Catalysis Letters Vol. 106, Nos. 1–2, January 2005 (© 2006)
DOI: 10.1007/s10562-005-9195-2

Catalytic wet air oxidation of Aqueous solutions of substituted phenols

Diana Posada[a], Paulino Betancourt[a,*], Fernando Liendo[b], and Joaquín L. Brito[c]

[a]*Universidad Central de Venezuela. Facultad de Ciencias. Escuela de Química. Centro de Catálisis, Petróleo y Petroquímica. Los Chaguaramos, Caracas AP 40679, Venezuela*
[b]*PDVSA-Intevep. Gerencia de Ecología y Ambiente. El Tambor. Edo., Miranda, Venezuela*
[c]*Instituto Venezolano de Investigaciones Científicas, IVIC. Centro de Química, Altos de Pipe, Estado Miranda Caracas 1020-A, Venezuela*

Received 11 November 2004; accepted 6 October 2005

Catalytic wet air oxidation (CWAO) of aqueous solutions of phenol, 2-chlorophenol and 4-nitrophenol were studied using Cu/CeO_2 with 4% of copper as catalytic material. The catalyst was prepared by an impregnation method and characterized by X-ray diffraction (XRD), BET surface area, oxygen storage capacity (OSC), temperature programmed reduction (TPR), electron paramagnetic resonance (EPR) and XPS. The reaction was carried out in a batch reactor at $T = 160$ °C and 1.0 MPa. Cu/CeO_2 catalyst was found effective in CWAO. On the basis of characterization data, it is suggested that the high activity of the copper–ceria catalyst is related to the modification of the structural and redox properties of the cerium oxide on copper addition. The ratio BOD_5/COD was measured to evaluate the biodegradability. Pretreatment by CWAO under operating conditions resulted in effluents whose biodegradation rates were significantly higher than those of the original.

KEY WORDS: Cu/CeO_2; characterization; wet air oxidation; phenol; 2-dichlorophenol, p-nitrophenol.

1. Introduction

Natural water pollution by organic compounds, among them phenol and its derivatives is the most harmful contamination and is increasing due both to industrial activities and accidents. As one of wastewater abatement technologies, wet air oxidation (WAO) has recently emerged, proving to have promising activity in oxidizing highly toxic and non-biodegradable industrial effluents. Normally a typical WAO process requires elevated pressures (0.5–20 MPa) and temperatures (125–320 °C) in order to enhance the solubility of oxygen in aqueous solution [1]. Such requirements will inevitably lead to high equipment and operational costs. To reduce these costs, catalysts are added to lower the reaction temperature and pressure, and to avoid the formation of harmful byproducts, including complete oxidation of organic contaminants to harmless carbon dioxide, water and nitrogen, which is referred to as CWAO process [2]. By using CWAO, the oxidation of phenol can be tremendously facilitated at milder conditions [2]. Aqueous phenol is a typical model pollutant of non-biodegradable wastewater in many studies of WAO or CWAO processes [3,4]. On the other hand, 2-chlorophenol (2CP), widely used in paper, pulp, pesticide, and herbicide industries, is a priority pollutant [5,6], being very toxic and poorly biodegradable.

The use of CeO_2-based catalyst has shown a rapid increase in the last years [7]. A high oxygen mobility [8], strong interaction with the supported metal phases (strong metal-support interaction) [9] and the modifiable ability [10] render the CeO_2-based materials very interesting for catalysis as a support. Cerium oxide has traditionally been used as a promoter in the so-called "three-way catalysts" (TWC) employed for the control of toxic emissions from automobile exhausts [11]. Several reports have shown that the activity of Ce-related oxides in complete oxidation reactions is greatly enhanced not only by noble metals (Rh, Pt, and/or Pd) [8,11,12], which generally form part of the TWC's, but also by base metals such as copper [13–16]. The promoting effect has been correlated with the synergism of the redox properties of the system, which is achieved by formation of copper–ceria interactions, with both components being significantly more readily reduced or oxidized than the corresponding independent components [15,17].

The focus of this paper is on the CWAO of phenol and substituted phenols over Cu/CeO2 catalysts.

2. Experimental

2.1. Materials

Hydrogen, nitrogen and helium gases used in the preparation and characterization of the catalysts were taken directly from cylinders, with a purity of at least 99.998%. Synthetic air, as reagent for the activity measurements was 99.990% purity. All gases were supplied by AGA gases.

---

* To whom correspondence should be addressed.
E-mail: pbetanco@strix.ciens.ucv.ve

1011-372X/06/0100–0081/0 © 2006 Springer Science+Business Media, Inc.

2.2. Catalyst preparation

2.2.1. Cerium oxide

Ceria was prepared by the ammonia precipitation method from an aqueous solution of cerium (III) nitrate hexahydrate. To this vigorously stirred solution it was added a mixture of aqueous ammonia and hydrogen peroxide (10:1), dropwise, over a period of 1 h until the solution reached a $pH = 10$. After the solution was stirred overnight at room ambient temperature the resulting precipitate was washed in distilled water and centrifuged. The solid was air-dried overnight at 383 K.

