

Photocatalytic Hydroxylation of Phenol to Catechol and Hydroquinone by Using Organic Pigment as Selective Photocatalyst

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Abstract: The application of photocatalytic reactions in organic synthesis has attracted extensive attentions because of recent developments in environmentally benign synthetic processes. For the first time, an organic pigment (C. I. Pigment Green 8) was used as selective photocatalyst to accomplish the photocatalytic hydroxylation of phenol to catechol (CAT) and hydroquinone (HQ) with the assistance of UV irradiation at room temperature. The prepared photocatalysts were characterized by FT-IR spectrum and UV-visible diffuse reflectance spectroscopy (UV-vis DRS), and the result found that the photocatalyst exhibits excellent adsorption ability both in the ultraviolet and visible light region. The effects of various affecting-parameters, such as catalyst amount, H₂O₂ amount, co-solvents and reaction time, on the photocatalytic hydroxylation of phenol were studied to optimize the reaction conditions. The desired products (CAT and HQ) on the photocatalyst can be facilitated with an increase in the selectivity. In this study, the conversion efficiency of phenol could reach high up to 87.8% with a total selectivity of 73.0% as well as the yield of 37.0% and 27.4% for CAT and HQ, respectively. The reaction is a photo-Fenton like process, and the iron ions cycle between Fe²⁺ and Fe³⁺ occurs with the light irradiation.

Keywords: Pigment photocatalyst, Selective photocatalysis, Hydroxylation, Phenol, Catechol, Hydroquinone.

1. INTRODUCTION

Hydroxylation of phenol to catechol (CAT) and hydroquinone (HQ) is an industrially demanding reaction, as the products widely used as photographical chemicals, antioxidants, polymerization inhibitors, pesticides, flavoring agent and medicine [1-2]. The traditional production of CAT and HQ requires a multistage process, a large amount of energy, and generates undesirable by-products. Thus, there have many attempts to direct hydroxylation of phenol to CAT and HQ by the thermal catalysis. And H₂O₂ as the oxidant becomes the most popular and cost-effective way to obtain CAT and HQ, due to its oxidant by-production is water [3-6]. The thermal catalysis reaction, however, generally demands a relatively high temperature and high concentration of H₂O₂ (60%) which would impose dangers to the operator [7-8]. So, it is highly desirable to develop a milder and more environmentally friendly method utilizing efficient catalysts to accomplish this reaction. Recently, there have been very broad interests in the photochemical transformations of organic compounds as a green and environmental friendly process [9-15], because the substrates can be photoactivated under mild reaction conditions. Since •OH can be generated on the UV-illuminated semiconductor photocatalyst surface, and thus the photocatalytic hydroxylation of aromatic compounds has been often attempted for synthetic purposes. Zhang *et al.* [13] investigated the photocatalytic hydroxylation of benzene to phenol over TiO₂ entrapped into hydrophobically modified siliceous foam, and the product selectivity can be enhanced by inhibiting the further conversion or degradation of phenol. Chen *et al.* [9] also reported that by taking advantage of the photocatalytic functions of Fe-g-

C₃N₄, the synthesis yield of the phenol can be markedly improved, and the conversion of benzene can be reached 11.9% under visible light irradiation. Shi *et al.* [16] also prepared silicate inorganic gel based photocatalyst Fe-Al-silicate as the photocatalyst for the organic synthesis of dihydroxybenzenes from phenol, and the phenol conversion efficiency could reach high up to 64.9%, and the yields of CAT and HQ can reach 39.3% and 22.3% respectively, with a high total selectivity of 95.0%. Thus, the photocatalytic hydroxylation of some organic compounds to desired industrially demanding products onto some certain efficient photocatalyst is an alternative method for other industrial processes.

Thus, in this paper, an organic pigment (C. I. Pigment Green 8, PG8) was attempted to use as an efficient photocatalyst for the photocatalytic hydroxylation reaction of phenol to CAT and HQ with high activity and selectivity, for the first time. Various affecting parameters were also optimized to find out the best reaction conditions for this desired reaction, and an attention mechanism for photocatalytic hydroxylation of phenol was also proposed to establish related fundamental study for a future clean industrial application.

