

## CHAPTER IV

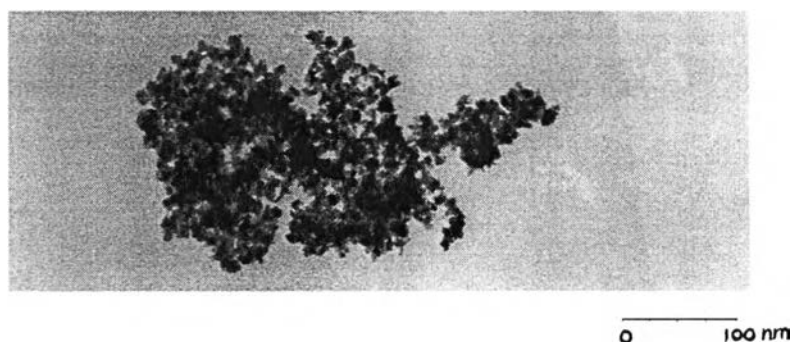
### RESULTS AND DISCUSSION

#### 4.1 Characterization of Photocatalysts Prepared by Microemulsion Technique

The microemulsion technique is the novel method to produce ultrafine particles that have vast applications including semiconductor application. In this study, the semiconductor photocatalysts were prepared by this method. The following are the physical properties of the catalysts.

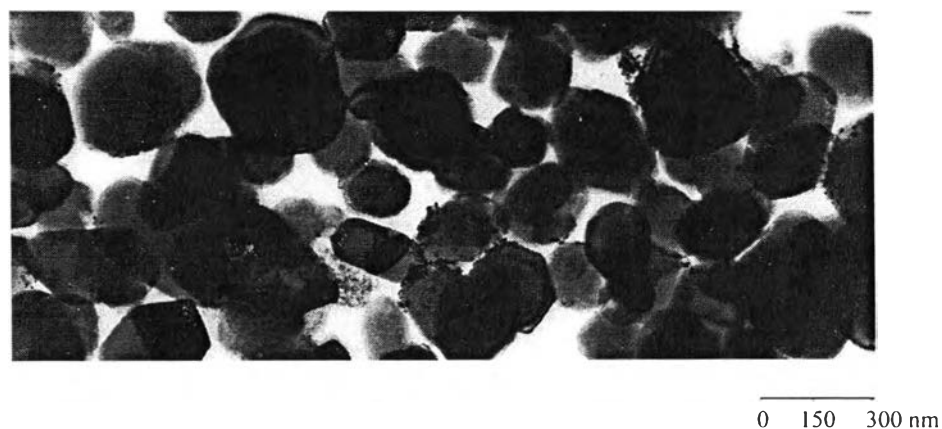
##### 4.1.1 *Particle Size and Size Distribution*

The particle size and size distribution of the catalysts prepared were observed by Transmission electron microscopy, Philips model 200 CX. The micrograph of the platinum particles is illustrated in Figure 4.1. The particle size of the platinum particles was measured to be around 3-5 nm.

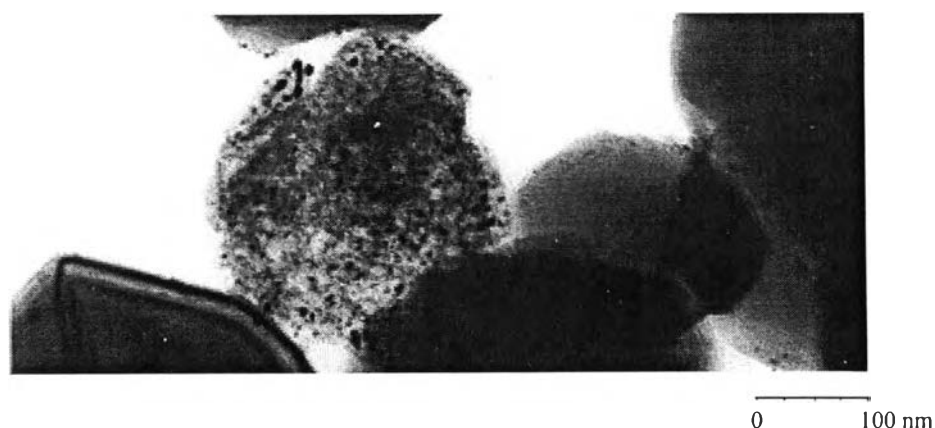


**Figure 4.1** A transmission electron micrograph showing a large cluster of tiny platinum particles produced by microemulsion technique

The particle size of the titanium(IV)oxide was also observed. Figure 4.2 shows a micrograph of the titanium(IV)oxide particles. It was found that the particles have a uniform size distribution around 70-100 nm in diameter. The micrograph of the platinized titanium(IV)oxide particles is given in Figure 4.3. The picture shows the adsorption of platinum particles onto the large particle of titanium(IV)oxide uniformly. The larger boundary represents the titanium(IV)oxide particle and the small black dots inside are platinum. These two types of the particles can be distinguished because of their different electron densities (Ohtani, 1997).



