Preparation and characterization of wet-proofed CuO/Al₂O₃ catalysts for the oxidation of phenol solutions

Paola Massa, Fernando Ivorra, Patricia Haure, and Rosa Fenoglio*

Instituto de Investigación en Ciencia y Tecnología de Materiales (INTEMA), CONICET- Universidad Nacional de Mar del Plata, J.B. Justo 4302, B7608FDQ Mar del Plata, Argentina

Two wet-proofed catalysts were prepared by subsequent coating steps with polytetrafluoroethylene fibers over a CuO/γAl₂O₃ catalyst. They were tested for the oxidation of phenol solutions in a semi-batch reactor. Phenol conversion as well as Chemical Oxygen Demand (COD) was recorded. The hydrophobic coverage reduces the loss of active phase by leaching. Therefore, deactivation was attributed to the deposition of carbonaceous residues on the catalytic surface.

KEY WORDS: wet-proofed catalysts; copper catalyst; phenol oxidation.

1. Introduction

A large portion of the wastes generated by chemical and related industries is in the form of aqueous streams. These effluents may contain organic pollutants that are either toxic or poorly biodegradable at the concentrations usually found, so that direct biological treatment is not feasible. In these cases, it is necessary to use less conventional techniques, such as partial chemical oxidation, to remove the pollutants. Organics are oxidized to carbon dioxide and water in a three-phase reactor operated at moderate temperatures and pressures. Sadana and Katzer [1] were the first who evaluated the catalytic liquid-phase oxidation as a potential wastewater treatment technology.

The key issue in the effective catalytic oxidation of organics in wastewater is, however, finding a suitable catalyst. The development of a stable, economic, active and selective catalyst is the objective of this contribution. Sadana and Katzer [1] determined that the copper-oxide supported over γ-alumina is effective for phenol oxidation in the temperature range of 96 to 246 °C. They observed an induction period followed by the transition to a state of higher catalytic activity. A mechanism involving heterogeneous and homogeneous reactions was proposed for the batch reactor. First order dependency with respect to phenol was suggested while the reaction order for oxygen changed from order 1 to 0.5 as reaction progressed. However, Ohta *et al.* [2] found different results working with the same catalyst. More recently, Pintar and Levec [3] and Fortuny *et al.* [4] used commercial catalysts developed for different reaction systems. Pintar and Levec [3] recommended the use of a Trickle Bed Reactor, with a low liquid/catalyst ratio, to avoid undesired homogeneous reactions such as polymerization. Stability studies reported in the literature indicated that the catalysts are deactivated mainly because of leaching of the active phase, a process that is favored by the hot acidic working conditions [3,5] and due to the deposition of carbonaceous intermediates [3].

In a previous work, we synthesized CuO/γ-alumina catalysts using a molten salt method [6,7]. Fresh and used samples were characterized by Atomic Absorption (AA), BET surface area, Temperature Programmed Reduction (TPR) and X-ray Diffraction (XRD). Activity essays were performed using commercial (Engelhard Cu0226S and Topsoe LK821) and CuO/γ-alumina catalysts synthesized in our laboratory. Experiments were conducted in a semi-batch agitated reactor, over a wide range of experimental conditions. Phenol consumption, Chemical Oxygen Demand (COD) and pH measurements were monitored to follow the reaction progress. For a given set of experimental conditions, all the samples tested gave a total phenol conversion of about 90%, however the necessary time to reach this conversion was smaller for the catalysts CuO/Al₂O₃. Stability test results indicate that catalyst activity decayed about 20% after 60 h of usage. Deactivation was due to the elution of the active phase and to the deposition of carbonaceous material on the active sites of the catalyst. To minimize deactivation by leaching, the catalyst must be resistant to fouling water, i.e. the catalyst should be wet-proofed and/or hydrophobic. The main advantage of using a hydrophobic material lies in the lower water adsorption capacity.

Few results are reported in the open literature concerning the development of wet-proofed catalysts, and none works are related to the preparation of

---

* To whom correspondence should be addressed.
 E-mail: rofeno@mdp.edu.ar

copper/alumina hydrophobic catalyst for the oxidation of phenol solutions. The use of wet-proofed catalysts for the oxidation of methanol in water has been proposed [8]. More recently, Horowitz [9] studied the oxidation of ethanol aqueous solutions using a Pd/alumina hydrophobic catalyst. High metal loadings are recommended for hydrophobized catalysts by Rangwala *et al.* [10] in order to increase the activity per unit volume of reactor.

In this contribution, we attempt to increase catalytic stability of conventional catalysts by means of a hydrophobic coverage. Comparison of conventional and hydrophobic copper/alumina catalysts performance for the oxidation of phenol solutions is reported.

