ARTICLES

CATALYST SYSTEMS FOR THE OXIDATION OF PHENOL IN WATER

P.A. MASSA, M.A. AYUDE, R.J. FENOGLIO, J.F. GONZALEZ and P.M. HAURE

Facultad de Ingeniería. Universidad Nacional de Mar del Plata.
Instituto de Investigación en Ciencia y Tecnología de Materiales. (INTEMA)-CONICET.
Juan B. Justo 4302. (7600). Mar del Plata. ARGENTINA
E-mail: phaure@fi.mdp.edu.ar

Abstract– **The oxidation of phenol solutions (5 g/L) has been studied in a semibatch autoclave reactor. Activity screening experiments were performed over two commercial catalysts: CuO+ZnO (Topsoe) and CuO+NiO (Engelhard), and CuO/Al_2O_3 prepared in our laboratory. Isothermal runs between 393 and 423 K were carried out under an oxygen pressure of 7 bar. Phenol conversion as well as pH and Chemical Oxygen Demand (COD) measurements were recorded. Almost complete phenol conversion was obtained for all catalysts. However, conversion to CO_2 was only partial. Laboratory prepared catalysts gave the best performance in terms of activity and selectivity with the lowest induction period. Stability tests showed that catalysts remained moderately active after 60 h of operation. A simple kinetic model fits experimental results.**

Keywords– **Catalytic oxidation of phenol, pollution control, copper catalysts.**

I. INTRODUCTION

There is an increasing need for decontamination of refractory compounds, such as phenolic contaminants, that cannot be degraded by conventional means. The phenol and derivatives are generally toxic even at very low concentrations. The Environmental Protection Agency of the USA has recommended discharge limits of 0.1 mg/L in wastewaters. These chemicals are present in the effluents of different industries, (*e.g.* petroleum refineries, petrochemical facilities, resin manufacturers, wood-preserving sites). Several methods have been proposed for treatment: recovery, incineration, adsorption, biological treatment and chemical oxidation (ozone, wet-air and catalytic, for example).

The oxidation of organic compounds over a solid catalyst has been recently proposed. The organic matter can be mainly converted to carbon dioxide and water, at temperatures and pressures much more moderate than those required for a non-catalyzed process. Nevertheless, the development of a satisfactory catalyst for this process has not been reported yet. Such catalyst should be able to oxidize low concentrations in aqueous media and possess resistance to inactivation by leaching. Relatively few studies exist on the catalytic oxidation of organic matter in aqueous solutions, and there is a large discrepancy in the results. Sadana and Katzer (1974a) determined that copper oxide supported over γ-alumina was effective for phenol oxidation in the temperature range of 96°C to 246°C. A transition to a state of higher catalytic activity was observed after an induction period. The authors postulated that the heterogeneously catalyzed aqueous-phase phenol oxidation occurs by a free radical mechanism, involving initiation on the catalytic surface, followed by homogeneous propagation. The kinetics seemed to be first order with respect to the phenol concentration in both cases, but the oxygen dependence changes from order 1 to 0.5. Ohta *et al.* (1980) found reaction orders of 0.44 and 0.55 for phenol and oxygen respectively, working with the same catalyst. More recent works (Pintar and Levec, 1992; Levec and Pintar, 1995; Fortuny *et al.*, 1995) used commercial catalysts with CuO, ZnO and alumina developed for different processes. Pintar and Levec (1995) studied the catalytic oxidation of p-chlorophenol and p-nitrophenol using a commercial catalyst (Süd-Chemie AG, Munich) with copper oxide, cobalt and zinc, modified with porous cement. The experiments were carried out in a fixed bed reactor filled with liquid at 30 bar and 150-190°C. These authors recommended working with low liquid/catalyst ratios so as not to favor undesired reactions (polymerization). Akyurtlu *et al.* (1998) studied the performance of six commercial catalysts in a batch autoclave. Depending on the operating conditions, complete phenol conversion was obtained within 90 min. In some cases, the reaction underwent an induction period after which there was a transition to a much higher activity regime. But when the reaction was started after preheating the aqueous solution saturated with oxygen, no induction period was observed. Vogel *et al.* (1999) studied the promoted oxidation of phenol in aqueous solution. Phenol was degraded at temperatures as low as 100ºC without observing induction time. The remaining solution mainly contained

acetic and formic acid.

