Optimized wet-proofed CuO/Al$_2$O$_3$ catalysts for the oxidation of phenol solutions: Enhancing catalytic stability

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

División Catalizadores y Superficies, INTEMA, Universidad Nacional de Mar del Plata/CONICET, Juan B. Justo 4302, 7600 Mar del Plata, Buenos Aires, Argentina

ARTICLE INFO

ABSTRACT

An optimized wet-proofed catalyst was prepared by successive immersion steps of conventional 37% CuO/γ-Al$_2$O$_3$ samples in a polytetrafluorethylene fibres suspension. Conventional and hydrophobic catalysts were tested for the oxidation of phenol solutions (5 g/L), at 140 °C and 7 atm of oxygen pressure, in a trickle bed reactor. For the conventional catalyst, phenol conversion decreased with reaction time. However, for the wet-proofed catalysts, phenol conversion levels remained almost constant with usage. The hydrophobic layer improved catalyst stability: prevented the formation of domains with cuprous species, minimized the solubilization of Cu^{2+} and the formation of bohmite phase during reaction.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

During the last decades, different non-conventional methods have been developed for the abatement of organic pollutants from industrial wastewaters. The Catalytic Wet Air Oxidation (CWAO) is a clean and effective alternative for the treatment of toxic, biorecalcitrant or highly concentrated systems. Phenol in aqueous solutions has been widely studied as model toxic and refractory pollutant [1–3]. Most of the low-cost catalytic systems used in CWAO of phenolic solutions are based on metal oxides that show good activity, but serious stability problems [1–3]. In fact, two combined effects are considered the main responsible of catalyst deactivation: the lixiviation of the metallic ions in the hot acidic reaction medium and the formation of less active phases onto the catalytic surface or carbonaceous deposits onto the active sites [3].

To minimize the deactivation/lixiviation processes, we proposed to cover conventional catalysts with a polytetrafluoroethylene (PTFE) layer [2,4]. The presence of this hydrophobic film would reduce the direct contact of the active phase with the aqueous reaction medium, allowing the reactants to diffuse and react into the catalyst. In order to effectively increase the stability of the system, a complete PTFE layer should be deposited on the catalyst.

We have previously developed a complete hydrophobic coating; however, the catalyst exhibited lower conversion levels than conventional systems, probably due to additional mass transport resistances at the thick PTFE film [4].

The objective of this contribution is to optimize the PTFE-impregnation process in order to obtain a wet-proofed catalyst with a thin and complete hydrophobic layer, able to improve catalyst stability without affecting the phenol conversion due to increased mass transport resistances compared to conventional catalysts. Catalyst activity and stability were tested for the CWAO of phenol in a trickle bed reactor (TBR) at 140 °C and 7 atm of oxygen pressure. Results are compared with those obtained with the conventional catalyst.

2. Experimental

2.1. Catalysts preparation

The CuO/Al$_2$O$_3$ catalyst was prepared with a 30 % w. of copper, from Cu(NO$_3$)$_2$·3H$_2$O (p.a., MERCK) and γ-Al$_2$O$_3$ (ALFA AESAR, dp = 4 mm, 214 m^2/g) following a molten salt method [2]. Part of the sample was reserved as reference (catalyst CNT) and the other part was further coated with hydrophobic fibres (catalyst CT), by successive immersion of the catalyst into an aqueous solution prepared from a commercial dispersion of polytetrafluorethylene (PTFE) fibres (Teflon®, PTFE30, Dupont) and Triton X-100 (Sigma-Ultra, SIGMA), with a final concentration of PTFE of 11%v/v and 0.15%v/v of surfactant. After each impregnation step, the samples were dried at room temperature and at 150 °C in an oven. The impregnation–drying process was repeated, and finally, the samples were calcined at 300 °C for 2 h, in air.

* Corresponding author.
  E-mail address: pamassa@fi.mdp.edu.ar (P. Massa).

Additionally, a CuC_2O_4/Al_2O_3 (5% Cu) catalyst was also synthesized, from an aqueous solution containing oxalic acid and copper nitrate in the stoichiometric ratio, left in contact with the γAl_2O_3 pellets for 24 h, with agitation. The catalyst was dried at room temperature and finally at 110 °C in an oven (24 h).

