ELSEVIER

Catalysis Today 48 (1999) 109–117

CATALYSIS TODAY

Overall rate of aqueous-phase catalytic oxidation of phenol: pH and catalyst loading influences

Aurora Santos, Eva Barroso, Félix García-Ochoa*

Dpto. Ingeniería Química, Facultad de Cecncia Quimica, Universidad Complutense, 28040-Madrid, Spain

Abstract

The catalytic oxidation of phenol in aqueous-phase has been investigated using a commercial catalyst $CuO–2(CuO)·Cr_2O_3–CrO_4Ba–Al_2O_3$ at 400 K and an oxygen pressure of 8 atm, changing the pH and catalyst concentration. The phenol conversion, TOC consumption, the intermediates and the pH variation with time have been determined. An irreversible bonding of phenol on the catalyst surface has been found as a previous step to the phenol oxidation reaction. An overall pseudo-first order kinetic constant has been calculated for phenol conversion and values obtained at basic pH are lower than those calculated for acid pH media. An important homogeneous contribution for the phenol oxidation rate was found. However, the intermediates mineralization is notably influenced by the catalyst load.

Keywords: Copper catalyst; Phenol oxidation; Mineralization; Catalyst/liquid ratio

1. Introduction

The problem of pollution reduction of the aqueous stream containing phenolic compounds is of great importance in waste waters from many industries (agroalimentary processes, pharmaceutical, fine chemical, petrochemical, etc.). These effluents cannot be treated through conventional processes of biological oxidation, because of their poor biodegradability. The process currently used is the wet oxidation or supercritical oxidation, which requires high pressures and temperatures, and consequently carries a high cost [1,2].

One of the most promising technologies for eliminating phenolic compounds in waste waters is the heterogeneous catalytic oxidation of these aqueous streams under supercritical or intermediate conditions [3–5]. After this treatment, the refractory organic compounds as phenol are mineralized to CO_2 and H_2O or converted to harmless intermediates which can be dealt with by a conventional process of biological degradation. Among the catalysts tested for phenol oxidation the copper oxides supported on alumina have been employed most frequently [6–12] often using the slurry reactors to carry out the reaction. Therefore, a low catalyst concentration is usually employed.

However, there is no agreement among the results reported by the previous works on the influences of variables such as pH, catalyst concentration and catalyst leaches. Studies carried out on this topic show that the reaction involves a free radical mechanism, with an induction period before the steady-state regime is achieved, considering both

---

*Corresponding author. Tel.: +34-1-3944176; fax: +34-1-3944171/14; e-mail: chapu@eucmax.sim.ucm.es

PII: S0920-5861(98)00364-2

homogeneous and heterogeneous reaction contribution [3,6–8,10].

In this work a copper-chromite catalyst from Engelhardt has been tested for the phenol oxidation reaction in a basket stirred tank reactor (BSTR) at an intermediate temperature (400 K) and oxygen pressure (P_{O_2}=8 atm). Experiments under different pH and catalyst concentration have been carried out and their influence on the phenol conversion, the remaining TOC, and copper leaches have been analyzed. Furthermore, an overall kinetic expression has been proposed and the kinetic constant values under the different operational conditions employed have been calculated.

2. Experimental

2.1. Catalyst

The catalyst employed in this work is a commercial one from Engelhard formed by copper oxide, copper chromite, barium chromate and alumina (CuO–$2(CuO)\cdot Cr_2O_3$–CrO_4Ba–Al_2O_3). The properties of the catalyst are given in Table 1.

2.2. Experimental set-up and procedure

A basket stirred tank reactor (BSTR) from Autoclave Engineers (500 ml Spectrum Reactor) was employed to carry out the experimental runs. A volume of 250 ml of the liquid phase containing 1000 ppm of pollutant (phenol) after setting the pH to an initial value (pH_0) was introduced in the reactor. The catalyst was boiled twice in distilled water before using it and placed in the basket of the reactor.