The literature survey on the catalytic oxidation of phenol shows considerable variability in activity and stability among the catalysts used. Since these parameters strongly influence the economics of the process, it is relevant to obtain comprehensive data on these areas. The preparation of an efficient and durable catalyst is still a critical step in the implementation of the catalytic oxidation process. Catalysts used until now presented serious activity losses and deactivations due to the strong oxidizing conditions.

We report here the catalytic oxidation of phenol in an autoclave batch reactor using commercial and a $CuO/\gamma\text{-}Al_2O_3$ catalyst developed in our laboratory.

II. METHODS

A. Sample preparation

CuO/γ Al_2O_3 catalysts were prepared in our laboratory by a molten salt method. Copper (II) nitrate trihydrate (MERCK, reagent grade) was used as metallic precursor. The alumina support (CK -300 Cyanamid KETJEN, BET N_2 surface area 190 m^2/g) was previously calcined at 650°C during 3 h with synthetic air. The metallic salt was molten at 250°C, to avoid decomposition. The alumina was also preheated at the same temperature. The molten salt and the support were mixed and left in contact for 30 min, at 150-200°C. The resulting preparation was cooled down at room temperature for 24 h. The sample was dried in a conventional oven at 110°C. A part of the sample was calcined at 400°C for 4 hours (catalyst **C1**) and the other at 900°C for the same time (catalyst **C2**). In addition, two commercial catalyst were tested:

C3:Engelhard Cu0226S: 12.5%CuO-0.32%NiO.

C4: Topsoe LK821: 52%CuO-25%ZnO.

B. Catalysts characterization

The laboratory prepared catalysts were characterized by Temperature Programmed Reduction (TPR), X-Ray Diffraction (XRD), Atomic Absorption (AA) and superficial area determinations by BET methods. The characteristics of the samples are given en Table 1.

The Surface Area measurements were performed using a FlowSorbI 2300 Micrometrics surface area analyzer. All the areas were derived from one point B.E.T. adsorption isotherms, with nitrogen at -195°C as the adsorbate. Temperature Programmed Reduction (TPR) was performed with 5% H_2/Ar with 0.04 g of catalyst in a conventional TPR set-up. The temperature was increased linearly at 5°C/min. The temperature range was 20 to 500°C and the H_2 uptake was monitored by a thermal conductivity detector. XRD patterns were obtained with a PW 1830/00 Philips XRD diffractmeter employing Cu Kα radiation. The X-ray was operated at 40 kV and 30 mA. Diffraction patterns were obtained using a scanning rate of 1.0 deg/min (in 2θ) with divergence slit and scatter slit widths of 1°. The overall metal composition of oxides was determined by atomic absorption spectrophotometry (AA–375 Varian). The samples were attacked with nitric acid to remove the Cu^{+2} species.

Table 1. Characterization results of the catalysts and the support.

Sample	S_{BET} (m^2/g)	Cu cont.[1] (%wt)	XRD phases Detected
$\gamma\text{-}Al_2O_3$	192	-	γ-alumina
C1 fresh	115	28.9	CuO, γ-alumina
C1 after 4 h of operation.	-	14.2	CuO, γ-alumina
C1 after 60 h of operation.	-	2.2	γ-alumina
C2 fresh	40	2.7	$CuAl_2O_4$, γ and α-alumina
C2 after 4 h of operation.	-	1.0	$CuAl_2O_4$, γ and α-alumina
C2 after 60 h of operation.	-	0.6	$CuAl_2O_4$, γ and α-alumina

[1] Copper extracted with nitric acid.

C. Determination of catalytic activity and selectivity

The experimental set-up consists of a stirred 0.5 L batch stainless steel autoclave reactor (Autoclave Engineers, Erie, PA) equipped with temperature control units and sampling facilities. The catalyst was placed into a catalytic basket. The kinetic basket is an annular cage (inner diameter: 3.7 cm; outer diameter: 5.3 cm; height: 7 cm), made of stainless steel screen. This device is useful for gas-liquid-solid reactions because catalyst particles can be used many times at identical operating conditions and a gradientless reactor can be realized. The total pressure in the system was kept constant by a backpressure regulator, the deviation not exceeding ±0.5% of the set value. The oxygen flow, introduced into the vessel below the impeller, was controlled by an electronic mass flow controller (Sierra Instruments 901C-PE).

