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Effects of Pt and Ag on the photocatalytic degradation of 4-chlorophenol and its by-products

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Abstract

Photocatalytic degradation of 4-chlorophenol (4-CP) was studied using TiO_2, Pt/TiO_2, Ag/TiO_2 prepared by the sol–gel methods and Degussa P25 as photocatalysts. The influence of dissolved oxygen on the reaction rate and amounts of intermediate products were determined. In the experiments, a photocatalyst was suspended in the 4-CP solution, which was then irradiated with an 11 W low pressure mercury lamp emitting UV light in 200–280 nm window. The results show that, with TiO_2 (sol–gel), the decrease of 4-CP concentration was much faster than that with Degussa P25. In contrast, the reduction rate of total organic carbon (TOC) with Degussa P25 was much higher than that with TiO_2 (sol–gel). The addition of a small amount of either Pt or Ag into TiO_2 (sol–gel) improved the catalyst activity significantly, the highest activity being obtained with 1.0% Pt/TiO_2 and 0.5% Ag/TiO_2. 0.5% Ag/TiO_2 showed the highest activity in terms of both 4-CP and TOC removals. Hydroquinone (HQ) and hydroxyhydroquinone were identified experimentally as the main intermediate products in the presence of dissolved oxygen. The availability of dissolved oxygen played a significant role in enhancing the photocatalytic degradation of 4-CP for all the catalysts.

Keywords: Total organic carbon; Photocatalysts; Hydroquinone

1. Introduction

4-Chlorophenol (4-CP), known as a toxic and non-biodegradable organic compound, is widely used for the production of dyes, drugs, and fungicide [1]. As a result, 4-CP is present in the wastewater of plants. The removal of this compound from wastewaters is currently performed by conventional treatment methods, such as biological treatment, chlorination and adsorption. However, the biological process usually requires a considerably long treatment time to break down organic pollutants leading to an unacceptable level of 4-CP in the final effluent. Chlorination poses another problem since it often generates carcinogenic by-products. Granular activated carbon adsorption is another commercialized process but the spent carbon needs to be disposed [2].

Photocatalytic oxidation has been accepted as a promising alternative to the conventional methods because, with suitable catalysts, most pollutants can be completely mineralized to carbon dioxide in the presence of UV or near-UV illumination. Moreover, this technique does not utilize any additional chemicals and can be operated at room temperature [3]. The photocatalytic process starts with illumination of a photocatalyst that is normally a semiconductor, with light of an appropriate wavelength. Interaction of the catalyst, with photons, produces electrons and holes that easily migrate to the catalyst surface and initiate the redox reaction. Although a wide range of catalysts has been tested, titania (TiO_2) seems to be the most widely used catalyst because it is stable in most working conditions, corrosion resistant, and relatively inexpensive [4].

It was reported that 4-CP was completely degraded in the presence of TiO_2 and Pt/TiO_2 but the total organic carbon (TOC) still remained at a high level [5]. This was because 4-CP was transformed to other intermediate products rather than carbon dioxide.

In this work, we report the results of our investigation of the formation of the intermediate products of photocatalytic degradation of 4-CP using TiO_2, Pt/TiO_2 and Ag/TiO_2. Ag/TiO_2 was employed to investigate the possibility of improving the activity of TiO_2 for the decomposition of

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4-CP. The effect of the Ag content on the decomposition of 4-CP along with the types and amounts of the intermediate products generated during the reaction and the effect of dissolved oxygen were also investigated.

2. Experimental

2.1. Catalyst preparation

Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6(H_2O)$) obtained from Aldrich, silver nitrate ($AgNO_3$) and tetraethylorthotitanate ($(C_2H_5O)_4Ti$) or TEOT supplied by Fluka, were used as precursors for platinum, silver and titania (TiO_2), respectively. Thirty-seven percent hydrochloric acid (HCl), 99.7% ethanol both from BDH, 65% nitric acid (HNO_3) from Lab-Scan and deionized water were used to prepare the premixed solution for TiO_2 synthesis. The activities of the photocatalysts prepared by the sol–gel methods were compared with commercially available titania (P25) obtained from Degussa Corporation.

The pure TiO_2 used in this experiment was prepared by two different methods. TiO_2 (sol–gel-1) was prepared by using the same method as described by Jung and Park [6]. TEOT was added into a premixed solution, which contained water, hydrochloric acid and ethanol at room temperature with vigorous stirring. White precipitates of hydrous oxides were produced instantly and the mixture was stirred for 24 h. The solution was heated at 75–80 °C for 5 h in a rotary evaporator to remove alcohol. After the ethanol evaporation, the solution was dried in an oven at 100 °C for 24 h followed by a 5 h calcination at 400 °C to obtain TiO_2 (sol–gel-1).