**Figure 4.2** A transmission electron micrograph of the titanium(IV)oxide particles



**Figure 4.3** A transmission electron micrograph of the platinized titanium(IV)oxide particles

#### 4.1.2 *BET Surface Area*

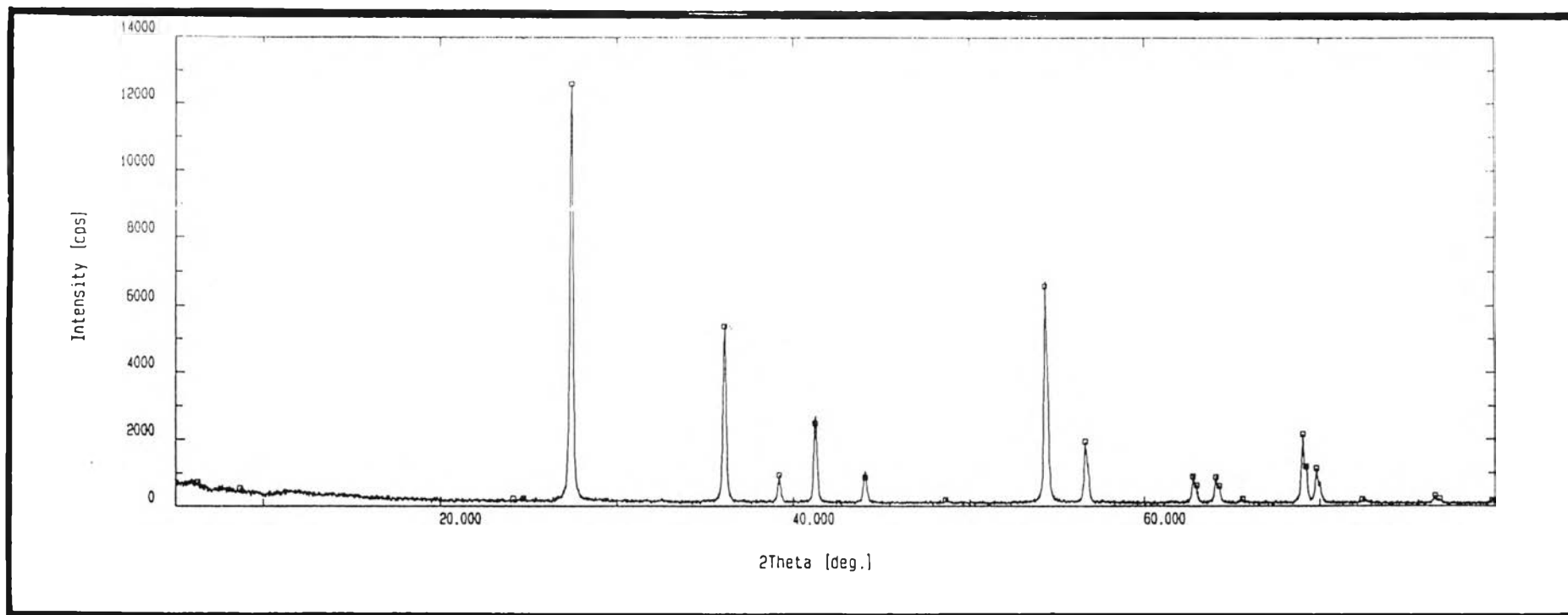
There were three types of the photocatalysts used in this study. The surface area of the catalyst particles is one of the important properties determining the activity of the catalysts. Table 4.1 shows the comparison of BET surface areas of the TiO<sub>2</sub> particles before and after heat treatment and with platinum deposited TiO<sub>2</sub> measured by Autosorb 1.

