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## CHARACTERIZATION OF CuO/Al<sub>2</sub>O<sub>3</sub> CATALYSTS USED IN THE OXIDATION OF PHENOL SOLUTIONS

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### Abstract

Two CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized at different calcination temperatures and used for the oxidation of phenol solutions. Deactivation is due to leaching of the active phase and deposition of carbonaceous material.

*Keywords:* Copper/alumina catalysts, catalytic oxidation of phenol

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## INTRODUCTION

The development of efficient processes for wastewater treatment at intermediate levels of phenol concentration is of considerable interest for industrial activities. The oxidation of organic aqueous solutions over a solid catalyst has been shown to be a useful and inexpensive non-conventional treatment process. Heterogeneous catalysts have been the subject of numerous studies [1-3]. However, the use of these catalysts is so far somewhat limited due to rapid deactivation. The hot acidic oxidation environment can result in the dissolution of the active component into the aqueous phase. In addition, catalyst deactivation can occur due to poisoning of active sites following the deposition of reaction intermediates.

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## EXPERIMENTAL

### Catalyst preparation and characterization

The CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by a molten salt method developed in our laboratory. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (MERCK, pro analysis) was used as the metallic precursor. The  $\gamma$ -alumina support (CK-300 Cyanamid KETJEN) with a surface area of 200 m<sup>2</sup>/g, was previously calcined at 650°C (3 h in synthetic air). The metallic salt was melted at 250°C and the alumina was 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 then calcined for 4 h in synthetic air. Calcination temperatures were 400°C for catalyst C1, and 900°C for catalyst C2.

Surface area measurements were performed using a FlowSorbI 2300 Micrometrics surface area analyzer. All surface areas were derived from one point B.E.T. adsorption isotherms, with N<sub>2</sub> at -195°C as the adsorbate. Temperature Programmed Reduction (TPR) was performed with 5% H<sub>2</sub>/Ar with 0.02 g of catalyst in a conventional TPR set-up. The temperature was increased linearly at 5°C/min. Temperature range was 20 to 500°C; a thermal conductivity detector monitored the H<sub>2</sub> uptake. X-Ray Diffraction (XRD) patterns were obtained with a PW 1830/00 Philips XRD diffractometer employing Cu K $\alpha$  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 2 $\theta$ ) with divergence slit and scatter slit widths of 1°. The overall metal composition of oxides was determined by Atomic Absorption spectrophotometry (AA-375 Varian). In order to determine the metal content the samples were pretreated with nitric acid to remove the Cu<sup>2+</sup> species.

### Reaction studies

The experimental set-up consisted of a stirred 0.5 L batch stainless steel autoclave reactor (Autoclave Engineers, Erie, PA), containing a rotating catalytic basket (RCB). The reactor was operated at 140°C and 7 atm of oxygen pressure at a gas flow rate of 0.9 L/min, with an initial phenol concentration of 5 g/L and catalyst concentration of 8.57 g/L. The particle diameter of the pellets was 2.6 mm.

In a typical run, a given amount of fresh catalyst was placed into the RCB, in contact with 0.35 L of phenol solution. First, the reactor was purged and heated under nitrogen flow. When the oxidation temperature was reached, pure oxygen

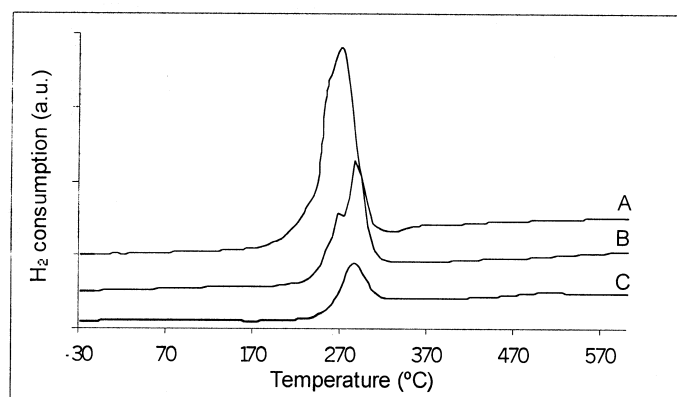
was introduced into the system at the required pressure and the reaction was initiated. Continuous stirring at 800 rpm (enough to avoid external mass transport limitations) was used in all experiments.

