

Conventional and wet proofed $\text{CuO}/\text{Al}_2\text{O}_3$ catalysts for phenol oxidation: deactivation studies in a trickle bed reactor

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Abstract: A large variety of catalytic systems have been studied for the catalytic wet air oxidation of phenolic solutions. Most of them show good activity, but serious stability problems. In this contribution, stability studies were performed over $\text{CuO}/\text{Al}_2\text{O}_3$ conventional (CNT) and polytetrafluorethylene coated (C3T) catalysts used for the oxidation of 5 g L^{-1} phenol solutions in a trickle bed reactor (140°C and 7 atm of oxygen pressure). For the hydrophilic catalyst, phenol conversion decreased with usage due to the formation of Cu_2O and copper oxalate phases. For the wet proofed catalyst, the hydrophobic layer prevented the appearance of those phases, and conversion levels remained practically constant with reaction time. After usage, both catalysts were oxidized at 400°C and tested for reaction: in the case of the C3T catalyst, the phenol conversion was increased over its initial level; for CNT catalyst, the phenol conversion was also increased, but initial levels were not completely restored. The deactivation mechanism of the CNT catalyst is associated with the formation of the Cu_2O and copper oxalate phases during reaction. For catalyst C3T, practically no deactivation was observed.

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Keywords: hydrophobic catalysts; phenol oxidation; CuO catalysts; copper oxalate; Cu_2O

INTRODUCTION

During the last three decades the development of efficient processes for wastewater treatment has gained increasing interest. From different non-conventional alternatives, catalytic wet air oxidation (CWAO) of organics has been extensively considered as a useful and inexpensive treatment technology. However, in order to obtain an effective reduction in contamination levels, it is crucial to find a suitable catalyst.

A large variety of catalytic systems have been studied for the CWAO of phenolic solutions.^{1–3} Most of these systems are based on metal oxides that show good activity, but serious stability problems.^{3–5} Frequently, the active components of the catalysts are soluble in the hot acidic conditions in which reaction occurs.⁶

Sadana and Katzer⁴ were the first to study this catalytic reaction. They determined that copper oxide supported over γ -alumina is effective for phenol oxidation in the temperature range of 96 to 246°C , using a batch reactor. Pintar and Levec⁵ also studied the oxidation of phenol in a slurry reactor, over a $\text{CuO}/\text{Al}_2\text{O}_3$ system, at 105 – 130°C . These authors observed an important reduction in the catalytic activity and an increase in the concentration of copper ions in the reaction medium with increasing operation

time. In previous work we reported results obtained in a semibatch reactor (Rotating Catalytic Basket Reactor, RCBR), working with a $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst with a high copper content (30% w/w).⁷ Phenol conversion and CO_2 production were monitored at 140°C and 7 atm of oxygen partial pressure. We observed two combined effects that would produce catalyst deactivation: the lixiviation of the copper ions and also the formation of carbonaceous deposits onto the active sites. Other authors have reported this second effect as produced by homogeneous polymerization of reaction intermediates.^{5,8} In order to minimize the production of carbonaceous deposits, trickle bed reactors are recommended, due to their low liquid-to-catalyst ratio.⁵

To prevent deactivation of the catalyst, two different strategies were proposed and tested separately. We reported an experimental study of the aqueous oxidation of phenol over conventional $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst carried out in a trickle bed reactor (TBR).⁹ Steady state as well as periodic on-off experiments were performed. Results indicate that catalyst leaching was less pronounced in the TBR. Polymer formation, even when markedly reduced, could not be neglected. This is not a typical observation; only a few authors observed the presence of carbonaceous deposits working with TBR.¹⁰

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(Received 11 January 2007; revised version received 22 February 2007; accepted 26 February 2007)

Published online 20 April 2007; DOI: 10.1002/jctb.1694

The second strategy was to cover conventional CuO/Al₂O₃ with a polytetrafluorethylene (PTFE) layer and test it for the oxidation of phenol solutions in a RCBR.³ The results showed that the hydrophobic coverage could effectively reduce the leaching of the active phase. The development of hydrophobic catalysts may significantly improve the efficiency of CWAQ, but additionally raises a number of issues that must be resolved prior to its implementation to industrial scale. Hydrodynamics, mass transfer and reaction mechanism in these unique three phase systems differ from conventional hydrophilic processes.¹¹

The objective of this work is to study the deactivation of hydrophilic and hydrophobic CuO/ γ -Al₂O₃ catalysts used for the CWAQ of phenol at 140 °C and 7 atm of oxygen. The experiments were carried out in a laboratory, continuous TBR operated at steady state.