**Table 4.1** The BET surface areas of the photocatalysts used in this study

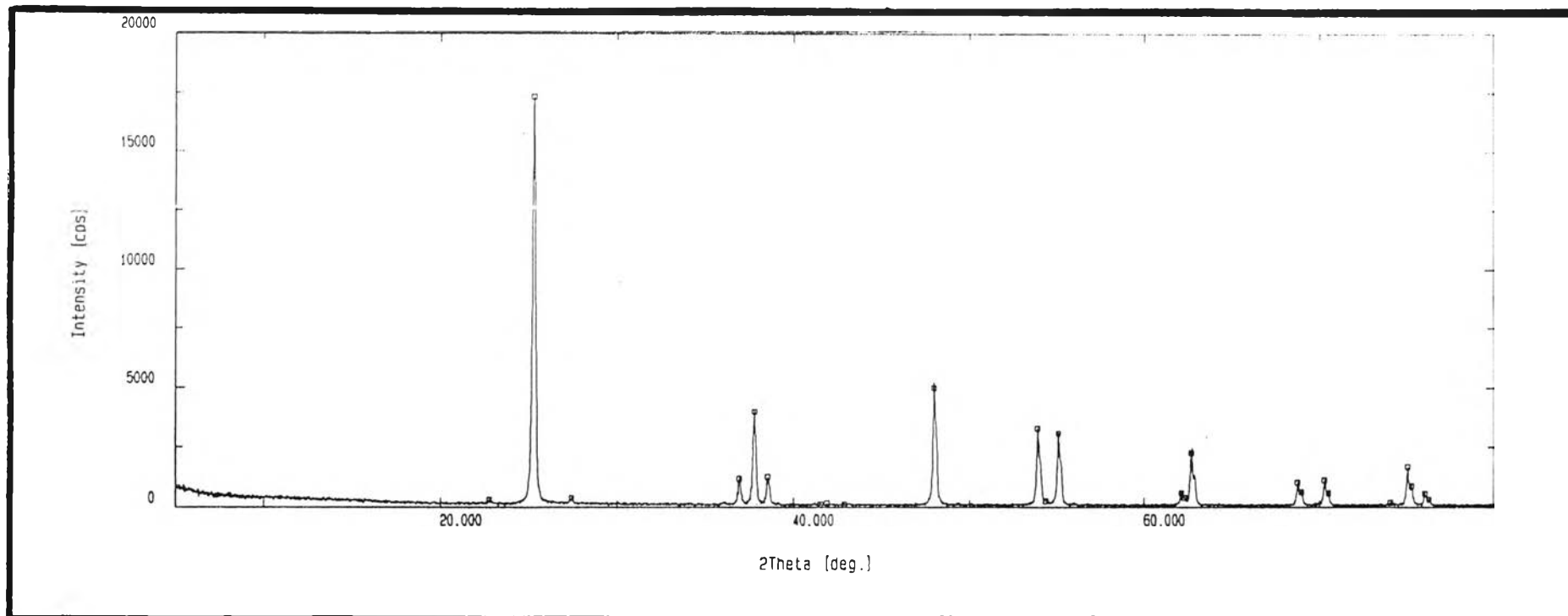
Photocatalysts	BET surface area (m <sup>2</sup> /g)
Commercial TiO <sub>2</sub>	13.79
Heat treated TiO <sub>2</sub>	10.48
0.23%Pt/TiO <sub>2</sub>	8.89

#### 4.1.3 *X-Ray Diffraction*

The molecular structure of the catalysts were also the factor that has an influence on the activity of the catalysts. Each form of the catalysts can be identified by x-ray diffraction. Titanium(IV)oxide normally has two forms that are rutile and anatase. Figure 4.4 represents the XRD patterns of commercial titanium(IV)oxide, which showed the rutile form while the heat treated titanium(IV)oxide and platinized titanium(IV)oxide are in the anatase form as illustrated in Figures 4.5 and 4.6, respectively. There were several studies show the different activity of these two forms of titanium(IV)oxide and reveal that titanium(IV)oxide in the anatase form gave higher activity in photocatalytic processes (Ohtani and Nishimoto, 1993). This conclusion is also confirmed by the results in this study as shown in Figure 4.7. The anatase titanium(IV)oxide gave much higher activity in IPA degradation than the rutile form of titanium(IV)oxide.