Liquid samples were withdrawn periodically. Phenol conversion as well as CO<sub>2</sub> production and pH were evaluated.

## RESULTS AND DISCUSSION

### Characterization

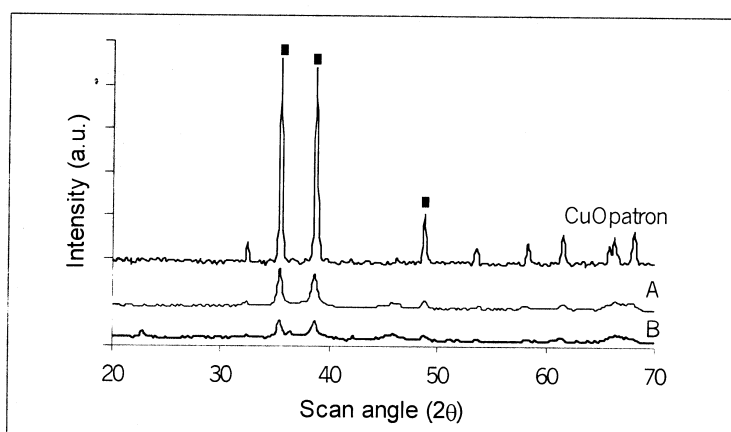
The TPR profiles obtained for catalyst C1 (fresh and after several hours of operation) show a maximum in H<sub>2</sub> consumption in the range 262-288°C (Fig. 1). These peaks can be assigned to CuO-like species, which species have been described as small Cu<sup>2+</sup> domains, and small and large CuO clusters [4]. The XRD analysis confirmed the presence of CuO phase due to two major



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

diffraction peaks centered at  $2\theta = 35.6^\circ$  and at  $38.8^\circ$  (Fig. 2). TPR profiles for used C1 are presented in Fig. 1 (curves B and C); they show a decrease in the amount of the active phase as operation time is increased. XRD (Fig. 2) and AA analysis (Table 1) confirm this observation. For fresh C2 catalyst the TPR profiles indicate the presence of two different copper species, as shown in Fig. 3, curve A. As in catalyst C1, at low temperatures the maximum in H<sub>2</sub>

consumption can be assigned to CuO-like species. Results show an additional contribution at higher temperatures, not observed for catalyst C1. This is attributed to a copper aluminate [5,6], probably induced by the higher calcination temperature.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a spinel-type structure in which the oxygen ions are cubic close-packed. The copper ions are able to fill defect sites of alumina and form CuAl<sub>2</sub>O<sub>4</sub>. At higher calcination temperatures the Cu<sup>2+</sup> species migrate into the alumina structure and form bulk aluminate phase [5, 6]. XRD patterns confirm the presence of these CuAl<sub>2</sub>O<sub>4</sub> species (Fig. 4). CuO phase was not detected by XRD because of its low content: AA analysis gave values below 5% Cu for all C2 samples.



**Fig. 2.** XRD patterns for C1 catalyst. A: fresh catalyst, B: after 4 h of operation

The XRD patterns for C2 catalyst show also the presence of  $\alpha$ -alumina that was not observed when only the support was calcined at 900°C or when it was attacked with nitric acid (Fig. 5). The presence of the metal induces the transformation of  $\gamma$ -alumina to  $\alpha$ -alumina at a lower temperature than in pure alumina [1,5], with a consequent loss in surface area (Table 1). The Cu contents obtained by AA for catalyst C2 are unusually low. They are only indicative of the copper present as CuO species since the nitric acid attack does not remove the Cu from the spinel structure. The TPR results confirm this hypothesis (Fig. 3).