2. Experimental

2.1. Catalysts preparation

The CuO catalysts were prepared from $Cu(NO_3)_2 \cdot 3H_2O$ (p.a., MERCK) and γAl_2O_3 (ALFA AESAR, 1/8″ pellets, BET surface area 214 m^2/g) following a molten salt method. 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 at room temperature for 24 h. The sample was dried in a conventional oven at 110 °C overnight, and calcined at 400 °C during 4 h with synthetic air. A part of the sample was coated with polytetrafluoroethylene (PTFE) fibers following Horowitz procedure [9]. During each impregnation cycle, the pellets were first dipped into water for 1 min in order to reduce further permeation of PTFE into the catalyst pores. Then, the catalyst was immersed into an aqueous suspension of fluoropolymer resin (Teflon® PTFE 30, DuPont) diluted with water and stabilized with Triton X-100 (SigmaUltra, SIGMA), with continuous agitation. After the impregnation, the liquid was drained and the samples were dried at room temperature. The drying process was completed in a stove at 150 °C during 1 h.

The following catalysts were prepared:

Catalyst CNT: Without PTFE.
Catalyst C1T: With one impregnation cycle with PTFE.
Catalyst C3T: With three successive impregnation cycles with PTFE.

After the corresponding impregnation cycles, both C1T and C3T catalysts were calcined at 300 °C during 1 h under air atmosphere. This temperature is well below the decomposition temperature of PTFE fibers.

2.2. Characterization

The morphology of the catalysts was examined by a SEM JEOL 35CF, operating at an acceleration voltage of 6 kV, resolution of 100 å and magnification values up to 10,000×. The analysis was accomplished on fresh and used samples. The latter were treated as follows: the catalysts were used for about 60 h, then they were oxidized at 400 °C during 4 h in synthetic air, and finally the samples were tested in the reactor for about three more hours.

Fresh and used samples were characterized by TPR. This analysis was performed with 5% H_2/Ar. A conventional TPR set-up was used. The temperature was increased linearly at 5 °C/min. The temperature range was 20 to 500 °C and a Thermal Conductivity Detector (TCD) monitored the H_2 uptake. For the calibration curve, pure CuO (p.a., Carlo Erba) was used.

The copper content of the samples was determined by AA and also confirmed by TPR, using an AANALYST 300 Perkin–Elmer Spectrophotometer, according to the procedure described in [11].

Specific surface area (BET), pore volume and pore size distribution were measured with a Micromeritics ASAP 2000 instrument using N_2 adsorption at the temperature of the liquid nitrogen. All samples were degassed at 130 °C for 10 h before analysis.

Carbonaceous residues over the catalysts were eliminated by oxidation in a flow of synthetic air at 16 mL/min and 400 °C, followed by chromatographic detection of the produced CO_2 with a GC Konik 2000C equipped with a Alltech CTR I column and with a TCD.

Thermogravimetric (TG) studies were performed to determine the Teflon decomposition temperature and the loss of mass due to thermal decomposition of the hydrophobic coverage. Experiments were conducted using a TGA-50 Shimadzu apparatus equipped with a Thermal Analyzer TA-50 WSI. Essays were conducted under oxygen atmosphere. Temperatures were increased up to 1000 °C.

2.3. Determination of catalytic activity and selectivity

Catalysts were used to oxidize phenol solutions in a stirred 0.5 L-batch stainless steel autoclave reactor (Autoclave Engineers, Erie, PA). Operating conditions are given in table 1. In a typical run, fresh catalyst was placed into the catalytic basket in contact with 0.35 L of phenol solution. First, the reactor was purged and heated under nitrogen flow. When the oxidation

Table 1
Summary of operating conditions

Temperature	140 °C
Oxygen pressure	7 bar
Gas flow rate	0.9 L/min
Agitation speed	800 rpm
Catalyst concentration	8.57 g/L
Catalyst particle diameter	2.6 mm
Initial phenol concentration	5 g/L

temperature was reached, pure oxygen was introduced into the system at the required pressure and the reaction was initiated with continuous stirring at 800 rpm to avoid external mass transport limitations.

Liquid samples were withdrawn periodically. Phenol conversion and COD were evaluated following standard determination techniques [11]. The COD measurement indicates the intensity of the oxidation process. So, production of CO_2 was then evaluated from COD decrease as:

$$CO_2 \text{ production } = (COD_i - COD_f)/COD_i$$

where COD_i and COD_f are initial and final COD values, respectively.

3. Results

3.1. Catalyst characterization

Scanning Electron Micrographs of conventional and wet-proofed catalysts were performed. Fresh catalyst CNT was used as reference. It has a rugged external and internal porous morphology; as shown in figure 1.