**Figure 4.4** XRD pattern of commercial titanium(IV)oxide in the rutile form



**Figure 4.5** XRD pattern of heat treated titanium(IV)oxide in the anatase form

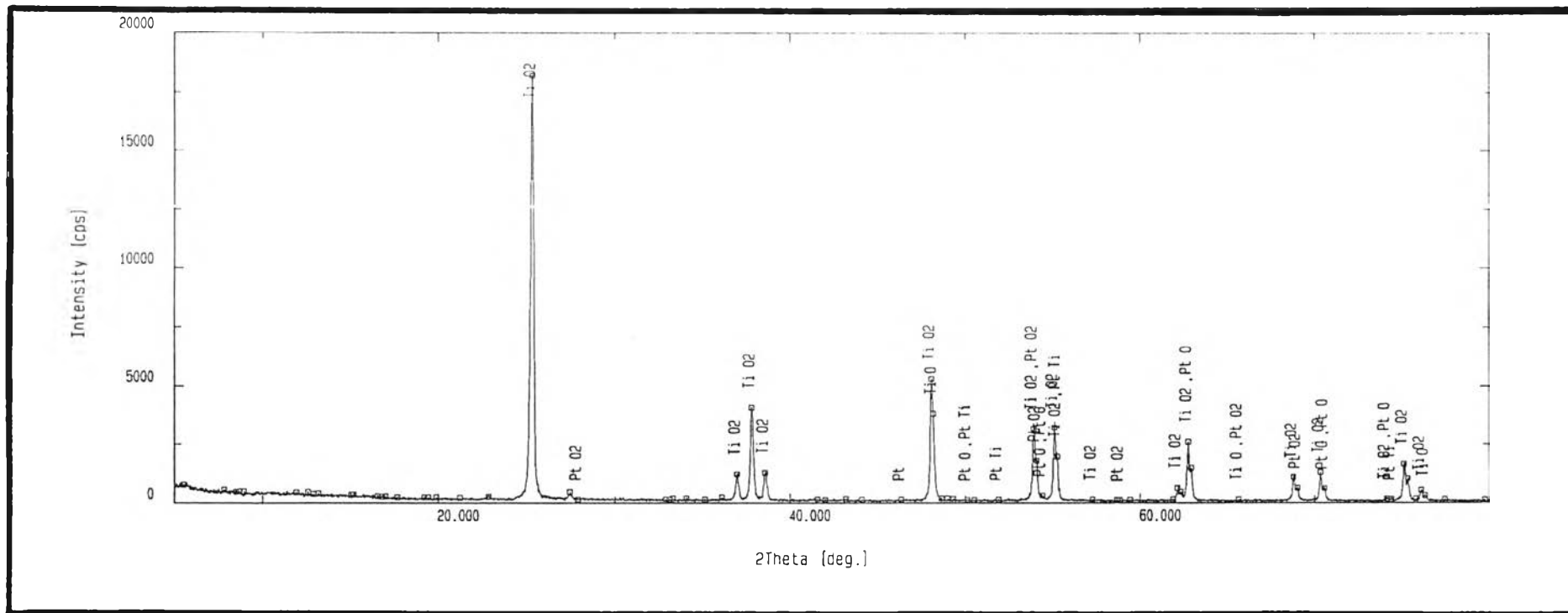


Figure 4.6 XRD pattern of platinumized titanium(IV)oxide in the anatase form