2.2.2. Cu/Cerium oxide

A slurry of ceria powder in a solution copper (II) nitrate trihydrate (to give a final copper load of 4 wt%) in distilled water was stirred vigorously at ambient temperature. The resulting suspension was then filtered and dried in air at 333 K.

2.3. Experimental procedure

In a typical run 0.5 g of catalyst was charged into a stainless-steel stirred tank reactor, Parr Instrument Co. model SS316, with 1 L capacity, and processed by a controller model 4851. It is equipped with a 4 bladed turbine type impeller mixer. A thermal sensor, cooling coil and external heating element are also included in the reactor for temperature control. The reactor was charged with a solution of known concentration of pollutant, and the reaction mixture was heated to the desired temperature. Once this temperature was achieved a first sample was withdrawn for analysis. This time was taken as "zero" time for a reaction; afterwards samples were taken at several reaction times. The model pollutants employed (phenol, 4-nitrophenol and 2-chlorophenol (all reagent grade, Merck) are frequently found in industrial waste waters and are generally considered to be resistant to degradation. At the chosen operating conditions the external as well as intraparticle mass transfer resistances were found to be negligible. The pH was not controlled in order to observe the pH changes by catalyst and intermediates.

2.4. Analytical procedures

Liquid samples, taken periodically from the reactor, were filtered through a 0.2 μm pore-size polycarbonate filter after being cooled to ambient temperature and analyzed for pH, COD and 5-day biochemical oxygen demand (BOD_5). Sample pH was measured with pH-meter (Orion) and COD concentration was determined with a direct reading spectrophotometer (Hash, DR/2000). The BOD_5 concentration was quantified according to *Standard Methods for Water Quality Analysis* using a traditional 5-day culture [18]. Biodegradability was defined as the BOD_5/COD ratio. This numerical value serves as a gross measure for the biological degradability of chemical substances.

Reaction intermediates and residuals were identified and quantified with a high performance liquid chromatograph (HPLC) (Perkin-Elmer, series 2000) equipped with a tunable absorbance detector. Separation of the components was achieved using a Nova-Pak C18 column. Elution was performed at 1 mL min^{-1} flow rate of mobile phase (Methanol: H_2O:$H_3PO_4 = 40{:}60{:}0.5$ vol.%).

Inductive coupled plasma (ICP) measurements were carried out to calculate the extent of copper leaching from the catalyst into the reaction medium.

2.5. Physical and spectroscopic measurements

The oxygen storage/release capacity (OSC) was estimated by thermo-gravimetric analysis. The CeO_2 sample was cyclically reduced using 20% H_2 for 5 min, and then oxidized with 50% O_2/Ar in 5 min at 773 K. The weight loss and gain were measured using a thermo-gravimetric analyzer. The value of the weight change between the reductive and oxidative conditions allows to the total OSC at 773 K, in terms of μmol O per gram of catalyst.

The specific surface areas of the samples were measured from the N_2 adsorption isotherm at 77 K by the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2010. The samples were degassed in flowing N_2 at 473 K for 20 min.

Powder X-Ray diffraction (XRD) experiments were carried out using a Bruker D-8 diffractometer with Cu-K_α radiation (1.5406 Å). Representative diffactograms were acquired over 5–90 ° in 2θ with 0.02° steps and 0.4 s acquisition times per step Phase identification was performed by comparison to the JCPDS database.

Catalysts reducibility (after calcination) was probed by temperature-programmed reduction (TPR) using a Micromeritics 2900 TPR/TPD system, utilizing approximately 60 mg of catalyst in the quartz U-tube flow reactor. TPR was carried out by heating the sample from room temperature to 500 °C (10 K min^{-1}) under 5% H_2/Ar (vol.%), with a flow rate of 30 mL min^{-1}.

Electron paramagnetic resonance (EPR) spectra were recorded at 298 K with a Varian E 104A spectrometer operating in the X-band and calibrated with reference to diphhenylpicrylhydrazyl (DPPH) standard ($g = 2.0036$).

X-ray photoelectron spectroscopic (XPS) analysis was conducted employing Mg K_α (1253.6 eV) radiation with VG ESCALAB 220i XL energy analyzer. The intensities were estimated by calculating the integral of each peak after subtraction of the "S-shaped" background (Shirley-type baseline) and taking into account experimental factors affecting quantitative data, viz., ionization cross section, electron escape depth, and instrumental sensitivity. The binding energy (E_b) of Cu was referred to C1s (284.4 eV) lines. The standard deviation of the binding energy (E_b) was typically ±0.3 eV (table 1).