2. EXPERIMENTAL

2.1. Materials and Reagents

Phenol, H₂O₂ (30%), acetonitrile, *t*-butyl alcohol, acetone, and alcohol were all analytical reagents and supplied by Kewei Chemical Reagents Company, China.

2.2. Preparation and Characterization of PG8 Catalyst

The synthesis of PG8 was prepared according to the previous reference [17-18], and the detail description of the preparation processes was shown in supporting information. FT-IR spectrum was characterized by NICOLET 380 (Thermo) using the KBr pellet technique, and the UV-vis diffuse reflectance spectrum (UV-vis

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DRS) was also performed with a Lambda 900 UV-vis spectrophotometer (Perkin-Elmer Co.).

2.3. Photocatalytic Hydroxylation of Phenol and Product Analysis

The photocatalytic hydroxylation of phenol by H_2O_2 was carried out in a photocatalytic reactor which consists of two parts: a 160 mL Pyrex glass bottle with an outer jacket and a 125 W high pressure Hg lamp (365 nm) placed parallel to the reactor as a light resource. All the experiments were conducted at ambient pressure and the reaction temperature was kept at $25 \pm 1^\circ C$ by the continuous circulation of water through the jacket around the reactor. The typical procedure was shown as follows: a suspension containing 0.05 g catalyst powder, 0.25 g phenol and 15.5 mL distilled water was prepared, and then 4 mL acetonitrile (*t*-butyl alcohol, acetone or alcohol) was added as co-solvent. After that, the suspension was stirred for about 20 min to ensure the well mixing, and finally 0.5 mL H_2O_2 was added into the suspension before the reaction. Prior to irradiation, the reaction suspension was stirred in dark for 20 min to establish an adsorption-desorption equilibrium. Then the solution was sampled after reaction at different intervals, and the phenol, CAT as well as HQ were analyzed with GC-FID (Agilent 6890N) with DB1701 chromatographic column and GC-MS (gas chromatography-mass spectrometry, Hiden HPR20-QIC)

The term of reaction performance was defined as follows:

$$\text{Conversion of phenol} = \frac{\text{mole of phenol reacted}}{\text{initial mole of phenol}} \times 100\%$$

$$\text{Yield of CAT} = \frac{\text{mole of CAT produced}}{\text{initial mole of phenol}} \times 100\%$$

$$\text{Yield of HQ} = \frac{\text{mole of HQ produced}}{\text{initial mole of phenol}} \times 100\%$$

$$\text{Selectivity} = \frac{\text{yield of CAT} + \text{yield of HQ}}{\text{conversion of phenol}} \times 100\%$$

3. RESULTS AND DISCUSSION

3.1. Photocatalytic Activity of Prepared PG8 Catalyst

Experiments of blank control (without catalyst) and dark control (without UV irradiation) were run first, and no CAT and HQ were detected (Table 1). It should be noted that, in the absence of UV irradiation and catalyst, phenol was not converted to CAT and HQ even adding excessive H_2O_2 . However, when the catalyst was added, both high yield and selectivity could be obtained under the UV irradiation, and the results showed that the prepared PG8 catalyst has excellent photocatalytic activity and good stability when the catalyst and UV light co-existed in this photocatalytic system. Within 4 h reaction, average 86.4% of phenol was transformed, and the yields of CAT and HQ were 35.8% and 25.4% respectively, meanwhile the selectivity is higher than 70.8%.

Fig. (1) shows the influence of the reaction time on the photocatalytic hydroxylation reaction of phenol. From the figure, it is observed that the phenol conversion efficiency increased gradually with the increase of the reaction time, meanwhile the accumulation of CAT and HQ was concomitant with the removal of phenol within the first 4 h. And the highest yields of CAT and HQ were achieved at 37.0% and 27.4%, respectively, while the selectivity

can be reached at 73.3%. However, the product yields and the selectivity for both CAT and HQ decreased gradually, while the phenol conversion efficiency increased steadily when the reaction time further extended. Thus the results indicate that exceeded reaction time is not beneficial to produce diphenols probably due to the increase of other byproducts and further oxidation degradation and mineralization in this system.