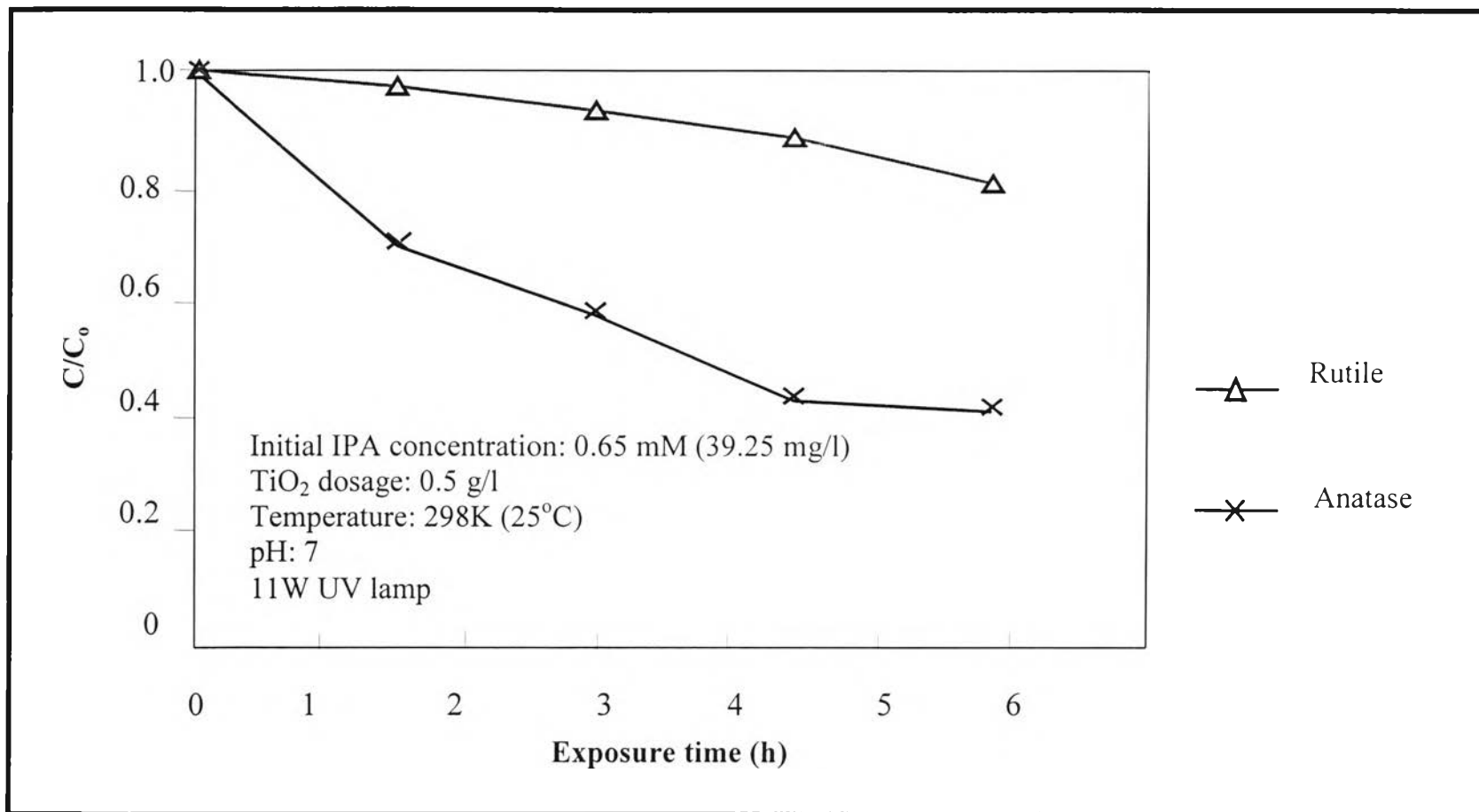


Figure 4.7 Photocatalytic degradation of IPA by using two different forms of titanium(IV)oxide catalysts

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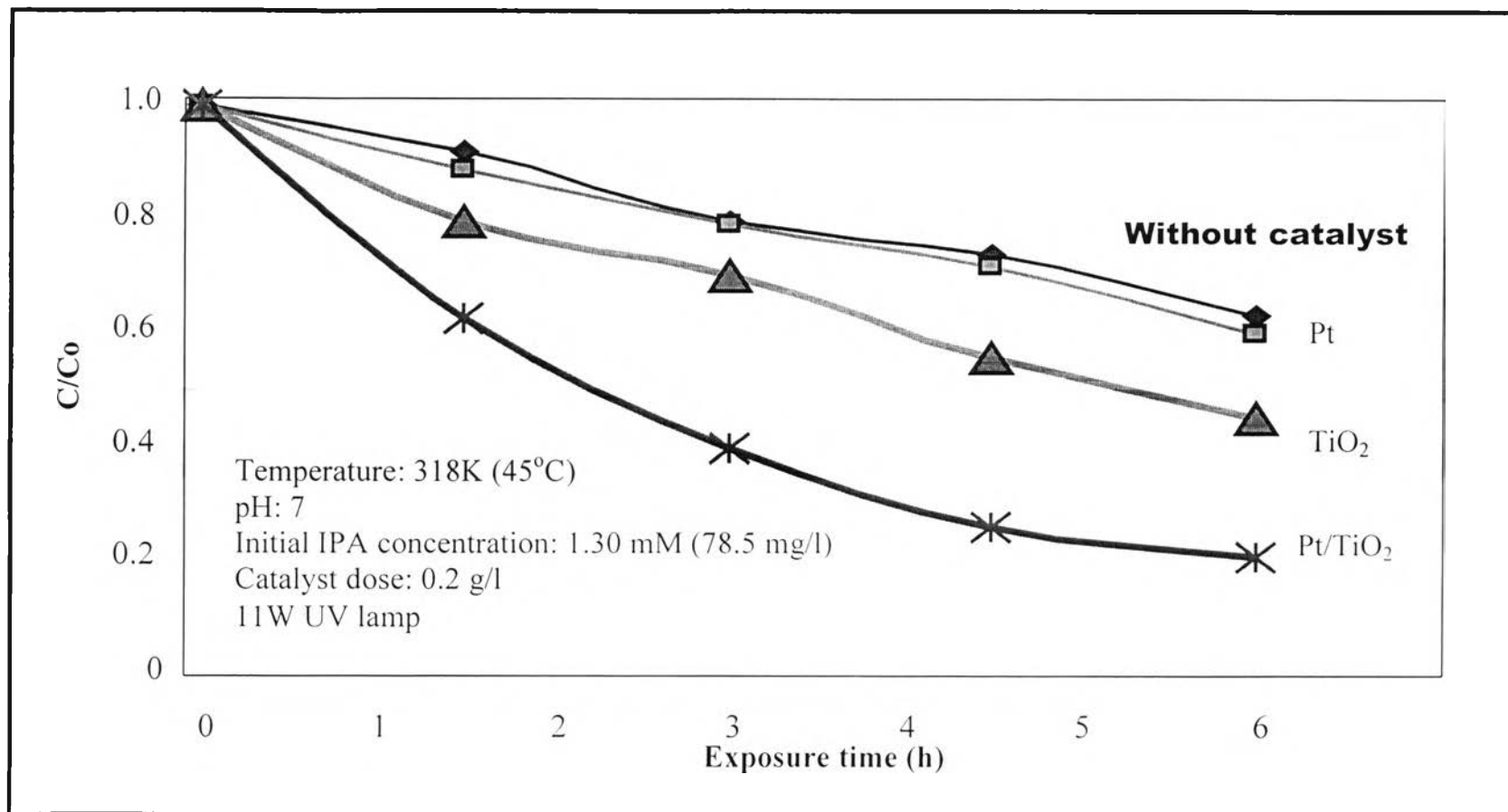
## 4.2 Photocatalytic Degradation of IPA by Using Different Types of Catalysts

