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Bimetallic catalysts for continuous catalytic wet air oxidation of phenol

A. Fortuny^a, C. Bengoa^b, J. Font^{b,*}, A. Fabregat^b

^a *Departament d'Enginyeria Química, E.U.P.V.G., Universitat Politècnica de Catalunya, Av. Víctor Balaguer, s/n, 08800 Vilanova i la Geltrú, Catalonia, Spain*

^b *Departament d'Enginyeria Química, E.T.S.E.Q., Universitat Rovira i Virgili, Carretera de Salou, s/n, 43006 Tarragona, Catalonia, Spain*

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Abstract

Catalytic wet oxidation has proved to be effective at eliminating hazardous organic compounds, such as phenol, from waste waters. However, the lack of active long-life oxidation catalysts which can perform in aqueous phase is its main drawback. This study explores the ability of bimetallic supported catalysts to oxidize aqueous phenol solutions using air as oxidant. Combinations of 2% of CoO, Fe₂O₃, MnO or ZnO with 10% CuO were supported on γ -alumina by pore filling, calcined and later tested. The oxidation was carried out in a packed bed reactor operating in trickle flow regime at 140°C and 900 kPa of oxygen partial pressure. Lifetime tests were conducted for 8 days. The pH of the feed solution was also varied. The results show that all the catalysts tested undergo severe deactivation during the first 2 days of operation. Later, the catalysts present steady activity until the end of the test. The highest residual phenol conversion was obtained for the ZnO–CuO, which was significantly higher than that obtained with the 10% CuO catalyst used as reference. The catalyst deactivation is related to the dissolution of the metal oxides from the catalyst surface due to the acidic reaction conditions. Generally, the performance of the catalysts was better when the pH of the feed solution was increased. © 1999 Elsevier Science B.V. All rights reserved.

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* Corresponding author. Tel.: +34-977-559646; fax: +34-977-559667; e-mail: jfont@etseq.urv.es

1. Introduction

Growing concern about the environment is making it necessary to develop techniques to treat waste waters containing compounds that are toxic to aquatic life. Phenol-contaminated waste waters are of particular interest because, aside from being toxic, phenol confers a particularly disagreeable taste and odor to water, even at concentrations below 0.001 mg/l. Phenols appear in the aqueous effluents from many industries, including petroleum refining and petrochemical manufacture. Moreover, phenol and its derivatives are powerful bactericides which prevents them from being treated in classical sewage processing plants even at concentrations as low as 50 mg/l [1]. Thus, phenolic aqueous effluents must be specifically treated before being biologically decontaminated.

Catalytic wet oxidation (CWO) of aqueous solutions of organics has largely demonstrated its effectiveness [2,3] when the organic concentration is too low to permit an economic recovery. This method converts the organics to carbon dioxide and water using oxygen or air as oxidizing agent, although the oxidation is rarely complete and many partial oxidation compounds may be produced. These oxidation intermediates are mostly less toxic than phenol or even nontoxic. The presence of a catalyst enables the process to be carried out at temperatures and pressures below 200°C and 10 MPa, which are much lower than operating conditions from uncatalyzed thermal processes. The key point of the oxidation in aqueous phase is, however, the catalyst. The lack of catalysts with the suitable chemical and mechanical properties for performing in the severe reaction conditions is the main drawback of CWO. Supported copper oxides [4–8] have been successfully investigated as catalysts for phenol oxidation. However, zinc and cobalt have also been included as second promoting metal for the oxidation of organics [8–13].

Although it has been shown that phenol oxidation occurs through a free-radical mechanism [4,5], there is still uncertainty about the actual role of the catalyst. It has been reported that the free-radical initiation takes place on the catalyst surface. However it is not well established if radical initiation occurs by dissociative adsorption of phenol or by hydroxide decomposition. Nonetheless, it has been postulated that the catalytic metal undergoes a redox cycle between two oxidation states. Thus, many inexpensive transition metals could be suitable oxidation catalysts. For instance, it has been reported that suspensions of manganese oxides effectively destroy the phenol in acidic aqueous solution [14]. Likewise, a combination of a soluble iron catalyst and hydrogen peroxide, i.e. the so-called Fenton reaction, has been used for years to oxidize many organic molecules [15]. Furthermore, many other metal oxides and mixtures of metal oxides, e.g. vanadium and rare metal oxides, have been examined for wet oxidation in both subcritical [2,3] or supercritical conditions [16].