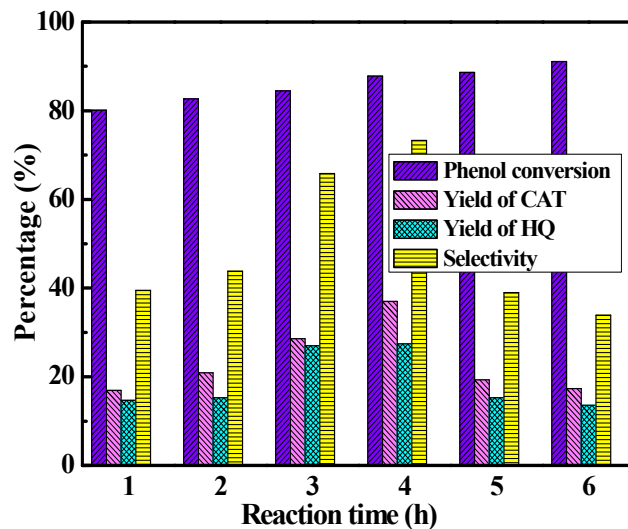


Fig. (1). Effect of the reaction time.

(phenol, 0.25g; H_2O , 15.5mL; catalyst, 0.05g; acetonitrile, 4.0mL; H_2O_2 , 0.5mL)

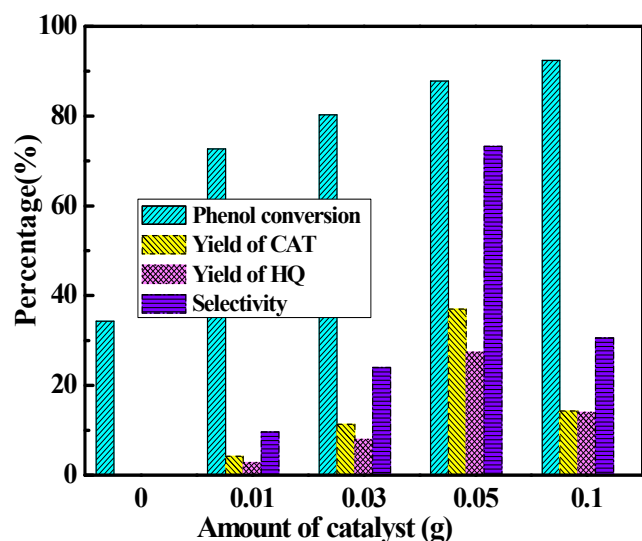
3.2. Effect of Catalyst Amount

The influence of the catalyst loading on the photocatalytic hydroxylation conversion efficiency of the phenol, the yields of CAT and HQ, as well as the selectivity of phenol is also investigated and the results are illustrated in Fig. (2). It is shown that almost no products were detected in the absence of the catalyst under the UV light irradiation, although the conversion efficiency of phenol reached about 34.3%. Surprisingly, when only 0.01 g of prepared catalyst was used, the conversion efficiency of phenol sharply increased from 34.3% to 72.7%, while the yield of diphenols increased to 4.2% for CAT and 2.8% for HQ, respectively, and the selectivity was obtained about 9.6%. Moreover, when the catalyst loading increased to 0.03 g, the conversion efficiency of phenol, the yields of CAT and HQ as well as the selectivity also continuously increased to 80.3%, 11.3%, 8.0% and 24.0%, respectively. Although the phenol conversion efficiency increased slightly to 87.8%, the highest yields of CAT and HQ as well as the selectivity were observed as 37.0%, 27.4% and 73.7% when 0.05 g of catalyst was added in the reaction suspension. However, further increasing the amount of catalyst, the yields of CAT and HQ as well as the selectivity sharply decreased to 14.3%, 14.0% and 30.6%, even though the phenol conversion efficiency continuously increased to 92.4%. Thus, the catalyst loading of 0.05 g was the optimum amount for photocatalytic hydroxylation of phenol in this case. The active catalytic sites may be considered to response to these phenomena, because the oxidation of the organic species adsorbed on the active sites of the catalyst may be associated with the delays for short reaction time, and the phenol was easy to be oxidized to other products [19].

