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Effect of operation conditions on Catalytic Oxidation of Phenol in Aqueous Solution

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Abstract

This work was conducted to study the oxidation of phenol in aqueous solution using copper based catalyst with zinc as promoter and different carrier, i.e. γ-Alumina and silica. These catalysts were prepared by impregnation method.

The effect of catalyst composition, pH (5.6-9), phenol to catalyst concentration ratio (2-0.5), air feed rate (30-50) ml/s, stirring speed (400-800) rpm, and temperature (80-100) °C were examined in order to find the best conditions for phenol conversion.

The best operating conditions which lead to maximum phenol conversion (73.1%) are : 7.5 pH, 4/6 phenol to catalyst concentration, 40 ml/s air feed rate, 600 rpm stirring speed, and 100 °C reaction temperature. The reaction involved an induction period and a steady state activity regime. Both of the regimes exhibiting first order behavior with respect to the phenol concentration. The rate constants k1 and k2 for the initial rate and steady state activity regime are represented by k1=1.9×10-3 ((cm3liq/gcat) 0.5s-1 and k2= 2.4×10-10 ((cm3liq/gcat) 2 s-1) respectively.

Introduction

The petrochemical, chemical and pharmaceutical industries produce waste waters containing organics, such as phenols, which are extremely toxic to aquatic life. It is difficult to oxidize them biologically, since biological processes are very time –consuming and operate well only in the case of relatively dilute wastes. Chemical oxidation of phenolic wastes offers an alternative treatment method such as incineration (1, 2), ozonation (3, 4, 5), wet air oxidation (6, 7), photo catalyst oxidation (8,9), supercritical wet oxidation (10), aerobic coupling (11), and electrochemical oxidation (12,13). However, the sever operation conditions and the investment needed in the most cases have prevented them from being widely implemented.

In the last decades, catalytic wet oxidation (CWO) using air or pure oxygen has received great attention (14-23). CWO is capable of destroying the phenolic compounds mainly yielding water and carbon dioxide or harmless product.

Catalytic wet oxidation is emerging as an economically and ecologically promising technique to convert refractory organized compounds, such as phenol, into carbon dioxide or harmless intermediates, which can later be treated biologically. In addition, the process can be carried out in mild pressure and temperature conditions.

The purpose of this research was to study the oxidation of aqueous phenol at atmospheric pressure in detail, that is, to investigate the effects of catalyst composition, pH, phenol to catalyst concentration, air feed rate, stirring speed, temperature on phenol conversion.

Experimental Work

Catalyst preparation

CuO.Al2O3 catalyst with composition of 10 wt. % of CuO was prepared by impregnation method. The carrier (γ-Alumina) was calcined at 873 K with air for six hours then placed in a desicator before impregnation step. Evacuation is operated to remove the air from pores of the carrier. The impregnation solution is prepared by dissolving 19 g of copper nitrate in 50 ml of deionized water. The impregnation process was carried out under vacuum accompanied with shaking for an hour at fixed temperature of 343 K. The impregnated alumina is dried at 383 K over night and calcined at 673 K for eight hours. The same procedure was followed to prepare the other. Table 1,shows the chemical composition and calcined temperature of prepared catalysts.

Table 1 lists the composition of the prepared catalysts and their calcinations temperature.

Catalyst	Composition	Calcinations Temperature, °C
A	CuO.Al2O3	400
B	CuO. Silica gel.	400
C	CuO. ZnO. Al2O3	400
D	CuO. ZnO. Al2O3	500

Experimental procedure

The runs were made in a four-neck, 250 ml Pyrex round-bottom flask. The necks housed a sampling tube, a contact thermometer, a sparger for oxygen introduction and a condenser connected to a gas-washing bottle open to the atmosphere. The gas washing bottle contained NaOH solution of known concentration for the absorption of carbon dioxide (figure 1). The flask was heated with a heating mantle and stirred magnetically. Oxygen was sparged through a coil containing 18 holes, each 0.15 cm in diameter.