This study deals with the effect of various metal oxide combinations on the catalytic oxidation of phenol in aqueous phase. The performance of four different bimetallic oxidation catalysts is compared with that of copper oxide supported over γ -alumina. Besides copper, the metals tested were cobalt, iron, manganese and zinc. The influence of the feed pH is also examined.

2. Experimental

2.1. Catalyst preparation

A set of proprietary catalysts with different combinations of active metals, i.e. Cu with either Co, Fe, Mn or Zn, were prepared by the pore-filling method. In this method, the support is impregnated with just the volume of salt solution needed to fill its pore volume. Two different techniques can be used if several species are to be supported: adding each species by successive impregnation, or co-impregnation. This latter technique was selected because it preferentially favors a homogeneous dispersion of the different metals added. The salt concentration of the impregnating solution is calculated to give the desired loading of metal oxides. γ -alumina (ALCOA CPN), received as 6-mm-diameter spheres, was selected as support because of its high surface area. The alumina was previously ground and sieved to take the fraction 20–50 mesh (0.7–0.3 mm). This fraction was washed to remove all fines and was then dried at 110°C overnight. Afterwards, the support was soaked, under proper vacuum conditions, with an acidic aqueous solution containing the appropriate concentration of salts until the liquid was essentially absorbed. The salts used in each case were respectively $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Merck ref. 2752), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka ref. 60833), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck ref. 3883), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka ref. 63547), and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka ref. 96482). Once impregnated, the alumina was successively dried at 110°C for 4 h and calcined at 400°C for 6 h in a glass packed bed reactor in a furnace. Both processes were conducted under an air flow rate of 400 ml/min in order to remove the nitrogen oxides formed during the calcination. The reference catalyst had a 10% CuO loading. The other catalysts were combinations of 2% of either CoO, Fe_2O_3 , MnO or ZnO with 10% of CuO. These catalysts are hereafter designated as, respectively, CuO, CuO–CoO, CuO– Fe_2O_3 , CuO–MnO and CuO–ZnO. Table 1 summarizes the physical properties of the catalysts as well as the alumina used as support. The characterization was carried out in a B.E.T. equipment (Micromeritics Model ASAP 2000).

2.2. Reaction set-up

The experimental equipment used to explore the catalytic performance on the wet oxidation of phenol is shown in Fig. 1. A pressurized 5-l glass tank contains the feed

Table 1
Physical characteristics of the support and catalysts

Name	Active metal (as oxide)	Surface area (m^2/g)	Average pore diameter (\AA)	Pore volume (cm^3/g)
Alcoa CPN	–	364	47	0.43
CuO	10% Cu	251	53	0.33
CuO–CoO	10% Cu/2% Co	252	53	0.33
CuO– Fe_2O_3	10% Cu/2% Fe	224	56	0.32
CuO–MnO	10% Cu/2% Mn	231	54	0.31
CuO–ZnO	10% Cu/2% Zn	218	60	0.33

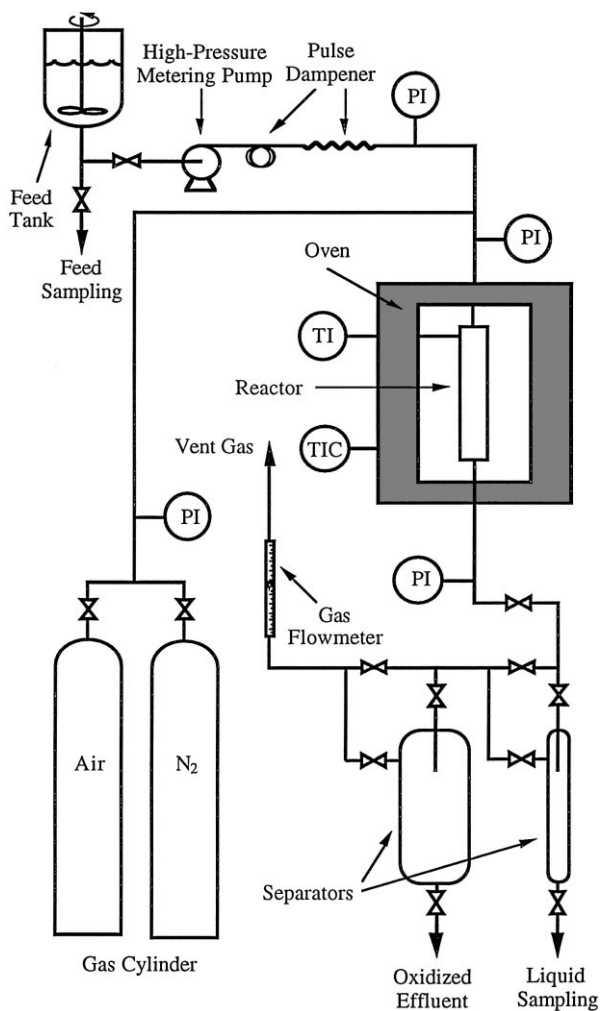


Fig. 1. Experimental set-up for catalytic wet oxidation of waste water.

