Short communication

Catalytic wet peroxide oxidation of phenol solutions over CuO/CeO$_2$ systems

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

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ABSTRACT

Three 5% CuO/CeO$_2$ catalysts were synthesized by sol–gel, precipitation and combustion methods, followed by incipient wetness impregnation with copper nitrate. The samples were characterized by XRD, TPR, BET and tested for the catalytic wet peroxide oxidation of a phenol solution (5 g/L). The reaction took place in a batch reactor at atmospheric pressure, in a temperature range of 60–80 °C, during 4 h. Phenol conversion, H$_2$O$_2$ consumption, pH and chemical oxygen demand were determined. The reaction temperature and the catalyst loading did improve the phenol and the H$_2$O$_2$ conversions. The effect on the selectivity towards complete mineralization was less marked, with levels among 60–70%. Stepwise addition of H$_2$O$_2$ was also tested.

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1. Introduction

Environmental pollution has become a very complex and extended problem. The worldwide increase of controls and regulations demands new technological strategies. One major area of study is associated with new developments and advances in wastewater treatment technologies.

Many methods have been proposed to deal with aqueous effluents containing organic pollutants. Recently, Advanced Oxidation Processes (AOPs) have become recognized as promising alternatives for the removal of hazardous chemicals, exploiting the high potential energy of hydroxyl radicals [1–4]. Among different pollutants, phenol is frequently chosen as a model compound for non-conventional detoxification studies, due to its high toxicity and poor biodegradability [5–7]. A variety of AOPs have been applied to treat wastewaters containing phenol, including the classic system discovered by Fenton more than a century ago [8]. Fenton's reagent (Fe^{+2}/H$_2$O$_2$) has demonstrated to be able to destroy toxic compounds such as phenols and herbicides [3,9–11]. However, the application of conventional Fenton reaction is seriously affected by the typical problems in homogeneous catalysis (catalyst separation, regeneration) and is also limited to an acid-range controlled pH [7,9].

Different heterogeneous Fenton-type systems have been proposed, using transition metals supported over different solid materials in the Catalytic Wet Peroxide Oxidation (CWPO) reactions [7,11,12].

We have previously studied the performance of CeO$_2$-supported catalysts for the CWPO of phenol solutions, working with Fe$_2$O$_3$ and WO$_3$ as active phases with promising results [11]. Now, we propose to study CuO/CeO$_2$ systems, taking into account the activity and selectivity of copper for oxidation of phenol [13–17]. Only a few CWPO studies dealing with copper-based catalysts have been reported. Nevertheless, none of them used ceria as support. We here present exploratory studies with nanostructured CuO/CeO$_2$ materials. The application of these catalytic systems is the current subject of extensive research [18–21]; however, so far, CuO/CeO$_2$ have not been used in CWPO processes.

In this preliminary approach we studied the effect of major process variables, such as temperature, hydrogen peroxide addition and catalyst loading, in the CWPO of phenol solutions (5000 ppm) performed at mild operation conditions (atmospheric pressure and 60–80 °C).

2. Experimental

2.1. Preparation of the catalysts

Three CeO$_2$ nanosized supports were synthesized by different methods:

- Sol–gel autocombustion method: the precursors Ce(NO$_3$)$_3$·6H$_2$O and citric acid (in 1:2 molar ratio) were dissolved in bidistilled water, vaporized at 60 °C with continuous stirring, up to gelation and dried at 120 °C overnight. The support was then calcined at 400 °C in air atmosphere for 4 h. (CeO$_2$-G)
- Calcination method: the precursor Ce(NO$_3$)$_3$·6H$_2$O was directly calcined at 400 °C in air atmosphere for 4 h. (CeO$_2$-C)

* Corresponding author. Tel.: +54 223 4816600; fax: +54 223 4810046.
E-mail address: pamassa@fi.mdp.edu.ar (P. Massa).

- Precipitation method: a solution was prepared dissolving $Ce(NO_3)_3 \cdot 6H_2O$ in bidistilled water (0.4 M) and KOH 1 M was added dropwise up to a pH 9. The powder was dried at 120 °C overnight, and then calcined in air atmosphere at 400 °C for 4 h. (CeO_2-P)
- All the supports were further impregnated using $Cu(NO_3)_2 \cdot 2.5H_2O$ as precursor (Incipient Wetness Impregnation, IWI, method). The solids were dried at room temperature for 24 h, then at 120 °C in air atmosphere (4 h) and finally calcined at 400 °C in air for 4 h. The final CuO loadings of the three catalysts (CuO/CeO_2-G; CuO/CeO_2-C; CuO/CeO_2-P) were 5 wt.%.