TiO_2 (sol–gel-2) was prepared by using the same method as described by Anderson and Bard [7]. TEOT was dissolved in ethanol and then nitric acid was added dropwise to the prepared solution at room temperature. Water was added drowise to the prepared solution with vigorous stirring. The gelation was allowed to proceed slowly and was complete within 1 h. The mixture was allowed to age at room temperature in a covered beaker for 10 h. The gel was dried at 100 °C for 5 h to obtain a glassy material and then calcined at 400 °C. The mole ratios of alkoxide to water, acid and alcohol of both methods are summarized in Table 1.

For the Pt/TiO_2 and Ag/TiO_2 preparation, the calculated amount of hexachloroplatinic acid or silver nitrate was dissolved in the premixed solution. Then, Pt/TiO_2 and Ag/TiO_2 were prepared by the same method as TiO_2 (sol–gel-1).

Table 1
Preparation conditions of TiO_2 prepared by two sol–gel methods

Catalyst	Mole ratio				
	TEOT	Ethanol	Water	HCl	HNO_3
TiO_2 (sol–gel-1)	1	1	100	0.2	–
TiO_2 (sol–gel-2)	1	52	13	–	0.8

2.2. Catalyst characterizations

The phase analysis of TiO_2 was carried out by an X-ray diffractometer (Rigaku D/max-2200) at room temperature. X-ray diffraction patterns of all TiO_2 particles were obtained by using a Phillips PW 1830/00 No. SY 1241 diffractometer equipped with a graphite monochromator and a Cu tube for generating a Cu Kα radiation (wavelength 1.5406 Å). The particles were spread on a glass slide specimen holder and the scattered intensity was measured between 5 and 90° at a scanning rate of $2\theta = 1.5°$/min with 0.02° increments. Cu Kα radiation of the X-ray source at $\lambda = 0.154$ nm was operated at 40 kV, 30 mA, and 1.20 kW. The digital output of the proportional X-ray detector and the gonimeter angle measurements were sent to an online microcomputer for storing and analysis. Peak positions were compared with the standard files to identify crystalline phases. X-ray diffraction patterns were used for the crystallite size (d) estimation by line broadening measurements in the Debye–Scherrer equation.

BET surface areas of all prepared TiO_2 particles were obtained by using a surface area analyzer (Autosorb I, Quanta Chrom). The TiO_2 powder was first outgassed to remove the humidity and volatile adsorbents adsorbed on its surface under vacuum at 300 °C for 3 h before starting the analysis to determine the surface area. Autosorb ANYGASl, Version 2.10 was used to analyze the results.

2.3. Photocatalytic reaction experiment

Ninety-eight percent purity of 4-chlorophenol (C_6H_5OCl) or 4-CP obtained from BDH was used as a model pollutant in this study. Benzoquinone (BQ) obtained from Fluka, hydroquinone (HQ) from Ajax and hydroxybenzoquinone (HHQ) from Aldrich were used for the analysis of intermediate products. HPLC grade of acetonitrile (CH_3CN) purchased from Lab-Scan was used as mobile phase for the HPLC analysis, and 99.8% high purity of oxygen and nitrogen were obtained from Thai Industrial Gases Public, Co. Ltd.

A 1000 ml reagent bottle was used as a batch reactor for the study. The UV light source was an 11 W low-pressure mercury lamp (Philips) with a wavelength in the range of 200–280 nm. The UV lamp was dipped into the reactor in order to illuminate throughout the solution. A thermostat bath and a magnetic stirrer were used to control the solution temperature and provide continuous mixing during the experiment. The reactor was covered by an opaque PVC box to prevent the evaporation and for UV protection.

For the irradiation experiments, 450 ml of a solution containing 0.5 mM 4-CP and 0.5 g/l catalyst were added into the reactor. Before the irradiation, the solution was stirred for 1 h to allow the system to reach adsorption equilibrium. Temperature was maintained at 25 °C by a thermostat bath. The experiment commenced when the UV lamp was turned on. A sample was taken every 30 min for 360 min during the irradiation.

Before analysis, the solution sample was centrifuged and filtered with a nylon filter membrane (0.2 μm pore size, 25 mm diameter) to remove all solid particles. The concentrations of 4-CP and intermediate products in the filtered sample were determined by a Hewlett-Packard HPLC equipped with an UV detector adjusted to 270 nm and the ODS-2 spherisorb column (125 mm length, 4 mm internal diameter, and 5 μm particle diameter). The mobile phase was a mixture of 40:60 (v/v) of acetonitrile to deionized water with a flow rate of 1.0 ml/min. Total organic carbon of the solution was also determined by a Shimadzu TOC analyzer (TOC-5000A).

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of TiO_2 (Degussa P25), TiO_2 (sol–gel-1), TiO_2 (sol–gel-2) and 1.0% Pt/TiO_2. For TiO_2 (Degussa P25), the major phase is anatase and rutile exists as the minor phase. For TiO_2 (sol-gel-1), anatase is the major phase, whereas brookite exists as the minor phase. TiO_2 (sol–gel-2) has only the anatase phase. The anatase peaks of TiO_2 (Degussa P25) has higher intensity than that of TiO_2 catalysts prepared by the sol–gel methods. For 1.0% Pt/TiO_2, there is only TiO_2 in the anatase form and no peaks of Pt at $2\theta = 40$ and 48° were observed. It can be explained that Pt is dispersed well on TiO_2. The XRD patterns of Ag/TiO_2 catalysts at different Ag loadings are shown in Fig. 2. For Ag/TiO_2 catalysts calcined at 400 °C and having 0.2–1.5 mol% Ag, anatase is the major phase.

