

## Catalytic Wet Oxidation of Phenol on Supported Platinum Catalysts

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**Abstract:** Catalytic wet oxidation of phenol was performed at 2.3MPa on the platinum catalysts supported on alumina, activated carbon and titania. When compared with the uncatalyzed reaction, the use of catalysts could increase the rate of phenol oxidation greatly. The Pt/TiO<sub>2</sub> catalyst was preferable to the other catalysts for the destructive oxidation of phenol. Reaction pathways of catalytic wet oxidation was proposed on the basis of the results from the temperature-programmed oxidation. Phenol was shown to be oxidized via the following species: hydroquinone, catechol, benzoquinone, maleic acid, fumaric acid, glycolic acid, acetic acid, formic acid and oxalic acid

**Keywords:** Catalytic Wet Oxidation, Phenol, Platinum Catalysts, Leaching, Reaction Pathways

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### I. INTRODUCTION

The industrial wastewater generated from various industries contains huge amounts of toxic and refractory organic compounds. However, conventional treatment technologies like biological treatment are used for domestic as well as non-toxic industrial wastewater. The wastewater containing toxic and refractory compounds requires advanced oxidation processes (AOPs) like Fenton, wet air oxidation (WAO), ozonation (O<sub>3</sub>), hydrogen peroxide oxidation, photocatalysis, etc. The hydroxyl radicals generated by AOPs are highly reactive and capable to oxidize various organic compounds.

Wet air oxidation is a very attractive and useful technique for treatment of effluent streams exhibiting high organic loading (10–100 g/L of COD) which is too dilute for incineration and toxic for biological treatment (Kim and Ihm, 2011), but it has a detrimental shortcoming that it should be operated under severe conditions of high temperature (150–350 °C) and high pressure (6–17 MPa). The severity of the process can be lowered by using catalysts. Catalytic wet air oxidation (CWAO) is a catalytic oxidation of oxidizable compounds with air or pure oxygen in an aqueous phase.

Homogeneous catalysts are in general more effective than heterogeneous oxidation catalysts (Fu et al., 2015; Yadav and Garg, 2014; Arena et al., 2010; Velegriki et al., 2011), but their use necessitates a separation step such as precipitation or membrane separation to remove toxic catalyst ions from the final effluent. Heterogeneous catalysts have also been used. The noble metal catalysts have been used for the treatment of various pollutants such as phenol, substituted phenols, carboxylic acids by CWAO process (Espinosa de los Monteros et al., 2015; Yang et al., 2015; Cau et al., 2014; Suarez-Ojeda et al., 2005; Gaállová et al., 2010).

As an early researcher on CWAO, Imamura et al. (1982a, 1982b) developed several heterogeneous catalysts to improve the liquid phase oxidation and found that Co/Bi composite oxides were remarkably active for the oxidation of many low molecular weight carboxylic acids. Ru, Pt and Rh were also proved to be active than a homogeneous copper catalyst toward the wet oxidation of phenols and other model compounds (Imamura et al., 1988). Mixed copper, zinc and cobalt oxide catalysts were used for the catalytic oxidation of phenol and substituted phenols, and the CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was proved to be effective for oxidation (Pintar and Levec, 1992). Perkas et al. (2005) studied CWAO of succinic, acetic and p-coumaric acids to demonstrate the activity of platinum and ruthenium metals supported on TiO<sub>2</sub> and ZrO<sub>2</sub> supports and reported that the Pt/TiO<sub>2</sub> catalyst showed higher activity. Espinosa de los Monteros et al. (2015) studied the oxidation of phenol using platinum and ruthenium metals supported on TiO<sub>2</sub>-CeO<sub>2</sub>. They reported that platinum was more efficient than rhodium catalyst and suggested that the activity of noble metals varies with the nature of support as well as metal dispersion on the support. The selectivity of support toward phenols and byproducts formed during CWAO reaction also varies with varying operating conditions of temperature and pressure.

Most of the investigations into catalytic wet oxidation were focused on the complete destruction of organic compounds to produce water and carbon dioxide. Little is known about the reaction pathways and identification of the intermediates compounds produced.

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This research was undertaken to gain further understanding of catalytic wet oxidation of phenol, the model pollutant compound, and the identification of reaction intermediates together with the elucidation of reaction pathways was carried out.