All the reagents were reagent-grade, from Aldrich.

2.2. Characterization of the catalysts

The supports and the catalysts were characterized using the following techniques:

- Temperature programmed reduction (TPR). The experiments were performed with 5% (v/v) H_2/Ar (flow: 20 mL/min), with a linear increase of 20 °C min^{-1} (20–1000 °C). A thermal conductivity detector monitored the H_2 uptake.
- X-ray diffraction (XRD). Powder X-ray diffraction patterns of the catalysts were obtained with a PW 1830/00 Philips diffractometer by using nickel-filtered Cu Kα radiation. The patterns were recorded over $10° < 2\theta < 70°$ range and compared to the JCPDS files to confirm phase identities. The main peaks corresponding to the cerium oxide phase (cerianite, cubic) are: $2\theta = 28,68°$ (999); 33,18° (285); 47,58° (458); 56,38° (361).
- Surface areas (BET method). Surface areas were calculated from the N_2 adsorption at −196 °C by using a Micromeritics FlowSorb II 2300 surface analyser.

2.3. Determination of catalytic activity and selectivity

The catalysts were tested for the phenol oxidation reaction in a batch reactor (250 mL) equipped with a thermocouple and a pH electrode. The experiments were performed at atmospheric pressure and different temperatures (60–80 °C), with continuous stirring (1200 rpm). In a typical run, a mass of 0.1 g of catalyst (powder) was added to 100 mL of phenol aqueous solution (5 g/L). When the reaction temperature was reached, 10 mL of hydrogen peroxide (30%) were charged into the reactor and the reaction started. The resulting phenol and hydrogen peroxide initial concentrations were 0.0048 M and 0.88 M, respectively; the H_2O_2/phenol molar ratio was 18.

Complementary experiments were performed changing some of the reaction conditions. Different catalyst loadings were tested, in the range of 0.05–0.3 g. Different dosages of the 10 mL addition of H_2O_2 were also tried (two-step and four-step addition of H_2O_2 solution every 120 and 60 min, respectively).

For all the runs the total reaction time was 4 h. Liquid samples were taken at different time intervals and analysed. Phenol and hydrogen peroxide concentrations were measured by standard analytical methods (colorimetric and iodometric methods, respectively) [22]. Chemical Oxygen Demand (COD) was measured by colorimetric method after reflux with $K_2Cr_2O_7$ [22], for the samples at 0 and 240 min of reaction time. Due to interferences in the COD measurements, the remnant H_2O_2 was eliminated from the reaction samples using a ruthenium catalyst. Percentage of phenol conversion and COD reduction were calculated. The CO_2 production levels were estimated from the COD reduction [16].

For all the experimental determinations, the error was evaluated to be in the range of ±5%.

Table 1
Surface area and particle diameters of the different samples.

Sample	BET surface area (m^2/g)	Particle diameter[a] (nm)
CeO_2-G	53	7.6
CuO/CeO_2-G	50	7.2
CeO_2-C	59	11.4
CuO/CeO_2-C	55	10.5
CeO_2-P	27	14.4
CuO/CeO_2-P	22	14.4

[a] By Scherrer equation, from the most intense peak of Ce in XRD patterns.

3. Results and discussion

3.1. Catalyst characterization

The surface area of the different supports and CuO/CeO_2 catalysts were determined, and are shown in Table 1. Only a slight decrease in the surface area was observed in the presence of copper species, probably as the theoretical monolayer of CuO was approached (corresponding to a 4 wt.% of CuO, approximately). These values are in agreement with literature reports on similar catalyst systems [19,23–25].

X-ray diffraction analysis revealed the characteristic diffraction peaks of CeO_2 phase, both for the support and the catalyst. No diffraction peaks of CuO (tenorite) were detected, suggesting that no segregation of CuO phase with a bulk-like structure occurred (Fig. 1), and copper species are well dispersed onto the support. Both the low copper content and the preparation method (IWI of a copper precursor onto CeO_2 supports) induce high dispersion of copper species and limit the formation of bulk mixed phases [19,26].

All the catalysts show defined XRD lines and the crystallite sizes calculated using the Debye–Scherrer method are in the range of 7–15 nm. The copper species deposition did not significantly affect the CeO_2 crystallites size. These results are also summarized in Table 1.