The crystallite sizes of the catalysts can be determined from the broadening of the anatase main peak by Debye–Scherrer equation. The crystallite sizes of all catalysts are shown in Table 2. The crystallite sizes of both sol–gel TiO_2 are smaller than that of TiO_2 (Degussa P25). Compared with TiO_2 (sol–gel-1), the addition of Ag did not significantly affect the crystallite size of the catalysts.

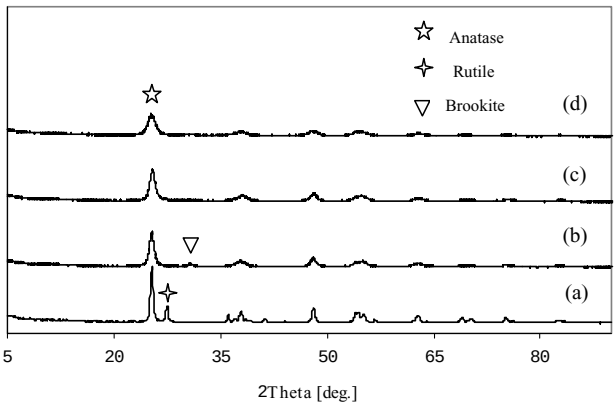

Fig. 1. X-ray diffraction patterns of: (a) TiO_2 (Degussa P25); (b) TiO_2 (sol–gel-1); (c) TiO_2 (sol–gel-2); (d) 1.0% Pt/TiO_2.

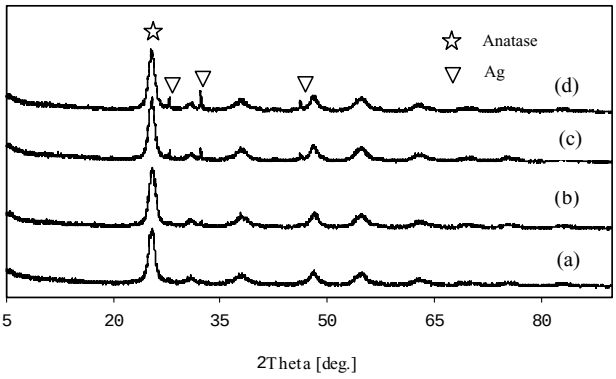

Fig. 2. X-ray diffraction patterns of Ag/TiO_2 catalyst at different Ag loadings: (a) 0.2% Ag/TiO_2; (b) 0.5% Ag/TiO_2; (c) 1.0% Ag/TiO_2; (d) 1.5% Ag/TiO_2.

Moreover, loading Pt into TiO_2 decreased significantly the crystallite size of the catalyst.

The surface areas of all catalysts are shown in Table 2. All catalysts prepared by the sol–gel methods have higher BET surface areas than those of TiO_2 (Degussa P25). The addition of Ag did not significantly affect the BET surface area.

3.2. Photocatalytic degradation of 4-CP

3.2.1. Effect of TiO_2 (Degussa P25)

Photocatalytic degradation of 0.5 mM 4-CP solution was carried out with TiO_2 (Degussa P25) loading of 0.5 g/l under UV irradiation. Samples were taken every 30 min to analyze for the concentration of 4-CP and other products. Fig. 3 shows the remaining fraction of 4-CP (C/C_0) and TOC (TOC/TOC_0) from the 4-CP degradation without any catalyst but with pure oxygen aeration. It was found that 4-CP decreased sharply and disappeared completely after 120 min but the TOC decreased only 38% after the irradiation for 360 min. In the presence of TiO_2 (Degussa P25) and with pure oxygen aeration, the TOC decreases 93% from the initial TOC after the irradiation for 360 min as shown in Fig. 4. However, 4-CP could not be completely degraded with TiO_2 (Degussa P25). The remaining 4-CP in solution is approximately around 0.0056 mM. Remarkably, the intermediate

Table 2
Surface areas and crystallite sizes of the studied catalysts

Catalyst	BET surface area (m^2/g)	Crystallite size (nm)
TiO_2 (Degussa P25)	55.9	24.04
TiO_2 (sol–gel-1)	101.2	12.80
TiO_2 (sol–gel-2)	137.1	11.30
1% Pt/TiO_2	112.2	7.54
0.2% Ag/TiO_2	105.7	9.37
0.5% Ag/TiO_2	113.5	10.67
1.0% Ag/TiO_2	105.0	14.78
1.5% Ag/TiO_2	122.7	9.85