Table 1
Range of operating parameters for activity measurements

Parameters	Range
Total pressure (MPa)	1
Temperature (K)	313–433
Initial phenol concentration, (mg L^{-1})	500
Catalyst concentration (g L^{-1})	0–1.5
Stirrer speed (rpm)	400

3. Results and discussion

Table 2 lists the investigated solids and their specific surface areas (SSA) and pore texture data. The undoped-ceria solid shows a relatively high surface area (69 $m^2 g^{-1}$). The addition of Cu decreases slightly the total surface area (ca. 12%), while the average pore diameter decrease from ~10 nm for CeO_2 to ca. 9 nm for Cu/CeO_2. The decrease in BET areas of the catalyst is presumably ascribed to the plugging of some micropores by copper. Isotherms for all the catalysts studied were of type IV with hysteresis indicative of mesoporous solids.

Figure 1 shows the X-ray diffractograms of the samples. The diffractogram of CeO_2 can be indexed according to its cubic fluorite structure (space group *Fm*3*m*, JCPDF 43-1002) with a cell parameter $a = 0.541$ nm. No CuO phase appeared in the pattern of Cu/CeO_2 (figure 1b). The lattice constant of CeO_2 remained almost unchanged when Cu was added. The XRD analysis of the Cu/CeO_2 confirmed that the fluorite lattice structure of ceria had been preserved during the impregnation process. These results suggest that copper forms metal oxide particles on the surface of CeO_2. However, the copper oxide particles are too small to show their XRD pattern. The size of the CeO_2 particle was close to 20 nm in the Cu/CeO_2 catalyst, calculated from the peak width at 28.6 degrees in the diffractogram using the Debye-Scherrer formula. TPR analysis was carried out in order to obtain information on the redox properties of the samples. Figure 2 shows the TPR profiles of the CuO, CeO_2 and Cu/CeO_2. CeO_2 did not show any peaks below 500 °C. CuO showed a broad single peak at around 340 °C. By supporting on CeO_2, the reducibility of Cu^{2+} was strongly enhanced, as the temperature of the Cu^{2+} reduction peak was much lower than that in the pure CuO. The shape of reduction profile observed for Cu/CeO_2 catalyst probably indicates the existence of different kinds of oxidic species (Cu_2O, CuO). Luo *et al.* [15] suggested that one kind was represented by small CuO particles, which are reduced at lower temperature; another was represented by large particle CuO and reduced at higher temperature. On the other hand, according to the work of Yao and Yao [19], there exist three types of oxygen in CeO_2, i.e. capping, bulk and shared oxygen. Capping oxygen may be produced by defects in the CeO_2 crystal. Zafiris and Gorte [20] have concluded that the relative ease of oxygen removal in CeO_2 may be due to the presence of defects. Copper in the catalyst would promote these crystal defects. As H_2 consumption, equates to oxidation of H_2 molecules by CeO_2, probably there exists a contribution of the capping oxygen in the H_2-TPR, indicating a higher oxidizing ability in the Cu/CeO_2 catalyst. The capping oxygen is considered to be the most active oxygen species in TWC catalysts. The catalytic ability of capping oxygen is attributed to its mobility with oxygen either in gas phase or in molecules adsorbed on the CeO_2, therefore undergoing a redox cycle between two oxidation states.

Table 2
Pore texture data for CeO_2, CuO and Cu / CeO_2 catalyst materials

Sample	SSA $m^2 g^{-1}$	Tot. pore vol. $cm^3 g^{-1}$	Av. pore diameter nm
CeO_2	67	0.168	10.3
CuO	13	–	–
Cu/CeO_2	59	0.137	9.4

For precious metals, it has been observed that the metal support on ceria can bring about a low-temperature reduction of surface capping oxygen anions of ceria [19,21]. This phenomenon has been attributed to hydrogen spillover supported precious metal to ceria [21]. The hydrogen spillover does not seem to be working in the Cu/CeO_2 system since hydrogen dissociation, would not occur easily on copper [22].

The results of OSC measurements for the support and Cu/CeO_2 catalyst were 61.7 and 98.6 μmol-O g^{-1}, respectively. The copper added increase, in significant proportion (37%), the OSC of ceria. This is linked to the reducibility of CeO_2, supporting the above discussion about the increase of capping oxygen with Cu doping. The availability of oxygen vacancies created by copper explains the increase of the oxygen storage capacity (OSC).

In the three consecutive cycles of the O_2–H_2 titration, the O_2 uptakes estimated according to O_2 consumption were similar, suggesting that the redox behavior is reversible. In a summary, based on the extent of oxygen uptake, one can see that the ability of storing oxygen coincide with the order of the oxygen vacancy density. The process for oxygen uptake involves a redox cycle between Ce^{4+} and Ce^{3+} and the oxygen vacancies generated by copper incorporation facilitate the reduction of Ce^{4+} to Ce^{3+}.