The three pH levels used in this work 3.6, 10 and 12, were achieved by adding H_2SO_4 (H), Na_2CO_3 (C) and NaOH (N), respectively. Catalyst concentration was changed from 4 to 120 g/l. The reactor was pressurized (at 8 atm) by means of a nitrogen flow (0.2 l/min STP). Constant flow rate and pressure values were achieved by means of a mass flow controller and a back-pressure control valve, respectively. The reactor was heated until the reaction temperature (400 K) is reached, this one being measured and controlled in the liquid phase, holding this value within a ±0.5 K range. The rotating speed of the stirrer was fixed at 700 rpm. When steady conditions were achieved, an oxygen stream at the same flow rate and reactor pressure replaced the nitrogen flow. A scheme of the experimental set-up is given in Fig. 1.

Gas and liquid samples were taken periodically from the reactor and analyzed. Residual phenol concentration and some intermediates in the samples from the reactor were determined by HPLC (Perkin-Elmer Model LC-100) using a Kromasil C_{18} column as stationary phase and a mixture formed by acetonitrile (75%) and water (25%) as mobile phase. Flow rate of the mobile phase was set at 0.7 ml/min and the UV detector was used at a 210 nm wavelength. Other reaction intermediates were identified and quantified by means of a GC/MS technique (Hewlett-Packard Model 6890). TOC values were obtained in a Rosemount-Dohrmann DC-190. Copper, chromium and aluminum leaches were determined by means of atomic absorption. The pH values of the liquid samples were also measured with time. For those runs carried out at acid pH_0, the carbon dioxide in the gas effluent from the reactor was analyzed on line by means of a Hewlett Packard GC (model 5890 series II).

Table 1
Characterization of the catalyst

Chemical composition	Bulk density (g/cm^3)	Total pore volume (cm^3/g)	Pore distribution		Surface area (m^2/g)	Geometry
			r_p (A)	V_p (cm^3/g)		
15% CuO			60	0.11		Extrudates 1.6 mm of diameter
44% (2 CuO)·Cr_2O_3	1.05	0.36	100	0.21	120	
12% CrO_4Ba			175	0.31		
29% Al_2O_3			5000	0.36		

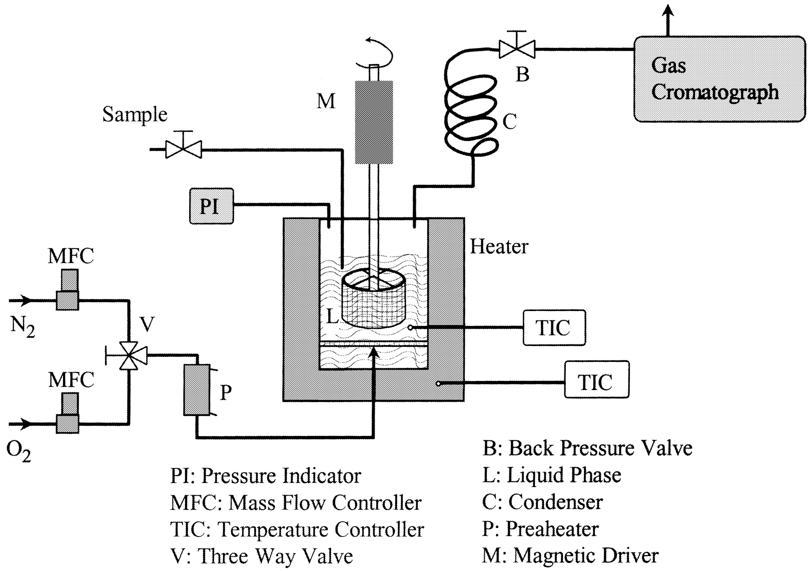

Fig. 1. Diagram of the BSTR apparatus employed to carry out the runs.

A blank run without catalyst was also carried out and a negligible conversion of phenol was observed after 24 h. Catalyst employed in the runs under acid and basic pH_0 were first stabilized by carrying out successive runs under those conditions, until the results from consecutive runs yielded the same induction period and phenol conversion evolution with time. In the first charges of the catalyst in the reactor, it was observed that phenol was removed from the liquid phase but neither intermediates or CO_2 were detected. Thus a particular interaction of the phenol with the fresh catalyst surface can be inferred which will be called from now "phenol-surface bonding".

This initial bonding of phenol was analyzed at different conditions. First at low temperatures (278 K), then at reaction conditions at acid and basic pH media (pH 3.6 and 10, respectively.) and under oxygen and nitrogen atmospheres.