Additionally, H_2-TPR experiments for the CeO_2 supports and the CuO/CeO_2 catalysts were performed (Fig. 2). For the pure ceria, two reduction peaks appeared, at 515–550 °C and 875–905 °C, corresponding to the reduction of surface and bulk ceria, respectively [19]. The presence of copper strongly modified the TPR patterns: overlapping reduction peaks appeared at temperatures much lower than for pure CeO_2 or CuO (170–220 °C), the ceria high temperature reduction peak (near 900 °C) remained unchanged and the peak of surface ceria at 500 °C disappeared [18]. Previous results using different CuO/CeO_2 preparation methods suggest that the dissolution of some copper and the formation of highly dispersed copper ions promote the reduction of surface ceria at lower temperatures
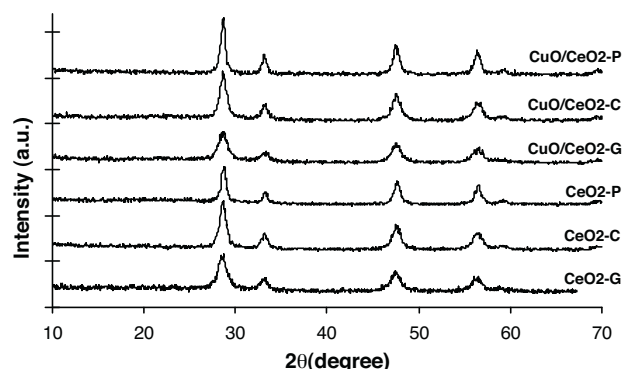

Fig. 1. XRD patterns for the different supports and catalysts.

Table 2
Summary of blank experiments results at 70 °C.

Sample	Reaction conditions				Conversions (%)[a]		
	C_{Phe}[b] (mol/L)	C_{Per}[c] (mol/L)	m_{CAT}[d] (mg)	m_{CeO2}[e] (mg)	Phenol[f]	H_2O_2[g]	CO_2[h]
CeO_2-G	0.048	–	–	100	<2	–	<2
CeO_2-C	0.048	–	–	100	<2	–	<2
CeO_2-P	0.048	–	–	100	<2	–	<2
CuO/CeO_2-G	0.048	–	100	–	<2	–	<2
CuO/CeO_2-C	0.048	–	100	–	6	–	<2
CuO/CeO_2-P	0.048	–	100	–	4.2	–	<2
CeO_2-G	–	0.88	–	100	–	92.7	–
CeO_2-C	–	0.88	–	100	–	31.6	–
CeO_2-P	–	0.88	–	100	–	31.6	–
CuO/CeO_2-G	–	0.88	100	–	–	100	–
CuO/CeO_2-C	–	0.88	100	–	–	100	–
CuO/CeO_2-P	–	0.88	100	–	–	100	–

[a] The reported conversions correspond to 4 h of reaction time.
[b] Initial phenol concentration.
[c] Initial hydrogen peroxide concentration.
[d] Mass of CuO/CeO_2 catalyst.
[e] Mass of CeO_2 support.
[f] Phenol conversion.
[g] Hydrogen peroxide conversion.
[h] CO_2 production.

[19]. Strong metal oxide–support interactions (SMSI) between CuO and CeO_2 would be responsible for the decrease in the reduction temperatures and would contribute to the complexity of thermorreduction profiles [20].

According to literature, these overlapping TPR peaks in the range 170–220 °C could be qualitatively attributed to the reduction of isolated Cu^{2+} ions (200–220 °C) and highly dispersed copper clusters (170–200 °C), both strongly interacting with the support [25]. Concurrent reduction of CeO_2 promoted by copper addition could not be neglected for any of these peaks [19,27,28]. In our study, the CuO/CeO_2-C catalyst showed thermorreduction peaks at approximately 170 °C and 200 °C; a similar behaviour, with slightly higher peak temperatures (200 and 220 °C) were registered for CuO/CeO_2-G and CuO/CeO_2-P systems.

The lower reduction temperatures observed for CuO/CeO_2-C could be explained taking into account the catalyst preparation procedure. Due to its explosive and less-controlled nature, the calcination method is likely to produce pores and a highly heterogeneous surface (confirmed by SEM studies). This morphology is probably favouring the formation of some larger (and more reducible) dispersed copper clusters than for CuO/CeO_2-G and CuO/CeO_2-P catalysts.

