up to 420°C for 100 h in air, water or HCl solution streams were carried out. There were not modifications of the Cu content of the catalyst, and the activity was not affected. So, only when reactants were present, the effect of temperature determined catalyst deactivation by the loss of Cu. Cu is lost in the form of $CuCl_2$, as it was detected on the reactor outlet wall. The $CuCl_2$ must be produced through the interaction of the Cl of chlorobenzene with Cu, because HCl alone, as mentioned above, did not produce a loss of Cu.

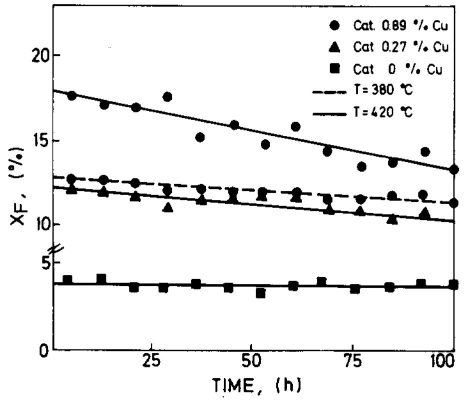


FIG. 5. Modifications of X_F at 380 and 420°C as a function of the time on stream for hydroxyapatites with different initial Cu contents. WHSV = 0.42 h^{-1}; $H_2O:C_6H_5Cl = 4.7$.

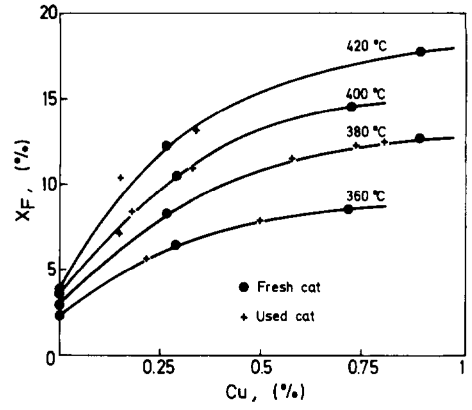


FIG. 6. Modifications of X_F with the Cu content of fresh and used catalysts, at different temperatures. WHSV = 0.42 h^{-1}; $H_2O:C_6H_5Cl = 4.7$.

Experiments in which the catalyst bed was separated in two layers were performed. The upper one, through which reactants were introduced, contained a 0.92% Cu-promoted hydroxyapatite, and the lower one had a nonpromoted catalyst. Water and chlorobenzene at a ratio 4.7 were fed for 100 h at 420°C, with reactivations after every 2 h of operation, as usual. After the experiment, the Cu content of the two zones was analyzed, producing the results presented in Table 6. The modification of Cu concentrations showed that the Cu lost by one layer of the catalyst was

TABLE 6

Modifications of Cu Content in Reactor Layers[a]

Cu (%)	Upper zone (uz)	Lower zone (lz)
Initial	0.92	0
Final	0.32	0.31

[a] $T = 380°C$; $H_2O:C_6H_5Cl = 4.7$; $w_{uz} = 2.5$ g; $w_{lz} = 2.5$ g; $F^{\circ}_{V}C_6H_5Cl = 1$ ml/h.

partially retained by the other one. The modifications of activity and selectivity during the run are shown in Fig. 7, and they can be explained from the modifications of activity and selectivity with the Cu content of the catalyst shown in Fig. 8.

The data of Fig. 7 shows that during the first 80 h of operation the activity increase due to the loss of Cu of one layer was compensated by the increment of the other. For a catalyst with initial 0.92% Cu, the initial loss of Cu decreased very little the activity (Fig. 8), while the same increment in the nonpromoted catalyst increased it much more. At the end of the run, when both layers were losing Cu, the activity decreased, as shown for the last 20 h of operation. Selectivity remained practically constant because there was a compensation between the increment of selectivity due to the loss of Cu of the upper layer and the decrease of selectivity with the lower layer Cu increment.

In order to maintain catalyst activity for a longer time, it is possible to place two layers of catalyst in the reactor, having a higher Cu concentration in the one through which reactants enter. The Cu lost by the first layer will be taken by the second one. There will be a compensation between the loss of activity of one layer, and the increase of activity of the second one.