The EPR spectra of the fresh (calcined in air at 500 °C) and used catalysts at room temperature are shown in figure 3. The fresh Cu/CeO_2 spectra (figure 3a) can be interpreted in terms of the overlapping of at least two components. The first one, characteristic of randomly isolated Cu^{2+} ions in an axially symmetric environment. The second consist of a broad single line shape, which can be assigned to two or more

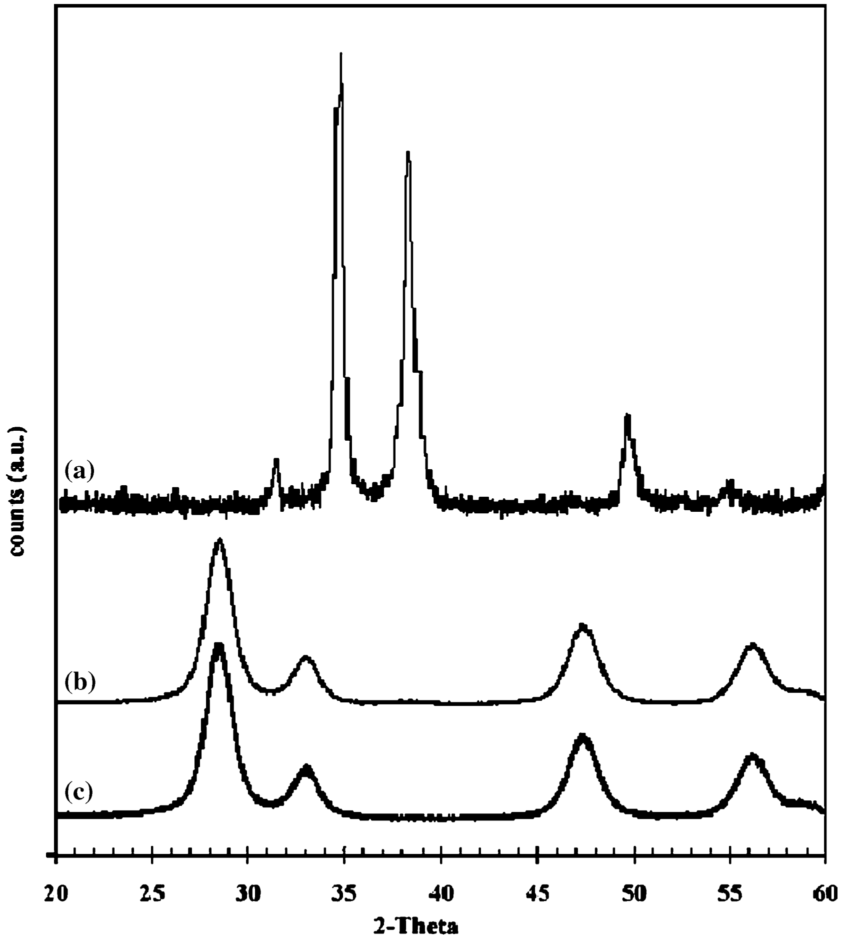

Figure 1. XRD patterns of (a) CuO; (b) Cu/CeO_2 and (c) CeO_2.

magnetically interacting Cu^{2+} ions, and their dipole broadening might cause the observed line shape.

Figure 3b shows EPR spectra after phenol CWAO reaction. On the basis of computer simulations, the spectra are formed by the overlapping of different signals, in agreement with previous results [17]. The spectra of the treated sample is formed by the overlapping of different signals: A major featureless broad signal showing extremes at $g = 2.23–2.20$ and $g = 2.04$, which must be due to Cu^{2+} ions; its large linewidth (leading to unresolved hyperfine splitting) can be attributed to dipolar broadening effects caused by mutual interactions between paramagnetic Cu^{2+} ions, indicating that the corresponding ions are located in a Cu^{2+}-containing aggregated phase of an oxidic type. The other axial signals, in which four-line hyperfine splittings can be resolved in each of its components, are typical of isolated Cu^{2+} ions, their different EPR parameters reflecting differences in the coordination environments of the corresponding ions.

Surfaces of catalyst were studied by XPS spectroscopy to reveal the nature of the active copper species involved in the catalytic CWAO of phenols. XPS data for calcined, spent and re-oxidized are reported in table 3.

For cerium, the position of the $3d_{5/2}$ XPS peak (882.1 eV), as well as the intensity of the satellite peak (916 eV), agrees well with a fully oxidized Ce^{4+} state [23–25]. On the other hand, the relatively small intensity of the peak appearing in the Ce 3d manifold at 915.2 eV (usually called u''') may suggest that the material studied contains Ce^{3+} in small amount [26] (it must be noted, however, that arguments have been put forward against the use of the u''' peak intensity for the quantification of the degree of Ce reduction in mixed oxides [27]). From these results, the coexistence of both Ce^{3+} and Ce^{4+} oxidation states are distinguishable, though the latter oxidation state is predominant. Close to 7% was ascribed to surface Ce^{3+} in fresh catalyst, which may exist as $Ce(OH)_3$ or as Ce_2O_3.