## II. METHODS

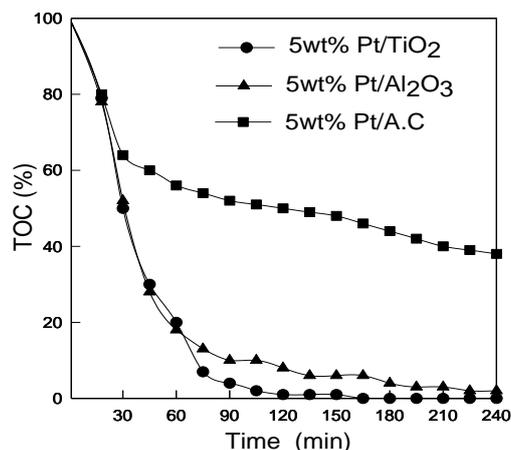
A stainless steel high pressure batch reactor was used for the catalytic wet oxidation of phenol. The operating pressure was kept at 2.3MPa. The concentration of phenol aqueous solution was 1,000mg/L. After heating up the aqueous solution to the desired temperature under nitrogen atmosphere at 1.7MPa, oxygen was fed continuously to the reactor at a partial pressure of 0.6MPa. The catalyst was introduced into the aqueous solution before the heating-up schedule.

Liquid samples were immediately filtered and then analyzed. Total organic carbon (TOC) was measured with a Shimadzu 5000A TOC analyzer whose operation is based on the combustion/non-dispersive infrared (NDIR) gas analysis. The TOC was determined by subtracting IC (Inorganic Carbon) from TC (Total Carbon). Reaction intermediates were identified by HPLC (Waters Associate) and Ion Chromatograph (Dionex 300). The detection was achieved with the UV detector and the products were analyzed with the Econosil C18 column using methanol/H<sub>2</sub>O/H<sub>3</sub>PO<sub>4</sub> (40/60/0.5) as a mobile phase.

Three different heterogeneous catalysts were used: Pt/A.C, Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/TiO<sub>2</sub>. The catalysts were prepared by impregnating H<sub>2</sub>PtCl<sub>6</sub> aqueous solutions onto the supports of activated carbon (Darco),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Strem Chemicals) and TiO<sub>2</sub> (Degussa P25), followed by calcination at 500°C for 24hrs.

## III. RESULTS AND DISCUSSION

Experiments were conducted with three different catalysts of Pt/A.C, Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pt/TiO<sub>2</sub>. Figure 1 shows the time dependence of TOC removal on the three different catalysts at 150°C. The Pt/TiO<sub>2</sub> catalyst seems to be the most effective for the oxidation of phenol, and the complete removal of phenol could be achieved after 150min of oxidation. The uncatalyzed oxidation of phenol was also carried out, but in all cases the TOC removal was negligible when compared with the catalytic reaction.



**Figure 1:** Time dependence of TOC removal on 5wt%Pt/TiO<sub>2</sub>, 5wt%Pt/Al<sub>2</sub>O<sub>3</sub> and 5wt%Pt/A.C at 150°C and 2.3MPa (1.5g catalyst)

Figure 2 shows the effects of the amount of the 5wt% Pt/TiO<sub>2</sub> catalyst introduced into the reactor on the removal of TOC. As the amount of the 5wt% Pt/TiO<sub>2</sub> catalysts is increased from 0.2 to 5.0g, the time needed for complete oxidation of phenol becomes shorter, and eventually most of the TOC is removed within 60min reaction with 5.0g catalyst.

The removal of TOC was also greatly affected by the oxidation temperature (Figure 3). The removal of TOC increases with increasing temperature. At 250°C a drastic TOC decrease is observed during the first 30min, implying that fast oxidation to CO<sub>2</sub> occurs. Through uncatalyzed oxidation TOC was not removed up to 150°C, and beyond that temperature 12% and 21% TOC were removed at 200°C and 250°C, respectively. When compared with the complete TOC removal through catalytic oxidation at those temperatures, the uncatalyzed reaction gives significantly lower oxidation rates. This indicates that the presence of the catalyst can lower greatly the severe wet air oxidation reaction conditions of high temperature and pressure as described before.

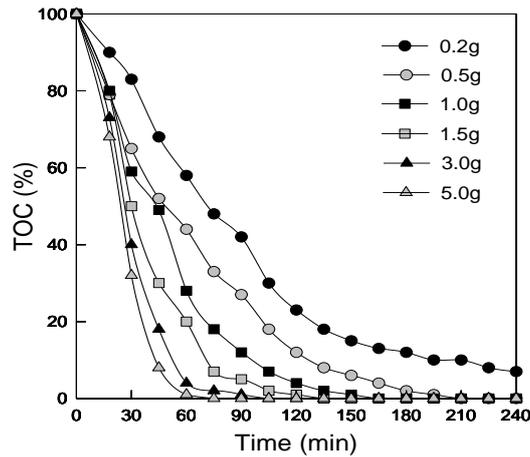


Figure 2: Effects of the amount of the 5wt%Pt/TiO<sub>2</sub> catalyst on TOC removal at 150 °C and 2.3MPa