DISCUSSION

Cu-promoted hydroxyapatites of Ca and P are good catalysts for chlorobenzene hydrolysis. Increasing the temperature there is an increment in catalytic activity as shown in Fig. 3, but as stability is related to the loss of Cu (Figs. 4 and 5) and the loss of Cu is related to the temperature (Fig. 5), the promoted catalyst is less stable at higher temperatures.

Several equations were derived to relate (a) the loss of Cu of the catalyst with time and the temperature of operation, and (b) the modifications of activity with the Cu content and the temperature.

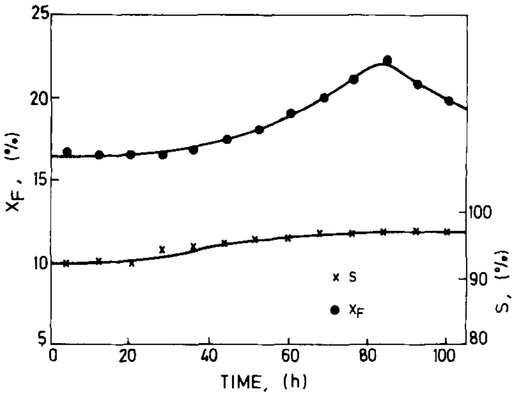


FIG. 7. Modifications of X_F and S with time on stream during a run in which the reactor was divided in two layers, the first one with Cu, and the second one without it. $T = 380°C$; $H_2O : C_6H_5Cl = 4.7$; $w_{uz} = 2.5$ g; $W_{lz} = 2.5$ g; $F^0_{C_6H_5Cl} = 1$ ml/h.

(a) Loss of Cu as a function of time and temperature: from studies of X_F as a function of time (partially presented in Fig. 5) and X_F as a function of percentage Cu (Fig. 6), curves of percentage Cu as a function of time at the different temperatures studied may be drawn, as shown in Fig. 9. For each temperature, the curves corresponding to catalysts with different initial Cu contents were overlapped. It was assumed that the percentage of Cu lost was independent of the instantaneous catalyst Cu content and only depends on the temperature.

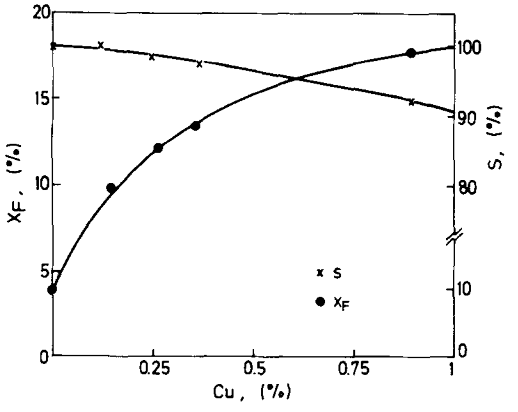


FIG. 8. Effect of Cu content of hydroxyapatite on X_F and S. $T = 420°C$; WHSV = 0.42 h^{-1}; $H_2O : C_6H_5Cl = 4.7$.

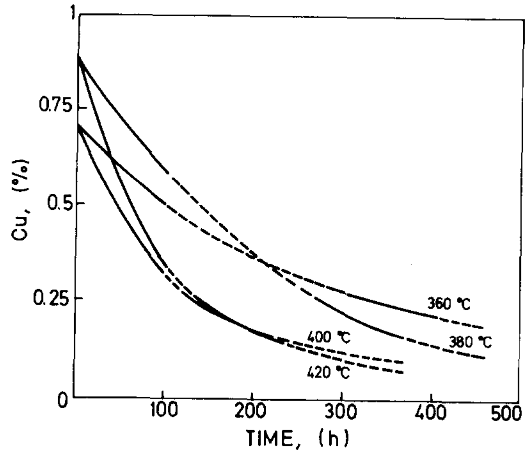


FIG. 9. Modifications of the Cu content of catalysts as a function of the time on stream at different temperatures. WHSV = 0.42 h^{-1}; $H_2O : C_6H_5Cl$ = 4.7.

Different expressions to correlate the data of percentage Cu as a function of time were considered, and in each case the optimum time to overlap the curves corresponding to catalysts with different initial Cu contents, at each temperature, were mathematically calculated.