MATERIALS AND METHODS

Catalysts preparation

Base CuO/ γ -Al₂O₃ catalyst (CNT) were prepared from Cu(NO₃)₂·3H₂O (p.a., Merck, Darmstadt, Germany) and γ -Al₂O₃ (Alfa Aesar, Ward Hill, MA, USA, 1/8" pellets, BET surface area 214 m²/g) following the molten salt method described elsewhere.⁷ Part of the sample was coated with PTFE fibers following the impregnation procedure described by Massa *et al.*,² for catalyst C3T (three successive impregnation cycles with PTFE). The samples were dried at 120 °C in an oven and calcined at 400 °C for 12 h in air.

Characterization methods

Scanning electron microscopy (SEM)

The morphology of the catalysts was examined using a SEM JEOL (Tokyo, Japan) 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.

Temperature programmed reduction (TPR)

Fresh and used samples were characterized by TPR. This analysis was performed with 5% v/v H₂/Ar. A conventional TPR set-up was used. The temperature was increased linearly at 5 °C min⁻¹. The temperature range was 20 °C to 500 °C and a thermal conductivity detector (TCD) monitored the H₂ uptake. For the calibration curve, pure CuO (p.a., Carlo Erba, Milan, Italy) was used.

Atomic absorption (AA)

The copper content of the samples was determined by AA and also confirmed by TPR, using an AANALYST 300 Perkin-Elmer (Waltham, MA, USA) spectrophotometer.²

X-ray diffraction (XRD). Powder X-ray diffraction patterns of the samples were obtained with a PW 1830/00 Philips (The Netherlands) XRD

diffractometer employing Cu K α radiation. The X-ray was operated at 40 kV and 30 mA. The patterns were recorded over 8° < 2 θ < 60° angles, and compared with X-ray powder files to confirm phase identities. The patterns of the detected phase are: aluminum oxide (γ -alumina) (2 θ = 38.23° (100), 32.41° (98), 45.72° (96) and 24.51° (72)); copper oxide (CuO, tenorite) (2 θ = 35.08° (100), 32.71° (96), 41.51° (28) and 35.24° (24)); copper oxalate hydrate (moolooite) (2 θ = 22.77° (100), 46.52° (100), 51.23° (25) and 51.7° (24)) and copper oxide (Cu₂O) (2 θ = 35.96° (100), 41.52° (35) and 58.73° (27)).

Carbonaceous residues

Carbonaceous residues over the catalysts used were eliminated by oxidation in a flow of synthetic air at 16 mL min⁻¹ and 400 °C, followed by chromatographic detection of the CO₂ produced with a GC Konik (Barcelona, Spain) 2000C equipped with a Alltech (Deerfield, IL, USA) CTR I column and with a TCD.

Determination of catalytic activity and selectivity

Phenol oxidation was studied in a packed bed reactor operated in the trickle regime. The experimental set-up and procedures are detailed elsewhere.⁹ The experimental conditions are given in Table 1.

Liquid samples were withdrawn periodically. Phenol conversion and chemical oxygen demand (COD) were evaluated following standard determination techniques.¹²

Phenol conversion was calculated as:

$$\text{Phenol conversion (percentage)} = \frac{(C_{\text{Ph } 0} - C_{\text{Ph } f}) \times 100}{C_{\text{Ph } 0}} \quad (1)$$

where $C_{\text{Ph } 0}$ and $C_{\text{Ph } f}$ are the initial and the final phenol concentrations, respectively.

The COD measurement indicates the completeness of the oxidation process. So, production of CO₂ was then evaluated from COD decrease as:

$$\text{CO}_2 \text{ production (percentage)} = \frac{(\text{COD}_i - \text{COD}_f) \times 100}{\text{COD}_i} \quad (2)$$

Table 1. Operating conditions

| Variables | TBR |
|----------------------------------|--------------------------|
| Phenol initial concentration | 5 g L ⁻¹ |
| Catalyst loading | 15 g |
| Particle diameter | 4 mm |
| O ₂ flow (STP conds.) | 0.46 L min ⁻¹ |
| Liquid flow | 1 mL min ⁻¹ |
| O ₂ pressure | 7 atm |
| Temperature | 140 °C |
| Initial pH* | 6.7 |

* Corresponding pH of a 0.057 mol L⁻¹ aqueous phenol solution in bidistilled water.