For a typical run, 250 ml of water and known weight of phenol and catalyst in powder form were loaded into the flask and heated to the desired temperature. The mixture was stirrer vigorously, slurrying the catalyst uniformly throughout the liquid. Cooling water was started and oxygen was spared into the flask. Representative samples were withdrawn periodically and the catalyst was separated from the aqueous phase by centrifugal forcing.

The samples prepared were analyzed with UV-spectrophotometer. A calibration curve was used to determine the unreacted phenol concentration in the reaction product in each run.

Kinetic Analysis of the Catalytic Oxidation of Phenol

In the Kinetic analysis of the reaction, the rate equations proposed by Sadana and Katzer (24) were tested. Equations 1 and 2 represent these equations for the initial rate and the rate in the steady state activity regime, respectively.

$$-\frac{V_1}{M_C}\frac{dC_{ph}}{dt} = k_1 \frac{C_{ph}}{(M_C/V_1)^{0.5}} \qquad (1)$$

$$-\frac{V_1}{M_C}\frac{dC_{ph}}{dt} = k_2 \frac{C_{ph}}{\left(M_C/V_1\right)^{3}} \qquad (2)$$

If these equations are written in terms of conversion and –ln(1-x) value are plotted versus time, the slop of the curve at x=0, t=0 gives k1 and the slope in the steady state activity regime gives k2.

Results and Discussion

Determination of the most Active Catalyst

Figure 2 presents a comparison of the activities of catalysts prepared. It can be seen that the catalyst composed of CuO.ZnO.Al2O3 (catalyst D) is the most active one. The catalyst can be ranked as follows in terms of activity in phenol oxidation:

Cat.D > Cat.C > Cat.A > Cat.B

The influence of the calcinations temperature on the catalyst activity is illustrated by figure 2, which compares the phenol conversion profiles for Cat.C and Cat.D, both with 10% of copper oxide and 2% of zinc oxide supported over γ-alumina. The catalysts were calcined at 400ºC and 500ºC receptively. Both catalysts behave similarity, so one can infer that the calcinations temperature does not have the significant effect on the catalyst activity except that the induction period of Cat.C is greater that Cat.D because of the “free oxide” caused by the calcinations temperature.

The evolution of the catalytic activity has been related to the presence of two different species of copper attached to the alumina surface. The first would be more active but also less stable in reaction condition. On the other hand, the second species would be more stable and responsible for the residual activity of the catalyst. A characterization of the catalysts (X-ray analysis) proved that these species are respectively “free” copper oxide and nonstochiometric copper aluminate. It is well-known that the most metal oxides, as copper oxide, dissolve in hot acidic media such as the one existing in the reactor. On the other hand, the treatment at high temperature, e.g. a calcinations temperature of 400°C and 500°C, of a mixture of copper and aluminum oxides forms copper aluminates that is more resistant to the acidic medium but is less catalytically active than the “free” copper oxide.

The loss in catalytic activity can be attributed to the leaching of copper from the catalyst during the process. This speculation is proved by figure 3 it should be noted that the total amount of Cu+2 that dissolves during the reaction time rapidly increases until giving the maximum Cu+2 concentration at (20,33,15, and 13) ppm for the catalyst A, B, C, D respectively. This behavior agrees with the presence of the two different species, the "free" copper oxide being easily dissolved during the first hours. When the pH is low, the catalysts show a fall in activity regardless the support, however after a variable period; the alumina-supported catalyst activity remains stable. In contrast, the silica- supported activity decreases sharply until the phenol conversion is negligible. These different trends are related to the presence of two active species in the alumina-supported catalyst, copper oxide and copper aluminates, whereas the silica-supported catalyst only has copper oxide.

Also for the phenol oxidation reaction it might be worthwhile to test the influence of promoter metal like Zn. This promoter changes the vulnerability of the copper oxide poisoning. Furthermore, it has been suggested that promoter also can protect the active metal against over–oxidation. Many researchers concluded that the presence of promoter caused that, lower sensitivity to poisoning and enhancement of the dehydrogenation activity.