Table 1. Hydroxylation of Phenol Under Different Condition ^a

Entry	Catalyst (g)	UV Irradiation	Phenol Conversion Efficiency (%)	Yield (%)		Selectivity (%)
				CAT	HQ	
1	No	Yes	34.3	N.D	N.D	-
2	0.05	No	9.0	N.D	N.D	-
3	0.05	Yes	86.4±1.6	35.8±1.3	25.4±3.2	70.8±3.6

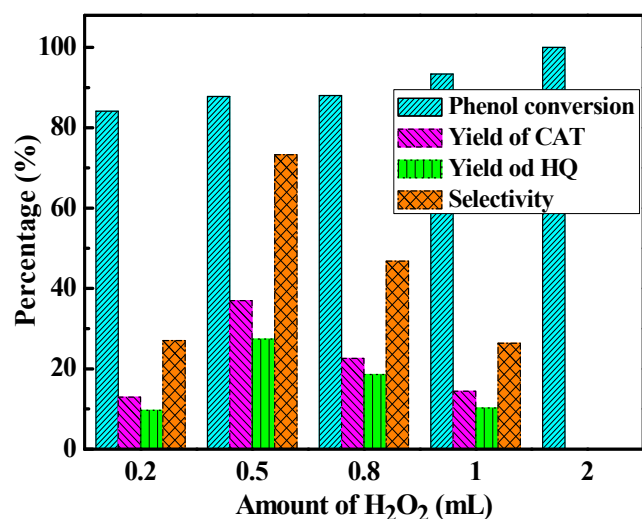
N.D: no detected;

^a The reaction conditions: phenol, 0.25g; water, 15.5mL; acetonitrile, 4.0mL; H₂O₂, 0.5mL; reaction time, 4.0h**Fig. (2).** Effect of catalyst amount.(phenol, 0.25g; H₂O, 15.5mL; acetonitrile, 4.0mL; H₂O₂, 0.5mL; UV time, 4.0h).

3.3. Effect of the Amount of H₂O₂

In the photocatalytic hydroxylation reaction of phenol, H₂O₂ is the main source of the active group of •OH, which can attack phenol to form the CAT and HQ [7]. The effect of H₂O₂ on the photocatalytic hydroxylation reaction of phenol is shown in Fig. (3). The increase of the addition amount of H₂O₂ from 0.2 to 2 mL can slightly increase the conversion efficiency of phenol, and 100% phenol conversion efficiency was accomplished when H₂O₂ amount was added up to 2 mL. In the case of the yields and selectivity, it was found that as the amount of H₂O₂ addition increased from 0.2 to 0.5 mL, the yields of CAT and HQ as well as the selectivity increased from 13.0%, 9.7% and 27.0% to 37.0%, 27.4% and 73.3%, respectively. However, further increasing the amount of H₂O₂ could lead to the decrease of the yields and selectivity. When the H₂O₂ addition was 0.8 mL, the yields of CAT and HQ as well as the selectivity were 22.6%, 18.6% and 46.8% which continuously decreased to 14.4%, 10.3% and 26.4% when the increase of the amount of H₂O₂ to 1.0 mL. And when the amount of H₂O₂ to 2.0 mL, the conversion efficiency can reach to 100%, but no diphenols was detected. All results mentioned above suggested that the higher content of H₂O₂ in the reaction suspension was beneficial for the phenol conversion efficiency but unfavorable for the yields of CAT and HQ, which would result in the lower selectivity. It is because H₂O₂ is so reactive and non-selective for the oxidative degradation and mineralization of phenol. So, it is very crucial to control the selective oxidation extent of phenol to produce CAT and HQ by changing the oxidant concentration. Therefore, controlling the H₂O₂

concentration and minimizing unwanted pathways such as oxidative degradation step is very important to achieve high selective hydroxylation of phenol [20].