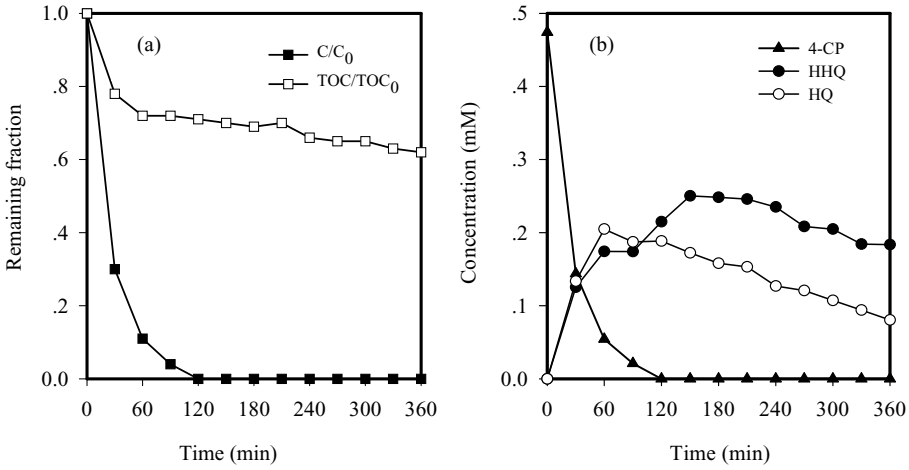

Fig. 3. Photocatalytic degradation of 4-CP as a function of irradiation time without catalyst with an oxygen saturated solution (a) remaining fraction of 4-CP and TOC, (b) concentrations of the intermediate products. Experimental conditions: 0.5 mM 4-CP, 298 K and 5.5 initial pH.

concentrations of HQ and HHQ reaches the maximum values at 90 and 120 min, respectively, when TiO_2 (Degussa P25) is added and the solution is aerated with pure oxygen as shown in Fig. 4b. Interestingly, the total concentration of the intermediates of the system with TiO_2 is much lower than that without TiO_2 catalyst. It can be concluded that the UV lamp with the short wavelength destroys the chemical bond in the 4-CP molecule and transforms into the intermediate products rather than CO_2 and the catalyst is necessary for further degradation of the intermediate products.

3.2.2. *Effect of TiO_2 (sol–gel)*

The photocatalytic degradations of 4-CP using two TiO_2 catalysts prepared by two sol–gel methods are shown in Fig. 5. Both have the same rate of 4-CP degradation and TOC reduction. Compared with the commercial TiO_2 (Degussa P25), the decrease of 4-CP concentration with either TiO_2 (sol–gel-1) or TiO_2 (sol–gel-2) is much faster and the 4-CP concentration disappears within 90 min. However, the TOC degradation rate with TiO_2 (Degussa P25) is higher than those with the two sol–gel TiO_2 catalysts. The results imply that the degradation rate of the intermediate products with TiO_2 (Degussa P25) is higher than that with the sol–gel TiO_2 catalysts.

Higher surface areas of both sol–gel TiO_2 catalysts resulted in larger amounts of 4-CP adsorbed on the catalyst surface leading to the higher degradation rates of 4-CP as compared to the commercial TiO_2 (Degussa P25). TiO_2 (Degussa P25) gives a higher degradation rate of TOC than TiO_2 (sol–gel) because of the higher crystallinity than both sol–gel TiO_2 catalysts. That, in turn, reduces the electron and hole (e^-/h^+) recombination. When the recombination effect decreases, there are more electrons and holes, which diffuse to the catalyst surface to react with the substrate

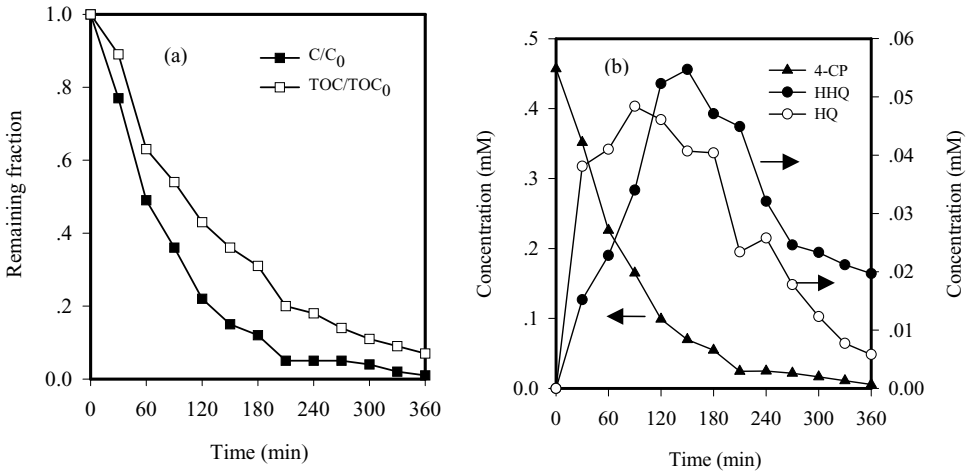

Fig. 4. Photocatalytic degradation of 4-CP as a function of irradiation time using TiO_2 (Degussa P25) with an oxygen saturated solution (a) remaining fraction of 4-CP and TOC, (b) concentrations of the intermediate products. Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP, 298 K and 5.5 initial pH.