Effect of Feed Solution pH

The previous results demonstrate the intrinsic relationship between the catalyst activity and the pH of the reactor solution. Therefore, cat. B (CuO. silica) was prepared using silica as support in order to find out whether or not a different support for the copper oxide could improve resistance against leaching. Run 1 in figure 4 shows the phenol conversion profile for cat. B feeding an unmodified phenol solution (pH=5.6). As can seen the catalyst shows very characteristic trends.

Cat. B has a short induction period in which the phenol conversion increases until it reaches a maximum conversion of about 41%. Then it losses its activity very fast after running for just 210 min the phenol conversion being very low and progressively approaching zero. This behavior could be explained by the existence of only "free" copper oxide linked to the silica, which is easily and continuously dissolved during the activity test. In this case, copper cannot form aluminates and all the copper loading is present as copper oxide.

In order to decrease the leaching of copper, various tests at higher pHs were conducted for cat. B and Cat.D. Figure 4 also displays the phenol conversion profiles for cat. B. At a feed pH of 7.5 (run2), the induction period almost greater giving an initial phenol conversion close to 55%. Then, the conversion begins to decrease, which indicates that this pH does not completely prevent the copper oxide from being dissolved. The reason for this behaviour is that, although the inlet pH is basic, the outlet pH (samples withdrawn) is still acid.

On the other hand, the induction period becomes greatest for run 3 in which the feed solution was fixed at pH = 9. It should be pointed out that this case has almost constant phenol conversion through out the first time. However, there is a significant difference between the conversions reached through out 120min. At pH = 9, the phenol conversion is nearly 50% while at pH = 7.5, the phenol conversion is higher. Thus, the higher the pH, the higher the remaining phenol conversion, so the inlet pH clearly affects the activity of the catalysts. This can be explained by the different rates of dissolution of the copper oxide in the aqueous solution. The solubility of any metal oxide is usually higher at low pH than at high pH. Hence, in run l, the rate of dissolution for the copper oxide should be the highest. A visual inspection through out the test certainly showed an intense decolouration of the catalyst due to the loss of copper. This decolouration was less important as the pH increased, which proves that a high pH prevents the leaching of copper.

Nonetheless, it is difficult to discern whether or not the remaining conversion is only due to the different rate of catalyst deactivation or there is also some change in the mechanism reaction. It has been shown that phenolate ion is much more reactive than phenol in basic media so the reaction occurs faster and gives a better phenol conversion. However, each of them shows similar reaction rates in acidic media because the phenolate concentration is very low.

The influence of the feed pH on the catalytic activity was also tested for Cat.D Figure 5 illustrates the dependence of the phenol conversion up on the pH using Cat.D as can be seen, behavior of this catalyst maintains the general trends given by cat. B, regardless of the pH, so two different activity curves are observed. In the first curve, the catalysts show high activity for a short period in which the phenol conversion nearly reach higher value, then after a progressive fall, the phenol conversions remains nearly constant and forms a second curve. The loss in catalytic activity can be delayed by increasing the pH but, in turn, the residual phenol conversion is lower at high basic solution. Thus, at pH of 5.6, the residual phenol conversion is slightly higher than 50% and increase to 60% at pH 9. As discussed above, the two curves can be explained because of the two different copper species over the alumina surface, both with different catalytic activity. The decrease in activity occurs when the most active copper oxide dissolves. Because of their characteristics, these oxides dissolve more slowly as pH increases so the first curve is longer in basic medium. However, the remaining conversion is also lower, which is opposite to what could be expected. A probable explanation for this lower conversion is that the basic medium interferes with the catalyst during the induction period, giving less active catalysts.

Effect of Phenol to Catalyst Concentration Ratio

Figure 6 shows the conversion of phenol versus time curves for different catalysts concentration. The highest phenol conversion was obtained with catalyst concentration of 6 g/l.