Figures 2 and 3 indicate that the distribution of the PTFE fibers over the external surface of the pellets is not the same for C1T and C3T samples. In fresh C1T catalyst, the thickness of the coating varies between 0.15 and 0.5 μ. A significant fraction of the PTFE is present as agglomerated fibers of different morphology. The layer is not homogeneous neither complete. There are zones without covering that present identical morphology than CNT. In some areas, the deposit is so thin that "copies" the surface morphology of the catalyst. The internal morphology of C1T is similar to that reported for CNT. The thickness of the coating for fresh catalyst C3T is about 3 to 8 μ in average. Close to the areas with low-density coverage, it is possible to observe domains with higher extent of coating (approximately 25 μ). For
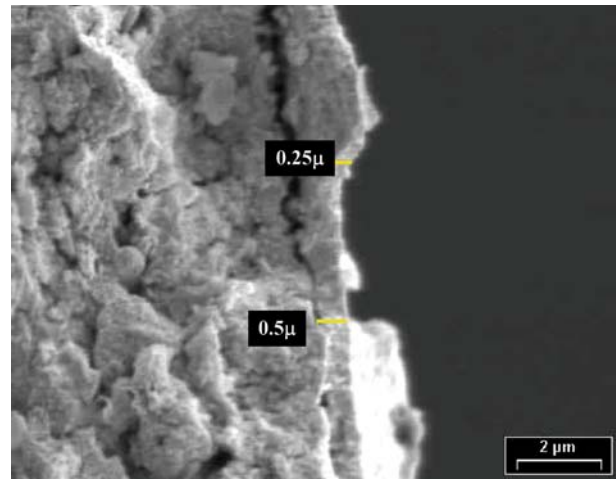

Figure 2. SEM photograph of the external surface of C1T (8600×).

this catalyst, the covering is complete but not homogeneous.

Table 2 shows the specific surface area, average pore diameter and pore volume of the different samples. Small differences can be observed in BET surface areas, average pore diameter, and pore volumes between the different catalysts and also with respect to the support.

Blank TPR assays were conducted on PTFE/alumina samples. No consumption of hydrogen was detected. TPR profiles for fresh, used and reoxidized catalysts are shown in figures 4–7. The corresponding curves for fresh CNT, C1T and C3T catalysts show a maximum in the H_2 consumption in the range of 310–320 °C, while the TPR profile for pure CuO shows a maximum rate temperature at 310 °C as shown in figure 4. Also, catalysts C1T and C3T have a small, additional peak for hydrogen consumption at 250 °C.

TPR profiles were also obtained after 60 h of usage. The area under the H_2 consumption curves for the used
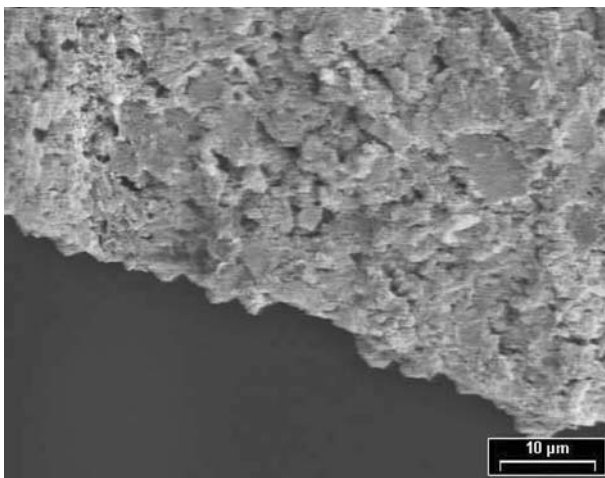

Figure 1. SEM photograph of the external surface of catalyst CNT (2000×).

Figure 3. SEM photograph of the external surface of catalyst C3T (2000×).

Table 2
Copper content, specific surface area, pore size and pore volume of the different samples

Sample	Cu content[a] (wt%)	BET surface area (m^2/g)	Average pore diameter (nm)	Average pore volume (cm^3/g)
γAl$_2$O$_3$	–	215	12.5	0.67
CNT fresh	30	154	11.7	0.46
CNT after 60 h	6	–	–	–
C1T fresh	27	157	12.4	0.49
C1T after 60 h	9	–	–	–
C3T fresh	25.5	152	11.6	0.45
C3T after 60 h	11	–	–	–

[a]Determined by AA and TPR assays.

catalysts diminishes. The reduction is more pronounced for catalyst CNT. Two overlapped peaks were distinguished at about 300 and 340 °C; for the three samples the 340 °C peak is broader.

After 60 h of reaction, all the catalysts were reoxidized at 400 °C to eliminate reversible carbonaceous deposits. This temperature was selected from preliminary experiments in which the samples were exposed to oxygen pulses at different temperatures and the production of CO$_2$ was followed by GC analysis. The deposits were completely eliminated at temperatures above 300 °C, but the PTFE coverage was not affected. Thermogravimetric analysis, performed on fresh hydrophobic samples, indicate that the PTFE coverage is stable up to 500 °C (figure 8).

TPR profiles were obtained with reoxidized samples. An increase in the total area under the thermoreduction peaks, with respect to the area registered before the reoxidation, is detected. Again, two peaks are observed but they have moved to lower temperatures: one appears at about 245–270 °C and the other at 295–320 °C. The

relative importance of these species depends on the catalyst. As seen in figure 5, for CNT the main proportion corresponds to the peak at 270 °C, while the other component (at 295 °C) represents approximately only the 20% of the total area. For C1T (figure 6) the high temperature signal represents approximately 35% of the total area under the curve, but the peak at 270 °C is still the most important. On the contrary, for C3T catalyst the high temperature peak (at 320 °C) is the main peak, representing near the 90% of the total area of H$_2$ uptake.