2.2. Characterization of the samples

– Scanning Electron Microscopy (SEM). The morphology of the catalysts (fresh and used) 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×.
– Temperature programmed reduction (TPR). The analysis was performed with 5% H_2/Ar, using a conventional TPR set-up. The temperature was increased linearly at 5 °C/min, in the range 20–500 °C; a Thermal Conductivity Detector (TCD) monitored the H_2 uptake.
– Atomic Absorption (AA). The copper content of the samples was determined by AA, using an AANALYST 300 Perkin–Elmer Spectrophotometer.
– X-ray Diffraction (XRD). Powder X-ray diffraction patterns of the samples were obtained with a PW 1830/00 Philips XRD diffractometer employing Cu Kα radiation. The X-ray was operated at 40 kV and 30 mÅ. The patterns were recorded over $8° < 2\theta < 65°$ angles, and compared to the X-ray powder files (JCPDS) to confirm phase identities, as mentioned elsewhere [4].
– Thermogravimetric Analysis (TGA). TGA studies were performed to determine the PTFE content of the hydrophobic catalysts analyzing the loss of mass due to thermal decomposition. Experiments were conducted using a TGA-50 Shimadzu apparatus equipped with a Thermal Analyzer TA-50 WSI, under oxygen atmosphere. Temperatures were increased up to 1000 °C.

2.3. Determination of catalytic activity and selectivity

Phenol oxidation was carried out in a TBR at 7 atm of O_2 pressure, 140 °C, liquid flow of 1 mL/min, gas flow of 0.46 L/min, phenol initial concentration of 5 g/L and a catalyst loading of 15 g. The experimental set-up and procedures were detailed elsewhere [5]. The catalysts were used in successive experiments up to 80 h of total reaction time. Liquid samples were withdrawn periodically until steady state; remnant phenol concentration and chemical oxygen demand (COD) were evaluated following standard determination techniques [6].

The percentage of phenol conversion was calculated as $(C_{Ph0}-C_{Phss})\cdot 100/C_{Ph0}$, where C_{Ph0} and C_{Phss} are the initial and the steady state phenol concentrations, respectively. The COD measurements indicate the completeness of the oxidation process. The percentage of carbon dioxide production was then estimated from COD decrease as $(COD_i-COD_{ss})\cdot 100/COD_i$, where COD_i and COD_{ss} are initial and steady state COD values, respectively.

3. Results and discussion

The wet-proofed catalyst preparation process was adjusted in order to improve hydrophobized catalysts overall characteristics and performance. The main variables considered were the impregnation conditions (PTFE and non-ionic surfactant concentration; contact time; number of immersion cycles) and the temperature of the drying step.

Based on previous studies [2,4], we decided to perform several consecutive immersion steps during the impregnation process. Additionally, in order to diminish the final thickness and to get a complete coverage, conditions were adjusted as to add only a limited amount of hydrophobic material in each impregnation cycle.

Successive immersion steps were tested up to a number of five. Different fluoropolymer suspension and surfactant concentrations in water were also tried (range 10–90%v/v and 0.03–0.55%v/v, respectively), and the contact time was varied from 10 to 60 min. From these preliminary experiments, the selected immersion conditions were three consecutive immersion cycles using 11 %v/v of PTFE, 0.15 %v/v of surfactant, with a contact time of 30 min at vigorous agitation.

The temperature of the drying process was varied from 110 to 150 °C. Higher temperatures (ca. 150 °C) were preferred to minimize the formation of pores in the resulting surface of the catalyst. Drying by vacuum extraction was also tested; however, it did not produce better coverage features.