At the lower temperature (278 K), 60 g fresh catalyst were in contact during 72 h with 1 l solution 1000 ppm on phenol. At reaction conditions (T=400 K, P_{O_2}=8 atm) initial bonding of phenol was studied taking an amount of 30 g of fresh catalyst, previously boiled in distillated water, being then introduced in the reactor with 250 ml of a solution of phenol. Remaining phenol concentration in the liquid phase of the reactor was analyzed with time. Three set of runs were carried out, each one with a charge of 30 g of fresh catalyst:

(S-1) A solution of 1000 ppm on phenol at pH_0=3.6 was charged with the catalyst in the reactor. Stable temperature and pressure were reached using a nitrogen and then (t=0) an oxygen flow was introduced. Four charges of the catalyst under these conditions were carried out.

(S-2) A solution of 5000 ppm on phenol at pH_0=10 was charged with the catalyst in the reactor. Stable temperature and pressure were reached using a nitrogen and then (t=0) an oxygen flow was introduced. Only one charge of the catalyst under these conditions was carried out.

(S-3) A solution of 5000 ppm on phenol at pH_0=3.6 was charged with the catalyst in the reactor. Nitrogen was used during the whole run. Only one charge of the catalyst under these conditions was carried out.

3. Results and discussion

3.1. Bonding of phenol on the fresh catalyst surface

From the runs carried out at the lower temperature (278 K) a negligible adsorption was obtained (about 0.7 mg phenol/g catalyst) when 60 g fresh catalyst were in contact during 72 h with a 1 l solution of 1000 ppm on phenol.

When the 30 g of fresh catalyst were in contact under reaction conditions with a solution of 1000 ppm on phenol at pH_0 3.6, (S-1) it was observed that phenol was totally removed from the liquid phase after four to five hours but no intermediates were detected, the TOC conversion was roughly the same as phenol conversion and carbon dioxide was not detected in the effluent gas. Likewise, an increase of the pH from 3.6 to 5.8 was noticed from the beginning and this last pH remained constant during the whole run, thus no acid compounds were produced. The catalyst used in these experiments needed four charges in the reactor until the reaction of phenol oxidation begun, that is, until intermediates and carbon dioxide were detected and a decrease in pH was observed.

When a basic pH_0, about 10, with an initial phenol solution of 5000 ppm was used (S-2) the oxidation reaction took place when about 70% of the initial phenol had been removed from the liquid phase.

As can be seen in Fig. 2(a) and (b), for both (S-1) and (S-2) experiments, the phenol removal from the liquid phase begun when the temperature was high enough, even while nitrogen was employed to reach stable temperature and pressure before the oxygen flow was introduced (t=0).

This bonding of phenol even with nitrogen flow was confirmed with the experiment (S-3) where a solution of 5000 ppm at pH_0=3.6 under nitrogen atmosphere was used. A removal of phenol while no intermediates were observed was also noticed and an increase of the pH at a value about 6 was found. An asymptotic amount of phenol removed from the liquid to the solid phase was obtained as is shown in Fig. 2(b).

When the catalyst was stirred for several hours in an aqueous solution free of phenol under the same pressure and temperature conditions (8 atm and 400 K), no compound removed from the solid to the liquid phase was observed. This irreversible bonding of phenol and the fact that a negligible adsorption takes place at low temperatures, indicates that the phenol is not physically adsorbed but chemically reacted on the catalyst surface.

This can also be justified from the FT-IR spectra for the catalyst after the use in phenol adsorption