The copper content of the samples was determined by AA and confirmed by TPR; the results are shown in table 2. The conventional CNT catalyst has 30 wt% of Cu. Even though the wet-proofed catalysts were prepared from catalyst CNT, their percentage of copper is lower due to the presence of PTFE fibers. Samples C1T and C3T have a copper content of 27 and 25.5 wt%, respectively. Copper present in used samples is also given in table 2. Catalyst C3T and C1T retain more active phase related with their initial content (43 and
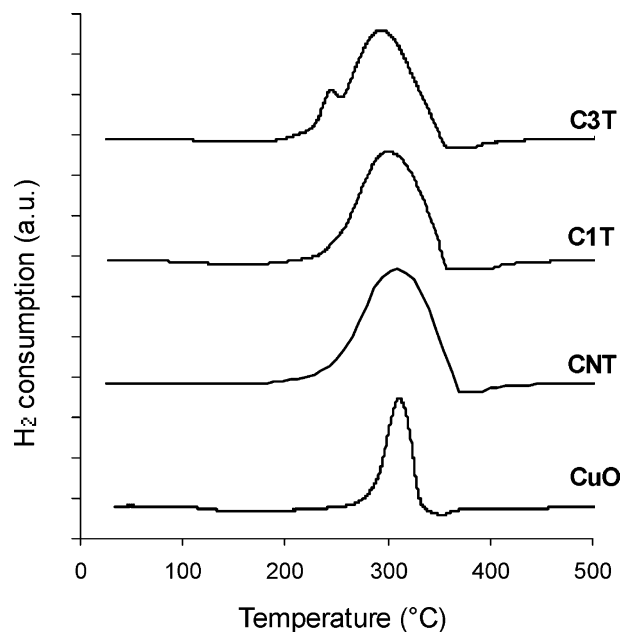

Figure 4. TPR profiles for patron CuO and fresh catalysts (CNT, C1T and C3T).
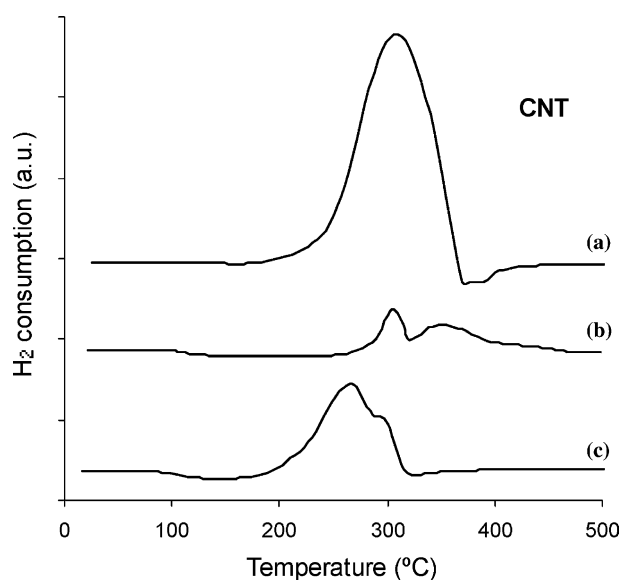

Figure 5. TPR profiles for CNT catalyst. (a) Fresh, (b) after 60 h of operation, and (c) after 60 h of operation and further reoxidation.
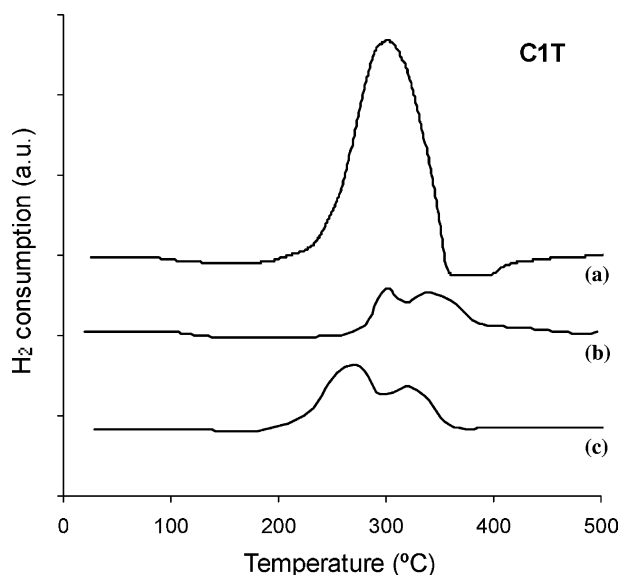
Figure 6. TPR profiles for C1T catalyst. (a) Fresh, (b) after 60 h of operation, and (c) after 60 h of operation and further reoxidation.

33%, respectively) than CNT does (only the 20% of the active phase is retained).