For copper, a broad and asymmetric main $Cu2p_{3/2}$ line has been observed in fresh Cu/CeO_2 catalyst, which can be due to the contribution of different copper species. A good deconvolution of the XPS peak is achieved by considering the contribution of two components at 933.1 and 934.1 eV, the later being the principal one. The $Cu2p_{3/2}$ binding energies and peak shapes cannot be used to distinguish between Cu_2O and Cu^0 because they are essentially identical. However, the Cu LMM Auger lines of Cu_2O and Cu^0 are separated by ~2.0 eV and

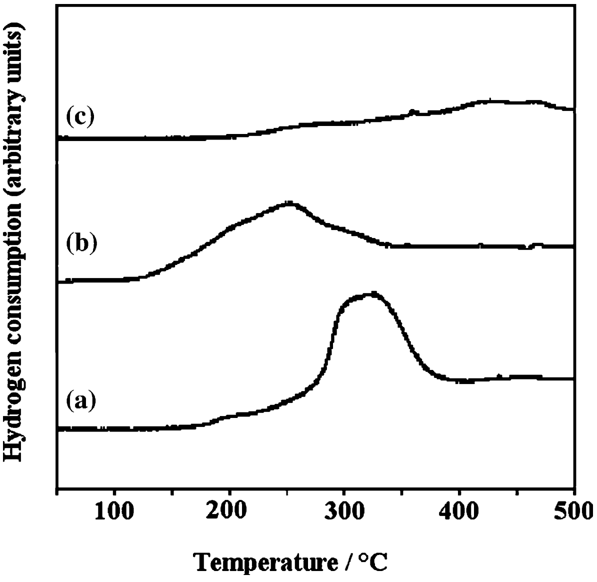

Figure 2. TPR profiles of (a) CuO; (b) Cu/CeO_2 and (c) CeO_2. Operating conditions: 10 K min^{-1}, 5% H_2/Ar, with a total flow rate of 30 mL min^{-1}; sample weight, 60 mg.

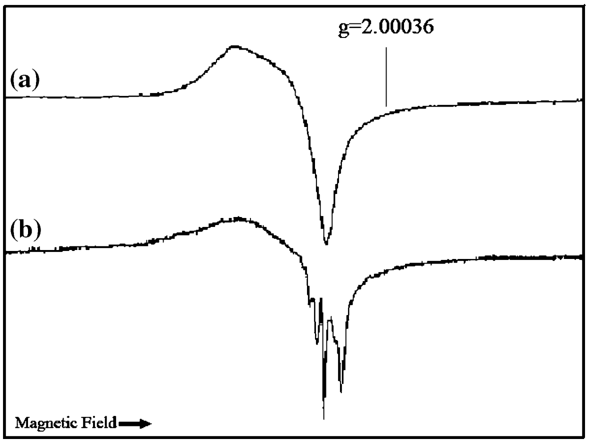

Figure 3. EPR spectra (a) fresh and (b) used of Cu/CeO_2.

their peak shapes are different, allowing easy distinction between the two species. The 918.5, 916.4 and 917.6 eV peaks in the Auger kinetic spectra correspond to Cu^0, Cu^+ and Cu^{2+} (CuO), respectively.

After reaction the XPS analysis shows: (i) the Ce^{4+} BE shift slightly (table 3), (ii) the Ce^{3+} proportion is four times higher than that detected on the corresponding oxidized sample, (iii) a noticeable reduction in oxygen (O 1 s), and the Cu^{2+} species in the Cu/CeO_2 catalyst were partially reduced to Cu^+ and Cu^0 during the CWAO process. An examination of deconvoluted C1s core level spectra of used Cu/CeO_2 catalyst showed that this region was dominated by an aliphatic carbon (284 eV).

The relative amount of CuO and Cu_2O on the surface of the copper species determined by XPS corresponds to the ratios of 2.9 and 6.8 for the fresh catalyst and the used catalyst, respectively. It seems that the Cu^{2+} species in the Cu/CeO_2 catalyst was reduced to Cu^+ in the CWAO process.

In a separate experiment, a spent catalyst (employed in CWAO of 2CP) was analyzed by XPS. Chlorinated-bonded CuO species in the Cu/CeO_2 were not observed in the XPS spectra. Thus, one may eliminate the possibility that copper is involved in the abstraction of Cl from 2CP in the CWAO process.

CWAO was been recognized as an innovative waste treatment process that can destroy organic species completely [references]. Development and rational design, control, optimization, analysis and evaluation of the CWAO process requires knowledge of reaction behavior that are also used to determine if further development of this technology would be warranted.

To assess the extent of the uncatalyzed thermal oxidation of organic compounds and the effect of support, WAO test were performed without catalyst and metal-free support at 160 °C. The uncatalyzed thermal oxidation did occur up to 20% in 100 min, and the use of metal-free CeO_2 support resulted in somewhat lower oxidation efficiency than uncatalyzed oxidation. Temperature effect can lead to the formation of oxygen radicals, which in turn can react with water to form hydroxyl radical. This radical might have oxidized phenol. Metal-free CeO_2, however, scavenged some of hydroxyl radical formed. Moreover, the CuO catalyst show an initial activity, but it strongly decay after few minutes of reaction.