The best equation found to fit the curves corresponding to the different temperatures was:

$$\%\ \mathrm{Cu} = \%\ \mathrm{Cu_i} e^{\alpha t} \qquad |\epsilon| < 0.05 \qquad (2)$$

where % Cu = Cu concentration at time t, % $\mathrm{Cu_i}$ = initial Cu concentration, T = temperature (°C), t = time (h), $\alpha = 0.02949 - 0.90195 \times 10^{-4}\ T$, and $|\epsilon|$ = absolute error.

(b) Modifications of activity as a function of the reaction temperature and the copper concentration of the catalyst: the following expression was derived from the data of Fig. 9:

$$X_F = a + b\ (\%\ \mathrm{Cu}) + c\ (\%\ \mathrm{Cu})^2 \qquad |\epsilon| < 1.1 \qquad (3)$$

where $a = -46.774 + 0.23115\,T - 2.625 \times 10^{-4}\ T^2$, $b = -92.58 + 0.298\ T$, and $c = 53.907 - 0.1693\ T$.

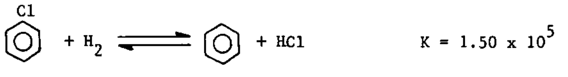
Equations (2) and (3) were used to predict the Cu content and the activity of two catalysts. The results are shown in Table 7, where they are also compared with experimental values.

It is important to observe that for catalyst A, the prediction was made for a period three times longer than the experimental data used to deduce Eqs. (2) and (3); nevertheless a good agreement between experimental and calculated values was obtained.

Reaction Mechanism

The hydrolysis of chlorobenzene over Ca and P hydroxyapatites is a very selective reaction. Only phenol is formed and there is coke deposition. The Cu-promoted catalyst is more active, but the selectivity to phenol decreases with the Cu content because benzene is also formed.

The possible reaction paths to benzene production are the following, with K the equilibrium constant:



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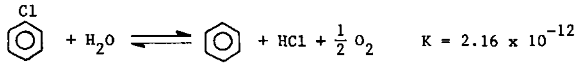

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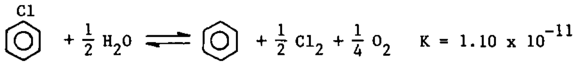

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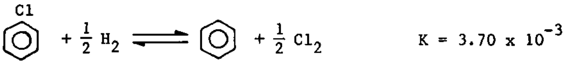

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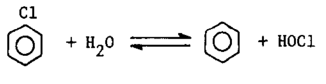
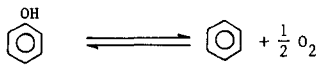


$K = 2.00 \times 10^{-6}$ (8)

$K = 1.58 \times 10^{5}$ (9)



$K = 2.29 \times 10^{-12}$ (10)

The equilibrium constants were calculated at 380°C; for reactions (1), (4–7), (9), and (10) they were calculated from data of Butler and Lielmezs (*19*) and for reaction (8) was used the van Krevelen method (*20*).

To know which of these reactions are those which take place, some experiments were carried out with a "microreactor" containing a copper-promoted hydroxyapatite. The reactor was directly connected to a chromatograph with a nitrogen stream passing through it. When samples of chlorobenzene perfectly dried with molecular sieves were injected to the nitrogen stream, phenol and benzene were detected, although water had not been fed to the system yet. Three different OH may be found in hydroxyapatites: structural ones (*21*), hydroxyls belonging to PO_4H^{2-} or from coordination water (*7*, *22*). Phenol could be formed from the interaction of chlorobenzene with one of those hydroxyls. When more chlorobenzene was fed, the production of benzene and phenol decreased with time and the amount of chlorobenzene detected at the reactor outlet increased until no more phenol and benzene were produced. When water was fed to the reactor, and then more chlorobenzene was injected, phenol and benzene were produced again, showing that water regenerated the active OH of the catalyst.

We have also found that a hydroxyapatite, partially transformed in chloroapatite by HCl treatment, was as active as the hydroxyapatite. The OH of PO_4H^{2-} are not the active ones, as it had been shown in Table 4 that stoichiometric and nonstoichiometric hydroxyapatites had the same activity for chlorobenzene hydrolysis.