Figure 8 shows the TG results for fresh CNT, C1T and C3T samples. For the three catalysts, it is observed a loss of weight at 150 °C due to water elimination. C1T and C3T samples show an additional weight loss at approximately 530 °C, attributed to PTFE decomposition. From these results, the percentage PTFE per unit mass of catalyst was calculated as 1 and 3% for C1T and C3T, respectively. Accordingly, Cu contents of 29.7 and 29.1% can be calculated for fresh C1T and C3T samples. These values differ slightly from those reported by TPR and AA. Discrepancies may be attributed to the pres-
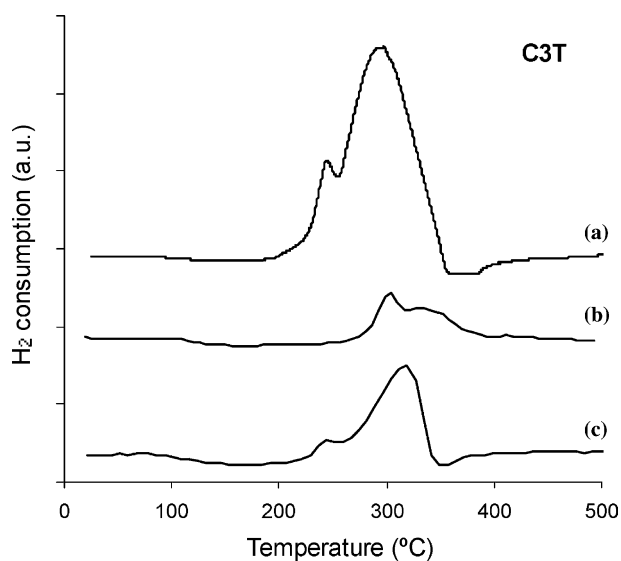
ence of the hydrophobic layer, that may interfere with the detection of Cu^{+2} species in TPR and AA studies.

3.2. Reaction results

Figure 9(a) and (b) present phenol conversion and CO_2 production vs. time. Results were obtained at 140 °C for CNT, C1T and C3T fresh catalysts. In all the runs, conventional and wet-proofed catalysts show similar behavior. Final phenol conversion is about 90% for CNT and C1T catalysts. However, the time necessary to reach this conversion (or induction period) is lower for the conventional catalyst. Finally, sample C3T exhibits lower final phenol conversion, approximately 80%, and longer induction period than CNT and C1T catalysts.

As shown in figure 9(b), the CO_2 production increases with time-run for all the fresh catalysts. Data given for catalyst CNT at 40 min indicate that phenol conversion is close to 80%, while CO_2 production is only 35%; that is, only 35% of the phenol converted goes to CO_2. The mass balance is completed considering the formation of intermediate products, mainly organic acids. The isolation and identification of these compounds is under study, but a preliminary HPLC analysis

Figure 7. TPR profiles for C3T catalyst. (a) Fresh, (b) after 60 h of operation, and (c) after 60 h of operation and further reoxidation.
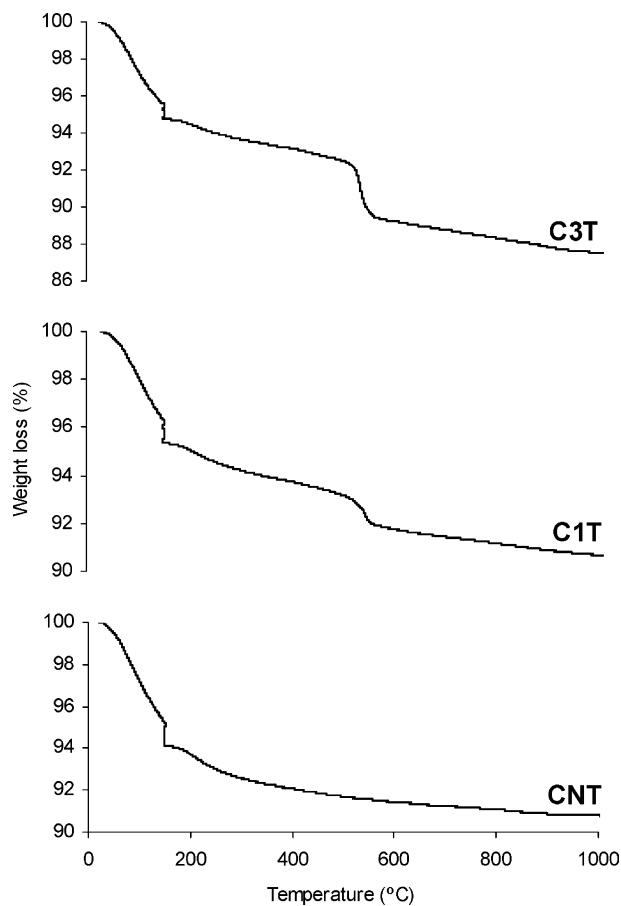