Therefore, an optimized wet-proofed catalyst (CT) was developed, as confirmed by characterization and reaction experiments.
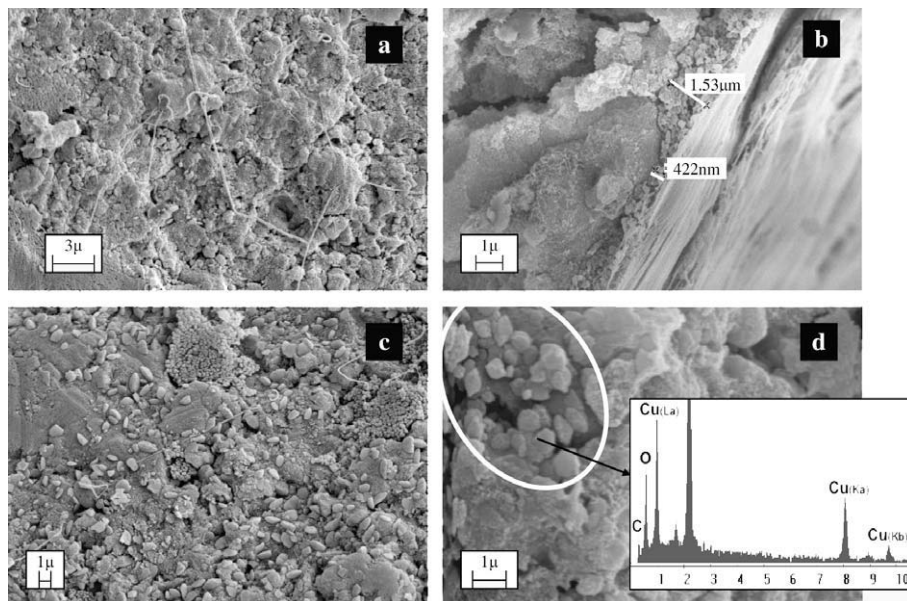

Fig. 1. SEM images of different catalysts: (a) fresh CT, surface (10,000×); (b) fresh CT, cross section (10,000×); (c) used CT surface (10,000×); (d) fresh CuC_2O_4/Al_2O_3, surface (10,000×), with EDX analysis.
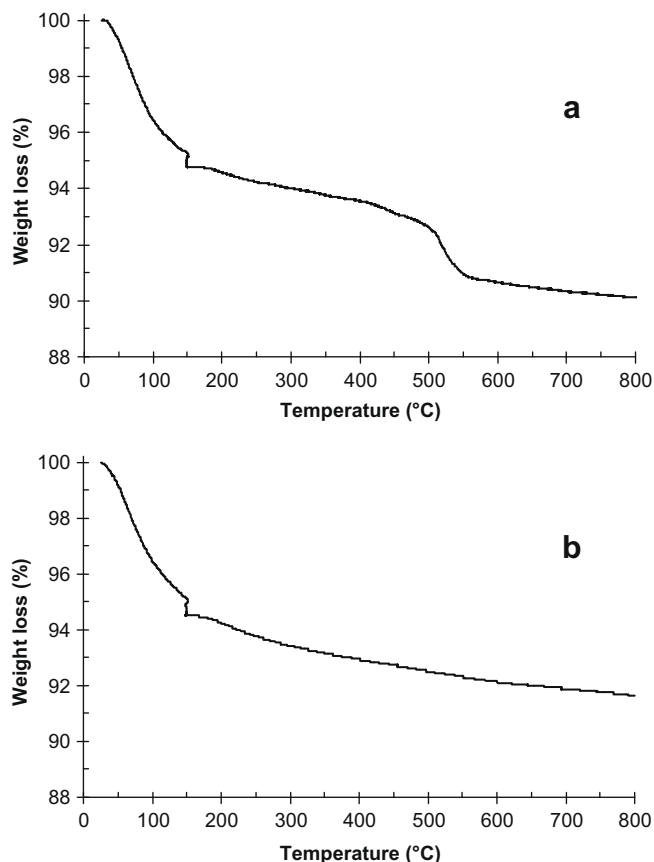
Fig. 2. TGA profiles: (a) CT catalyst; (b) CNT catalyst.

Fig. 4. TPR profiles for CT and CuC_2O_4/Al_2O_3 catalysts.

SEM results indicated that the PTFE coverage obtained for CT was complete and irregular (Fig. 1a–b). The PTFE thickness was relatively thin (0.1–1 µm in average) with some isolated areas with higher accumulation of fibres up to 8 µm. No pores or crackings were detected on the surface.