To address about the importance of internal mass transfer limitations, one experiment with

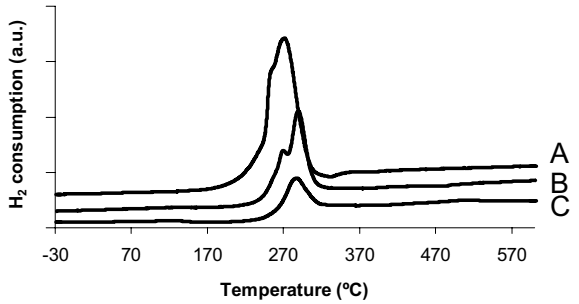

Figure 1: TPR profiles for catalyst C1. A- fresh catalyst, B- after 4 h of operation and C- after 60 h of operation.

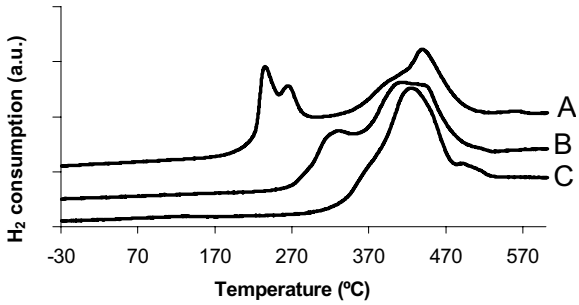

Figure 2: TPR profiles for catalyst C2. A- fresh catalyst, B- after 4 h of operation and C- after 60 h of operation.

powdered catalyst was performed. Essentially we did not observe significant improvements on reaction performance. The experiments with powdered catalysts are difficult to perform in our system, because the particles run away from the catalytic basket. To minimize catalyst loss and deactivation by leaching, all the experiments were done with pellets, as recommended by Ohta *et al*. (1980).

In a typical run, a given amount of fresh catalyst was charged into the reactor containing 0.35 L of bidistilled water with a known quantity of phenol. Once the reactor was closed, nitrogen was passed through in order to purge the air left in the reactor, which was then heated. No phenol conversion was detected during the preheating period under nitrogen flow. When the oxidation temperature was reached, pure oxygen at 0.9 L/min was introduced into the system at the required pressure, the stirrer was turned on, and the reaction was thus initiated. Preliminary experiments were performed in which the rotating speed was varied from 500 to 900 rpm while other conditions were held constant. Conversion with time curves were independent of rotating speed and we confirmed that interphase mass transfer resistances could be neglected. Consequently, all the tests were done at 800 rpm, a velocity enough to neglect interphase mass transfer resistances. The theoretical time required to saturate the liquid with oxygen under the experimental conditions is in the order of a few minutes.

Liquid samples were withdrawn periodically through a liquid sampling line and were analyzed for phenol content by a direct photometric method (SPECTROPHOTOMETER Shimadzu, UV 1601 PC). Intermediates were recognized by a GC/MS equipped with a HP-5M5 (crosslinked 5% PH ME Siloxane) capillary column and HPLC analysis using an AMINEX HPX-87 H column.

Chemical Oxygen Demand was determined by a closed reflux colorimetric method, which is a rapid system for measuring the amount of oxygen consumption in the solution by $K_2Cr_2O_7$. The pH of the samples was measured by a digital pH meter. Carbon dioxide was detected as barium carbonate obtained when the gas outlet stream was continuously bubbled into a saturated barium hydroxide solution (Pintar and Levec, 1992).

III. RESULTS AND DISCUSSION

A. Characterization studies

The TPR profiles obtained for the C1 and C2 catalysts (fresh and used) are shown in Figs. 1 and 2. The results indicate the presence of different copper species in the two catalysts.

The TPR profiles for fresh and used catalyst C1 show a maximum in the H_2 consumption in the range 262-288 ºC, as seen in Fig. 1. These peaks can be assigned to CuO-like species (Anderson *et al.*, 1997). The XRD analysis confirmed the presence of CuO phase, as indicated in Table 1. Activity measurements were performed following the procedure described in section 2.3. After several hours of reaction, the TPR profiles show a decrease in the amount of the active phase. The XRD and AA analysis reported in Table 1, confirm this observation.