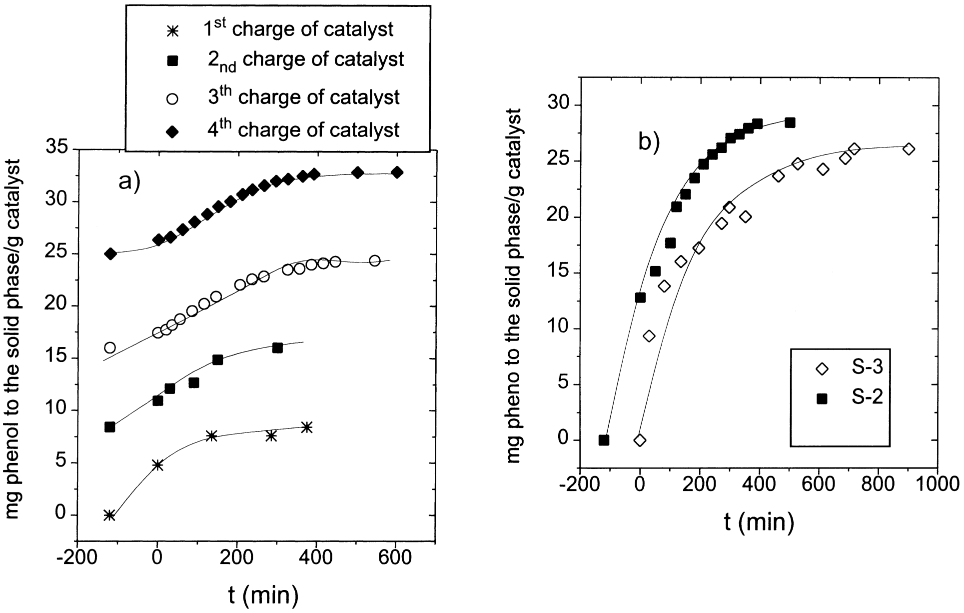

Fig. 2. Runs with fresh catalysts: T=400 K, P=8 atm 30 g catalyst, 250 ml liquid phase: (a) Experiment (S-1): pH_0=3.6, N_2 until t=0 then Oxygen, ppm_0 phenol=1000, (b) experiment (S-2): pH_0=10, N_2 until t=0 then Oxygen, ppm_0 phenol=5000, and (c) experiment (S-3): pH_0=3.6, N_2 during all run, ppm_0 phenol=5000.

and phenol oxidation runs, because aromatics groups (1200–1600 cm^{-1}) were detected on the catalyst surface.

The amounts of phenol bonding to the catalyst surface was about 35 mg phenol/g catalyst for adsorption experiments under acid conditions and with oxygen flow (S-1), and about 28 and 25 mg/g for experiment at basic conditions (S-2) and with nitrogen flow (S-3), respectively. These aromatic compounds bonded to the catalyst surface were also noticed by Levec [9] and could also explain the finds of Goto et al. [8] who observed a much slower reaction rate for the phenol conversion, a different induction period and a change in the catalyst color from the first to the second charge of the Harshaw copper catalyst used by these authors. Because the reaction takes place only after an amount of phenol has reacted with the catalyst surface, it can be questioned whether those aromatic groups are responsible for the catalyst activity. A deep discussion of the nature of these compounds (adsorbed phenolic surface radicals as suggested by Levec [9] or a polymeric product strongly adsorbed on the catalyst surface as proposed in other works [3,10]) is out of the scope of this work, and should be the object of further studies.

3.2. *Influence of the pH and catalyst loading on the phenol conversion and TOC reduction*

Phenol and TOC conversions progress obtained for runs carried out at pH_0 about 3.6 are shown in Fig. 3(a). In all of these runs the catalyst used had an amount of phenol adsorbed of 35 mg/g. The pH and carbon dioxide evolution with time for these runs are shown in Fig. 3(b) and (c), respectively.

Phenol and TOC conversions obtained for runs carried out at pH_0 about 10 and 12 are shown in Fig. 4(a) and (b), respectively. The pH evolution with time for those basic runs is given in Fig. 4.

It should also be noticed that an increase on the pH_0 takes place when the catalyst is in contact with the phenol solution, increasing from 3.6 to 5.5 at zero time, as can be seen in Fig. 3(b), while a decreasing of the pH from initial pH_0 is found for basic runs, as shown in Fig. 5.

Phenol conversions were found to be bigger for acid than for basic media. In most of the cases, the catalyst concentration had scarcely any influence on phenol conversion, therefore an important contribution of the homogeneous reaction can be inferred, at least at low catalyst loading. On the contrary, TOC conversion increased notably when the catalyst concentration increased. As an explanation for this fact, a strong homogeneous contribution for the oxidation of phenol may be suggested (according to a free radical mechanism), while the oxidation of the intermediates should mainly be due to a heterogeneous reaction.