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

RESULTS

Characterization

Scanning electron micrographs of conventional and wet proofed catalysts were performed. Figures 1 and 2 show the different surface morphologies of both fresh and used catalysts. Fresh CNT samples exhibited a rough external and internal porous morphology (Fig. 1). PTFE coverage of C3T was initially complete but irregular (Fig. 2), with an average thickness of 3–8 µm. The PTFE content was determined by TG, and was estimated at 3%.²

After 80 h of use in the TBR, CNT samples showed the presence of a new crystalline phase, with a laminar structure, self-crossed all over the catalyst surface. An elemental analysis of these species revealed Cu, O and C. Small irregular deposits containing Cu and O were observed by SEM-EDX over this crystalline phase. After 80 h of reaction, the samples were oxidized. As seen in Fig. 1, the crystalline phase was removed by oxidation; significant changes in the surface morphology could also be observed after the thermal treatment.

When used C3T samples were examined by SEM (Fig. 2), no deposits were detected over the PTFE coverage. A crystalline phase was observed only on discontinuities of the hydrophobic layer and also between the PTFE and the alumina support. This

phase could be associated with the same laminar phase detected in CNT samples. However, neither Cu₂O nor copper oxalate phases were detected by XRD and TPR. No marked changes to the surface morphology were observed after the oxidation process.

XRD analyses were also performed (Fig. 3). For all the examined samples, CuO and γ -Al₂O₃ phases were confirmed. However, for used CNT catalyst, two additional phases were observed, identified as cuprous oxide and copper oxalate. These two phases were not detected after oxidation at 400 °C.

No changes were observed for XRD profiles among C3T samples (Fig. 4). Neither Cu₂O phase nor copper oxalate phase appeared after 80 h of reaction time.

Figures 5 and 6 exhibit TPR profiles for both CNT and C3T catalysts (fresh, used and used+oxidized). The H₂ uptake maximum appears at 310–320 °C for fresh CNT and C3T. A pure CuO sample was also examined, showing a maximum hydrogen consumption rate at 310 °C.

For the two used samples, a reduction in the area under the TPR curves was detected. In the case of used CNT, the decrease in hydrogen consumption was markedly pronounced (ca. 60% of area reduction). Two peaks at 230 °C and 275 °C were recorded, the latter with a slight shoulder at 255 °C. After oxidation at 400 °C, the TPR curve was practically restored to its initial profile.

The differences observed in the TPR profiles for C3T are less significant: only a small decrease in the peak area (ca. 20% loss) was detected after use. The