The influence of the catalyst amount on the rate of phenol oxidation and the selectivity to CO2 and H2O or harmless compound was studied at conditions with 2, 4, 6, 8 g/l of catalyst. It was found that the conversion of phenol increased as the amount of catalyst increased. However, the relationship between the conversion and the catalyst concentration does not appear to be linear as can see in figure 6. A low phenol conversion of 30% was obtained at steady state when 2 g/l of catalyst was used. This can be explained by an insufficient amount of catalyst used.

With 6 g/l of catalyst, phenol conversion of about 60% was obtained during the first 210 min of reaction time, however, after 210 min a gradual decline in conversion was noted. Similarly, using 8 g/l of catalyst, phenol conversion of 60% was obtained during the first 180 min of reaction time, however after 180 min, catalyst deactivation occurred. In addition to the formation of polymeric products, analysis of the brownish colored liquid showed increased formation of p-benzoquinone, maleic acids, and other low molecular weight acid.

This unusual dependence on catalyst loading can be explained by the phenomena of a heterogeneous-homogeneous reaction mechanism which was first proposed by Sadana and Katzer (1974). According to this mechanism, the reaction begins on the catalyst surface, and after the homogenous propagation step, the chain carriers are destroyed by a homogeneous or heterogeneous termination process depending on the catalyst concentration.

Effect of Air Feed Rate

Figure 7 shows the conversion of phenol versus time curves for different air feed rates. The highest phenol conversions were obtained with air feed rate of 40 ml/s.

It is evident that phenol removal increases with increasing amounts of bubbled air gas. the decrease in phenol conversion observed with an air feed rate of 50 ml/s , interface and shortened residence time of large air bubbles formed by the collapsing of fine bubbles at air rates greater than a critical value.

Also, it can be seen that when insufficient oxygen is fed, the reaction is dominated by the formation of low pH with low selectivity to CO2. At high air rate, both p-benzoquinone and maleic acid were detected in high concentration in the brownish coloured liquid. As the intensity of the brownish color in the reactor solution increased, insoluble compounds, attributed to polymeric products, are also formed in addition to the increase of the p-benzoquinone concentration. These results support the hypothesis that the extents of oxygen converge on the catalyst surface influences the selectivity of the reaction.

Effect of Stirring Speed

Figure 8 presents the variation of phenol conversion with time at different stirring speed in experiments of 6 hours. As the stirring speed increases from 400 rpm to 600 rpm, the conversion of phenol increases appreciably and the induction time decreases significantly.

The stirring speed was 600 rpm in all the runs in this study, ensuring vigorous mixing and uniformity throughout. Thus, increasing the liquid to particle mass transfer coefficient causes the absence of liquid to particle mass transfer resistance, also increasing in turbulence of mixing causes an increase in interfacial area of mass transfer. At 400 rpm, some parts of the catalyst particles remained at the bottom due to gravity causing significant decrease in phenol consumption.

Increasing the stirring speed to 800 rpm, increased the rate of break-up and hence decreasing the bubble size of dispersed phase, this can result in making the bubble rigid spheres. In this condition, there is no internal movement within the spheres, no new surfaces are produced and the oxidation rate is slow.

Effect of Temperature

Figure 9 presents the variation of phenol conversion with time at different temperatures viz (80, 90, and 100ºC). It was found that at temperatures of 90 and 80 ºC, phenol conversion were about 53% and 32% respectively. At lower temperatures the residual phenol concentration increased gradually, while a decline in the activity of the catalyst was observed, analysis of the liquid samples obtained at 80ºC, which was characterized by a brownish colour, showed increased formation of p-benzoquinone and maleic acid.

These observations indicate that a high temperature enhances the reaction and the activity of the catalyst. At high temperature the catalyst can handle higher oxygen and intermediate compound loads are employed deactivation by over–oxidation takes place. However, at high temperature the activity of the catalyst was enhanced.