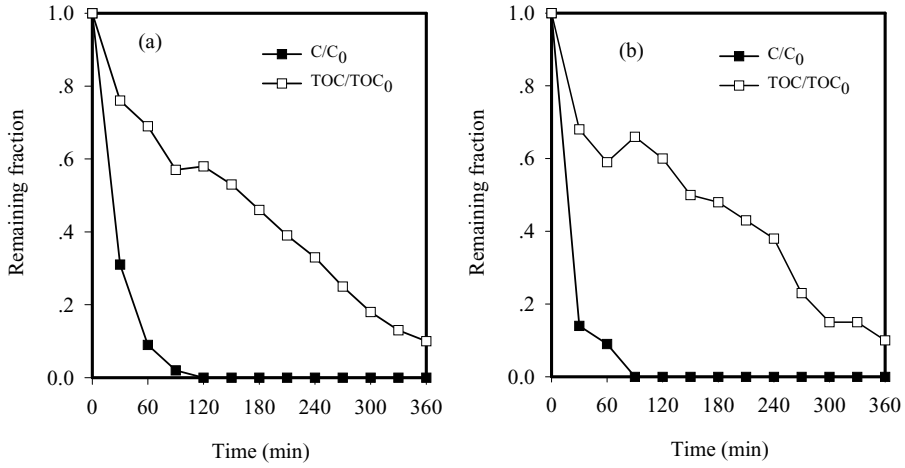

Fig. 5. Photocatalytic degradation of 4-CP as a function of irradiation time with an oxygen saturated solution using (a) TiO_2 (sol–gel-1), (b) TiO_2 (sol–gel-2). Experimental conditions: 5 g/l catalyst, 0.5 mM 4-CP, 298 K and 5.5 initial pH.

molecules adsorbed on the surface at the faster rate [5–8]. The results are also consistent with the work done by Guillard et al. [9]. They investigated the 4-CP degradation using different TiO_2 catalysts, TiONA PC 10, TiLCOC HC 120, Hombikat UV 100 and Degussa P25. Although TiO_2 (Degussa P25) had the lowest surface area, it was observed that the TiO_2 (Degussa P25) had the highest TOC degradation rate. It was explained that TiO_2 (Degussa P25) decreased the readsorption rate of the intermediate products.

3.2.3. *Effect of dissolved oxygen*

In order to determine the effect of dissolved oxygen on the 4-CP degradation, the solution was aerated with nitrogen to obtain zero dissolved oxygen while other experiments were carried out at a very high dissolved oxygen level by bubbling pure oxygen gas into the solution. The remaining fractions of TOC at the irradiation time of 360 min for each catalyst are shown comparatively in Table 3. As seen from the experimental results, in the presence of dissolved oxygen, the degradation rates of 4-CP and TOC are much higher than those of the systems in the absence of dissolved oxygen for both with and without catalysts. For TiO_2 (sol–gel-1), the three intermediates, HQ, BQ and HHQ, are generated during the 4-CP degradation in the absence of dissolved oxygen but BQ is not generated during the 4-CP degradation in the presence of dissolved oxygen. It can be concluded that the dissolved oxygen not only reduces the intermediate concentrations but also reduces the types of the intermediate products.

The presence of dissolved oxygen plays a significant role in the photocatalytic degradation of 4-CP. As explained by Litter [10], the oxygen molecule can act as an electron scavenger to trap and separate electron out from the positive hole that helps to reduce the chance of electron–hole pair recombination. Furthermore, the oxygen molecule can affect the fate of the photogenerated species. The oxygen molecule reacts with the conduction band electrons to form the superoxide anion radical, which reacts further with hydrogen ions to give a perhydroxyl radical. Consequently, the perhydroxyl radical can form hydrogen peroxide, which, in turn, gives rise to the hydroxyl radical [4]. Additionally, the oxygen flow serves as the stirring medium to increase the mass transfer in the irradiated systems [10].

3.2.4. *Photocatalytic degradation of 4-CP with Pt/TiO_2*

In this study, the photocatalytic degradation of 4-CP using 1% Pt/TiO_2 prepared by the sol–gel method in either the presence or absence of dissolved oxygen was investigated. Fig. 6 shows the comparative photocatalytic activity of 4-CP with different photocatalysts in the presence and absence

Table 3
Intermediate products and remaining fractions of TOC at 360 min from 4-CP degradation using different photocatalysts with and without dissolved oxygen

Catalyst	Nitrogen aeration		Oxygen aeration	
	TOC/TOC_0	Intermediate product	TOC/TOC_0	Intermediate product
Without catalyst	0.76	HQ, HHQ	0.62	HQ, HHQ
TiO_2 (Degussa P25)	0.42	HQ, HHQ	0.07	HQ, HHQ
TiO_2 (sol–gel-1)	0.41	HQ, HHQ, BQ	0.10	HQ, HHQ
1% Pt/TiO_2	0.27	HQ, HHQ, BQ	0.20	HQ, HHQ