**Fig. (3).** Effect of the amount of H₂O₂(phenol, 0.25g; H₂O, 15.5mL; catalyst, 0.05g; acetonitrile, 4mL; UV time, 4.0h).

3.4. Effect of co-solvents

In the present photocatalysis reaction system, water was used as a main solvent. Moreover, various other organic solvents such as acetonitrile, *t*-butyl alcohol, acetone, and alcohol were also employed as a co-solvent to investigate their effects on the photocatalytic hydroxylation of phenol, and the results were shown in Fig. (4). When no co-solvents added in reaction suspension, the conversion efficiency of phenol, the yields of CAT and HQ as well as the selectivity were 89%, 23.6%, 13.4% and 41.6%, respectively. However, when *t*-butyl alcohol, acetone and alcohol were used as co-solvent, only a trace amount of CAT and HQ was detected, although the phenol conversion efficiency can be reached at 67.4% and 78.7%, respectively. This may be because the *t*-butyl alcohol, acetone and alcohol can scavenge the •OH in the photocatalytic system [21-24], and the limited active group of •OH will not effectively attacks phenol to form the CAT and HQ. Therefore, adding *t*-butyl alcohol, acetone and alcohol into the reaction system can significantly decrease the phenol conversion efficiency, the yields of CAT and HQ as well as the selectivity.

Acetonitrile was another typical co-solvent in the hydroxylation reaction. When adding 4 mL acetonitrile as co-solvent in the reaction system, the conversion efficiency of phenol, the yields of CAT and HQ as well as the selectivity were 87.8%, 37.0%, 27.4% and 73.3%, respectively. Although the conversion efficiency was low

compared with no-solvent, the yields of CAT and HQ as well as the selectivity were increased obviously. The effect of acetonitrile on the photocatalytic hydroxylation conversion efficiency of phenol was shown in Fig. (6). It is observed that as the adding amount of acetonitrile increased from 2 to 4 mL, the conversion efficiency of phenol, the yields of CAT and HQ as well as the selectivity increased from 78.5%, 18.7%, 14.5% and 42.3% to 87.8%, 37%, 27.4% and 73.3%, respectively. However, further increasing the amount of acetonitrile could lead to the decrease of the yields and selectivity. When the adding amount of acetonitrile up to 10 mL, the conversion efficiency of phenol, the yields of CAT and HQ as well as the selectivity decreased to 52.8%, 2.9%, 1.8% and 8.9%, respectively. Therefore, 4 mL of co-solvent, acetonitrile, was used throughout the remained experiments of this work. The possible reasons were presented below. In the preliminary stage of the reaction, the addition trace of acetonitrile can compete with $\bullet\text{OH}$, it can decrease the concentration of $\bullet\text{OH}$, which can prevent the produce of by-product, thereby the selectivity can be increased subsequently. However, the selectivity of phenol decreased with further increasing the amount of acetonitrile, because in the high concentration of acetonitrile state, the hydrogen of hydroxyl radical interacts with the electronegative nitrogen of the acetonitrile to form a more stable transition state complex [25]. In addition, water molecule which is an essential precursor of hydroxyl radicals was significantly reduced and then led to the decrease of the production of $\bullet\text{OH}$ as well the OH adducts. Therefore, the selectivity of phenol in high concentration acetonitrile was lower than that of low concentration of acetonitrile. The relative results regarding the solvent effect of acetonitrile were in agreement with the previously obtained results both from Park's [11] and our group [16]. Moreover, it is reported that the addition of acetonitrile can effectively improve the photocatalytic hydroxylation of phenol with proper addition dosage because it can prevent the volatilization of phenol from water during the reaction [11].