Figure 4 shows the results of catalytic test performed on the Cu/CeO_2 sample with phenol, 2CP and 4NF. The use of Cu/CeO_2 catalyst enhanced the oxidation appreciably. Complete degradation of phenol could be obtained in 100 min, and a 100% of conversion of chlorophenol was obtained within 130 min. About a 60% destruction of nitrophenol could be achieved at the final steady state (200 min.). The conversion of the

Table 3
Binding and kinetic energies of Cu/CeO_2 catalyst

Cu/CeO_2	Ce $3d_{5/2}$	Cu $2p_{3/2}$		Cu LMM Auger		
	CeO_2	Cu^0/Cu_2O	CuO	Cu^0	Cu_2O	CuO
Fresh	882.1	933.1	934.1	–	916.4	917.6
Used	882.4	933.1	–	918.5	916.4	917.6
Re-oxidized	882.2	933.1	934.1	–	916.5	917.6

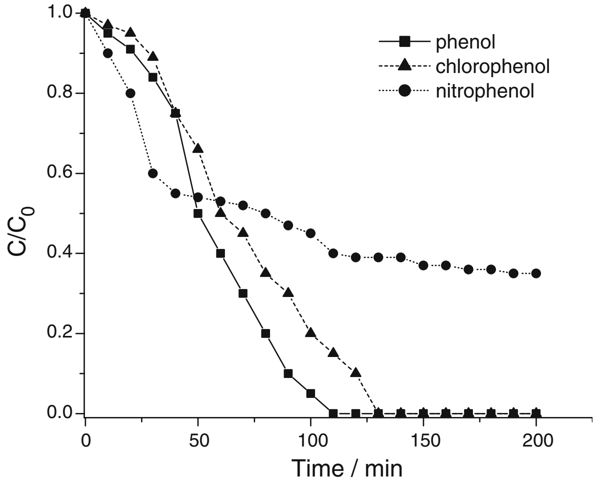

Figure 4. Conversion of phenol, 2CF and 4NF as a function of reaction time.

composite Cu/CeO_2 catalyst toward the oxidation of phenols is greater than either of the two individual oxides. This observation indicates the occurrence of both chemical and physical changes that affect the nature of the catalyst material.

In an experiment apart, a Cu/γ-Al_2O_3 catalyst was studied, which is usually employed as CWAO commercial catalyst. It showed conversions of 71%, 62% and 39%, for phenol, 2-CP and 4-NP, respectively. Comparing the performance of the Cu/CeO_2 catalysts in the CWAO of phenol, 2-CP, and 4-NP. We see that Cu/CeO_2 had much higher catalytic abilities than the commercial copper oxide supported over γ-alumina. This corresponds to our OSC and H_2-TPR result, i.e., the Cu/CeO_2 is the one with the highest oxygen mobility and therefore the highest catalytic ability, for both H_2 consumption and for phenols conversion.

The hypothesis that the decrease in the catalytic activity is due to a catalyst leaching was ruled out by analyzing the Ce content in the solution after reaction. As on unpromoted samples, no Ce leaching was detected (Ce content in reaction mixture after 4 h was <1 ppm) from the doped catalyst. On the other hand, a somewhat higher concentration of Cu was detected in the liquid phase (up to 50 ppm) after reaction. Because Cu^{2+} ions present an important homogeneous activity in the phenol oxidation [28], the high amount detected (54.5 ppm) of this ions in solution include that they can be partially responsible of high conversion observed on the Cu/CeO_2 catalyst.

It has been reported that ceria is a good catalyst in the oxidation of phenol and substituted phenols. In this regard, de Leitenburg et al. have suggested that the activity of CeO_2 in the wet oxidation is related to the mobility of surface oxygen associated with deficient Ce sites, which activate oxygen [29]. Oxygen vacancies are further formed when ceria is doped by divalent or trivalent ions [30–33]. Doping ceria with copper resulted instead in more active catalysts. The reason for the activity enhancement is likely to be found in the structure modification due to the incorporation of Cu ions which favor the oxidation activity as already reported on doped-ceria catalyst, such as Mn, Zr and Ru [3,11,25,29,34–41].

As a result, it is conceivable that the distinct enhancement of conversion is due to the synergistic effect of copper oxide and the surface oxygen vacancies of ceria by means of formation of interfacial active centers, Cu–Ce, as shown by earlier discussions on characterization of this work.

The HPLC analysis of reaction products has shown that intermediates of phenol CWAO are: catechol, hydroquinone, *p*-benzoquinona, oxalic and formic acid. The intermediaries observed are in agreement with the reaction pathways proposed for phenol oxidation by Santos *et al.* [42]. For 2CP were identified 4-chloro-1,2-benzenediol, 1,4-benzenediol and oxalic acid. The presences of benzenediols were also identified in a previous study [43].

The pH value change between the use of catalyst and without catalyst. With reaction in progress, the pH initially decreases because the formation of organic acids (e.g. acetic acid), and then organic acids were decomposed, increasing the pH.