The total PTFE content was estimated in a 2 % w., according to TGA results shown in Fig. 2 (the weight loss corresponding to the fluoropolymer decomposition, near 500 °C, was compared to the weight loss of CNT, in the same temperature range [2]).

XRD results obtained for fresh and used CT are shown in Fig. 3. As expected, only CuO (tenorite) and γ-Al_2O_3 phases were detected for the fresh sample. These results were confirmed by TPR studies (Fig. 4). The H_2 uptake maximum at 290 °C could be assigned to CuO-like spec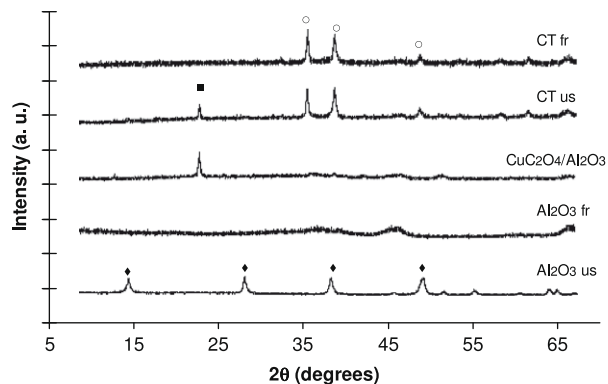ies [2,7]. It is well established that the main active phase in these catalytic systems is the copper oxide [4]. However, for the TPR profiles of the wet-proofed catalyst, additional overlapped components were detected at approximately 215 and 245 °C (arrows, Fig. 4). As observed with similar systems, these less significant contributions appeared in the presence of PTFE over the catalytic surface and they could be associated with diffusion effects [2,4]. Nevertheless, this still remains as an open discussion and further studies are required in order to completely elucidate the effects that this kind of hydrophobic coating has on TPR results.

The catalyst CT was tested in a TBR at 140 °C, for 80 h; the results are shown in Fig. 5. For the sake of comparison the performance of CNT catalyst is also presented. Phenol conversion levels reached with the wet-proofed catalyst were similar to those obtained at initial reaction times for CNT. This could be considered as a certain indication that the thickness of the hydrophobic layer in CT was appropriate to minimize mass transfer restrictions. A pronounced reduction in phenol conversion was observed for the conventional catalyst during reaction. For CT catalyst, phenol conversion remained practically constant (near 30%) with reaction time. The catalyst exhibited a high selectivity towards complete mineralization (near 85%) during the 80 h of reaction time.

Table 1 presents the copper contents detected for the fresh and used samples (AA experiments). For CNT catalyst, approximately a 22% of the initial copper loading was solubilized in the reaction medium [4]. For CT catalyst the lixiviation was lower, near a 13%. Though, these differences alone could not explain the improving in catalyst stability observed for CT catalyst. For the conventional catalyst CNT it was observed that the deactivation was mainly due to the formation of other copper species (copper oxalate and

Fig. 3. XRD results for alumina support (fresh and used), CT (fresh and used) and CuC_2O_4/Al_2O_3 catalysts. (The marks indicate the phase assignation: (○) for copper oxide (tenorite); (■) for copper oxalate hydrate (moolooite) and (♦) for hydrated aluminum oxide (bohmite).)
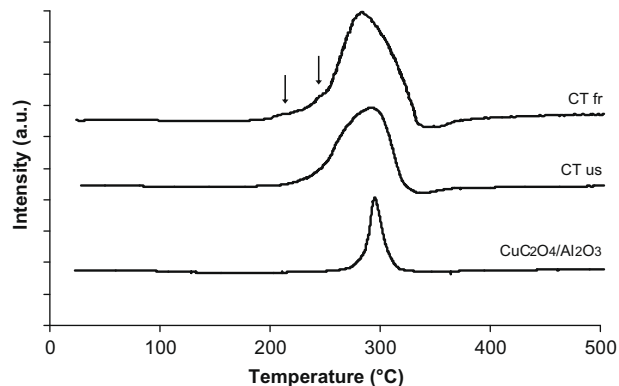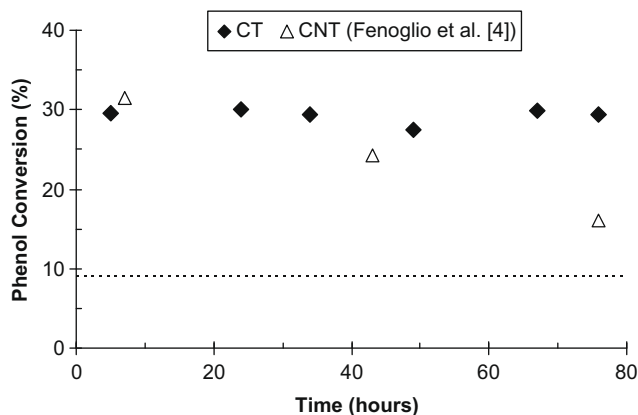