To make sure that the small differences obtained for phenol conversion at higher catalyst loading are not due to a strong resistance for the oxygen transport to the liquid phase, the experiment at 120 g/l of Fig. 3 was repeated, increasing the rotating speed at 1000 rpm and the oxygen flow rate at 1 l/min. Results are shown in Fig. 6. It can be observed that no differences were found for phenol and TOC conversion, thus the small effect of the catalyst loading on the phenol conversion can be attributed to the homogeneous contribution. This has been also confirmed for the low rate of phenol oxidation found when not slurry but fixed bed is employed [11].

Some of the intermediates identified by HPLC and GC/MS in the runs carried out under acid pH were 1,2 benzenediol, 1,4 benzenediol with 2,5-cyclohexadiene-1-4dione, and branched 1,2 benzenedicarboxylic acids (BDA) as 1,2 BDA, bis(2-metoxyethyl) ester; 1,2 BDA, diethyl ester; 1,2 BDA, butyl 2-methyl propyl ester; 1,2 BDA, butyl 2-methylpropyl; 1,2 BDA, dibutyl ester, etc. Under basic conditions, 1,2 and 1,4 benzenediol were not detected, but the 1,2 benzenedicarboxylic acids above quoted were also found. Concurrently with the appearance of 1,2 BDA, a decrease of the pH was observed, and 1,2 BDA became more branched with the reaction progress. While the pH decreases, the color of the liquid samples turn from transparent to light yellowish brown, then blackish brown. This brown color remains with time when low catalyst loading is used but turns to lighter brown for higher catalyst concentration. When 120 g/l of catalyst are used, almost transparent samples are obtained at 200 min. This remaining brown color concurs with the lower TOC conversion observed in the runs at lower catalyst loading.

In the runs carried out at acid pH_0, the conversion vs. time curves show sigmoidal profiles, the initial time corresponding to the induction period. The inflection point of these curves coincides with the appear-