The biodegradability is defined as the ratio of the BOD to the COD. The figure 5 showed the ratio BOD_5/COD for each organic compound. The ratio increased respect to initial solutions for the three studied compounds indicating improved biodegradability. Phenol is a slightly biodegradable substance and further oxidation may yield biodegradable compounds. This increased biodegradability showed a good possibility for biological treatment as a post CWAO step. Chlorophenol shows little or no biodegradability ($BOD_5/COD < 0.01$), but after CWAO process, by-products show increasing biodegradability (up to $BOD_5/COD = 0.7$). After

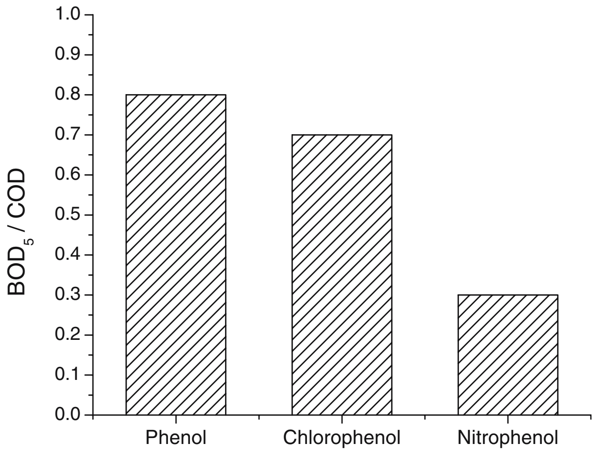

Figure 5. The variation of the ratio BOD_5/COD after CWAO reaction.

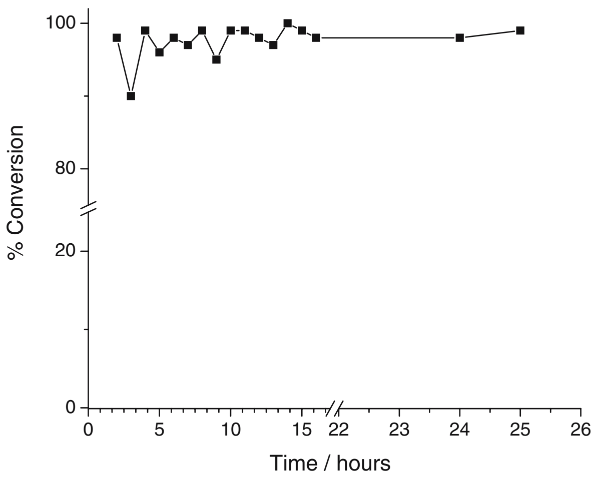

Figure 6. Stability tests of Cu/CeO_2 catalyst for the wet air oxidation of phenol at 160 °C. Phenol concentration = 500 ppm.

CWAO reaction the 4-nitrophenol increase the ratio from 0 to 0.30.

In the isothermal CWAO of phenol at 160 °C over a 25 h period (shown in figure 6), phenol conversion was maintained at ~99% for the duration of the test. This demonstrates that any effect of the phenol oxidation products H_2O and CO_2 was insignificant, and also that the Cu/CeO_2 catalyst showed excellent stability.

4. Conclusion

Catalytic wet air oxidation of phenol, 2CP and 4NP were carried out with Cu/CeO_2 catalyst at 160 °C and 1 MPa. Based on the results of this work, the following conclusions can be made:

1. The conversion enhancement is inferred to result from the synergistic effect of copper oxide and the surface oxygen vacancies of ceria by means of the formation of interfacial active centers.
2. When copper oxide is supported on CeO_2 support, the resulting synergistic effect between copper oxide and the surface oxygen vacancies of ceria lowers the TPR peak temperature of the copper oxide species.
3. The relative amount of CuO and Cu_2O on the surface of the copper species determined by XPS, show that the Cu^{2+} species in the Cu/CeO_2 catalyst was reduced to Cu^{+} in the CWAO process.
4. EPR shows that, fresh catalyst, the copper (II) is present as a mixture of isolated Cu^{2+} ions and aggregates of Cu^{2+} ions. After reaction, the same species are presents, but the coordination environment change.
5. The ratio BOD_5/COD increased respect to initial solutions for the three studied compounds indicating improved biodegradability.

Acknowledgment

Thanks are given to the FONACYT (Project No. QF-10) and to PDVSA-INTEVEP (Project No. 2001-00139/2003-056) for financial help, which allowed us to carry out the research, reported here.

References

[1] V.S. Mishra, V.V. Mahajani and J.B. Joshi, Ind. Eng. Chem. Res. 34 (1995) 2.

[2] Y.I. Matatov-Meytal and M. Sheintuch, Ind. Eng. Chem. Res. 37 (1998) 309.

[3] A. Sadana and J.R. Katzer Ind. Eng. Chem. Fundam, 13 (1974) 127., J. Levec, Appl. Catal., 63 (1990) L1.

[4] H.R. Devlin and I.J. Harris, Ind. Eng. Chem. Fundam. 23 (1984) 387.

[5] L.R. Suntio, W.Y. Shiu and D. Mackay, Chemosphere 17 (1988) 53.