Kinetic Analysis of the catalytic oxidation of phenol

In the kinetic analysis of the reaction, the rate constants k1 and k2 were calculated from the –ln(1-x) Vs. time curve. The rate constant k1 was determined from the initial rate equation at the point x=0 , t=0 by means of the differential method and k2 for the steady state activity regime was established from the slope of the -ln(1-x) Vs. time line drawn using the least square techniques of the steady state activity region data. The linearity of the experimental data in the steady state activity regime displays first order kinetics with respect to phenol concentration. The rate constants k1 and k2 given in figure 10 were found to be:

With phenol/catalyst ratio = 4/6

K1 = 1.9*10-3((cm3liq/gcat)0.5s-1)

K2 = 2.4*10-10((cm3liq/gcat)2s-1)

The difference in the result with other researchers (24) may arise from the reaction conditions and the type of conditions and the type of catalyst used.

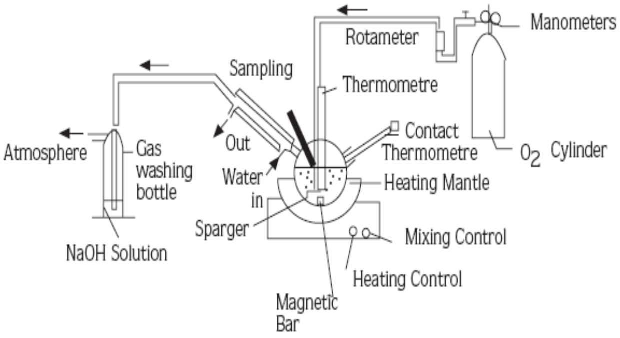

Fig. 1: Experimental setup

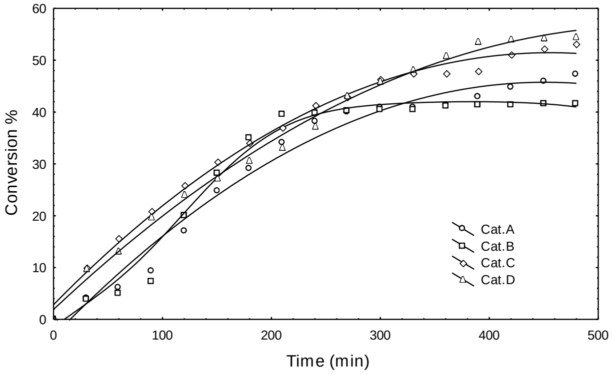

Fig. 2, Comparison of the Activities of the Catalyst
Reaction conditions: initial phenol concentration=4g/l, catalyst conc.=6g/l, air flowrate=30ml/s, stirring speed=600rpm, temperature=100ºC.

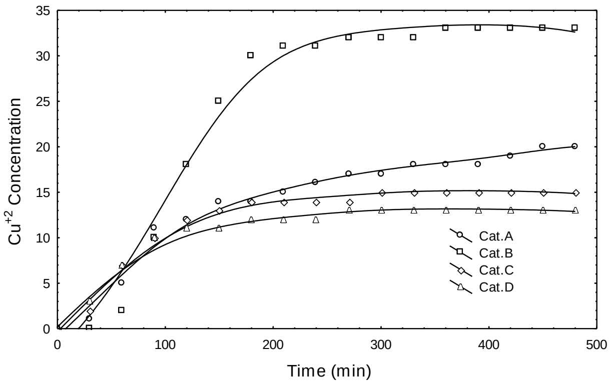

Fig. 3, Copper concentration profile of the reaction mixture
Reaction conditions: initial phenol concentration=4g/l, catalyst conc. =6g/l, air flowrate=30ml/s, stirring speed= 600rpm, temperature=100ºc