3.2. Phenol oxidation reaction

Different "blank" runs were performed at 70 °C and are summarized in Table 2.

Preliminary experiments were carried out to observe the extension of the phenol oxidation process over the supports and the catalysts, in the absence of H_2O_2. Negligible conversions were registered at 70 °C.

The ability of the three supports to decompose the H_2O_2 was also examined. From these results it can be inferred that nano-CeO_2 are promising for the CWPO reaction due to its rate of H_2O_2 consumption, especially in the case of CeO_2-G. The decomposition of H_2O_2 was also tested in the presence of phenol and significant differences were observed (Table 3). Indeed, the presence of phenol diminished the H_2O_2 conversion, especially for CeO_2-G support (probably because of sorption of phenol to the surface sites that promote decomposition of H_2O_2, [29]). In the presence of phenol and H_2O_2, the supports exhibited minor phenol conversion levels (lower than 10%) and relatively high selectivity towards complete mineralization. The best performance corresponded to the support prepared by the gelation method.

The catalysts were tested at 70 °C and at typical reaction conditions (catalyst loading of 0.1 g; phenol initial concentration of 0.048 M; H_2O_2 initial concentration of 0.88 M). The results are also presented in Table 3. No marked differences were detected among the three performances. Again, the catalytic system prepared by the sol–gel method exhibited higher conversion and CO_2 production levels. On the basis of characterization results, we can relate the best performance of CuO/CeO_2-G with both a more homogeneous dispersion of small copper clusters and a relatively high surface area. Thus, it was selected for more detailed reaction studies.
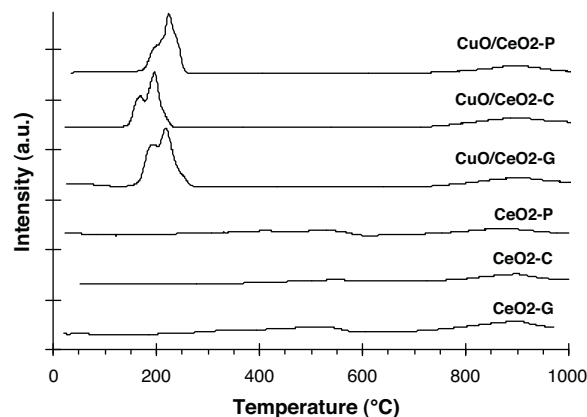
Table 3
Reaction results at 70 °C with the different supports and catalysts. (m_{SAMPLE} = 100 mg; 0.048 M of phenol; 0.88 M of H_2O_2).

Sample	Phenol conversion (%)	H_2O_2 conversion (%)	CO_2 production (%)	Selectivity
None	<2	3.5	<2	–
CeO_2-G	7.1	34.8	4.1	0.58
CuO/CeO_2-G	100	57.0	67.0	0.67
CeO_2-C	2.7	20.5	<2	–
CuO/CeO_2-C	96.2	55.1	57.8	0.61
CeO_2-P	4.4	27.3	<2	–
CuO/CeO_2-P	97.6	48.9	63.0	0.64

Fig. 2. H_2-TPR profiles for the different supports and catalysts.

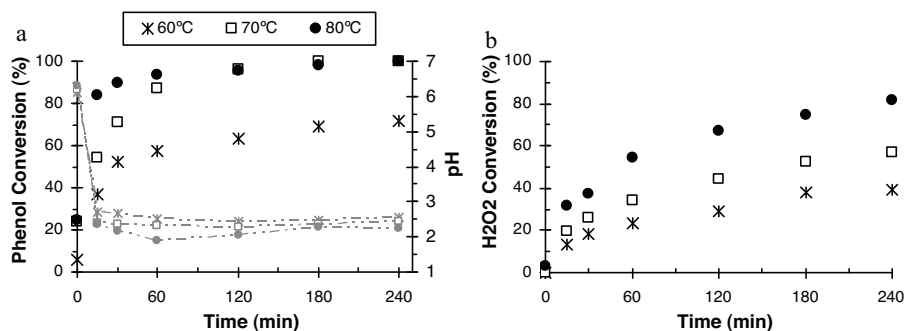**Fig. 3.** Reaction results for CuO/CeO$_2$-G, at different temperatures. (a) Phenol conversion and pH evolution (dashed lines) against time; (b) H$_2$O$_2$ conversion against time (m_{CAT} = 100 mg).
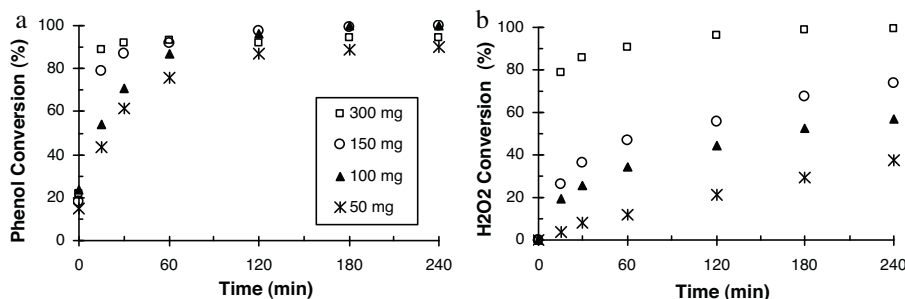