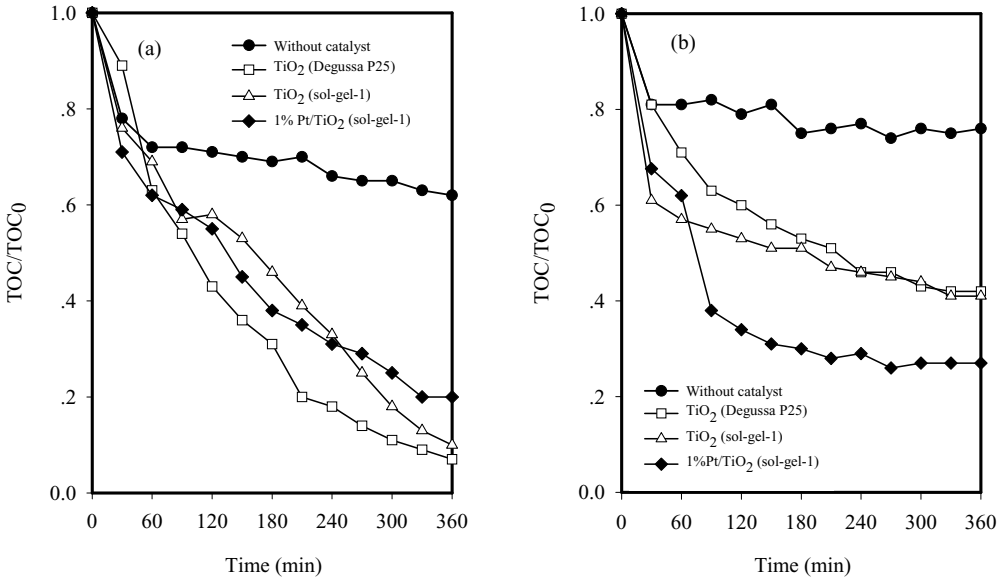

Fig. 6. The remaining fraction of TOC as a function of time for different photocatalysts: (a) in the presence of dissolved oxygen; (b) in the absence of dissolved oxygen.

of dissolved oxygen. Compared to pure TiO_2, an addition of 1% Pt on TiO_2 could increase the photocatalytic activity when the system was operated in the absence of dissolved oxygen. Surprisingly, a significant decrease in the photocatalytic degradation of 4-CP was found when 1% Pt was added in TiO_2 with the presence of dissolved oxygen. As reported by Blazkova et al. [11], the increase of oxygen flow significantly enhanced the photocatalytic activity of phenol with Pt/TiO_2 but too high of an oxygen flow damaged the activity.

3.2.5. *Photocatalytic degradation of 4-CP with Ag/TiO$_2$*

Effects of adding Ag to TiO_2 prepared by the first sol–gel method on the degradation of 4-CP were investigated systematically. A series of Ag/TiO_2 was prepared at different Ag loadings from 0.2 to 1.5 mol%. 0.5 mM 4-CP and 0.5 g/l catalyst were used. The remaining fractions of 4-CP and TOC are compared in Fig. 7. It is clear that the amount of Ag does not significantly affect the degradation rate of 4-CP but has some effect on the intermediate products and TOC degradation. It was found that the 0.5% Ag/TiO_2 has the lowest TOC at 360 min. Therefore, a small amount of Ag added to TiO_2 improves the photocatalytic activity of TiO_2 and the optimum amount of Ag loading under the investigated condition is 0.5 mol%.

Comparison of all studied catalysts (Fig. 8) shows that 0.5% Ag/TiO_2 gives the highest photocatalytic activity in terms of the remaining fraction of TOC at 360 min. We speculate that a small amount of Ag on TiO_2 increases the rate of generation of the superoxide radical anion, $O_2^{\bullet -}$, resulting in a decrease in the recombination process while enhancing

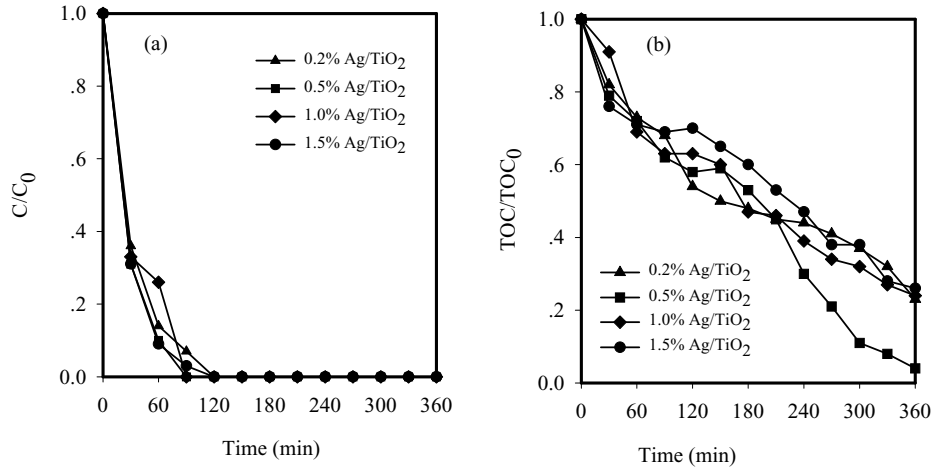

Fig. 7. Photocatalytic degradation of 4-CP with Ag/TiO_2 catalysts having different Ag loadings: (a) remaining fraction of 4-CP; and (b) remaining fraction of TOC.