The TPR profiles obtained for fresh C2 catalyst indicate the presence of two different copper species (Fig. 2). As for catalyst C1, at low temperatures, the maximum in H_2 consumption can be assigned to CuO-like species. Results show an additional contribution at higher temperatures attributed to the formation of copper aluminate (Dumas *et al.*, 1989). The XRD patterns confirm the presence of $CuAl_2O_4$. Similar results were obtained by Alejandre *et al.* (1998). The interactions between the copper oxide and the alumina produce a non-stoichiometric copper aluminate. This process is favored by high calcination temperatures. The Cu content for catalyst C2 was obtained by AA, as reported in Table 1. The values are unusually low. However, they are only indicative of the Cu present as CuO, since the nitric

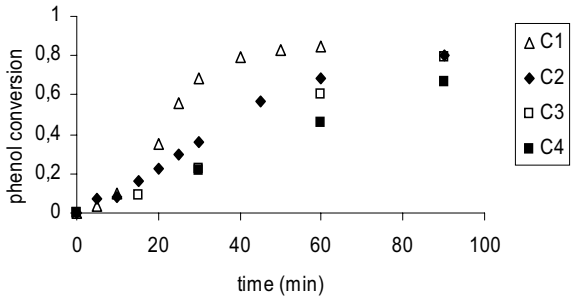

Figure 3: Phenol conversion vs. time, for the different catalysts. Conditions: C_{cat}= 8.57 g/L, $C_{Ph,0}$=0.053 mol/L, PO_2= 7 bar, T=140ºC.

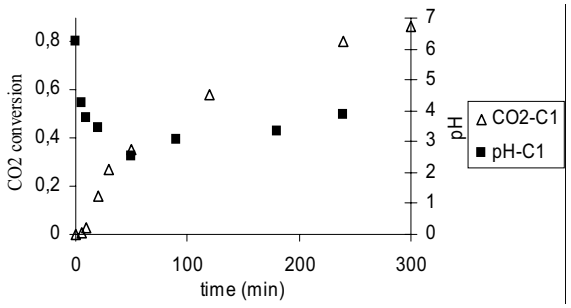

Figure 4: Phenol conversion to CO_2 and pH vs. time, for catalyst C1. Conditions: C_{cat}= 8.57 g/L, C_{Ph0}=0.053 mol/L, PO_2= 7 bar, T=140ºC.

Table 2: Activity results for the different catalysts at 140ºC.

	C1	C2	C3	C4
Induction period (min)	50	110	120	150
Final phenol conversion	0.90	0.91	0.88	0.90
Final CO_2 production	0.80	0.67	0.62	0.57

acid attack does not remove the Cu^{+2} species presented in the spinel structure. These species represent about the 85% of the total Cu content of the C2 catalyst, as observed in TPR and AA experiments. After 4 h of operation, TPR profiles show also two thermoreduction peaks for C2 catalyst. The H_2 consumption for the total reduction of the species present in used C2 catalyst is approximately the same as reported for fresh C2 catalyst, but the amount of spinel species is higher in the used sample. This may be attributed to the transformation of the active phase CuO into the inactive spinel structure. Finally, after 60 h of operation, the amount of CuO is negligible and practically all the Cu^{+2} is in the spinel structure. The XRD and AA results confirmed that the Cu^{+2} species initially present as CuO, migrate into the surface of defective spinel-type γ-Al_2O_3 (Ozawa *et al.*, 1996). This diffusion process is favored by the reaction conditions.

B. Catalytic studies

Figure 3 presents the activity results obtained at 140°C for all the catalysts. Final phenol conversion is about 90% for all the samples. However, the necessary time to reach this steady state conversion (induction period) is smaller for the catalysts synthesized in our laboratory (C1 and C2), as shown in Table 2.

In all the runs, commercial and laboratory prepared catalysts show similar behavior. Sadana and Katzer (1974b) found that slurry oxidation of phenol in aqueous solution with copper oxide catalysts occurred by a free radical mechanism. The reaction involved a free radical initiation on the catalyst surface, homogeneous propagation and either homogeneous or heterogeneous termination processes. Intermediate products formed are quinones and organic acids. Pintar and Levec (1992) additionally reported the formation of polymers by the homogeneous route. Alejandre *et al.* (1998) performed a comparative study of Cu and Ni based catalysts in a trickle bed reactor. They found that all the copper catalysts drive a mechanism of partial phenol oxidation to carboxylic acids and quinone related products with very high specific rates.

Our experimental results followed the mechanism proposed by Sadana and Katzer (1974b). The color of the samples turned from transparent to light brown and finally to blackish brown as conversion of phenol increased. Even at very high conversions, samples did not become clear. But, when the liquid samples were centrifuged at 3000 rpm, blackish brown precipitates appeared for the samples in which the reaction time exceeded 30 min. An elementary analysis of the solid precipitates mainly detected carbon.