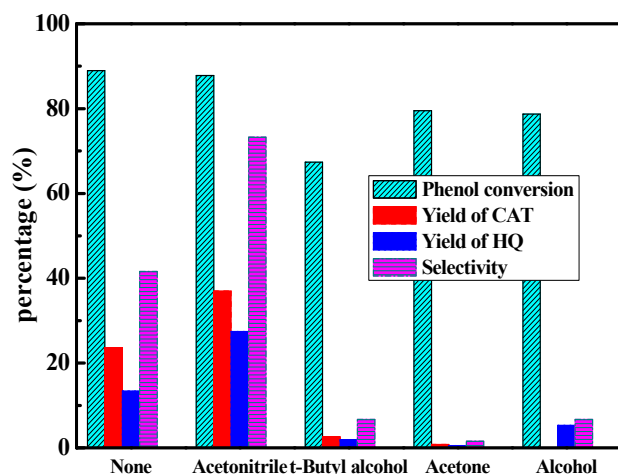


Fig. (4). Effect of various co-solvents (phenol, 0.25g; H_2O , 15.5mL; catalyst, 0.05g; H_2O_2 , 0.5mL; UV time, 4.0h; co-solvent, 4.0mL).

3.5. The Mechanism of Photocatalytic Hydroxylation

As described above, the synthesized PG8 catalyst can catalyze the photocatalytic hydroxylation of phenol to CAT and HQ in the

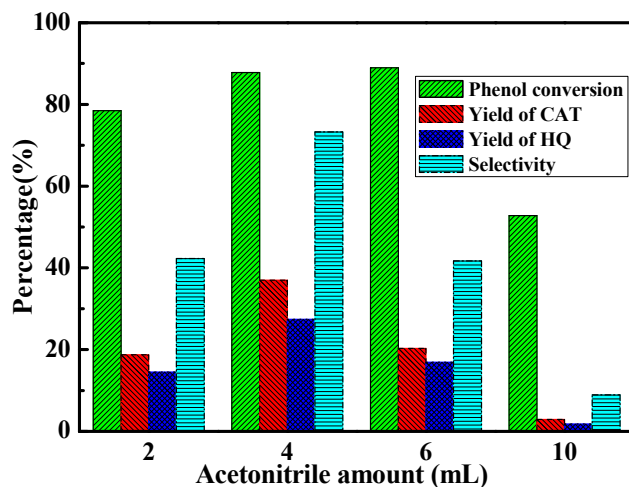
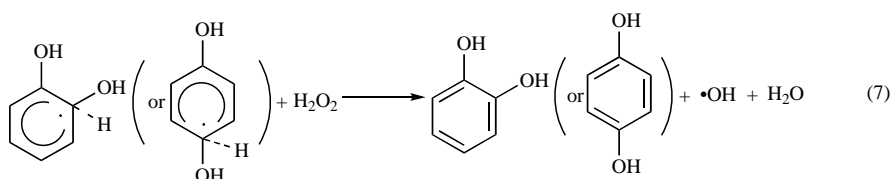
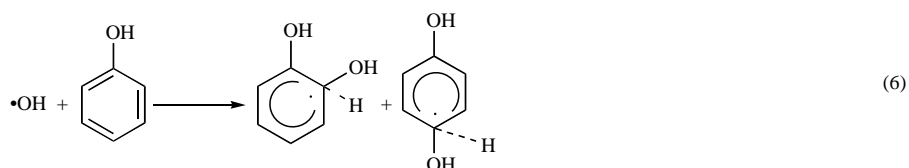
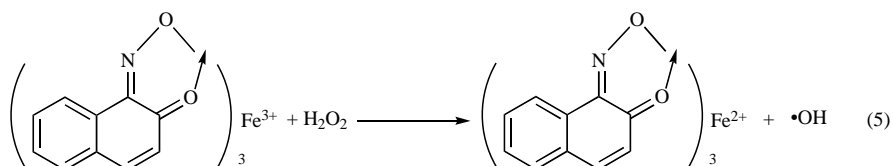
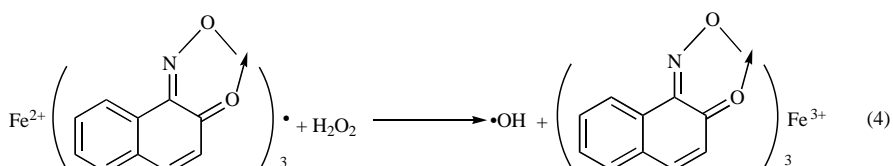
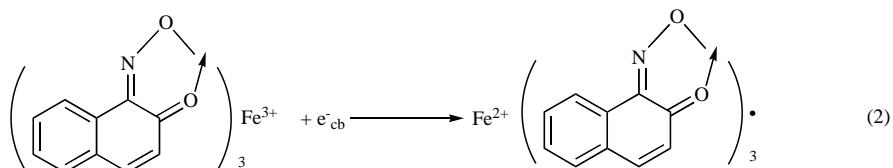
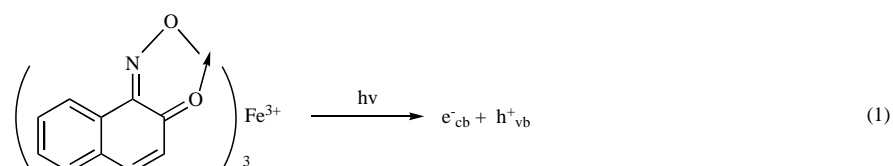