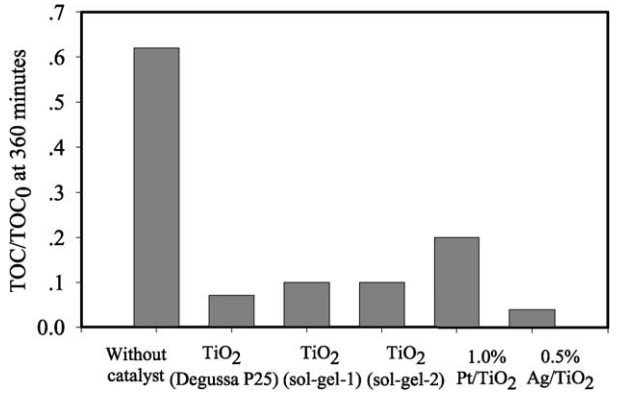

Fig. 8. Remaining fraction of TOC at 360 min for different catalysts in the presence of dissolved oxygen.

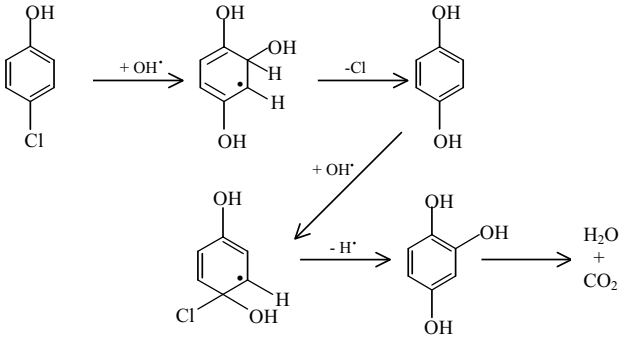

Fig. 10. Reaction pathway for the photocatalytic degradation of 4-CP in the presence of dissolved oxygen.

the photocatalytic activity. When the amount of Ag increases to a certain level, the photoelectrons will transfer from the semiconductor support to the metal particles and decrease the amount of $O_2^{\bullet -}$. The net result is lower photocatalytic activity [11]. Another possible explanation for the enhancement, seen with small amounts of Ag, is that Ag increases the rate of direct hole oxidation pathway leading to improved photocatalytic activity [12].

3.2.6. Intermediate pathways in the photocatalytic degradation of 4-CP

During the photocatalytic degradation with each catalyst, the aromatic intermediates were detected by HPLC. All species in the solution were identified by comparison of the retention times of the observed peaks with the retention times of standard HPLC peaks. For the studied catalysts, the two intermediates generated during the 4-CP degradation are HQ and HHQ when the photocatalytic system was operated in the presence of dissolved oxygen. However, TiO_2 (sol–gel-1) and Pt/TiO_2 with aerated nitrogen condition or without dissolved oxygen were found to generate three intermediates of HQ, HHQ and BQ.

Fig. 9 illustrates the profiles of the intermediate products during the 4-CP degradation using TiO_2 (Degussa P25) with dissolved oxygen. The concentration of HHQ increases almost linearly until the irradiation time of 150 min, whereas, the concentration of HQ increases and reaches a maximum after 90 min before both concentrations decreases progressively. The shape of the HQ curve is typical for a compound formed as a primary intermediate in a consecutive reaction.

For a better understanding of the degradation pathway of 4-CP in the presence of the dissolved oxygen condition, an analogous experiment was carried out for the degradation of HQ under the same experimental conditions as used for the irradiation of 4-CP. HHQ was only detected during the photocatalytic degradation of HQ. Accordingly, the proposed reaction pathway for the photocatalytic degradation of 4-CP is shown in Fig. 10. 4-CP is first oxidized into HQ and HQ is further oxidized into HHQ. Eventually, HHQ is mineralized to CO_2.