The color of the supernatant liquid changed from yellowish to brownish and finally, in some cases, became clear as pH increased. Figure 4 shows pH changes and the amount of phenol converted to CO_2 as function of time for catalyst C1, at 140°C. The pH decreases up to a minimum of 2.5 at 40 min and then increases gradually with time. Catalyst C2 exhibited similar trends. These results may be an indication that the organic acids produced during the initial step of phenol oxidation (40 min) are gradually oxidized to final products.

As shown in Fig. 4, CO_2 production increases with the time-run. At 40 min, phenol conversion is close to 80% while CO_2 production is 35%. The mass balance is completed considering intermediate products, mainly organic acids. The isolation and identification of these compounds is under study, but a preliminary HPLC analysis reported the presence of oxalic, formic and malonic acids. GC/MS detected

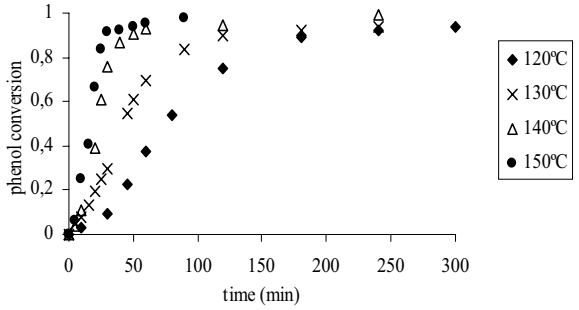

Figure 5: Phenol conversion vs. time, for catalyst C1 at different temperatures. Conditions: $C_{Ph,0}$=0.053 mol/L, PO_2= 7 bar, C_{cat}= 8.57 g/L.

Table 3: Induction period for catalysts C1 and C2, as a function of temperature.

	120ºC	130ºC	140ºC	150ºC
Induction period for C1 (min)	180	120	50	30
Induction period for C2 (min)	210	130	100	90

acetic, malic and formic acid, and quinones, as well as residual phenol. The minimum value of pH reported corresponds to the maximum intermediate concentration. As the oxidation of intermediates progresses, phenol conversion remains almost constant while CO_2 production and pH increase.

Taking into account the results shown in Table 2, we conclude that catalysts C1 and C2 exhibited the best performance in terms of activity and selectivity. Catalysts C1 and C2 were tested at different temperatures. An activity enhancement and a decrease in the induction period was found at higher temperatures, in agreement with literature results (Akyurtlu *et al.*, 1998). Figure 5 shows the results for the catalytic runs performed with C1. Catalyst C2 shows similar behavior, but longer induction periods than catalyst C1 (Table 3).

According to Fortuny *et al.* (1995), catalytic activity is directly related with the amount of active species. Catalyst C1 has a CuO content of 28%, while catalyst C2 only has 2.7% CuO, however, activity differences are not so pronounced. One possible explanation is that the amount of active species present in catalyst C1 could be in excess.

C. Catalytic stability studies

Catalytic stability is an important factor for industrial applications. A catalyst batch of 3 g has been retained and used for several cycles without treatment between cycles. The sample and reactants were placed in the reactor following the procedure previously described. The steady state phenol conversion (estimated at 4 h of operation) for C1 and

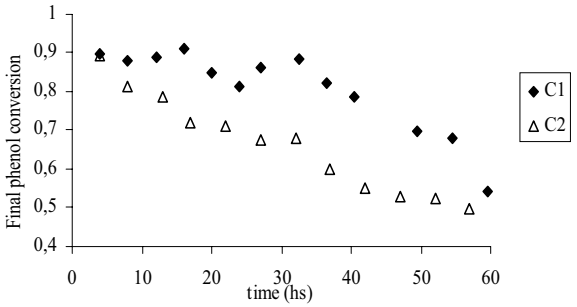

Figure 6: Steady state phenol conversion as a function of time of operation, for catalysts C1 and C2 reused several times. Conditions: $C_{Ph,0}$=0.053 mol/L, PO_2= 7 bar, T=140ºC, C_{cat}= 8.57 g/L.

Table 4: Performance after 60 h of operation.

	C1	C2
Phenol conversion	0.60	0.55
Final CO_2 production	0.40	0.35
Final pH	2.7	2.9
Induction period (min)	300	>400

C2 samples is plotted against time in Fig. 6. Performance of these catalysts after 60 h of operation is shown in Table 4.

For catalyst C1, two different zones can be distinguished. Catalyst activity seems to decrease very slowly with usage during the first 40 h. After this time, phenol conversion decrease is more pronounced.