Fig. 5. Phenol conversion vs. reaction time, for CNT and CT catalysts. (Dashed line corresponds to the phenol conversion of Al_2O_3 support.)

Table 1
Copper loading for CNT and CT catalysts, before and after reaction.

Catalyst	Copper content (% w.)	
	Fresh	Used for 80 h (CWAO)
CNT	30	23.5
CT	29.4	25.6

cuprous oxide) and morphology changes in the support during reaction [4].

For used CT catalyst, XRD results shown in Fig. 3 revealed the presence of copper oxalate phase formed during reaction; no copper (I) species were detected as observed for other wet-proofed systems [4].

The formation of copper oxalate detected by XRD was quantitatively less significant for catalyst CT than for CNT (the latter reported in previous work [4]). Two major reasons were considered: First, the lower level of copper lixiviation detected for CT, and also the presence of the PTFE coating that could hinder the deposition of the CuC_2O_4 on the surface. As described by Santos et al. [8], the oxalic acid, as an oxidation intermediate, is able to complex copper in solution and to precipitate it as copper oxalate on the catalyst.

SEM images of used CT showed the presence of crystalline deposits on the catalyst surface (Fig. 1c) that could reasonably correspond to the CuC_2O_4 phase [8].

TPR results also confirmed XRD observations. The presence of copper oxalate phase on used CT catalyst did not exhibit major changes with respect to the fresh sample (Fig. 4). However, after usage, a moderate reduction in the area under the H_2 uptake maximum was observed for the wet-roofed catalyst, and it could be attributed to the solubilization of copper in the reaction medium.

According to the results obtained working with hydrophobized and conventional systems, some aspects of the deactivation process of copper catalysts were also considered.

The role of copper oxalate was evaluated. A CuC_2O_4/Al_2O_3 catalyst was synthesized and additional experiments were carried out in order to investigate its performance under the same reaction conditions. The fresh sample was characterized. The formation of copper oxalate on the surface was confirmed by XRD (Fig. 3) and also by SEM–EDX studies (Fig. 1d). TPR analysis was also performed on the copper oxalate samples, but practically no changes in the position of the hydrogen consumption peak were detected if compared to CuO/Al_2O_3 catalysts (Fig. 4). The reduction of copper (II) species, either from CuO or from CuC_2O_4, occurred at similar temperature (the differences in the area under the thermoreduction profile between both systems correspond to the different amount of copper of the samples). This must be considered when TPR results for used CT catalyst are analyzed: The main difference that appeared on CT after usage was the formation of copper oxalate phase. However, it can not be properly differentiated from fresh CT (CuO phase) by performing TPR studies.

For the reaction tests with fresh CuC_2O_4/Al_2O_3 catalyst, the stationary state conversion (after 4 hours of reaction) was 22%, with

selectivity towards complete mineralization in the order of 70% (Table 2). Thus, it was confirmed that the copper oxalate resulted active (and selective) for the phenol oxidation reaction [9], and it should not be considered a main responsible for catalyst deactivation.