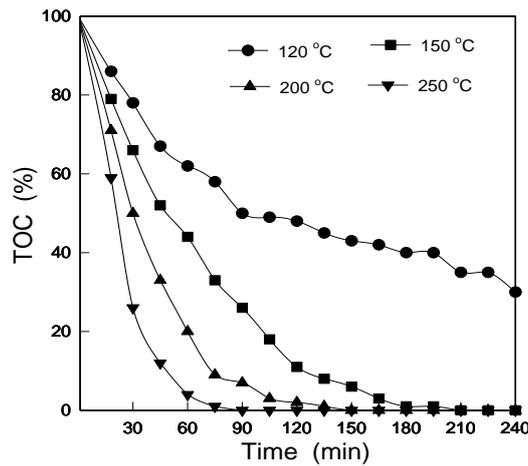


Figure 3: Effects of oxidation temperature on TOC removal with 0.5g 5wt%Pt/TiO<sub>2</sub> catalyst at 2.3MPa

As expected the reactivity changed greatly with the Pt loading in the Pt/TiO<sub>2</sub> catalyst. As shown in Figure 4 the TOC removal increases greatly with Pt loading.

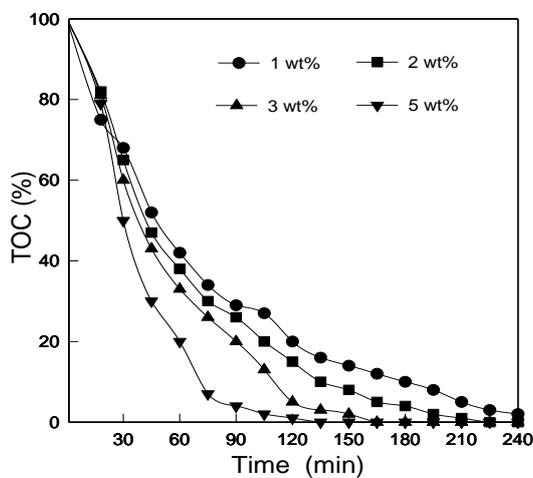
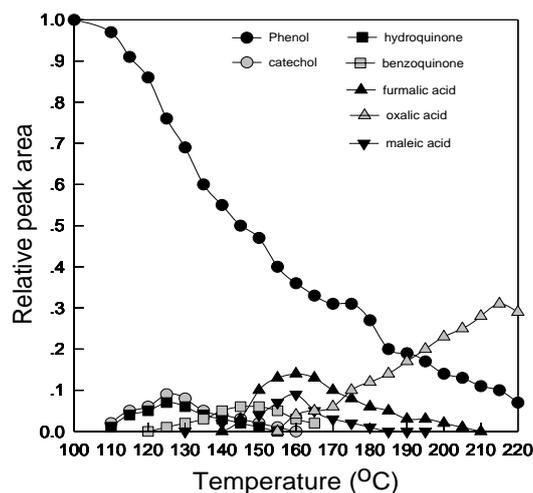


Figure 4: Effects of Pt loading in the 1.5g Pt/TiO<sub>2</sub> catalysts on TOC removal at 150 °C and 2.3MPa



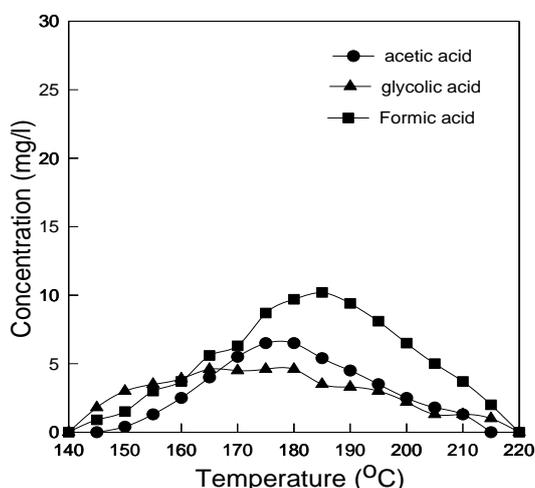
**Figure 5: Changes in product concentrations during temperature-programmed oxidation with 0.5g 5wt%Pt/TiO<sub>2</sub> catalyst (temperature increase rate: 1K/min)**

Another point to be emphasized from the aforementioned results is the changes in pH with reaction time. The pH rapidly dropped to around 2 probably due to the production of organic acids. Under these low values of pH, catalyst leaching may occur. The concept of catalyst leaching is important in wastewater treatment. Dissolved metal ions must be responsible for homogeneous catalytic reaction, and a homogeneous-heterogeneous reaction system should be considered rather than a pure heterogeneous reaction. Besides an additional processes such as membrane separation and precipitation may be needed to remove any leached catalyst compound from the effluent. Continuous leaching would lead to the progressive deactivation of the heterogeneous catalyst.