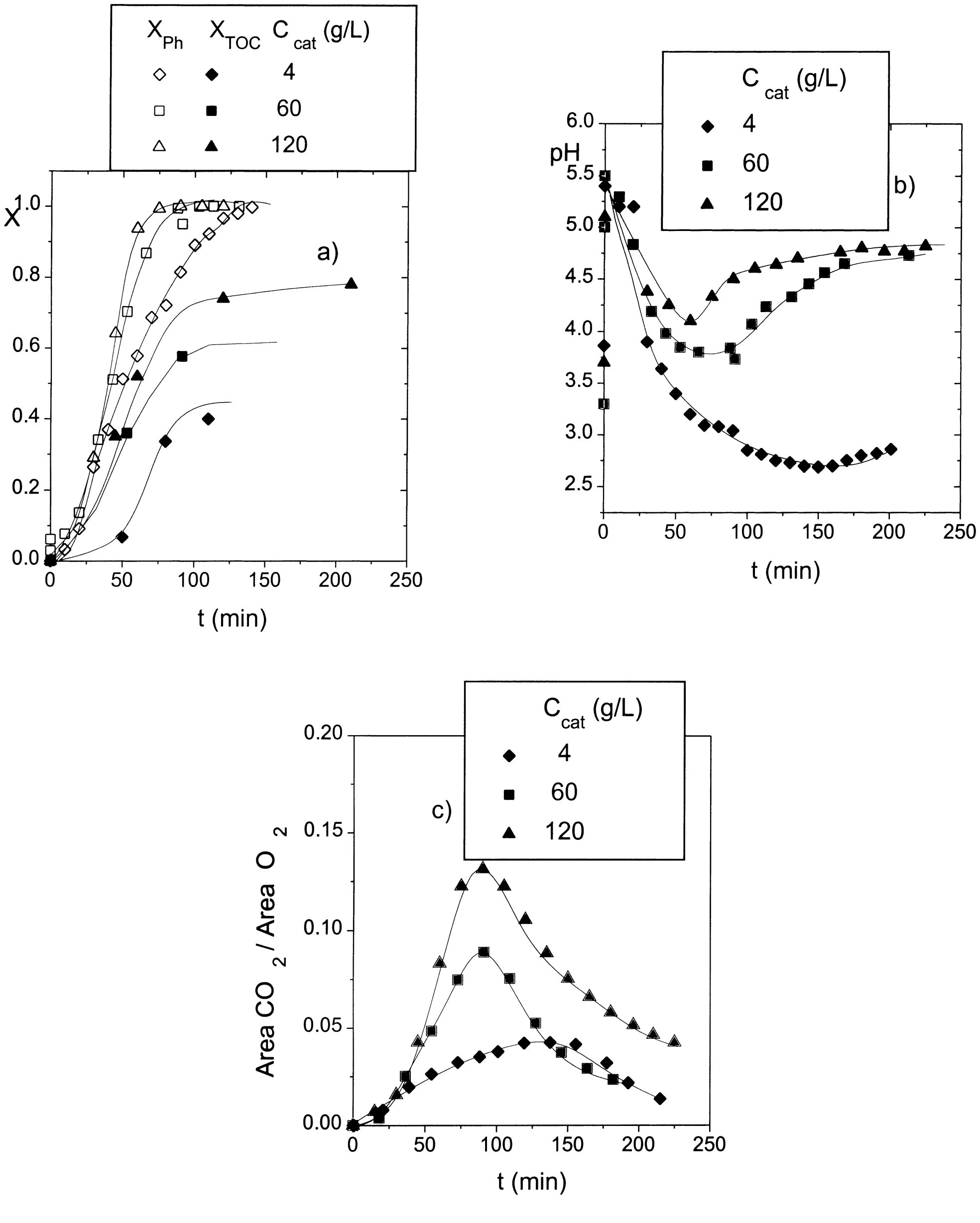

Fig. 3. Experimental results for runs carried out at pH_0 about 3.6: T=400 K, P_{O_2}=8 atm, ppm_0 phenol=1000: (a) phenol and TOC conversion, (b) pH evolution, and (c) CO_2 production.

ance of the acids, as can be deduced from the results shown in Fig. 3(a) and (b). On the other hand, when the conversion of phenol is already very high, the appearance of carbon dioxide is still small, as can be seen in Fig. 3(c). The maximum on the appearance of carbon dioxide coincides with the minimum in the pH vs. time curve, therefore the acids seem to be the most difficult compounds to be mineralized. Similar pH effects were noticed repeatedly in literature for slurry reactors and phenolic compounds oxidation [8,12] and also for catalytic oxidation of other organic compounds [5].

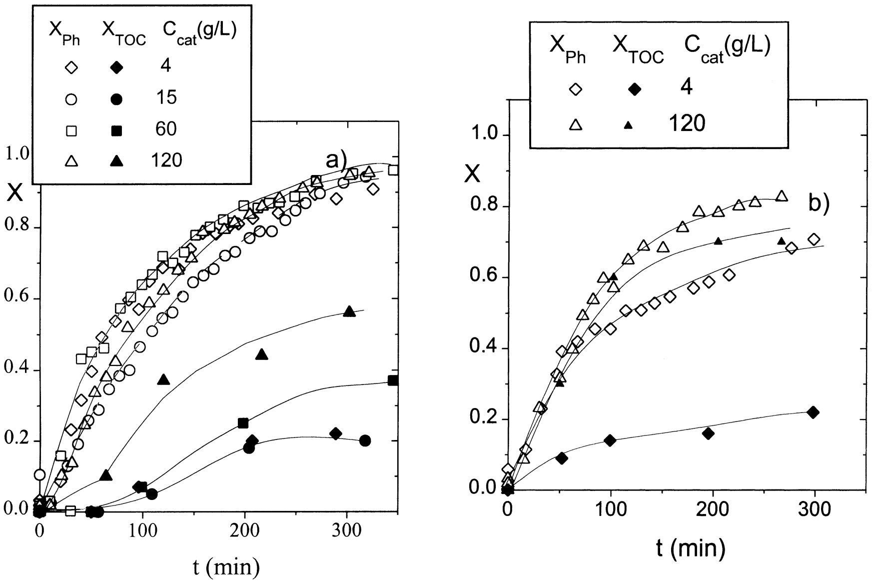

Fig. 4. Experimental results for runs carried out at basic pH. Operational conditions: T=400 K, P_{O_2}=8 atm, ppm_0 phenol=1000: (a) data for pH_0 about 10, and (b) data for pH_0 about 12.