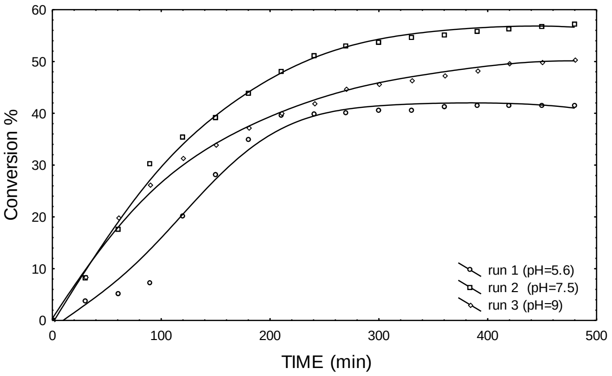

Fig. 4, Effect of the feed solution pH on Cat.B performance
Reaction conditions: Cat.B conc. =4 g/l, initial phenol concentration=4 g/l, air flowrate=30 ml/s, stirring speed=600 rpm, temperature=100ºC

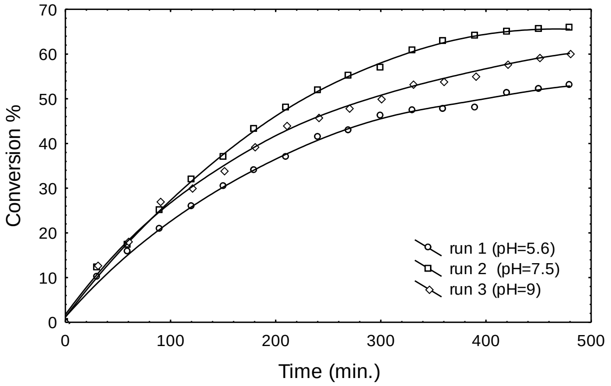

Fig. 5, Effect of the feed solution pH on Cat.D performance
Reaction conditions: Cat.D conc.=6 g/l, initial phenol concentration=4 g/l, air flowrate=30 ml/s, stirring speed=600 rpm, temperature=100ºC

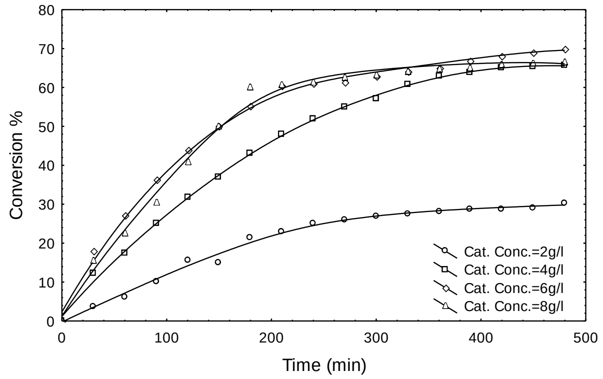

Fig. 6 Effect of catalyst concentration on phenol oxidation.
Reaction conditions: initial phenol concentration=4g/l, air flowrate=30 ml/s, stirring speed= 600 rpm, temperature=100ºC

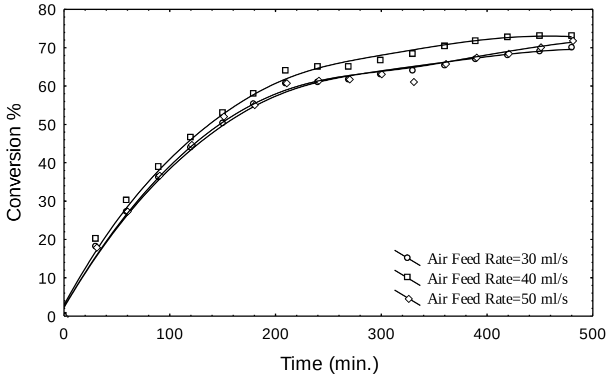

Fig. 7, Effect of Air Feed Rate on Phenol oxidation. Reaction conditions: phenol/catalyst concentration ratio=4/6 g/l, cat. Conc. =6g/l stirring speed= 600rpm, temperature=100ºC