The objective of this study was to determine the role of each type of catalyst on the degradation rate of IPA. In this study, the catalysts used were Pt, TiO<sub>2</sub>, and Pt/TiO<sub>2</sub>. Figure 4.8 illustrates the results of the IPA degradation by using each catalyst compared to the degradation without catalyst. The results showed negligible activity of Pt when compared with no catalyst while the degradation of IPA by TiO<sub>2</sub> was slightly higher. It can be explained that Pt as a metal has a continuum between valence band and conductance band, so e<sup>-</sup>/h<sup>+</sup> pair produced by photoirradiation can recombine easily and reduce the chance to react with other species. TiO<sub>2</sub> can act well as a photocatalyst to accelerate the reaction. As can be seen in Figure 4.8, Pt gives significantly high activity when together with TiO<sub>2</sub>. We speculate that the degradation rate was enhanced by adding of Pt due to better adsorption of IPA onto the catalyst surface which increased the transfer of electrons from TiO<sub>2</sub> to IPA. Consequently, the reaction rate increased significantly. In addition, Pt or the noble metal deposits have been known to act as catalysts for the H<sub>2</sub> evolution by e<sup>-</sup>, because they reduce the activation energy of the reaction (Ohtani *et al.*, 1997).

## 4.3 Effect of Influencing Parameters on the Degradation Rate of IPA

There are several parameters affecting the rate of IPA degradation maybe by changing the mechanism. These parameters are light intensity, initial concentration of reaction substrate, type of catalyst, amount of catalyst, temperature, pH, dissolved oxygen, and electrolytes. In this study, the effects of four parameters of IPA concentration, catalyst dosage, initial pH, and the





**Figure 4.8** Photocatalytic degradation of IPA by using different types of catalysts under UV illumination

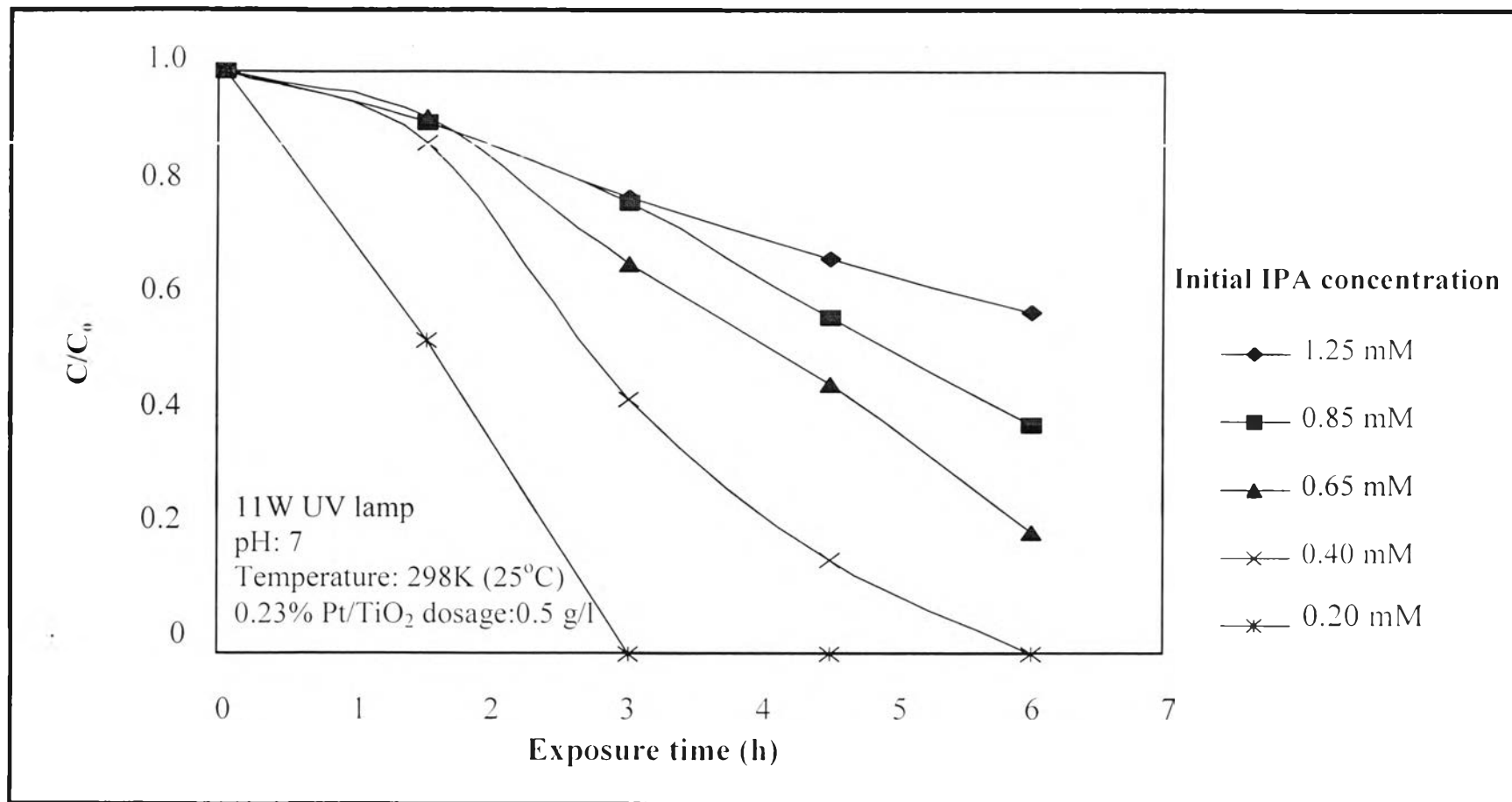
dissolved oxygen were determined. Since Pt/TiO<sub>2</sub> was the most effective catalyst in degrading IPA, this catalyst was then employed in this study.