Figure 7 shows steady state CO_2 production. In this case the variations are more significant, changing from 0.7 to 0.3 at 60 h. Analysis of phenol and CO_2 production (Figs. 6 and 7) indicates that selectivity towards complete oxidation decreases reaction time. The pH measurements, also presented in Fig. 7, confirm this hypothesis. The final pH decreases with usage up to 40 h, reaching a minimum of 2 and then increases with the run-time. After 40 h, the catalyst activity decays and so does the production of intermediate compounds responsible for the pH increase.

For catalyst C2 the phenol conversion decays with reaction time from 80 to 55%. Its selectivity towards CO_2 is lower than that reported for C1. Induction time also increases with usage.

For both C1 and C2, activity and selectivity towards CO_2 production decrease with time of operation. For catalyst C1, this behavior could be partially attributed to the loss of CuO species. Leaching is confirmed by TPR, XRD and AA techniques reported in section 2.1. It is known that hot acidic solutions can promote the solubility of some metal oxides (Alejandre *et al.*, 1998). For catalyst C2, a different deactivation mechanism is proposed: the formation of spinel structures. This is confirmed by

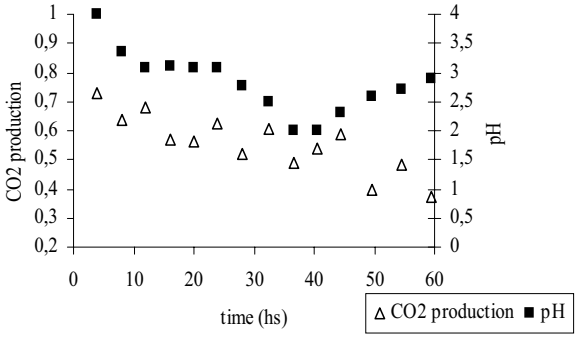

Figure 7: Phenol conversion to CO_2 and pH vs. time, for catalyst C1 reused several times. Conditions: $C_{Ph,O}$=0.053 mol/L, PO_2= 7 bar, T=140ºC, C_{cat}= 8.57 g/L.

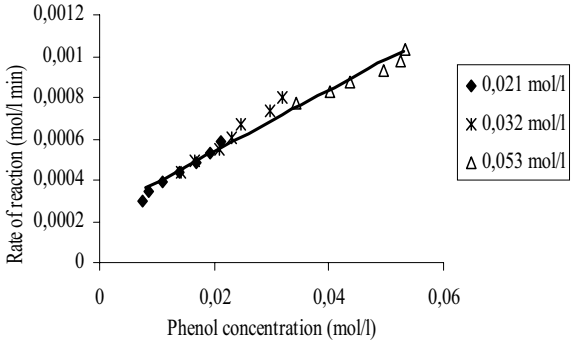

Figure 8: Reaction rate vs. phenol concentration, for different initial phenol concentrations. Conditions: PO_2= 7 bar, T=140ºC. C_{cat}= 8.57 g/L.

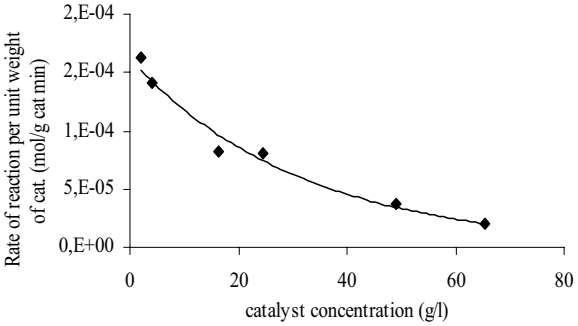

Figure 9: Reaction rate vs. catalyst concentration. Conditions: T=140ºC, PO2= 7 bar, CPh,O=0.053 mol/L.

TPR, XRD and AA analysis.

Nevertheless, after 60 h of operation, catalyst C1 has a CuO content of 2.2 %. This amount is close to the CuO content of fresh C2, however, activity and selectivity for used catalyst C1 are significantly lower than for fresh C2. This could be attributed to the deposition of carbonaceous material formed during the reaction. The solid intermediates are deposited on the active sites, further reducing the catalytic activity.

Since catalyst C1 exhibited the best performance in terms of activity, selectivity, and stability, it was selected to perform additional experiments.

D. Reactant concentration effect

The impact of phenol concentration on the initial oxidation rate is illustrated in Fig. 8; three different initial phenol concentrations were used. These data suggest a first order dependence with respect to phenol, in agreement with literature results (Sadana and Katzer, 1974b). The effect of oxygen pressure was also tested (6, 7, and 9 bar). The induction period and steady state phenol conversion were slightly affected by the oxygen pressure.