The role of the bohmite phase in the deactivation process was also taken into account. Morphological changes were detected for the used conventional catalyst [4]. XRD analysis confirmed the formation of a different aluminum-containing phase (bohmite) on used CNT catalyst. The formation of bohmite by rehydration of gamma alumina is possible to occur at the hydrothermal conditions of the reaction [9]. Fig. 3 shows the XRD results obtained after a blank reaction run, where only alumina was used instead of catalyst. These results confirmed that the rehydration process of the support occured at the reaction conditions, and bohmite phase was detected. The formation of bohmite phase would induce different morphological changes on the catalyst that could affect its performance (deactivation).

According to characterization results, the formation of bohmite could be significatively minimized by using wet-proofed catalysts. For CNT and CT catalysts the reaction conditions were similar; however, practically no bohmite phase was detected for the hydrophobized system (only a slight, incipient signal of bohmite could be observed, after a detailed examination of used CT XRD results). While preventing the direct contact of the catalyst with the aqueous reaction medium, the PTFE layer resulted very promising to reduce the formation of bohmite by rehydration.

4. Conclusions

- The proper selection of the PTFE impregnation variables allowed obtaining an improved hydrophobic coating, continuous, without pores and crackings, with thinner and more regular thickness distribution.
- The presence of an optimal wet-proofed coating enhanced catalyst performance in terms of phenol conversion and stability with reaction time.
- The presence of a hydrophobic layer exhibited the following advantages, with respect to the conventional catalyst:
  – The loss of active phase due to solubilization in the reaction medium was minimized.
  – No domains of cuprous species were formed on the catalyst.
  – The formation of bohmite phase during reaction was markedly minimized.
  – The overall mechanical resistance of the catalyst was enhanced.
  – With a controlled thickness of the hydrophobic layer the reactants diffusion remained practically unaffected, and phenol conversion levels are constant and similar to those reached with the conventional system at short reaction times.

Table 2
Phenol conversion and CO_2 production for the fresh catalysts.

Catalyst	Phenol conversion (%)[a]	CO_2 production (%)[a]
CNT[b]	31.5	27.5
CT	29.8	25
CuC_2O_4/Al_2O_3	22	15.5

[a] Conversion obtained for the fresh catalyst at stationary state, after 4 h of reaction.
[b] Previous results, reported in [4].

References

[1] S.K. Bhargava, J. Tardio, J. Prasad, K. Foger, D.B. Akolekar, S.C. Grocott, Wet oxidation and catalytic wet oxidation, Ind. Eng. Chem. Res. 45 (2006) 1221–1258.

[2] P. Massa, F. Ivorra, P. Haure, R. Fenoglio, Preparation and characterization of wet-proofed CuO/Al$_2$O$_3$ catalysts for the oxidation of phenol solutions, Catal. Lett. 101 (2005) 201–209.

[3] A. Pintar, J. Levec, Catalytic oxidation of organics in aqueous solutions. I. Kinetics of phenol oxidation, J. Catal. 135 (1992) 345–357.

[4] R. Fenoglio, P. Massa, F. Ivorra, P. Haure, Conventional and wet proofed CuO/Al$_2$O$_3$ catalysts for phenol oxidation: deactivation studies in a trickle bed reactor, J. Chem. Technol. Biotechnol. 82 (2007) 481–487.

[5] P. Massa, M. Ayude, F. Ivorra, R. Fenoglio, P. Haure, Phenol oxidation in a periodically operated trickle bed reactor, Catal. Today 107–108 (2005) 630–636.

[6] L.S. Clesceri, A. Geenberg, A. Eaton (Eds.), Standard Methods for the Examination of Water and Waste water, 20th ed., American Public Health Association, Washington DC, 1998.

[7] P. Massa, M. Ayude, R. Fenoglio, J. Gonzalez, P. Haure, Catalyst systems for the oxidation of phenol in water, Latin Am. Appl. Res. 34 (2004) 133–140.

[8] A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, F. García-Ochoa, Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: causes and effects, Appl. Catal. B: Environ. 61 (2005) 323–333.

[9] A. Alejandre, F. Medina, A. Fortuny, P. Salagre, J.E. Sueiras, Characterisation of copper catalysts and activity for the oxidation of phenol aqueous solutions, Appl. Catal. B: Environ. 16 (1998) 53–67.