Fig. 4. Reaction results for CuO/CeO$_2$-G at 70 °C, using different catalyst mass. (a) Phenol conversion against time; (b) H$_2$O$_2$ conversion against time.

Catalytic runs with CuO/CeO$_2$-G were performed at different temperatures. Phenol conversion, H$_2$O$_2$ consumption and pH evolution against time are presented in Fig. 3. As the temperature was increased, an increase in initial reaction rates was observed. Above 70 °C, almost complete phenol conversion was reached after 60 min of reaction. The selectivity towards complete mineralization, estimated as the ratio of the CO$_2$ production and the phenol conversion, was also determined from COD measurements. No changes in selectivity were observed in the 60–80 °C temperature range (Table 4).

In all the cases, the mass balance is completed considering the formation of several reaction intermediates: hydroquinone and benzoquinone (responsible for initial darkening of the reaction solution) and organic acids (responsible for pH decrease).

Taking into account the low content of active phase in the reaction system (a total of 36 ppm of Cu), additional experiments were carried out using different catalyst loadings. The results (phenol conversion and H$_2$O$_2$ consumption against time, at 70 °C) are shown in Fig. 4. The increase in catalyst mass induced higher initial consumption rates for phenol and hydrogen peroxide. However, no significant changes in the mineralization were detected (Table 5).

For the catalytic runs using 300 mg of CuO/CeO$_2$-G, a distinctive behaviour was observed. This high catalyst loading produced a practically complete H$_2$O$_2$ consumption (at 120 min of reaction), and consequently, the progress of the phenol oxidation was halted.

Table 5
Effect of the CuO/CeO$_2$-G catalyst loading. Phenol conversion and CO$_2$ production results, after 4 h of reaction at 70 °C. (0.048 M of phenol; 0.88 M of H$_2$O$_2$).

Catalyst mass (mg)	Phenol conversion (%)	CO$_2$ production (%)	Selectivity
50	90.2	61.3	0.68
100	100	67.0	0.67
150	100	71.0	0.71
300	94.6	65.1	0.69

Thus, a lower final phenol conversion and also a lower mineralization degree of the reaction solution was achieved.

Step-wise additions of hydrogen peroxide solution (30%) were also performed; for all the experiments, the total amount of added H$_2$O$_2$ was kept constant. The results are presented in Table 6. The best results were those obtained for the higher initial concentration of H$_2$O$_2$ (one step addition). The other dosages induced lower initial rates of phenol oxidation, that could not be compensated by further addition of peroxide.

Fig. 5 shows the evolution of phenol and H$_2$O$_2$ conversion during the reaction; the results of an experiment with one-step addition of H$_2$O$_2$ at the stoichiometric molar ratio (H$_2$O$_2$/phenol = 14) are also included. A marked increase of the initial phenol degradation rate was registered for higher initial concentration of H$_2$O$_2$ [30]. There is agreement with considering that the H$_2$O$_2$ could participate in

Table 4
Effect of different reaction temperatures. Phenol conversion and CO$_2$ production results, after 4 h of reaction, using CuO/CeO$_2$-G catalyst (m_{CAT} = 100 mg; 0.048 M of phenol; 0.88 M of H$_2$O$_2$).