solution which is vigorously stirred to prevent phenol concentration gradients in the tank. A high-pressure metering pump (Eldex AA-100-S2, Napa, CA, USA) is connected to this tank and feeds the reactor. This pump can perform at a flow rate from 10 to 150 ml/h. The packed bed reactor consists of a 20-cm-long and 1.1-cm-i.d. SS-316 tube filled with catalyst. A metal sintered disk placed at the bottom of the reactor prevents the catalyst from being drawn out. A thermocouple is axially inserted in the center of the reactor to measure the temperature inside the catalytic bed. Fig. 2 shows a detailed scheme of the reactor. This reactor is heated by an air convection oven with a temperature control device which allows working at almost isothermal conditions ($\pm 1^\circ\text{C}$). The air used as oxidizing agent comes from a high-pressure gas cylinder

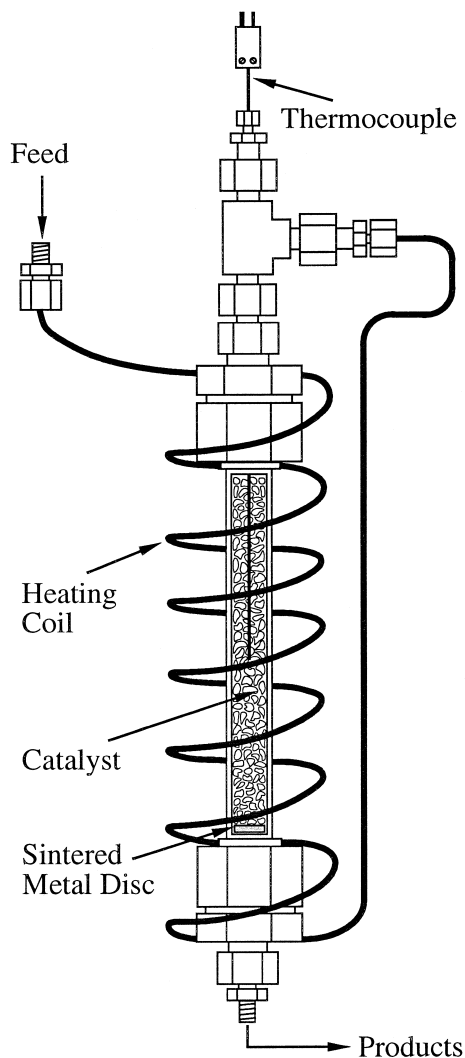


Fig. 2. Detail of the packed bed reactor.

provided with a pressure regulator that permits control of the operation pressure. The gaseous and liquid streams are mixed and driven to a heating coil placed in the oven where they are heated to the operating temperature before entering the reactor. Then, the mixture flows downwards through the reactor. The outlet products pass into two separators where the gaseous and liquid phases are separated. The smallest separator (2 ml) is also used as a liquid sampler whereas the largest (2 l) is used more for liquid product storage. The air flow rate is measured and controlled by means of a gas flowmeter coupled with a needle valve installed at the outlet to the second separator.

2.3. Reaction procedure

Feed solutions of phenol (5 g/l; analytical grade, Aldrich) were prepared using degassed deionized water from a Millipore system. The temperature was set at 140°C and the process was operated at an oxygen partial pressure of 900 kPa. The oxygen pressure was achieved by feeding high purity synthetic air at a total pressure of 4700 kPa which also includes the water vapor pressure at 140°C. The air flow rate was always fixed at 2.4 ml/s in STP conditions. In these conditions, there is a considerable excess of oxygen so oxygen pressure does not influence the reacting system. The space time was kept constant at 0.42 h, 2.4 h^{-1} of WHSV (weight hourly space velocity), in all the tests. Therefore, the liquid flow rate was adjusted for each test depending on the weight of the catalytic bed, which were different due to the slightly different apparent density of each catalyst prepared. As a result, the liquid flow rate oscillated between 32 and 35 ml/h. The above reaction conditions were selected according to data in previous works [8] in order to obtain phenol conversions around 50%, which permit a better comparison of the results. In these conditions, the operating regime of the reactor falls in the trickle flow zone [17], and this improves the mass transfer between the liquid and gaseous phases.