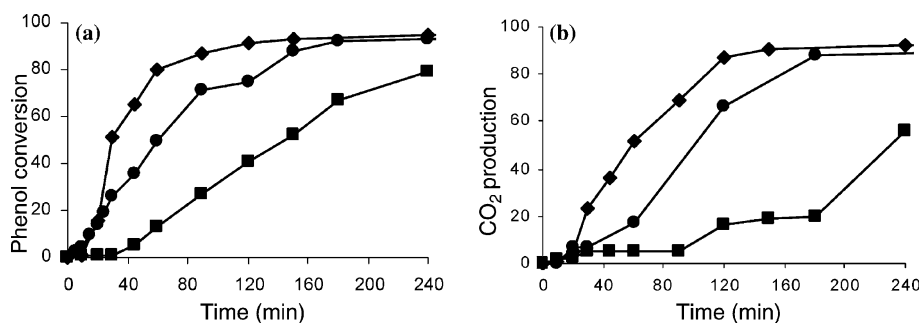Figure 8. Thermogravimetric results for fresh CNT, C1T and C3T catalysts.

Figure 9. Conversions vs. time for fresh catalysts. (a) Phenol conversion (b) CO$_2$ production . -◆-CNT catalyst, -●-C1T catalyst, -■-C3T catalyst.
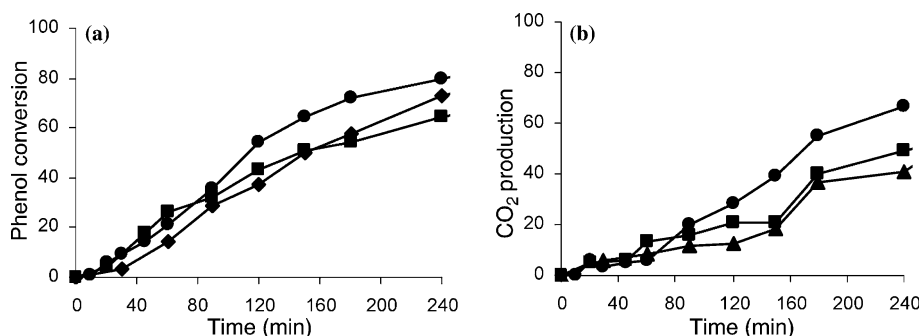

Figure 10. Conversions vs. time for used catalysts, in a run after 60 h of operation. (a) Phenol conversion, and (b) CO$_2$ production. -◆- CNT catalyst, -●- C1T catalyst, -■- C3T catalyst.

reported the presence of oxalic, formic and malonic acids. GC/MS detected acetic, malic and formic acid, and quinones, as well as residual phenol. As the oxidation reaction progresses, the amount of phenol converted to CO$_2$ is close to 100% for both catalysts CNT and C1T at 240 min of reaction. Sample C3T does not show a complete mineralization of phenol at 240 min of reaction, and only about the 70% of phenol is converted to CO$_2$.

To test catalytic stability, a batch of 3 g of each catalyst was preserved and used for several cycles of reaction. Fresh phenol solution was used in each run. All the runs lasted at least 4 h. Phenol conversion and CO$_2$ production against time are plotted in figure 10(a) and (b), for the three catalysts. These results correspond to a run after 60 h of operation. Phenol conversion and

CO$_2$ production decrease with usage, as seen in table 3. The effect is more pronounced for CNT catalyst, especially in terms of CO$_2$ production. The highest phenol conversion and CO$_2$ production are those exhibited by used C1T catalyst. No marked changes were observed for used C3T catalyst with respect to its low initial performance: phenol conversion and CO$_2$ production diminish only 19 and 12%, respectively.

The presence of carbonaceous compounds formed during the reaction was detected even by visual observation of all used catalysts. Air oxidation followed by chromatographic detection of CO$_2$ confirmed the presence of these species, although an accurate quantification was not possible.

After reoxidation at 400 °C, the catalysts were used for the oxidation of a fresh phenol solution. Reaction

Table 3
Phenol conversion and CO$_2$ production, for the different catalysts[a]

Catalyst	Phenol conversion			CO$_2$ production		
	Fresh (%)	Used for 60 h (%)	Used for 60 h and reoxidized (%)	Fresh (%)	Used for 60 h (%)	Used for 60 h and reoxidized (%)
CNT	95	73	90	92	41	80
C1T	93	84	94	89	72	83
C3T	79	64	88	56	49	53

[a]The conversion values correspond to the ones registered at 240 minutes of reaction.

results are given in figure 11(a) and (b) and in table 3. Almost complete restoration of catalytic properties is achieved: phenol conversion is close to that obtained with fresh catalysts, while CO_2 production increases notably. The final phenol conversion is practically the same for all samples, but catalyst C3T presents longer induction period than the other samples. Differences are also observed in terms of CO_2 production. After 120 min of reaction, C1T produces the highest amount of CO_2, followed by catalysts CNT and C3T.

4. Discussion

Small differences can be observed in BET surface areas, average pore diameters, and pore volumes between the different catalysts and also with respect to the support, as indicated in table 2. Alejandre *et al.* [5] observed similar trends, attributed to a good dispersion of the CuO phase on the support. Furthermore, it is evident that the hydrophobic coverage does not modify these characteristic parameters.