E. Catalyst concentration effect

To test the effect of the catalyst concentration on the global rate, experiments with variable catalyst concentration were carried out. Reaction rates per unit weight of catalyst are plotted against catalyst concentration in Fig. 9 for an initial phenol concentration of 0.053 mol/L.

As the catalyst loading is increased, the rate decreases with the order of -0.48. This is characteristic of oxidation reactions that proceed through a free radical mechanism (Ramachandran and Chaudhari, 1983) and was also observed by Ohta *et al.* (1980) and Sadana and Katzer (1974b). The negative dependence of rate per unit catalyst on catalyst concentration could indicate that termination steps occur on the catalyst surface (Sadana and Katzer, 1974b). The studies reported on heterogeneously catalyzed liquid-phase oxidation of aqueous phenol solutions in slurry reactors have all concluded that the observed phenol disappearance rate is dependent on the catalyst concentration (Pintar and Levec, 1992). This implies that a heterogeneous-homogeneous free-radical mechanism is involved. In many oxidation reactions reported, the rate is proportional to the square root of catalyst concentration (Ramachandran and Chaudhari, 1983). When the reaction occurs only on the catalyst surface, either via a radical or nonradical mechanism, the observed rate per unit weight of catalyst is independent of catalyst concentration (Pintar and Levec, 1992).

Final phenol conversion and CO_2 production per unit weight of catalyst also show a dependence on mass of catalyst, as indicated in Fig. 10. The difference between phenol conversion and CO_2 production is appreciable at low catalyst loadings, but virtually all the phenol is converted to CO_2 when catalyst concentration is increased. This is in agreement with the assumption that catalyst surface participates on termination steps. Note that carbon dioxide yield is a measure of the selectivity rather than just a production parameter. Since the distribution of intermediate products, and conse-

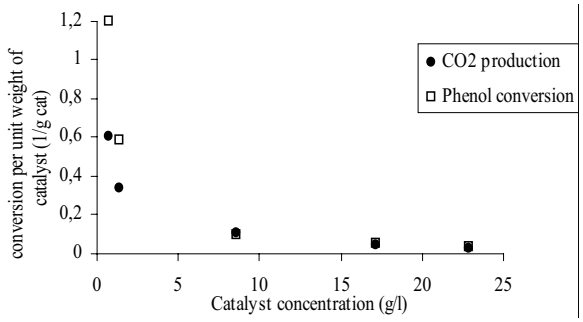

Figure 10: Final phenol and phenol conversion to CO_2 as a function of catalyst mass. Conditions: T=140ºC, PO_2= 7 bar, $C_{Ph,O}$=0.053 mol/L.

quently the selectivity, depends on the *mass of catalyst/volume of liquid* ratio, a reactor with low liquid to catalyst ratio such as a trickle bed would be more suitable to favor the selectivity towards complete oxidation

F. Kinetic model

For catalytic oxidation, the reaction kinetic is usually simplified to a power law expression (Ohta *et al.*, 1980; Pintar and Levec, 1992). Taking into account the experimental results reported previously, the following expression for the oxidation rate can be written:

$$-r_{ph} = k'.C_{ph}.m_c^{-0.48}$$

where $-r_{ph}$ (mol.g cat^{-1}.min^{-1}) is the phenol degradation rate, k' (min^{-1}) is the apparent pseudo-first order kinetic constant that accounts for internal mass transport limitations, C_{ph} (mol.L^{-1}) is the phenol concentration at the surface of the catalyst for the bulk phenol concentration in absence of external mass transport limitations and m_c (g cat/L) is the catalyst concentration. It is important to point out that power-law rate expressions can be only considered as equations. that describe the general trend of experimental data, but they do not describe at all any detail of the complex oxidation chemistry.

Using experimental results obtained with an initial concentration of phenol of 0.053 mol/L and catalyst loading of 8.57 mol/L, k' was evaluated at different temperatures for catalyst C1. A subsequent Arrhenius representation of k' allowed the calculation of the apparent activation energy for the heterogeneous reaction, which results in Ea_{app}=91 kJ/mol. This value is in agreement with the results reported by Ohta *et al.* (1980) and Pintar and Levec (1992), 85.3 and 84 kJ/mol respectively, for phenol oxidation over a $CuO.ZnO.Al_2O_3$ catalyst in slurry reactors. The kinetic parameters reported in both studies are broadly accepted to be intrinsic (Fortuny *et al.*, 1995).