Eight-day (192 h) tests were conducted for each catalyst. Samples of the liquid product were periodically withdrawn in duplicate, usually every 6 h, and rapidly analyzed as described in Section 2.4. To verify that only the catalyst causes the oxidation of the phenol, two more tests were made using an inert material and the alumina used as support. In the test with the inert material, the reactor was filled with carborundum spheres of the same size as the catalysts (SiC, Carlo Erba, Milan, Italy). In both cases, the phenol removal was negligible, less than 1%, which falls within the experimental error.

The catalyst tests were conducted with the feed solution at two different pH's. Phenol is formally an acid that gives at the feed solution of 5 g/l a pH of 5.9. Thus, the first tests were carried out at this pH. In addition, to check the catalyst performance in basic conditions, a second catalyst screening was completed by adding sodium hydroxide to the feed solution until the pH was 10. The pH of the effluent was periodically examined by means of a pH meter (CRISON microph 2001).

2.4. Product analysis

The phenol concentration of the outlet liquid product was determined by HPLC (Beckman System Gold, San Ramon, CA, USA). Phenol separation was attained by a C_{18} reverse phase column (Spherisob ODS-2 5μ , 25×0.4 cm). The mobile phase consisted of a mixture of methanol (35%) and distilled water (65%) with a flow rate of 1 ml/min. Phenol was detected and measured by UV absorbance at a wavelength of 254 nm. The chromatograms obtained were monitored and recorded, and then the area of the phenol peak was determined. The phenol concentration was calculated by comparison with a calibration curve, which was periodically obtained using phenol sample solutions of known concentration. When analyzed, the copper concentration in the outlet samples was determined by atomic absorption (Hitachi Z-8200).

3. Results and discussion

The phenol conversion profiles obtained for the different catalysts at a feed pH of 5.9 are shown in Fig. 3. Phenol conversion, X_{Ph} , is defined as

$$X_{\text{Ph}} = \frac{[\text{Ph}]_{\text{in}} - [\text{Ph}]_{\text{out}}}{[\text{Ph}]_{\text{in}}} \times 100 \quad (1)$$

where $[\text{Ph}]_{\text{in}}$ and $[\text{Ph}]_{\text{out}}$ respectively denote the inlet and outlet reactor phenol concentration. The main trend common to all the catalysts is the severe deactivation observed during the first 24–48 h of operation. Thus, the phenol conversion during the first 6 h ranges from 80% for Cu–ZnO to 99% for CuO–MnO. It must be noted that the time required to saturate the catalytic bed in anoxic conditions was determined to be lower than 1 h since these catalysts do not show significant adsorption capacity. After 24 h, phenol conversion decreases to 50%, which is almost identical for all the catalysts. At this point, the CuO–ZnO activity begins to stabilize whereas the remaining catalysts continue to lose activity although the rate of deactivation is significantly lower. CuO–MnO and CuO–CoO show steady activity only after 96 h of operation. In turn, beyond 96 h, the activity of CuO and CuO–Fe₂O₃ still slowly decreases until the end of the test.

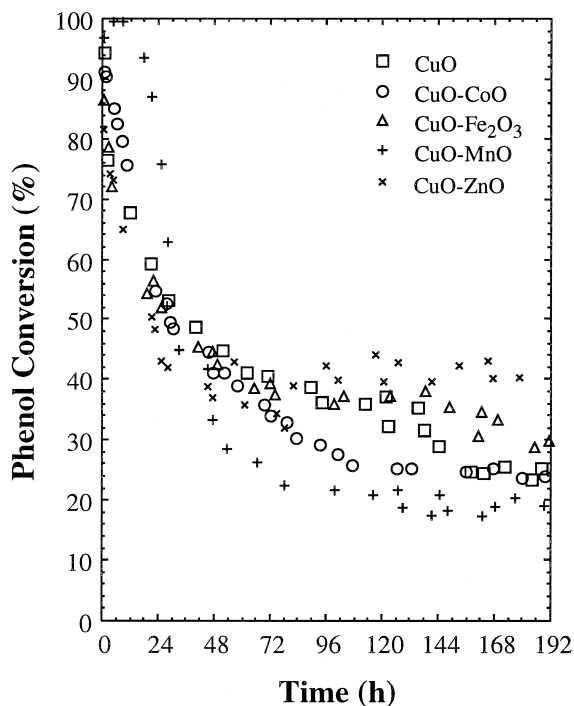


Fig. 3. Phenol conversion profiles for different bimetallic catalysts at a feed pH of 5.9.