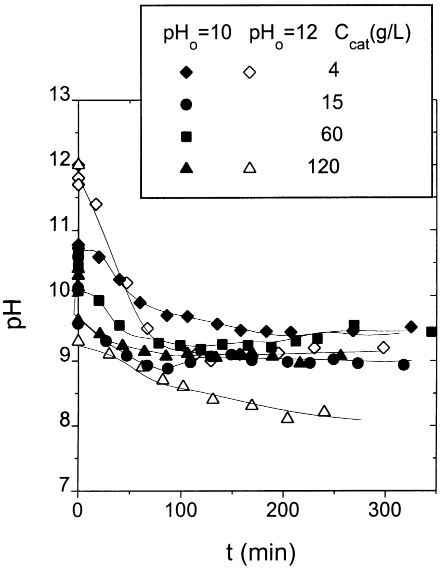

Fig. 5. Evolution of pH vs. time for runs carried out at basic pH.

The lower TOC conversion found in the basic runs compared to that obtained in the acid runs could be due either to a lower homogeneous or to a heterogeneous contribution. When carbonate is used to achieve the basic pH_0 almost no influence of the catalyst loading is found, thus mainly a homogenous contribution for the phenol oxidation can be deduced and an inhibition effect of the anions (OH^- or $CO_3^=$) in the propagation step presumed. When NaOH is used to get basic conditions (pH_0 about 12) a lower conversion is obtained for a catalyst loading of 4 g/l than when carbonate is employed (pH about 10). Thus the negative effect of OH^- anions can be confirmed, affecting the propagation step. When the catalyst loading is 120 g/l, this bigger catalyst concentration produces a higher decrease in the pH at zero time, thus the effect of the OH is lower and therefore a bigger phenol conversion is achieved.

After the induction period, when steady-state is reached, the values of $\ln(1-X_{Ph})$ plotted vs. time yield a straight line for each run. Therefore a linear relationship is observed in all cases with a constant slope for each run, under different operational conditions of both pH and catalyst load. Thus, at least under the operational conditions studied, a pseudo-first order kinetic model can be assumed, the kinetic equation for phenol disappearance at steady-state being given by the following function,

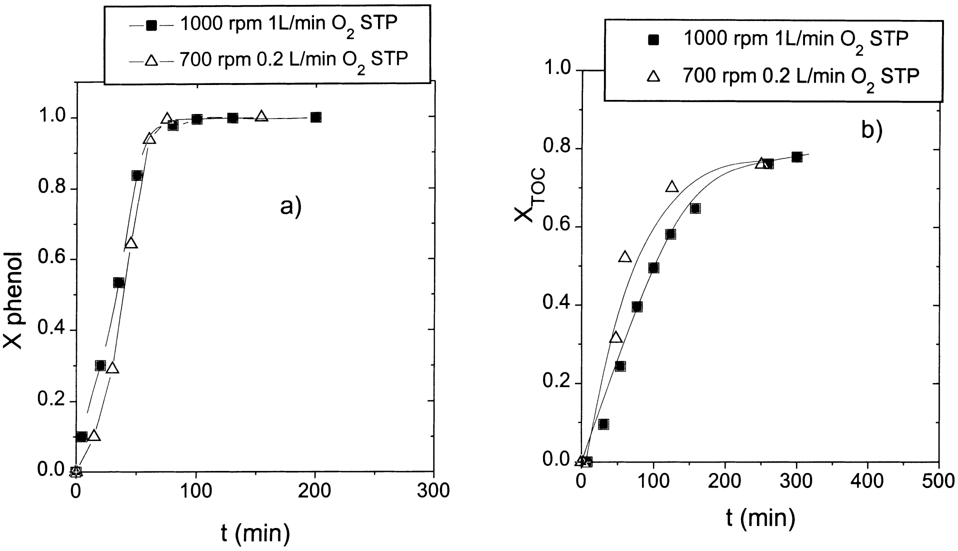

Fig. 6. Effect of the rotating speed and oxygen flow: P_{O_2}=8 atm, C_{Cat}=120 g/l, pH_0 about 3.6, ppm_0 phenol=1000: (a) phenol conversion and (b) TOC conversion.