Reaction temperature (°C)	Phenol conversion (%)	CO$_2$ production (%)	Selectivity
60	71.8	48.9	0.68
70	100	67.0	0.67
80	100	67.7	0.68

Table 6
Step-wise addition of H$_2$O$_2$ solution (30%). Phenol conversion and CO$_2$ production results, after 4 h of reaction at 70 °C, using CuO/CeO$_2$-G catalyst, (m_{CAT} = 100 mg; 0.048 M of phenol).

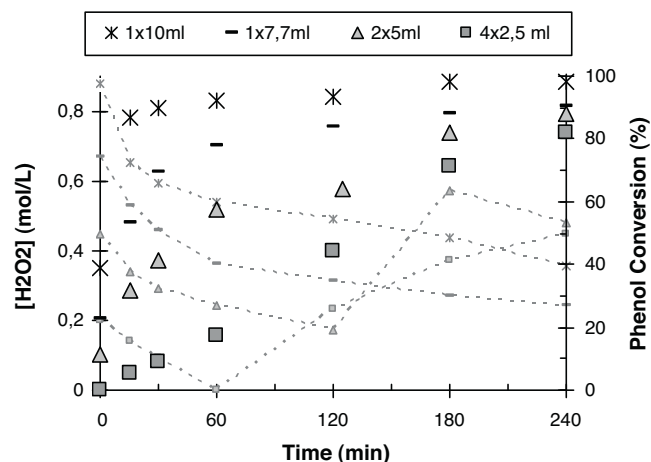| H$_2$O$_2$ solution addition	Phenol conversion (%)	CO$_2$ production (%)	Selectivity
1 × 10 mL	100	67	0.67
2 × 5 mL	87.8	51.5	0.59
4 × 2.5 mL	82.1	47.6	0.58

Fig. 5. H_2O_2 concentration and phenol conversion against time for different H_2O_2 dosages.

three major competitive reactions: (1) the thermal decomposition giving water and oxygen (2) the formation of hydroxyl radicals and (3) the scavenging of the OH* radicals (the last reaction being more significant for high H_2O_2 concentration) [1,5,9]. Thus, a suitable catalyst for these CWPO processes should minimize the thermal decomposition of H_2O_2, the main cause of inefficient consumption of the hydrogen peroxide, and favour the activation to form oxidant radicals.

For other catalytic systems, it was reported that the step-wise addition of the oxidant improved the oxidation performance [17]. However, in the present study a different behaviour was detected. During the 4 h of reaction time, the consumption of hydrogen peroxide was gradual and not complete. Two and four-step addition increased the remaining H_2O_2 levels at long reaction times. However, this effect did not improve final phenol conversion or mineralization levels. The contribution of catalyst deactivation processes could not be neglected. Exploratory experiments were performed adding more fresh catalyst during reaction runs, and no significant changes in the mineralization rates were observed. More experiments are under study in order to investigate catalyst stability.

4. Conclusions

According to the present study, we conclude that 5% CuO/CeO$_2$ nanocatalysts resulted active and selective for the CWPO of phenol reaction, at mild operation conditions (60–80 °C and atmospheric pressure).

The different preparation methods of CeO$_2$ had a moderate influence on the physicochemical properties and catalytic performance of the CuO/CeO$_2$ catalysts. The catalyst CuO/CeO$_2$-G exhibited the highest conversion levels and selectivity towards complete mineralization. This was related to both a more homogeneous dispersion of small copper clusters and a relatively high surface area.

The reaction temperature and the catalyst loading did improve the initial phenol and H_2O_2 consumption rates. However, no marked effect on the selectivity towards complete mineralization was observed.

The catalyst CuO/CeO$_2$-G produced a gradual consumption of H_2O_2. The stepwise addition of the oxidant agent increased the remaining H_2O_2 levels at long reaction times. However, this effect did not improve the selectivity of the oxidation towards complete mineralization.