The final residual phenol conversion found was 20% for CuO–MnO, about 25% for both CuO–CoO and CuO, close to 30% for CuO–Fe₂O₃, and about 40% for CuO–ZnO. It has already been reported that CuO–ZnO supported over γ -alumina performed better than a CuO catalyst or a copper–manganese–lanthanum catalyst in the aqueous oxidation of organics [18] although the very different sources and compositions of these catalysts make it very difficult to compare their respective performances. It should be noted that the initial behavior of CuO–MnO was notably different since its activity increased for the first 12 h until it reached its highest phenol conversion (over 99%). Later, this phenol conversion underwent a sudden drop. As noted above, this catalyst finally gives the lowest residual phenol conversion of the catalysts tested.

Catalyst deactivation has been related to the attack on the catalyst by the extremely hot acidic medium where the oxidation takes place. The acidic medium is provided by the phenol itself because it is capable of dissociating to form phenolate, however the partial oxidation products are the main cause of the total acidity of the aqueous reaction system. The intermediates in the phenol oxidation have been found to be mainly mono- and di-carboxylic acids such as oxalic, acetic or formic acid [19]. In particular, due to its refractory properties towards oxidation, acetic acid has often been identified as one of the most abundant end products in the phenol oxidation in liquid phase.

The direct correlation between catalyst activity and the reaction pH is illustrated in Fig. 4, which plots the pH of the aqueous stream at the outlet against the operation time.

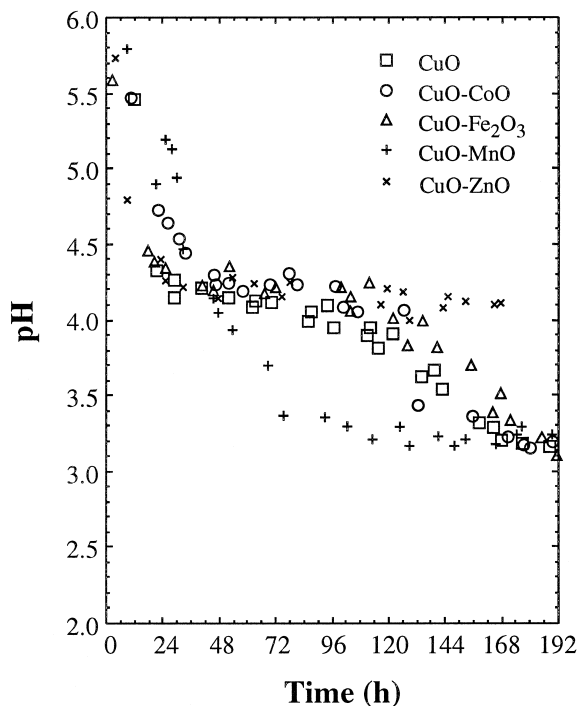


Fig. 4. Evolution of the effluent pH for different bimetallic catalysts at a feed pH of 5.9.

As mentioned above, the pH of the feed solution was 5.9 for all the catalysts. The pH profile behaves like phenol conversion, showing a rapid decrease during the first hours of operation. In most cases, the pH at the end of the run is about 3. Only when CuO–ZnO was used, was the final pH close to 4, which clearly agrees with the higher residual phenol conversion rendered by this catalyst. It should also be noted that the faster deactivation found in the case of CuO–MnO also correlates very well with its quick fall in the pH.

One possible reason for the catalyst deactivation could be the dissolution of the metal oxides in the acidic medium. In fact, some copper was detected in the reactor effluent as Fig. 5 illustrates for the CuO catalyst. However, the total loss of copper oxide throughout the test was calculated to be less than 2% of the initial CuO loading in the catalyst, which is not enough to explain the considerable decrease in catalytic activity. One can speculate about the existence of various copper species on the catalyst surface, the most active but least abundant being easily dissolved. The least active would remain in the catalyst and would be responsible for the residual phenol conversion obtained at the end of the tests. However, without intense investigation into this specific aspect, which is presently ongoing, the reason for this effect is entirely speculative.