Table 2
Values of $k\,C^n_{cat}\,P^m_{O_2}$ (min^{-1})

pH_0	C_{cat} (g/l)			
	4	20	60	120
3.6 (H)	0.0586	–	0.0957	0.105
10 (C)	0.0077	0.0074	0.0093	0.0102
12 (N)	0.0030	–	–	0.0062

with the pseudo-first order kinetic constant values summarized in Table 2:

$$\frac{-dC_{Ph}}{dt} = k.C^n_{cat}P^m_{O_2}C_{Ph}.$$

As can be deduced from Table 2, the *n* value is lower than unity, as also found by other authors [5,8]. This can be due to an important homogeneous contribution. Notice also the lower values of the pseudo-first order kinetic constant obtained when runs are carried out at basic than acid pH_0.

3.3. Catalyst leaching

The catalyst leaches of copper were always less than 2 mg/g catalyst of the initial copper after five consecutive runs for both acid and basic pH. Chromium and aluminum leaches after 20 h of reaction were negligible for runs under acid conditions and about 30 and 6 mg/g catalyst for chromium and aluminum, respectively, for runs carried out under basic conditions.

4. Conclusions

Previous to the reaction of phenol oxidation, an irreversible bonding of phenol in the surface of the copper–chromite catalyst used in this work is observed, the amount bonded being slightly greater in the acid media (35 mg of phenol/g of catalyst) that in the basic media (28 mg of phenol/g of catalyst).

Under the operational conditions employed, an important homogeneous contribution for the phenol oxidation reaction rate was observed. This fact suggests that the reaction must take place by free radicals mechanism, the catalyst being an initiator of such reaction. However, the total mineralization of the intermediates is affected by the catalyst concentration, specially when the reaction takes place under acid conditions.

In the basic media, the propagation step elapses very slowly, which seems to indicate an inhibitor effect of the OH^- anion. Assuming first order for the phenol concentration in the oxidation kinetic equation, this inhibitor effect is also translated in a kinetic constant one order of magnitude lower in basic media than that obtained in acid media.

5. Nomenclature

C_{cat}	catalyst concentration (g/l)
k	kinetic constant for phenol oxidation
m	kinetic order for oxygen pressure
n	kinetic order for catalyst concentration
pH_0	initial pH of the phenolic solution
Ph	phenol
P_{O_2}	oxygen pressure (atm)
T	temperature (K)
t	time (min)
TOC	total organic carbon
X	conversion

Acknowledgements

This work has been supported by CAM under contract no. 06M/063/96. Authors wish to thank Engelhardt for the catalyst supply.

References

[1] T.D. Thornton, P.E. Savage, J. Supercritic. Fluids 3 (1990) 240–248.
[2] S. Gopalan, P.E. Savage, AIChE J. 41 (1995) 1864–1873.
[3] A. Pintar, J. Levec, Catal. Today 24 (1995) 51–58.
[4] Z. Ding, S.N. Aki, M.A. Abraham, Environ. Sci. Technol. 29 (1995) 2748–2753.
[5] S.H. Lin, S.J. Ho, Appl. Catal. B 9 (1996) 133–147.
[6] A. Sadana, J.R. Katzer, J. Catal. 35 (1974) 140–152.
[7] A. Sadana, J.R. Katzer, Ind. Eng. Chem. Fundam. 13 (1974) 127–134.
[8] H. Ohta, S. Goto, H. Teshima, Ind. Eng. Chem. Fundam. 19 (1980) 180–185.
[9] J. Levec, Appl. Catal. 63 (1990) L1–L5.
[10] A. Pintar, J. Levec, Chem. Eng. Sci. 47 (1992) 2395–2400.
[11] A. Pintar, J. Levec, Ind. Eng. Chem. Res. 33 (1994) 3070–3077.
[12] D. Mantzavinos, R. Hellenbrand, A.G. Livingston, I.S. Metcalfe, Appl. Catal. B 7 (1996) 379–396.