The TPR results indicate the presence of only one active phase, recognized as CuO-like species [12,13]. For catalysts with copper contents over 4 wt% Cu per 100 m^2/g of alumina, segregation of CuO phase occurs due to saturation of adsorption sites with Cu^{+2} ions [14–16]. The high metal loading used in this work could be responsible of the presence of large bulk-like CuO crystallites on the catalysts.

The thermoreduction temperature of CuO-like species (320 °C) obtained for the three catalysts is higher than that given elsewhere [12,17,18]. However, copper loading and calcination temperature of our samples differ from literature values. Both parameters are key factors in determining the extent of metal-support interaction and consequently, the TPR behavior.

No marked changes in the shape of the TPR principal peaks are observed in the presence of PTFE. However, for fresh C1T and C3T catalysts, the TPR profiles shows a small thermoreduction peak at lower temperature (250 °C); this could be an indication for the effect of the hydrophobic coating on the diffusion

of hydrogen during the reduction process. Discrepancies between Cu contents, evaluated directly from TPR and AA and indirectly from TG analysis, may be attributed to the presence of the PTFE layer. This film may act as an additional mass transport resistance which prevents the exposure, and therefore the detection, of Cu^{+2} species. Therefore, TPR and AA analysis may not be accurate techniques to determine Cu contents of hydrophobic catalysts, although they can be used to predict tendencies.

From results expressed in table 2, it is evident that the metal content decreases with the exposure to the hot acidic reaction conditions [5,12]. However, the PTFE coating reduces the loss of active phase. This effect is more evident for catalyst C3T, which holds a complete covering. As detected by SEM analysis, the hydrophobic coating of C1T is not complete. Thus, it does not act as an efficient barrier to avoid the solubilization of Cu^{+2} ions.

After 60 h of operation, all the catalysts exhibited a reduction in the area under the TPR profiles. A shifting of the peaks to higher temperatures was also observed. As expected, these effects are more significant for conventional CNT and for C1T; the complete hydrophobic coating of catalyst C3T reduces the contact with the aqueous solution and practically no peak displacement was registered. The lixiviation process decreases the amount of the CuO-like species. In addition, the presence of carbonaceous deposits would affect the availability of the CuO phase, diminishing the reducibility of copper species and splitting the original peak into two components. The same general behavior was observed for the three catalysts.

Under the experimental conditions examined, the reaction follows the free radical mechanism proposed by Sadana and Katzer [20]. The following steps are involved: free radical initiation on the catalyst surface, homogeneous propagation and either homogeneous or heterogeneous termination processes. Pintar and Levec [3] additionally reported the formation of polymers or carbonaceous solids by the homogeneous route. These carbonaceous deposits may also participate in the
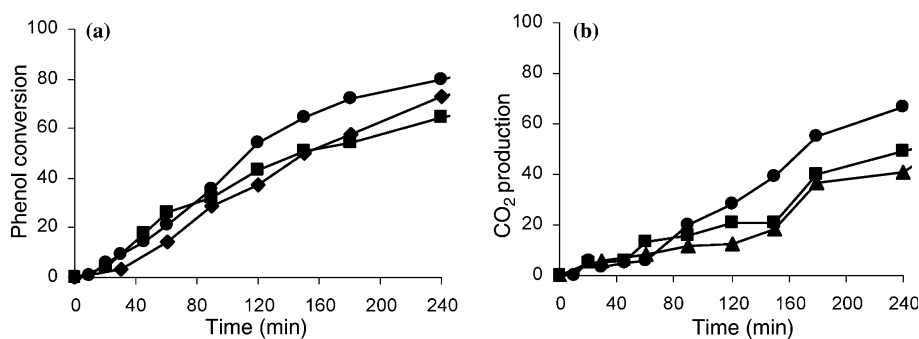

Figure 11. Conversions vs. time for used and oxidized catalysts. (a) Phenol conversion, and (b) CO_2 production. -◆- CNT catalyst, -●- C1T catalyst, -■- C3T catalyst.

deactivation process. To address this issue, used samples were calcined. After reoxidation at 400 °C, an increase of the active phase content was detected by TPR experiments. The removal of the carbonaceous deposits may increase the availability of the copper species on the catalytic surface. This effect produces an increase in the amplitude of the peaks in the H_2 uptake curve, and a shifting to lower temperatures. Two overlapped peaks were also registered: The higher temperature peak could be related with the main CuO peak observed for the fresh catalysts, and the lower temperature peak might be associated with the reduction of other copper species or with less dispersed CuO. It must be consider that the resulting copper content of the used catalysts is slightly above the threshold value for CuO phase segregation (ca. 8.5 wt% for the γ-alumina used in our work). Thus, other phases, such as surface spinel, could be detected by TPR [13,19].

Reaction results reported previously indicate that fresh CNT shows the best performance, closely followed by fresh C1T sample since both catalysts reach the same final phenol conversion and CO_2 production. The behavior of CuO/Al_2O_3 catalyst is directly proportional to the amount of active phase [4]. Initially, the three samples had similar CuO content, though catalyst C3T may have strong diffusional limitations that affect its performance.