[6] K.-S. Lin and H.P. Wang, Appl. Catal B: Environ. 22 (1999) 261.

[7] A. Trovareli, C. de Leitenburg, G. Dolcetti, Chemtec, june (1997) 32.

[8] P. Fornasiero, G. Balducci, R.D. Monte, J. Kaspar, V. Sergo, G. Gubitosa, A. Ferrero and M. Graziani, J. Catal. 164 (1996) 173.

[9] L. Fan and K. Fujimoto, J. Catal. 172 (1997) 238.

[10] M. Pijolat, M. Prin and M. Soustelle, J. Chem. Soc., Faraday Trans. 91 (1995) 3941.

[11] A. Trovarelli, Catal. Rev.-Sci. Eng. 38 (1996) 439.

[12] S.H. Overbury, D.R. Huntley, D.R. Mullins and G.N. Glavee, Catal. Lett. 51 (1998) 133.

[13] Lj. Kundakovic and M. Flytzani-Stephanopoulos, J. Catal. 179 (1998) 203.

[14] W. Liu, A.F. Sarofim and M. Flytzani-Stephanopoulos, Chem. Eng. Sci. 49 (1994) 4871.

[15] M.-F. Luo, Y.-J. Zhong, X.-X. Yuan and X.-M. Zheng, Appl. Catal. A 162 (1997) 121.

[16] A. Martínez-Arias, J. Soria, R. Cataluña, J.C. Conesa and V. Cortés Corberán, Stud. Surf. Sci. Catal. 116 (1998) 591.

[17] A. Martínez-Arias, M. Fernández-García, J. Soria and J.C. Conesa, J. Catal. 182 (1999) 367.

[18] Standard Methods for the Examination of Water and Wastewater, 20th Edition.

[19] H.C. Yao and Y.F. Yao, J. Catal. 86 (1984) 254.

[20] G.S. Zafiris and R.J. Gorte, J. Catal. 139 (1993) 561.

[21] A. Trovarelli, G. Dolcetti, C. de Leitenburg, J. Kaspar, P. Finetti and A. Santoni, J. Chem. Soc. Faraday Trans. 88 (1992) 1311.

[22] S.J. Teichner, Appl. Catal. 62 (1990) 1.

[23] Y Sun and P.A. Sermon, J. Mater. Chem. 6 (1996) 1025.

[24] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz and H.S. Gandhi, J. Catal. 114 (1988) 23.

[25] M. Fernández-García, E. Gómez-Rebollo, A. Guerrero Ruiz, J.C. Conesa and J. Soria, J. Catal. 172 (1997) 146.

[26] J.Z. Shyu, W.H. Weber and H.S. Gandhi, J. Phys. Chem. 92 (1988) 4964.

[27] P.J. Schmitz, R.K. Usman, C.R. Peters, C.W. Graham and R.W. McCabe, Appl. Surf. Sci. 72 (1993) 181.

[28] C.H. Yoon, S.H. Cho, S.H. Kim and S.R. Ha, Water Sci. Technol. 43 (2001) 229.

[29] C. de Leitenburg, D. Goi, A. Primavera, A. Trovarelli and G. Dolcetti, Appl. Catal. B: Environ. 11 (1996) L29.

[30] D.J. Ileh and M.S. Islam, J. Chem. Soc., Faraday Trans. 89 (1993) 3833.

[31] D. Wolf, Catal. Lett. 27 (1994) 207.

[32] T. Miki, T. Ogawa, M. Haneda, N. Nakuta, A. Ueno, S. Tateishi, S. Matsuura and M. sato, J. Phys. Chem. 94 (1990) 644.

[33] G. Neri, A. Pistone, C. Milone and S. Galvagno, Appl. Catal. B: Environ. 38 (2002) 321.
[34] S. Imamura, I. Fukuda and S. Ishida, Ind. Chem. Res. 27 (1988) 718.
[35] A. Pintar and J. Levec, Ind. Eng. Chem. Res. 33 (1994) 3070.
[36] A. Pintar and J. Levec, J. Catal. 135 (1992) 345.
[37] S. Imamura, Y. Okumura, T. Nishio, K. Utani and Y. Matsumura, Ind. Eng. Chem. Res. 37 (1998) 1136.
[38] P.W. Park and J.S. Ledford, Catal. Lett. 50 (1998) 41.
[39] S. Hamoudi, F. Larachi, G. Cerrella and M. Casanello, Ind. Eng. Chem. Res. 37 (1998) 3531.
[40] J. Barbier, F. Delanoe, F. Jabonille, D. Duprez, G. Blauchard and P. Isnard, J. Catal. 177 (1998) 378.
[41] A. Trovarelli, *Catalysis by Ceria and Related Materials, Catalytic Science Series* 2(Imperial college Press, London, 2002).
[42] A. Santos, P. Yustos, A. Quintanilla, S. Rodríguez and F. García-Ochoa, Appl. Catal. B 39 (2002) 97.
[43] C. Sheck and F.H. Frimmel, Water Res. 29 (1995) 2346.