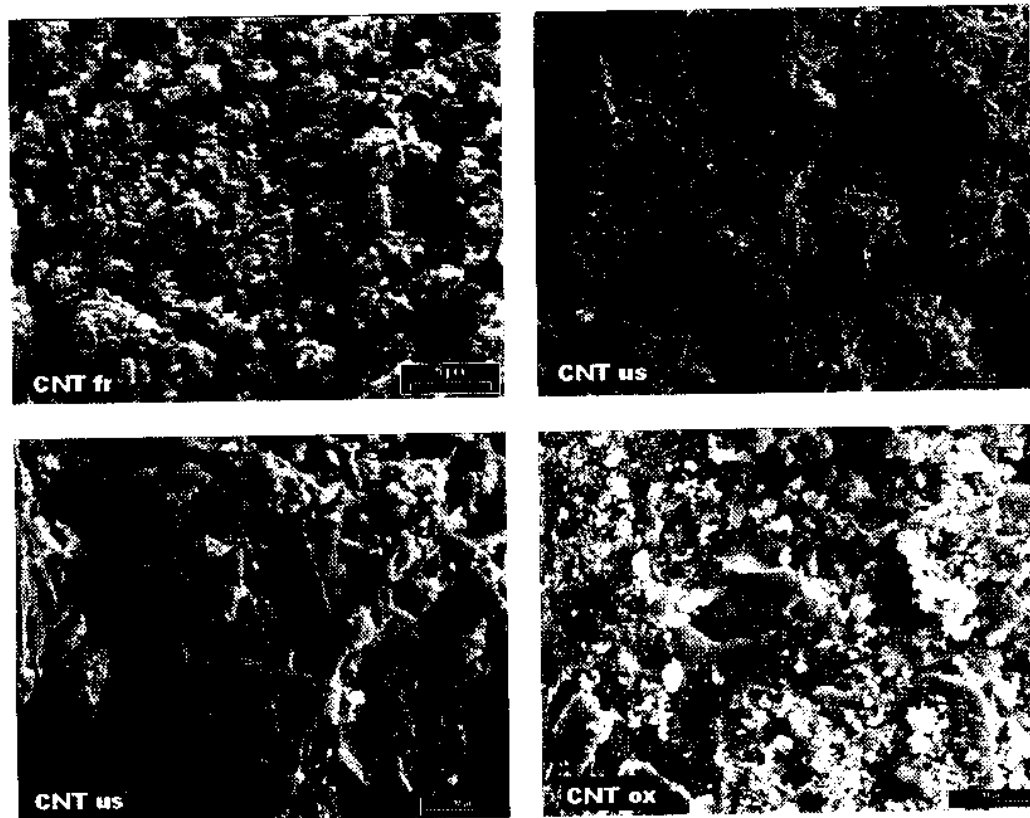


Figure 1. SEM photographs of CNT catalyst: fresh (*fr*), used in the TBR (*us* and *us*²) and used + oxidized at 400 °C (*ox*).

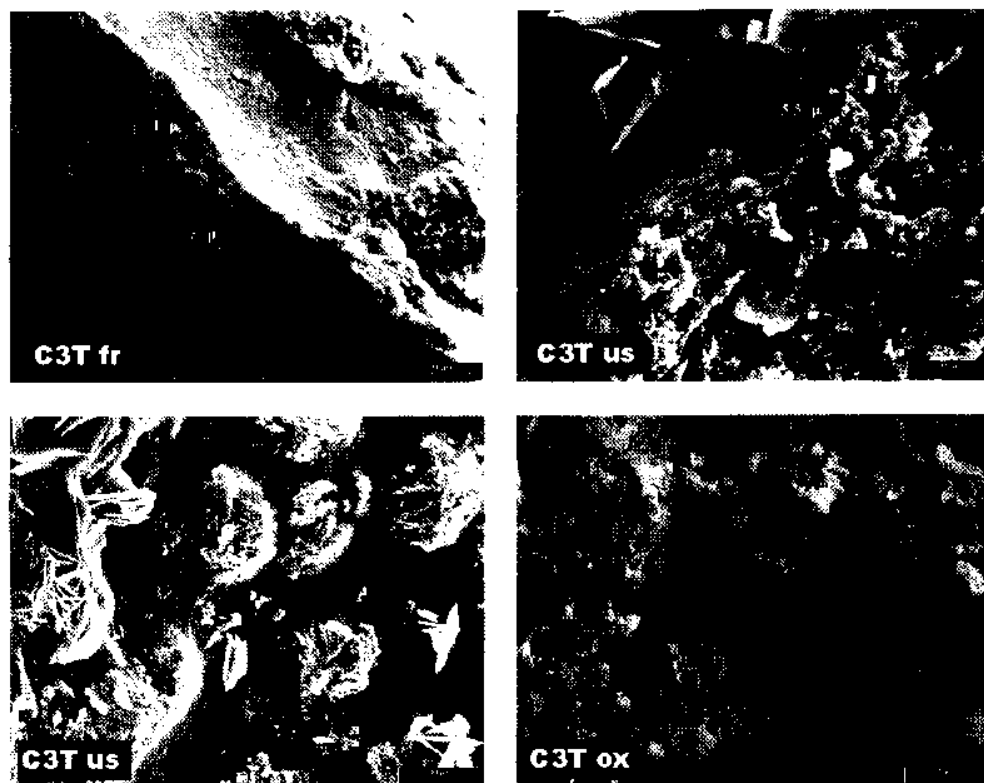


Figure 2. SEM photographs of C3T catalyst: fresh (*fr*), used in the TBR (*us* and *us*²) and used + oxidized at 400 °C (*ox*).