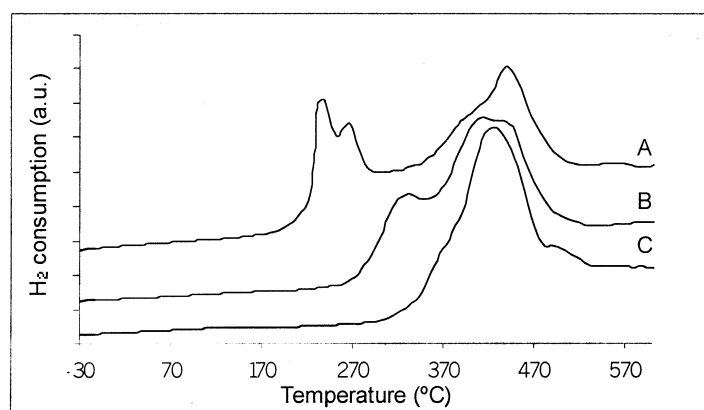
The comparison of TPR profiles for fresh and used C2 catalyst indicates that the catalyst undergoes morphological changes with increasing operation time (Fig. 3). These phase redistribution phenomena were not observed for catalyst C1. After 4 h of reaction, the CuO-like species observed for fresh C2 catalyst

(below 275°C) disappeared and a different thermoreduction signal was registered at *ca.* 300°C (Fig. 3, curve B). This peak can be assigned to the formation of an intermediate aluminate phase or to the superficial restructuring of CuO aggregates [4]. After 60 h of operation, this species disappears and only bulk CuAl<sub>2</sub>O<sub>4</sub> was observed. Hot acidic reaction conditions favor this migration process.

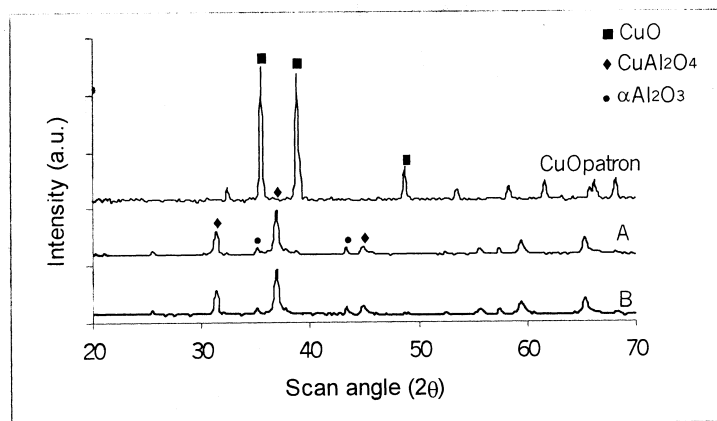
**Table 1**  
Summary of experimental results

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Cu content (wt.%)	XRD phase detected	Phenol conversion	Induction time (min)	Final pH	CO <sub>2</sub> production
C1 A	115	28.9	CuO, γ-Al <sub>2</sub> O <sub>3</sub>	90%	50	4	75%
C1 B		14.2	CuO, γ-Al <sub>2</sub> O <sub>3</sub>	88%	150	3.5	60%
C1 C		2.2	CuO, γ-Al <sub>2</sub> O <sub>3</sub>	67%	300	2.7	37%
C2 A	40	2.7	CuAl <sub>2</sub> O <sub>4</sub> , γ and α-Al <sub>2</sub> O <sub>3</sub>	85%	110	2.9	55%
C2 B		1.0	CuAl <sub>2</sub> O <sub>4</sub> , γ and α-Al <sub>2</sub> O <sub>3</sub>	80%	250	2.9	55%
C2 C		0.6	CuAl <sub>2</sub> O <sub>4</sub> , γ and α-Al <sub>2</sub> O <sub>3</sub>	55%	>400	2.9	32%