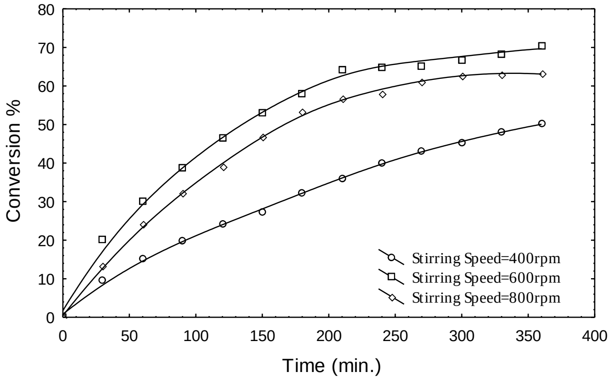

Fig.8 Effect of stirring speed on phenol oxidation. Reation conditions: phenol/catalyst concentration ratio=4/6 g/l, catalyst conc.=6g/l, air flowrate=30ml/s, temperature=100ºc.

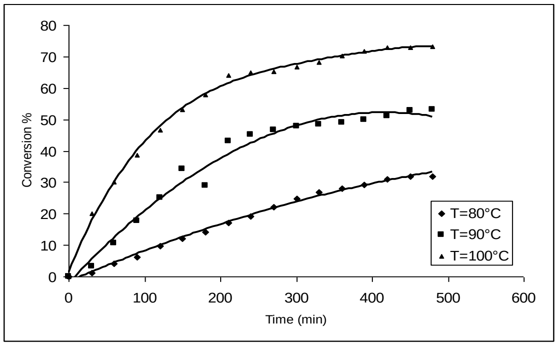

Fig. 9 Effect of temperature on phenol conversion

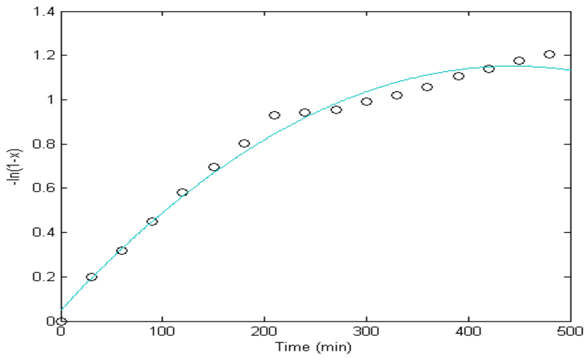

Fig. 10 –ln(1-x) versus time curve for phenol/catalyst ratio of 4/6

CONCLUSIONS

1- In this study, the oxidation of phenol in aqueous solution over a supported copper oxide, zinc oxide catalyst was investigated at atmospheric pressure. The oxidation rate of phenol was low due to the solubility of oxygen in these conditions. The reaction comprised an induction period and a steady state activity regime. The initial rate and steady state activity regime exhibited first order behavior with respect to phenol concentration. The rates show an unusual dependence on catalyst loading. The initial rate and the rate in the steady state activity regime, per unit mass of catalyst, decreased as the catalyst concentration increased. These observations support the conclusion that the reaction involves a heterogeneous-homogeneous free radical mechanism that is, as the catalyst concentration increases, the chain termination on the catalyst surface becomes significant.
2- The experiments showed that the length of the induction period decreased as the ratio of initial phenol concentration to catalyst concentration increased.

3- When the pH is low, the catalyst shows a fall in activity regardless the support, however, after variable period, the alumina-supported catalyst activity decreases sharply until the phenol conversion is negligible.
4- In alumina supported catalyst, two active spices present i.e. copper oxide and copper aluminate, whereas the silica supported catalyst only has copper oxide.
5- An increase in stirring speed, as expected increased conversion of phenol appreciably and decreased the induction time significantly.

Nomenclature

C_{ph}	Concentration of phenol	mol/cm^3
k_1	Rate constant for initial rate	(cm^3 of liquid/g of catalyst)$^{0.5}$ (s)$^{-1}$
k_2	Rate constant for steady state activity	(cm^3 of liquid/g of catalyst)^2 (s)$^{-1}$
M_C	Weight of catalyst	g
t	Time	s
V_1	Liquid phase volume	cm^3
x	Conversion of phenol	

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