Fig. (5). Effect of the acetonitrile amount (phenol, 0.25g; H_2O , (19.5-V_{acetonitrile})mL; catalyst, 0.05g; H_2O_2 , 0.5mL; UV time, 4.0h).

presence of H_2O_2 with the assistance of UV irradiation, and the possible mechanism of the photocatalytic hydroxylation with high conversion efficiency and high selectivity was also attempted and illustrated in Scheme 1. In this system, PG8 catalyst exists mainly in the form of the aqua complex, the photogeneration electron-hole pairs was formed when the photocatalyst was irradiated with UV light (Eq. 1), and the excitation of PG8 can cause an intermolecular electron transfer from the ligand to Fe^{3+} , then Fe^{3+} can be reduced to Fe^{2+} (Eq. 2). Subsequently, the reduced Fe^{2+} complex immediately reacts with H_2O_2 to produce the powerful oxidant $\bullet\text{OH}$ (Eq. 4) [26]. The h^+ reacts with H_2O also to produce $\bullet\text{OH}$ (Eq.3), and phenol was directly converted into OH adducts, CAT and HQ by adding onto the benzene ring with $\bullet\text{OH}$ (Eq. 5 and 6). That is the photo-Fenton process, which consists of a combination of the Fenton reagents ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and light energy, and iron cycles between Fe^{2+} and Fe^{3+} are enhanced by the light irradiation. In other words, Fe^{3+} ions are constantly reduced to Fe^{2+} ions under irradiation and the Fenton reaction is improved by the participation of the photogenerated Fe^{2+} , then $\bullet\text{OH}$ generated in the reactions (Eq. 3, 4 and 5) can react with target phenol to produce the desired products [27-28]. According to the proposed mechanism, the selective hydroxylation phenol in presence of PG8 catalyst under irradiation with UV light can be well explained without involving in high-valence iron-oxo or iron-peroxo complexes [29].

4. CONCLUSION

The photocatalytic hydroxylation of phenol in the liquid phase was investigated under various conditions with a new prepared organic PG8 as a photocatalyst. The experiments demonstrate that the PG8 photocatalyst has a high activity for the selective photocatalytic conversion of phenol to CAT and HQ under mild conditions. And the product selectivity could be enhanced by inhibiting the further conversion (or oxidative degradation) of phenol. The high activity of PG8 photocatalyst is due to the efficient transfer of e^- from the inner of the pigment to the surface Fe^{3+} , and leads to a quick charge separation between e^- and h^+ as well as promotes the efficient phenol hydroxylation on the catalyst surface. The basic concept on the selective photocatalytic hydroxylation of phenol presented here, may contribute to the development of photocatalytic



Scheme 1. photocatalytic mechanism reaction equations of phenol hydroxylation.

systems for industrial application in green and selective synthesis of some desired fine chemicals.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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