A reaction mechanism for chlorobenzene hydrolysis over hydroxyapatites was proposed by Reichle (*1*): a chlorobenzene molecule enters the Ca–Cu–Ca triangles of the hydroxyapatite, and from the interaction with the structural OH, a phenol molecule is formed, leaving a chloroapatite. According to Reichle the chloroapatite is then transformed by water vapor into hydroxyapatite. But we have found that at reaction temperature the last transformation does not occur, and Elliott and Young (*23*) found

TABLE 7

Comparison of Experimental Results with Those Obtained Applying Eqs. (2) and (3)

Catalyst	Temperature (°C)	Cu_i[a](%)		X_F°	Cu_t[b](%)	X_{F_t}	$Time_t$ (h)
A	370	0.88	Experimental	12.1	0.24	7.5	332
			Calculated	11.0	0.24	6.5	
B	380	0.49	Experimental	10.2	0.29	8.5	100
			Calculated	10.6	0.30	8.4	

[a] Cu_i = initial Cu content.
[b] Cu_t = Cu content at time *t*.

that the transformation of a chloroapatite into hydroxyapatite is only possible at temperatures above 1100°C.

When a phenol solution was fed to the catalyst, no benzene was produced, indicating that benzene was formed through a reaction parallel to (1). In such a case reactions (9) and (10) previously proposed for benzene formation may be neglected. From the values of the equilibrium constants, and considering the amounts of benzene produced in some of our experiments, reactions (5)–(8) may be also neglected. So, benzene must be formed through reaction (4). It is necessary to remember that in the presence of H_2 in the feed, there was a decrease in selectivity of the promoted catalyst, as was shown in Table 5. The nonpromoted catalyst did not produce benzene in any of the cases.

Reaction (4) needs H_2 which may be produced through reaction (11), as was supposed by Rennard and Kehl (*24*) for the formation of toluene from chlorotoluene hydrolysis.

$$C + 2\,H_2O \rightleftharpoons CO_2 + 2\,H_2 \qquad (11)$$

Hydrogen may also be formed through reactions (12) or (13):

$$x\,C_6H_5Cl \rightleftharpoons \text{Coke} + y\,H_2 + x\,HCl \qquad (12)$$

$$m\,C_6H_5OH \rightleftharpoons \text{Coke} + n\,H_2 + m\,H_2O \qquad (13)$$

However, from some unpublished results (25) which are shown in Fig. 10, it was demonstrated that when a catalyst was used without regenerations for 15 h, there was a decrease of coke deposition velocity with time, with a consequent decrement of H_2 production, according to Eqs. (12) and (13). If that was the H_2 source for reaction (4), then selectivity should have increased with time, while it remained constant. So hydrogen must be produced through reaction (11).

Reaction (11) is not easy at the operating temperature (around 380°C), but it may be catalyzed by Cu, as other metals, like Fe (*26*) were found to be catalysts for the reaction.

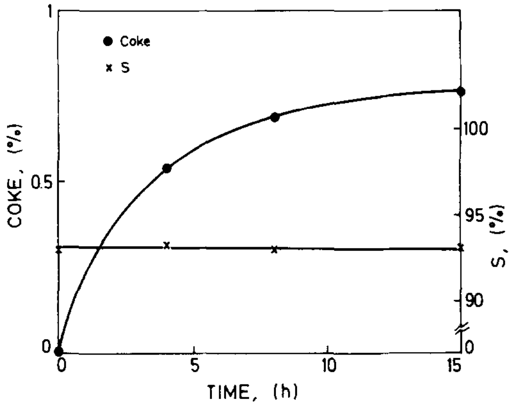


FIG. 10. Modifications of the amount of coke on the catalyst and of selectivity with time on stream during a run without regenerations. T = 380°C; WHSV = 0.42 h^{-1}; $H_2O : C_6H_5Cl$ = 4.7.

For hydroxyapatites (Fig. 8) and also for other catalysts (*6, 27*) it was found that by increasing the Cu concentration there is a decrease of selectivity. We have assumed that Cu is a catalyst for reaction (11) through which hydrogen is produced. When more Cu is present, reactions (11) and (4) will continue more quickly and there will be a decrease in selectivity. There will also be higher amounts of HCl than that corresponding to phenol formation, as our analysis has shown, as well as the results of Freidlin *et al.* (*3, 28*).

The presence of Cu and P is fundamental for chloroaryl compound hydrolysis, as lanthanum and cerium phosphates (*29*), zirconium phosphates (*6*), or hydroxyapatites (*1, 2, 28*), all of them promoted by Cu, are good catalysts for the reaction. The oxidation state of Cu does not affect catalyst behavior, as was shown in Table 2.

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