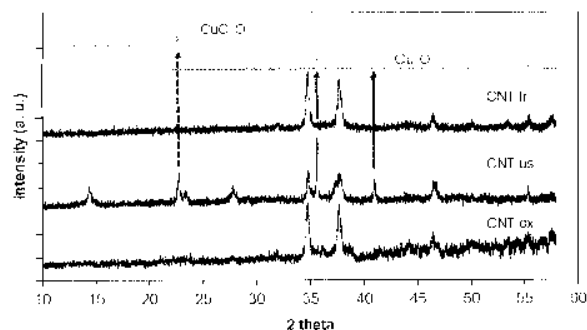


Figure 3. XRD patterns for CNT catalyst: fresh, used in the TBR (80 h), and used + oxidized at 400 °C.

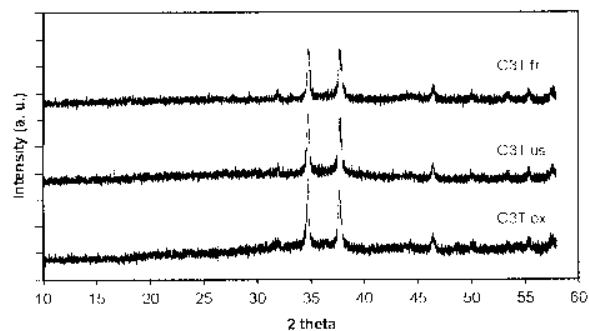


Figure 4. XRD patterns for C3T catalyst: fresh, used in the TBR (80 h), and used + oxidized at 400 °C.

treatment at 400 °C did not result in any significant modifications to the species present on the catalyst.

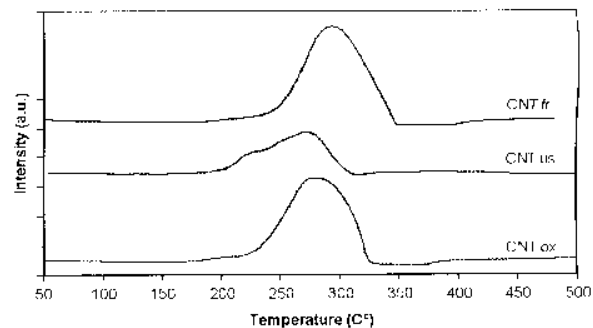


Figure 5. TPR profiles for catalyst CNT: fresh, used in the TBR (80 h), and used + oxidized at 400 °C.

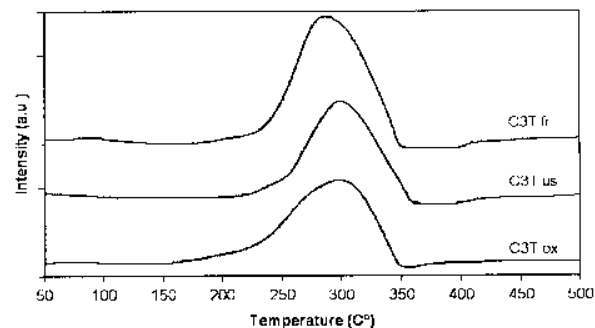


Figure 6. TPR profiles for catalyst C3T: fresh, used in the TBR (80 h), and used + oxidized at 400 °C.

The copper content of the used samples are also given in Table 2. Relative values of copper retention are determined by AA and confirmed by

TPR analysis.² The metal content decreased with the exposure to the hot acidic reaction conditions.⁶ However, according to its initial content, catalyst C3T retained more active phase than CNT. The PTFE coating prevented lixiviation, reducing copper leaching levels.

TBR reaction studies

Preliminary blank runs were performed in the presence of Al₂O₃ and negligible phenol conversion levels were obtained. The catalysts were tested in a trickle bed reactor for 80 h. Phenol conversion vs. reaction time curves are plotted in Fig. 7. For C3T, phenol conversion was always lower than for the conventional catalyst. However, for the coated catalyst no marked changes of phenol conversion with reaction time were observed.

On the contrary, catalyst CNT presents a pronounced reduction in phenol conversion with usage: the conversion diminished by almost 50% during 80 hours of reaction (Fig. 7).

Similar trends were registered for CO₂ production results (Table 3). The selectivity to complete mineralization to carbon dioxide was high, but not completed (91% for fresh CNT and 92% for fresh C3T).

Practically no suspended solids were observed in the withdrawn reaction samples.