The possibility that deposition of phenol condensation products on the catalyst surface causes the catalyst deactivation was rejected because no adsorbed organic compounds were detected in the used catalyst. After each test, the catalyst was washed,

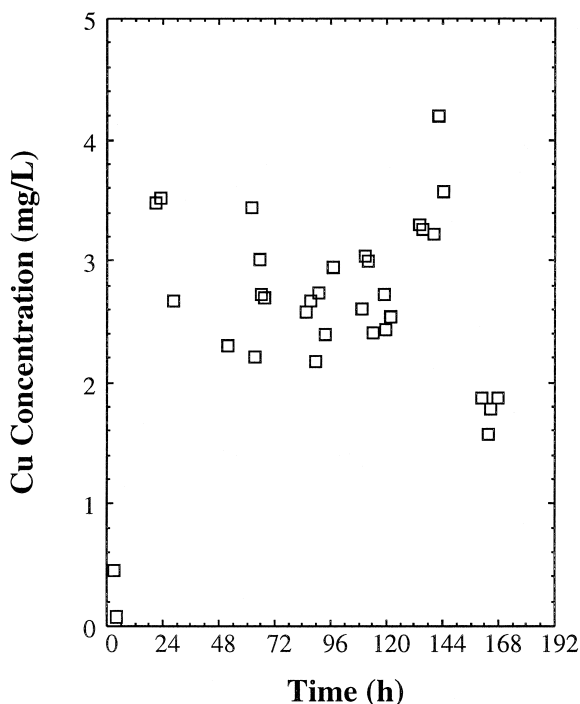


Fig. 5. Cu concentration in the effluent for the CuO catalyst at a feed pH of 5.9.

dried and weighed but only minor differences with respect to the initial catalyst weight were observed. In addition, temperature-programmed desorption tests were performed in air atmosphere for each catalyst. A mass spectrometer did not detect significant carbonaceous compounds so one can infer that no polymers exist in the catalyst surface. Unlike the batchwise experiments, formation of polymers has not been reported when phenol wet oxidation is conducted in a catalytic fixed bed operating in trickle regime [8]. This was due to the high catalyst to liquid ratio used in this kind of reactor.

It is well known that cuprous salts effectively catalyze the condensation of phenol compounds by oxidative coupling in homogeneous phase [20]. So, the copper dissolved during the tests could promote the homogeneous catalytic removal of phenol. To verify that only the supported CuO catalyst causes phenol oxidation, an experiment was conducted by feeding a phenol solution containing cuprous chloride with a concentration of 40 mg/l in copper, which is forty times greater than the concentration encountered in the outlet effluent for the CuO catalyst case. In this experiment the reactor was filled with inert carborundum (SiC) and the reaction was completed under the same temperature and oxygen partial pressure, i.e. 140°C and 900 kPa. The phenol conversion attained was a maximum 3% so homogeneous catalysis is not significant in comparison with heterogeneous catalysis.

In order to examine the influence of the pH on the ability to oxidize phenol, a new catalyst set was screened by feeding a phenol solution with a pH adjusted to 10 by adding sodium hydroxide. Fig. 6 plots the respective phenol conversion profiles from the

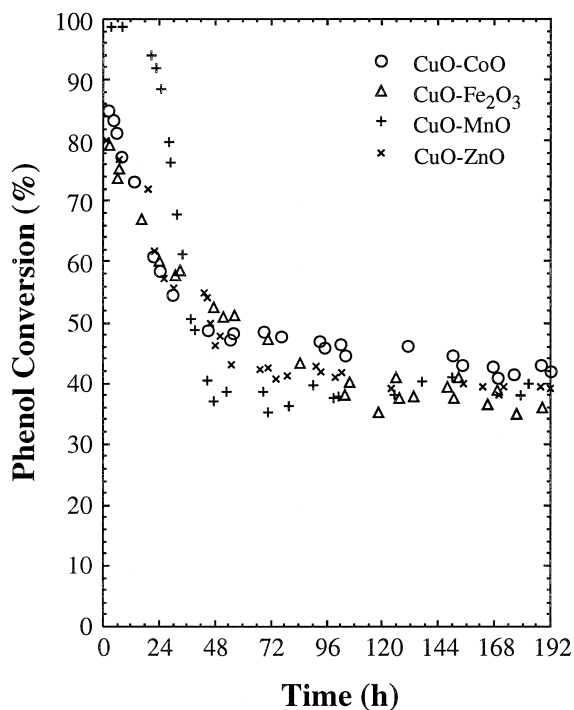


Fig. 6. Phenol conversion profiles for different bimetallic catalysts at a feed pH of 10.