In the presence of dissolved oxygen, hydroxyl radical can be formed by the following reactions [4]:

$$H_2O + h^+ \rightarrow OH^\bullet + H^+ \quad (1)$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (2)$$

$$2H_2O + O_2^{\bullet -} \rightarrow 2H_2O_2 \quad (3)$$

$$H_2O_2 \rightarrow 2OH^\bullet \quad (4)$$

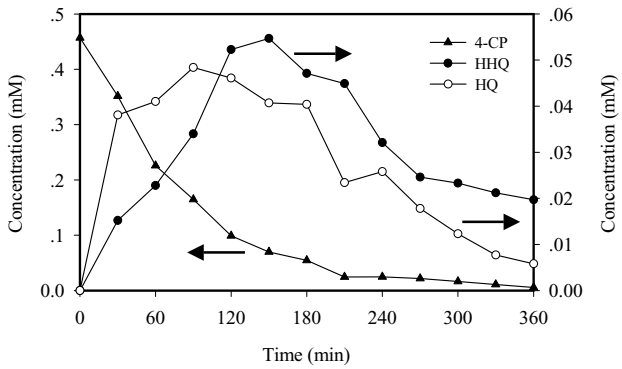

Fig. 9. Photocatalytic degradation of 4-CP as a function of irradiation time using TiO_2 (Degussa P25) under the presence of dissolved oxygen.

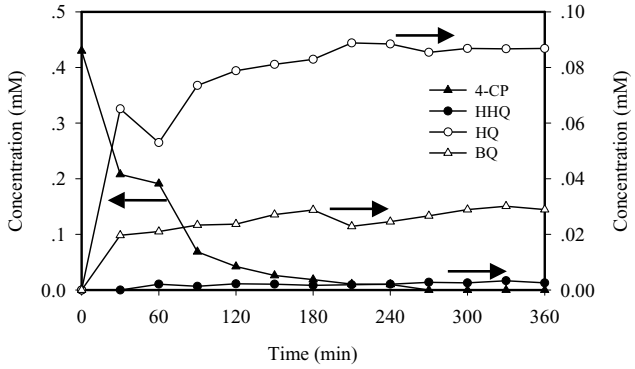

Fig. 11. Photocatalytic degradation of 4-CP as a function of irradiation time using 1.0% Pt/TiO_2 in the absence of dissolved oxygen.

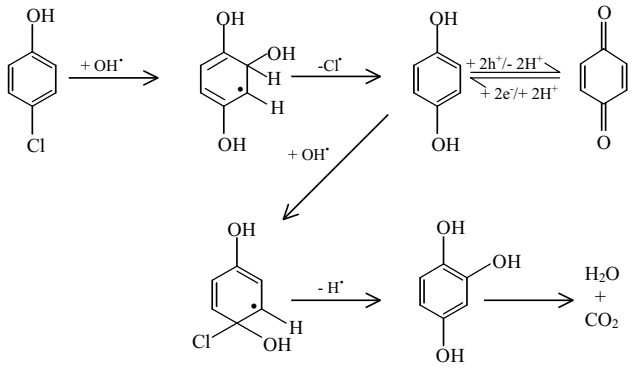

Fig. 12. Reaction pathway for the photocatalytic degradation of 4-CP in the absence of dissolved oxygen.

In the absence of oxygen, there is a small amount of hydroxyl radical since it is only generated from Eq. (1). Consequently, the oxidation rate of HQ to HHQ decreases. In the presence of a mild oxidizing agent, oxidization of HQ produces BQ and the reaction is reversible [13]. As seen from Fig. 11, there is a small amount of HHQ while the concentration of HQ and BQ are relatively constant. Accordingly, the proposed reaction pathway for the photocatalytic degradation of 4-CP in the absence of oxygen is shown in Fig. 12.

4. Conclusions

The photocatalytic degradation of 4-chlorophenol (4-CP) using different catalysts, TiO_2 (Degussa P25), TiO_2 (sol–gel-1), TiO_2 (sol–gel-2), Pt/TiO_2 and Ag/TiO_2 was investigated. For TiO_2 prepared by the sol-gel methods, TiO_2 (sol–gel-1) and TiO_2 (sol–gel-2), in the presence of dissolved oxygen, the decrease of 4-CP concentration was much faster than that with TiO_2 (Degussa P25) because of their higher surface areas. On the contrary, the reduction rate of TOC with TiO_2 (Degussa P25) in the presence of oxygen was higher than those with TiO_2 (sol–gel-1) and TiO_2 (sol–gel-2) because of its higher crystalinity.

For Pt/TiO_2 with nitrogen aeration, the presence of 1.0 mol% Pt on TiO_2 enhanced the degradation rate of TOC but with dissolved oxygen, it decreased the photoactivity. However, Ag did not have any effect on the degradation rate on 4-CP but adding 0.5 mol% Ag to TiO_2 enhanced the degradation rates of the intermediate products. Furthermore, 0.5% Ag/TiO_2 showed the highest activity compared to the other catalysts. A small amount of Ag on TiO_2 increases the rate of superoxide radical anion formation resulting in decreasing the recombination process and Ag also increases the rate of direct hole oxidation pathway leading to improving the photocatalytic activity.

The main intermediate products generated during the photocatalytic reaction in the absence of dissolved oxygen were found to be HQ, BQ and HHQ but BQ was not observed in the presence of dissolved oxygen. The presence of dissolved oxygen played an important role in the photocatalytic degradation of 4-CP. When the oxygen was present in the solution, both types and concentrations of intermediate products decreased significantly because dissolved oxygen can act as an electron scavenger and increase the hydroxyl radical concentration.

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