To investigate the stability of the Pt/TiO<sub>2</sub> catalyst with respect to metal leaching, samples were taken after the reaction at various temperatures. The catalyst loading and the concentration of dissolved Pt and Ti metals were analyzed using atomic absorption. No detectable amounts of the dissolved Pt and Ti metals were measured. Accordingly at the reaction conditions employed in this research it can be said that no leaching occurred.

Analysis of the reaction products was performed under temperature-programmed oxidation conditions to determine the sequence in which the reaction intermediates are formed. The rate of temperature increase during the temperature-programmed was controlled to be 1K/min, and the sample was taken at 10min intervals.

Figure 5 shows the changes in product concentrations taken during the temperature -programmed oxidation with 0.5g 5wt%Pt/TiO<sub>2</sub> catalyst. Since the separation of glycolic and formic acid was not successful in the HPLC, the concentration of both acids was analyzed with the Ion Chromatograph. The change in the concentration of glycolic acid and formic acid are plotted separately in Figure 6.

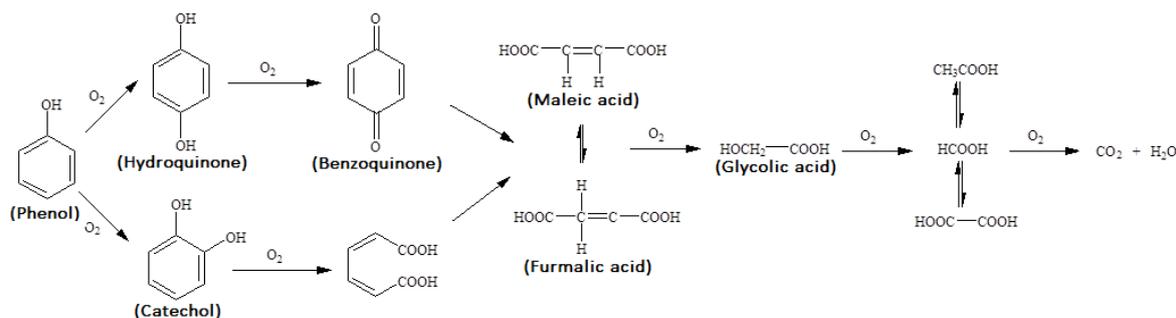


**Figure 6: Changes in acetic acid, glycolic acid and formic acid concentrations during temperature-programmed oxidation with 0.5g 5wt%Pt/TiO<sub>2</sub> catalyst (temperature increase rate : 1K/min)**

As the concentration of phenol gradually falls, many kinds of reaction intermediates appear depending on the temperature. A small amount of catechol and hydroquinone is observed in the temperature interval of roughly 110~150°C. At the temperature of the maximum catechol, hydroquinone and benzoquinone begin to appear and go through a maximum as the temperature is increased. Since the chemical structure of benzoquinone is somewhat similar to that of hydroquinone but not to that of catechol, benzoquinone is believed to be formed through the oxidation of hydroquinone.

The disappearance of benzoquinone is then followed by the formation of both the maleic acid and fumaric acid. Acetic acid and formic acid are found in somewhat wide temperature region, and oxalic acid concentration continues to grow up to 210°C and then decreases.

On the basis of the results in the plot of relative concentration as a function of temperature for each intermediate, the reaction pathways of the catalytic wet oxidation of phenol on the Pt/TiO<sub>2</sub> catalyst can be proposed as the sequential step in Figure 7.



**Figure 7: Proposed pathways for the catalytic wet oxidation of phenol on Pt/TiO<sub>2</sub> catalyst**

#### IV. CONCLUSIONS

The catalytic wet oxidation of phenol as the model pollutant compound was studied. The platinum catalysts supported on alumina, activated carbon and titania had been investigated with respect to their efficiency for oxidizing phenol.

The Pt/TiO<sub>2</sub> catalyst was preferable to the other catalysts for the destructive oxidation of phenol. The stability of the catalyst was monitored in terms of metal leaching, and it was found that the metal leaching was almost negligible under the operation conditions employed in this study. Reaction intermediates had been identified, and possible reaction pathways were proposed on the basis of the results from the temperature-programmed oxidation of phenol. Phenol was partially oxidized into both catechol and hydroquinone, the latter being converted further into benzoquinone. Ring cleavage was then followed to produce such low molecular weight organic acids as maleic acid and fumaric acid. Both acids were believed to be oxidized into CO<sub>2</sub> and H<sub>2</sub>O via glycolic acid, acetic acid, oxalic acid and formic acid.

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