lifetime tests and Fig. 7 shows the pH evolution of the outlet liquid product for each catalyst. In general terms, the trends at a feed pH of 5.9 are the same as at a pH of 10. Thus, there is a severe decrease in activity during the first 48 h, which means that a high pH does not completely prevent the catalysts from being deactivated. The outlet pH ranges from 7 to 8 for all the catalysts and is considerably more stable throughout the test.

The most significant difference in the catalytic behavior lies in the residual phenol conversion, which is mostly independent of the catalyst employed, within the experimental error. In this case, the final phenol conversion is around 40% for every catalyst. This suggests that the pH indeed affects the catalyst performance although it is not clear whether or not this involves a lower deactivation at high pH. At basic pH, a larger amount of phenolate in solution is expected due to a more extensive phenol dissociation. In addition, it has been proved that the phenolate ion is more reactive than undissociated phenol [21]. Thus, at pH 10, the rate of phenol disappearance could be enhanced by the predominance of phenol as phenolate rather than by the larger activity of the catalyst. The coupled action of both effects is difficult to discern and both factors probably account for the higher phenol conversions. At a feed pH of 10, the liquid oxidation product was a brown liquid in contrast with the clear liquid obtained at pH 5.9. This brown color was attributed to a higher production of quinones. Although not quantified,

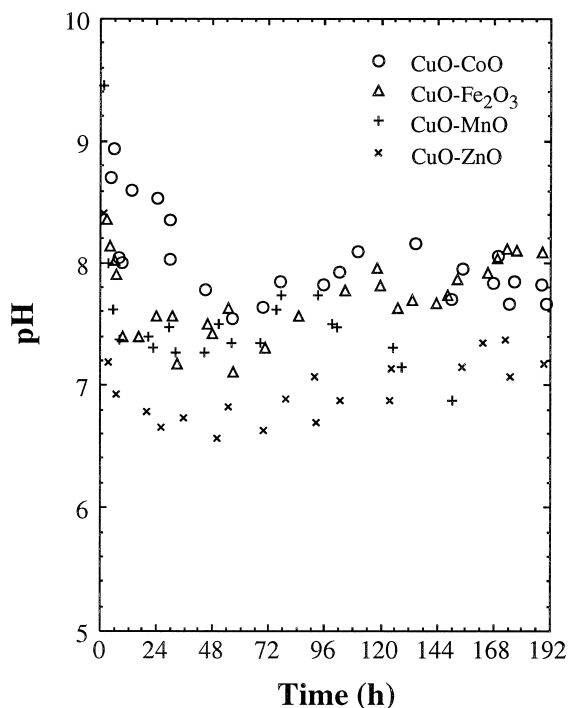


Fig. 7. Evolution of the effluent pH for different bimetallic catalysts at a feed pH of 10.

this aspect was confirmed in the analysis of the samples by liquid chromatography since the peaks corresponding to quinones were remarkably larger.

4. Conclusions

Catalytic wet air oxidation of phenol has been efficiently carried out in a packed bed reactor operating in trickle flow regime. A screening of proprietary bimetallic supported catalysts was completed in the oxidation of aqueous phenol at mild temperature (140°C), oxygen partial pressure (900 kPa), and space time (0.42 h) using air as oxidizing agent. A set of catalysts consisting of combinations of either cobalt, iron, manganese or zinc with copper supported on γ -alumina was successfully prepared by the pore filling method. The examination of their lifetime shows a severe deactivation during the first 48 h of operation following a zone of steady activity. The residual phenol conversion ranges from 20% for the CuO–MnO catalyst to 40% for the CuO–ZnO catalyst. The decrease in the rate of phenol disappearance is assumed to be due to the dissolution of the metal oxides from the catalyst surface since the presence of metal cations in the outlet reactor solution was detected. The loss of the catalyst surface metal oxides is believed to be caused by the hot acidic reaction environment. Adding sodium hydroxide to the feed solution until the pH was 10 does not completely prevent the catalysts from being deactivated. At a feed pH of 10, every catalyst renders a similar residual phenol conversion of about 40%.

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