DISCUSSION

From characterization results, and in agreement with previous reports^{2,13} it can be stated that CuO predominates as the active phase of the system. However, after use, the formation of additional phases was also observed: copper oxalate and cuprous oxide were detected on CNT catalyst. Alejandro *et al.* and Santos *et al.*^{14,15} detected a copper oxalate phase

Table 3. Phenol conversion and CO₂ production

| | Phenol conversion (%) | | | |
|-----|-----------------------|-----------|-----------|------------------------|
| | Fresh | Used 40 h | Used 80 h | Used 80 h and oxidized |
| CNT | 31.5 | 24 | 16 | 25 |
| C3T | 15 | 12 | 12 | 20 |

| | CO ₂ Production (%) | | | |
|-----|--------------------------------|-----------|-----------|------------------------|
| | Fresh | Used 40 h | Used 80 h | Used 80 h and oxidized |
| CNT | 27.5 | 21 | 14.5 | 20 |
| C3T | 13.5 | 11 | 11 | 18 |

during the phenol oxidation reaction using CuO catalysts. These observations are associated with the accepted reaction mechanism, which involves the formation of oxalic acid as one of the intermediates. The oxalic acid is able to react with Cu²⁺ and to precipitate as copper oxalate on the catalyst surface. Alejandro *et al.*¹⁴ suggested that this new crystalline phase of copper oxalate could retain catalytic activity after several hours of operation in a trickle bed reactor. Santos *et al.*¹⁵ proved that the formation of the copper oxalate layer prevents copper leaching, but diminished notably the phenol conversion, probably due to a decrease in the homogeneous contribution in the overall degradation process.

The work presented by Alvarez *et al.*⁸ reported the formation of another organocupric by product of the reaction, in their case, formed with acetate ions. They reported that both the carbonaceous and copper-acetate polymeric products blocked the pores of the catalyst and fouled it. The loss of copper is proposed to be due to the reaction of copper oxide with carboxylic acids.

The formation of Cu₂O phase was also detected. The presence of Cu^{II} species has not been previously reported in literature. However, some authors have proposed a free radical mechanism involving the formation of Cu^{II} species in an initial step, and their further participation during propagation and termination reactions.^{4,15} According to this pathway, cuprous species would also take part in the oxygen adsorption process, which regenerates the catalyst to its initial form. For CNT the O₂ provision was probably not enough to completely regenerate the cupric species of the catalyst. It could be proposed that the oxygen would reach the active sites by overcoming two mass transfer resistances: gas-liquid and liquid solid, from gas bulk towards the wet catalyst surface, requiring oxygen dissolution in the liquid phase.¹⁶

The Cu₂O phase was completely removed when the oxidation was performed at 400 °C; however, in the prevailing conditions during reaction the regeneration from Cu^{II} → Cu^{I2} could not be performed.

TPR results obtained for fresh conventional and PTFE coated catalysts showed one main reducible specie, identified as CuO phase. After use of the

Table 2. Copper contents, for fresh and used catalysts

| Catalyst | Fresh | Used 80 h and oxidized |
|----------|-------|------------------------|
| CNT | 30.0% | 23.5% |
| C3T | 29.1% | 26.3% |

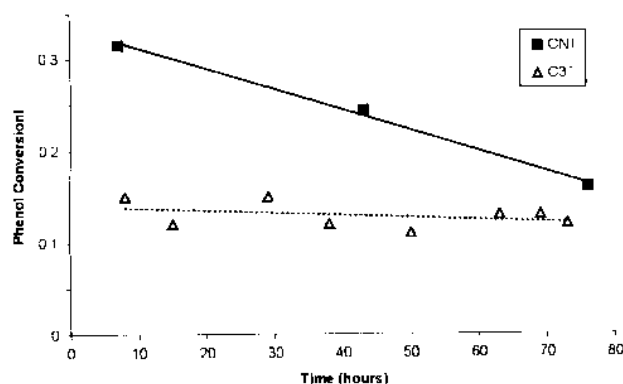


Figure 7. Phenol conversion vs operation time for CNT and C3T catalysts (trickle bed reactor).

CNT sample two overlapped peaks of hydrogen consumption were registered. This could be related to the coexistence of different copper species on the CNT catalyst. The presence of Cu^{+1} could be the major reason for the significant area reduction observed in the TPR curves. This could be confirmed by further oxidation of the sample. The phases Cu_2O and copper oxalate were not detected by XRD after the oxidation at 400°C and the TPR curve was practically restored to its initial profile.