#### 4.3.1 *Effect of Initial Concentration of IPA*

To study the effect of this parameter, the experiment was carried out by varying the initial concentration of IPA from 0-1.3 mM (0-78.5 mg/l). Figure 4.9 illustrates the IPA concentration profile with time at different initial concentration of IPA when Pt/TiO<sub>2</sub> was used. For the studied conditions, the result of IPA degradation rate shows a linear relationship fit to an empirical kinetic equation of zero order. It can be concluded that the rate of IPA degradation is not depending on the initial concentration of IPA under the studied condition. The results followed the zero equation mean the rate of degradation may be limited by an active species and the reaction at the surface is not fast enough so the initial concentration of IPA is not a significant factor.

#### 4.3.2 *Effect of Catalyst Dosage*

In this experiment, the IPA concentration was fixed at 0.65 mM (39.25 mg/l) and the catalyst dosage was varied from 0 to 0.75 g/l. Figure 4.11 shows the effect of catalyst dosage of Pt/TiO<sub>2</sub> on the IPA degradation. The results showed that the reaction rate of IPA degradation depended on the dosage of Pt/TiO<sub>2</sub> significantly. Increasing the catalyst dosage, concentration of active species to react with organic molecules is increased consequently increasing the reaction rate. The cooperation of light and catalyst is very important for the photocatalytic process. At a low initial IPA concentration with relatively high amount of catalyst, the rate increases with catalyst amount will not be observed. But for a higher concentration of IPA, an insufficient catalyst leads to the low reaction rate. So the increasing of catalyst will increase the overall reaction rate. However, increases of either substrate concentration and catalyst dosage also have the limitation on the light penetration that affects the reaction.