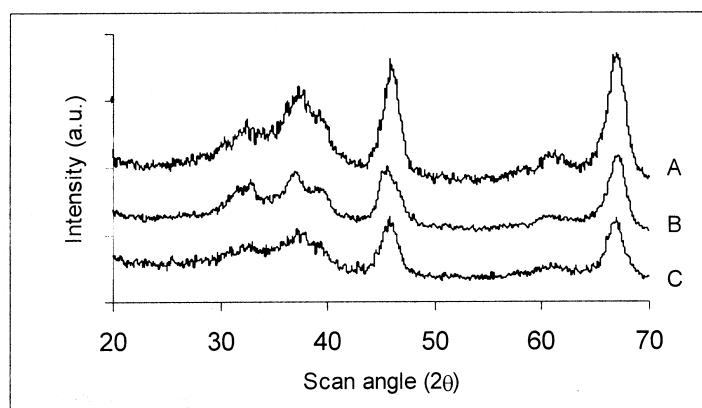
A: fresh catalyst; B: after 4 h of operation and C: after 60 h of operation.



**Fig. 3.** TPR profiles for catalyst C2. A: fresh catalyst, B: after 4 h of operation and C: after 60 h of operation



**Fig. 4.** XRD patterns for C2 catalyst. A: fresh catalyst, B: after 4 h of operation



**Fig. 5.** XRD patterns for the  $\text{Al}_2\text{O}_3$  support. A: Calcined at 500°C. B: Calcined at 900°C. C: Calcined at 500°C and extracted with  $\text{HNO}_3$

The deactivation mechanism of C2 catalyst does not involve a significant loss of metal content. The TPR peaks (below 350°C) have moved to higher temperatures, however, the total area under the  $\text{H}_2$  consumption curves remains practically constant.

## Reaction studies

Table 1 summarizes the results obtained with C1 and C2 in the oxidation of phenol aqueous solutions. With fresh samples, a significant difference in the induction time is observed. Even though the final phenol conversions are quite similar, CO<sub>2</sub> production is higher for C1 because it has a higher CuO content. Phenol oxidation occurs *via* a heterogeneous-homogeneous free radical chain mechanism which involves initiation on the catalyst surface, propagation in the homogeneous solution and either homogeneous or heterogeneous termination depending on the catalyst concentration [2,3]. The higher concentration of active sites found in catalyst C1 favors the heterogeneous termination to CO<sub>2</sub>. This is also confirmed by the higher pH value reported for fresh C1. The pH values are an indication of the intermediates of phenol degradation present as organic acids. By HPLC and GC/MS analysis it was possible to detect the following compounds: acetic, oxalic, formic, malic and malonic acids, residual phenol and quinones. The results confirm that phenol oxidation follows a complex pathway composed by parallel and consecutive reactions [7].

To investigate catalytic stability, a batch of 3 g was used for several consecutive runs. In every run, the reused catalyst was in contact with a fresh phenol solution. The experimental conditions and procedure were the same as described above. Results are presented in Table 1. For catalyst C1, phenol conversion remains almost constant at about 85% for 4-16 hours. The amount of free CuO is high, as reported in Table 1. Then, phenol conversion decreases up to 67%, and so does the amount of free copper oxide. The loss of CuO species, confirmed by TPR, XRD and AA techniques, also explains the increase of the induction time and the decrease of the production of CO<sub>2</sub> with usage.

For catalyst C2, phenol conversion decays from 85 to 55%. As expected, CO<sub>2</sub> production is lower than that reported for C1 and induction times increase with usage. This behavior is probably due to a different deactivation mechanism. From TPR, XRD and AA results, it is seen that the Cu<sup>2+</sup> initially present as CuO may migrate into the structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [5, 6]. The copper aluminate that results from this migration is not accessible to the reactants, and it is much less active than the CuO original species.

In addition, another deactivation process is involved. The presence of carbonaceous compounds, formed mainly by the homogeneous mechanism, is detected by visual observation of both used catalysts. The deposits were eliminated by reoxidation of the samples at 400°C and phenol conversion and CO<sub>2</sub> production increased.

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