TPR and XRD experiments performed over C3T catalyst did not report any important changes after 80 h of usage. However, SEM photographs showed also the presence of a new crystalline phase (similar to the copper oxalate observed for CNT catalyst). This phase was only detected on the areas of discontinuities of the PTFE layer, where the reaction medium is in direct contact with the CuO species. This new phase would probably be not sufficiently quantitatively significant to be detected by the other characterization techniques used.

For C3T catalyst after 80 h of operation no Cu_2O phase was detected. Lavelle and McMonagle suggest the existence of a surface gas envelope surrounding the catalyst particle (for completely hydrophobic catalysts).¹¹ The presence of this zone could be expected to have a profound effect on the mass transfer and chemical kinetics of the overall oxidation reaction. According to Horowitz *et al.*,¹⁶ the wetting efficiency of a TBR would decrease on hydrophobized catalyst, improving the oxygen transport towards the catalyst surface. If a similar reaction mechanism is assumed for both catalysts, then the presence of a wet proofed coating improves the oxygen supply favouring the complete regeneration of the catalyst by oxidizing Cu^{+1} to Cu^{+2} species. This is reasonable taking into account the semiconductor nature of the catalyst. In catalytic processes the semiconductor does act as an active participant and takes part in the intermediate stages of the reaction as one of the reaction components.¹⁷ The surface of a metal oxide catalyst has a dynamic character that depends on the properties of the reactants. Therefore, catalyst activity will be modified as the catalyst is exposed to different oxygen concentrations.¹⁰

Tables 2 and 3 show that CNT and C3T samples had, initially, similar CuO content; however the performances of the two catalysts were significantly different. Phenol conversion levels for C3T catalyst remained practically constant with use, but they were lower than those obtained for CNT (Fig. 7). This lower performance could be explained by the mass transfer resistance of phenol through the additional hydrophobic coating.²

After 80 h of use, both catalysts were oxidized at 400°C and tested for reaction. For C3T the phenol conversion was increased over the initial levels obtained for the fresh catalyst. Again, this could be connected with a partial damage to the PTFE layer

resulting from thermal treatment which improved the mass transfer of the reactants to the active sites.

For CNT catalyst, after the oxidation process, the phenol conversion was also increased. This could be related to the regeneration of the CuO phase on the surface, as observed by XRD. However, conversion levels were not completely restored. Two contributing causes are attached. One of them, and probably the most likely, is related to the major morphological changes taking place on the catalyst surface during reaction. As shown in SEM images, after oxidation and elimination of the copper-containing phases formed during reaction, CuO phase was restored. However, copper oxide phase morphology appeared markedly different from that present in the fresh sample, which looked more rough and dispersed. As reported by AA and TPR experiments, the copper content of CNT was decreased with reaction and it could also affect the conversion after oxidation.

CONCLUSIONS

Both CNT and C3T catalysts are active for the phenol oxidation reaction (140°C and 7 atm of oxygen pressure) performed in a trickle bed reactor. The selectivity towards carbon dioxide was practically complete over both catalytic systems. Phenol conversion levels for C3T catalyst remained practically constant with usage, but they were lower than those obtained for CNT. This could be explained by the mass transfer resistance of phenol through the additional hydrophobic coating.

The deactivation mechanism of the CNT catalyst was mainly associated with the Cu_2O and copper oxalate phases evolved during reaction. By further oxidation at 400°C of the used CNT samples these two phases were eliminated. However the initial levels of phenol conversion could not be completely restored, probably due to critical changes of the surface morphology exhibited after the thermal treatment.

The presence of a wet proofed coating improved the oxygen provision favouring the complete regeneration of the catalyst by oxidizing Cu^{+1} to Cu^{+2} species. However, at the same time, a strong mass transfer resistance was introduced because reactants must diffuse through the PTFE layer before reaching the $\text{CuO}/\text{Al}_2\text{O}_3$.

To prevent the latter effect, we propose to prepare hydrophobic catalysts, in which the active phase will be deposited over a hydrophobic support.

ACKNOWLEDGEMENTS

This work was supported 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 Héctor Asencio, Ms Carmen Rodríguez for technical support, and to Eng. Maria Julia Yáñez (CRIBABB) for the SEM studies.

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