References

[1] W.H. Glaze, J.W. Kane, D.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, Ozone: Sci. Eng. 9 (1987) 335–352.
[2] C.P. Huang, C. Dong, Z. Tang, Advanced chemical oxidation: its present role and potential future in hazardous waste treatment, Waste Manage. 13 (1993) 361–377.
[3] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.
[4] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.
[5] R. Alnaizy, A. Akgerman, Advanced oxidation of phenolic compounds, Adv. Environ. Res. 4 (2000) 233–244.
[6] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.
[7] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288.
[8] H.J.H. Fenton, Oxidation of tartaric acid in presence of iron, J. Chem. Soc. 65 (1894) 899–911.
[9] P. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.
[10] C. Jiang, S. Pang, F. Ouyang, J. Ma, J. Jiang, A new insight into Fenton and Fenton-like processes for water treatment, J. Hazard. Mater. 174 (2010) 813–817.
[11] P. Massa, A. Dafinov, F. Medina Cabello, R. Fenoglio, Catalytic wet peroxide oxidation of phenolic solutions over Fe$_2$O$_3$/CeO$_2$ and WO$_3$/CeO$_2$ catalyst systems, Catal. Commun. 9 (2008) 1533–1538.
[12] L. Xiang, S. Royer, H. Zhang, J.M. Tatibouet, J. Barrault, S. Valanges, Properties of iron-based mesoporous silica for the CWPO of phenol: a comparison between impregnation and co-condensation routes, J. Hazard. Mater. 172 (2009) 1175–1184.
[13] A. Sadana, J.R. Katzer, Catalytic oxidation of phenol in aqueous solution over copper oxide, Ind. Eng. Chem. Fundam. 13 (1974) 127–134.
[14] 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 16 (1998) 53–67.
[15] 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 61 (2005) 323–333.
[16] 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.
[17] R.M. Liou, S.H. Chen, CuO impregnated activated carbon for catalytic wet peroxide oxidation of phenol, J. Hazard. Mater. 172 (2009) 498–506.
[18] A. Gurbani, J.L. Ayastuy, M.P. González-Marcos, J.E. Herrero, J.M. Guil, M.A. Gutiérrez-Ortiz, Comparative study of CuO–CeO$_2$ catalysts prepared by wet impregnation and deposition–precipitation, Int. J. Hydrogen Energy 34 (2009) 547–553.
[19] T. Caputo, L. Lisi, R. Pirone, G. Russo, On the role of redox properties of CuO/CeO$_2$ catalysts in the preferential oxidation of CO in H$_2$-rich gases, Appl. Catal. A 348 (2008) 42–53.
[20] P. Djinovic, J. Batista, A. Pintar, Calcination temperature and CuO loading dependence on CuO–CeO$_2$ catalyst activity for water-gas shift reaction, Appl. Catal. A 347 (2008) 23–33.
[21] D. Delimaris, T. Ioannides, VOC oxidation over CuO–CeO$_2$ catalysts prepared by a combustion method, Appl. Catal. B 89 (2009) 295–302.
[22] L.S. Clesceri, A. Geenberg, in: A. Eaton (Ed.), Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington DC, 1998.
[23] G. Avgouropoulos, T. Ioannides, H. Matralis, Influence of the preparation method on the performance of CuO–CeO$_2$ catalysts for the selective oxidation of CO, Appl. Catal. B 56 (2005) 87–93.
[24] L. Li, Y. Zhan, Q. Zheng, Y. Zheng, C. Chen, Y. She, X. Lin, K. Wei, Water–Gas shift reaction over CuO/CeO$_2$ catalysts: effect of the thermal stability and oxygen vacancies of CeO$_2$ supports previously prepared by different methods, Catal. Lett. 130 (2009) 532–540.
[25] W. Yang, D. Li, D. Xu, X. Wang, Effect of CeO$_2$ preparation method and Cu loading on CuO/CeO$_2$ catalysts for methane combustion, J. Nat. Gas Chem. 18 (2009) 458–466.
[26] A. Martínez-Arias, M. Fernández-García, J. Soria, J.C. Conesa, Spectroscopic study of a Cu/CeO$_2$ catalyst subjected to redox treatments in carbon monoxide and oxygen, J. Catal. 182 (1999) 367–377.

[27] H. Zou, X. Dong, W. Lin, Selective CO oxidation in hydrogen-rich gas over CuO/CeO$_2$ catalysts, Appl. Surf. Sci. 253 (2006) 2893–2898.

[28] X. Tang, B. Zhang, Y. Li, Y. Xu, Q. Xin, W. Shen, CuO/CeO$_2$ catalysts: redox features and catalytic behaviors, Appl. Catal. A 288 (2005) 116–125.

[29] K. Hanna, T. Kone, C. Ruby, Fenton-like oxidation and mineralization of phenol using synthetic Fe(II)–Fe(III) green rusts, Environ. Sci. Pollut. Res. 17 (2010) 124–134.

[30] S. Zrncevic, Z. Gomzi, CWPO: an environmental solution for pollutant removal from wastewater, Ind. Eng. Chem. Res. 44 (2005) 6110–6114.