For used catalysts, the highest phenol conversion and CO_2 production were reached by catalyst C1T. This sample retains more active phase that CNT but less than catalyst C3T. In all the experiments, the conversion for catalyst C3T is the smallest, due to additional mass transport restrictions provided by the thick hydrophobic layer.

On the other hand, as registered by TPR and also by AA analysis, the leaching process is less important for C3T sample. This catalyst has a complete, thick hydrophobic coating that prevents lixiviation. Catalysts C1T holds an incomplete coverage with zones without PTFE fibers in which the active phase is directly exposed to the reaction medium. Even though the PTFE coating is not complete, it can partially prevent the solubilization of the metal oxide. With usage, the coating presents a cracked morphology detectable by visual observation and confirmed by SEM measurements.

Carbonaceous deposits formed during reaction [20] were eliminated by reoxidizing the samples at 400 °C. Reoxidized samples were then used with fresh phenol solutions. Results are reported in table 3 and figure 10(a) and (b). Restoration of catalytic activity is present in all the samples. This is an indication that the presence of carbonaceous deposits affects significantly catalysts performance.

Therefore, the lixiviation of the active phase does not influence phenol conversion results obtained with these catalysts, mainly because they have a high initial metal content. However, selectivity towards mineralization depends on the amount and availability of active sites and is favored in catalyst C1T.

5. Conclusions

Two wet-proofed $CuO/\gamma Al_2O_3$ catalyst were prepared by subsequent coating steps with polytetrafluoroethylene fibers (PTFE). Conventional (CNT) and hydrophobic samples (C1T and C3T) had a high initial metal content. Samples were tested for the oxidation of phenol solutions during several hours. Reaction results indicate that the catalyst prepared by one immersion cycle (C1T) has the best, long-standing performance in terms of phenol conversion, production of CO_2 and stability. It was demonstrated that the PTFE layer partially prevents the solubilization of the metal oxide. However, to provide a better shelter, the coverage must be complete and homogeneous, but thin enough as to minimize mass transport resistances.

The operating conditions induced the lixiviation of the active phase. However, through the reaction times studied, this phenomenon is not the main responsible of catalytic deactivation.

References

[1] A. Sadana and J.R. Katzer, Ind. Eng. Chem. Fundam. 13 (1974) 12.
[2] H. Ohta, S. Goto and H. Teshima, Ind. Eng. Chem. Fundam. 19 (1980) 180.
[3] A. Pintar and J. Levec, J. Catal. 135 (1992) 345.
[4] A. Fortuny, C. Bengoa, J. Font and A. Fabregat, Catal. Today 24 (1995) 79.
[5] A. Alejandre, F. Medina, A. Fortuny, P. Salagre and J.E. Sueiras, Appl. Catal. B: Environ. 16 (1998) 53.
[6] R. Fenoglio, P. Rolandi, P. Massa, J. Gonzalez and P. Haure, React. Kinet Catal. Lett. 1 (2004) 83.
[7] P. Massa, M. Ayude, R. Fenoglio, J. Gonzalez and P. Haure, Latin American Appl. Res. 34 (2004) 133.
[8] S. Chen and K.T. Chuang, Can. J. Chem. Eng. 70 (1992) 727.
[9] G. Horowitz, Estudio de reactores trickle-bed: Aplicación al tratamiento de aguas residuales (Study of trickle bed reactors: Aplication to the polluted water treatment), PhD. thesis (Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires, Buenos Aires, Argentina, 1999).
[10] H.A. Rangwala, S.E. Wanke and F.D. Otto, Can. J. Chem. Eng. 72 (1994) 296.
[11] L.S. Clesceri, A.E. Greenberg and A.D. Eaton (eds), *Standard Methods for the Examination of Water and Waste water*, 20th ed.

(American Public Health Association, Washington DC, 1998), pp. 5–17 and 5–43..

[12] J.A. Anderson, C. Márquez-Alvarez, M.J. López-Muñoz, I. Rodríguez-Ramos and A. Guerrero-Ruiz, Appl. Catal. B: Environ. 14 (1997) 189.

[13] J.M. Dumas, C. Geron, A. Kribii and J. Barbier, Appl. Catal. 47 (1989) L9.

[14] B.R. Strohmeier, D.E. Leyden, R.S. Field and D.M. Hercules, J. Catal. 94 (1985) 514.

[15] R.M. Friedman, J.J. Freeman and F.W. Lytle, J. Catal. 55 (1978) 10.

[16] G. Centi and S. Perathoner, Appl. Catal. A: General 132 (1995) 179.

[17] W. Dow and T. Huang, J. Catal. 147 (1994) 322.

[18] G.M. Fierro, M. LoJacono, M. Inversi, P. Porta, R. Lavecchia and F. Cioci, J. Catal. 148 (1994) 709.

[19] P.O. Larsson and A. Andersson, Appl. Catal. B: Environ. 24 (2000) 175.

[20] A. Sadana and J.R. Katzer, J. Catal. 35 (1974) 140.