IV. CONCLUSIONS

The catalytic studies on the degradation of phenol in aqueous solution gave the following results:

- The copper oxide supported on γ-alumina catalysts, prepared by a molten salt method developed in our laboratory, were active for the oxidation of phenol at temperatures above 120°C and 7 bar of oxygen. A simple kinetic model fits experimental data. Results obtained are only suitable for the reaction conditions used in this study.
- The distribution of intermediate products, and consequently the selectivity, depends on the *mass of catalyst / volume of liquid* ratio. A reactor with low liquid to catalyst ratio would be more suitable to favor the selectivity. Future studies will be performed in a trickle bed reactor.
- Catalyst stability tests show that catalyst remains moderately active up to 60 h. The loss of active species and the deposition of carbonaceous material on the catalytic sites are responsible of the activity loss. Efforts are in progress to improve stability by coating the pellets with a hydrophobic material. In this way, we expect to minimize the leaching process.

ACKNWOLEDGEMENTS

This work was supported by funds provided by the Agencia Nacional de Promoción Científica y Tecnológica ANPCyT and the Universidad Nacional de Mar del Plata. We want to express our gratitude to Mr. Hector Asencio, Mr. Jorge Cechini, Mr. Fernando Ivorra and Ms. Carmen Rodriguez for the technical support and to Eng. P. Bonelli who performed the elementary analysis.

REFERENCES

Akyurtlu, J., A. Akyurtlu and S. Kovenklioglu, "Catalytic oxidation of phenol in aqueous solutions," *Catal. Today* **40**, 343-352 (1998).

Alejandre, A., F. Medina, A. Fortuny, P. Salagre and J.E. Sueiras, "Characterisation of copper catalysts and activity for the oxidation of phenol aqueous solutions," *Appl. Catal. B: Environmental* **16**, 53-67 (1998).

Anderson, J., C. Marquez Alvarez, M.J. Lopez Muñoz, I. Rodriguez Ramos and A. Guerrero Ruiz, "Reduction of NO_x in C_3H_6/air mixtures over Cu/Al_2O_3 catalysts," *Appl. Catal. B: Environmental* **14**, 189-202 (1997).

Dumas, J.M., C. Geron, A. Kribii and J. Barbier "Preparation of supported copper catalyst. II. Reduction of copper/alumina catalysts," *Appl. Catal.* **47**, L9-L15 (1989).

Fortuny A., C. Ferrer, C. Bengoa, J. Font and A. Fabregat, "Catalytic removal of phenol from aqueous phase using oxygen or air as oxidant," *Catal. Today* **24**, 79-83 (1995).

Levec J. and A. Pintar, "Catalytic oxidation of aqueous solutions of organics. An effective method for removal of toxic pollutants from waste waters," *Catal. Today* **24**, 51-58 (1995).

Otha, H., S. Goto and H. Teshima, "Liquid-phase oxidation of phenol in rotating catalytic basket reactor," *Ind. Eng. Chem. Fundam.* **19**, 180-185 (1980).

Ozawa, M., H. Toda, O. Kato and S. Suzuki, "Solid-state thermal behavior of copper-modified alumina toward lean-burn exhaust NO removal catalyst," *Appl. Catal. B: Environmental*, 8, 123-

Pintar, A. and J. Levec, "Catalytic oxidation of organics in aqueous solutions," *J.Catal*. **135**, 345-357 (1992).

Pintar, A. and J. Levec, "Catalytic oxidation of aqueous p-clorophenol and p-nitrophenol solutions," *J. Chem. Eng. Sci*. **49**, 4391-4396 (1995).

Ramachandran, P.A. and R.V. Chaudhari, "Three-Phase Catalytic Reactors," Gordon and Breach Science Publishers Ltd., New York (1983).

Sadana, A. and J.R. Katzer, "Catalytic oxidation of phenol in aqueous solution over copper oxide," *Ind. Eng. Chem. Fundam.***13**, 127-134 (1974a).

Sadana, A. and J.R. Katzer, "Involvement of free radicals in the aqueous-phase catalytic oxidation of phenol over copper oxide," *J. Catal*. **35**, 140-152 (1974b).

Vogel, F., J. Harf, A. Hug and P. Von Rohr, "Promoted Oxidation of phenol in aqueous solution using molecular oxygen at mild conditions," *Environmental Progress,* **18**, 7-12 (1999).

Received: November 15, 2002.
Accepted for publication: September 15, 2003.
Recommended by Editor A. Bandoni.