**Figure 4.9** IPA concentration ratio as a function of exposure time for different initial IPA concentrations

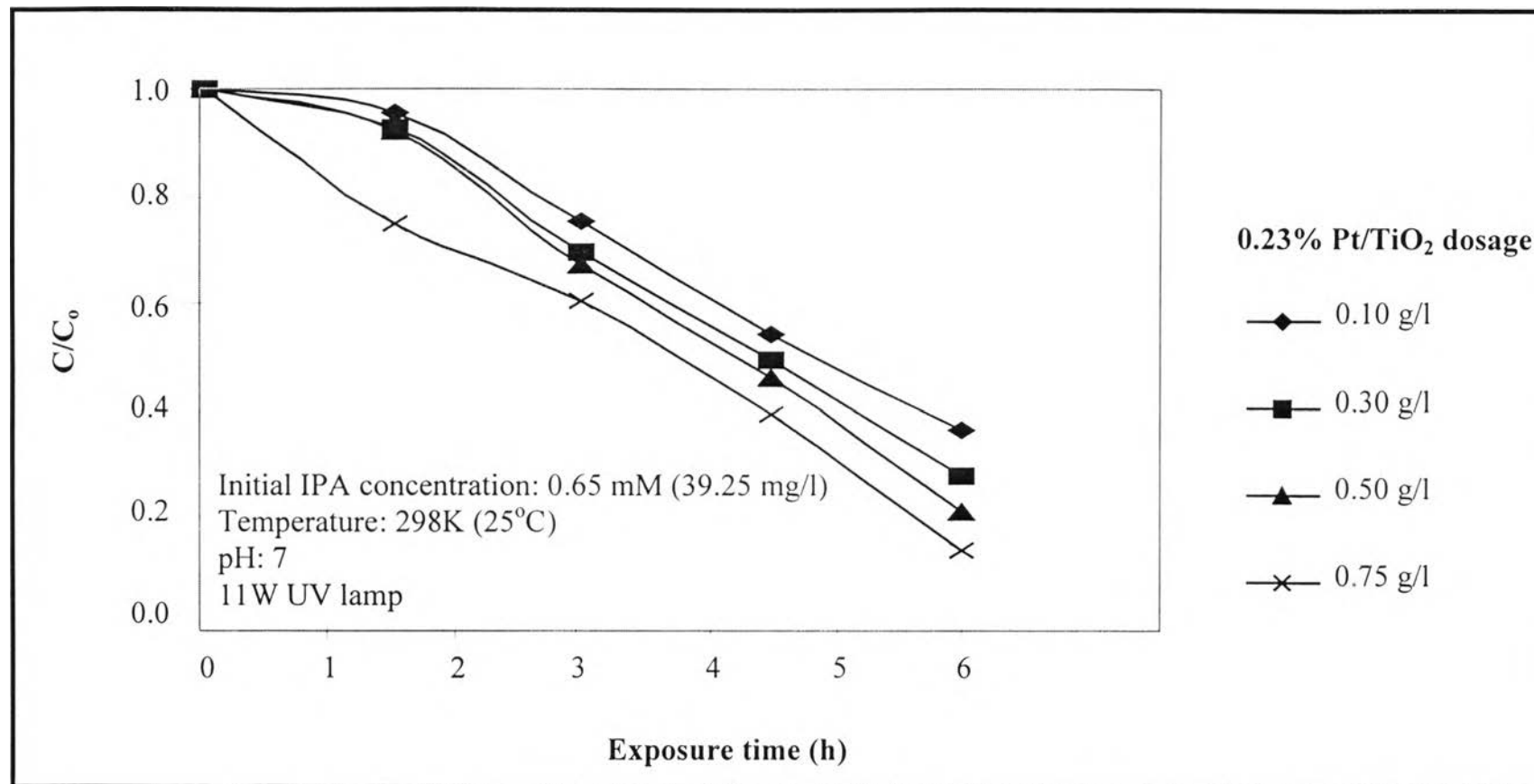


Figure 4.10 IPA concentration ratio as a function of exposure time for different dosages of Pt/TiO<sub>2</sub>

#### 4.3.3 *Effect of Initial pH*

From Figure 4.12, the results show that the IPA degradation rate becomes relatively efficient under acidic condition and decreases drastically with increasing pH but the degradation rate increases again at pH around 12. The acidity and alkalinity have an effect on the degradation of organic molecules since they change the adsorption of the substrate onto the surface of the catalysts and also the hydroxyl radical (OH) concentration which participates in the reaction. Moreover, pH also has an influence on the surface charge of the catalyst and the form of the substrate so that the adsorption of substrate onto the catalyst surface will be changed. TiO<sub>2</sub> has an amphoteric surface, IPA can adsorb more on the TiO<sub>2</sub> surface in the acidic condition. Thus, the direct oxidation is predominant as decreasing pH. Under a very high pH condition (pH 12), the reactive hydroxyl radical becomes more concentrated to enhance the IPA degradation rate so a higher rate of oxidation is seen again at high pH.

#### 4.3.4 *Effect of Dissolved Oxygen*

This experiment was conducted in order to determine the effect of dissolved oxygen on the IPA photocatalytic degradation. The first run was done in the deaerated condition by flowing nitrogen gas through the reaction vessel to obtain zero dissolved oxygen throughout the experiment. The second one was aerated with air to obtain the dissolved oxygen around 8.8 mg/l. The third one was carried out at a very high dissolved oxygen level by flowing pure oxygen gas to get the saturated dissolved oxygen around 37.7 mg/l.

The effect of dissolved oxygen on IPA degradation is shown in Figure 4.12. For the saturated dissolved oxygen of 37.7 mg/l, IPA was degraded rapidly and completely within 1.5 hours and gave nearly the same result for aerated condition which has the dissolved oxygen around 8.8 mg/l. For the experiment of deaerated condition, the results showed a slightly decreased of

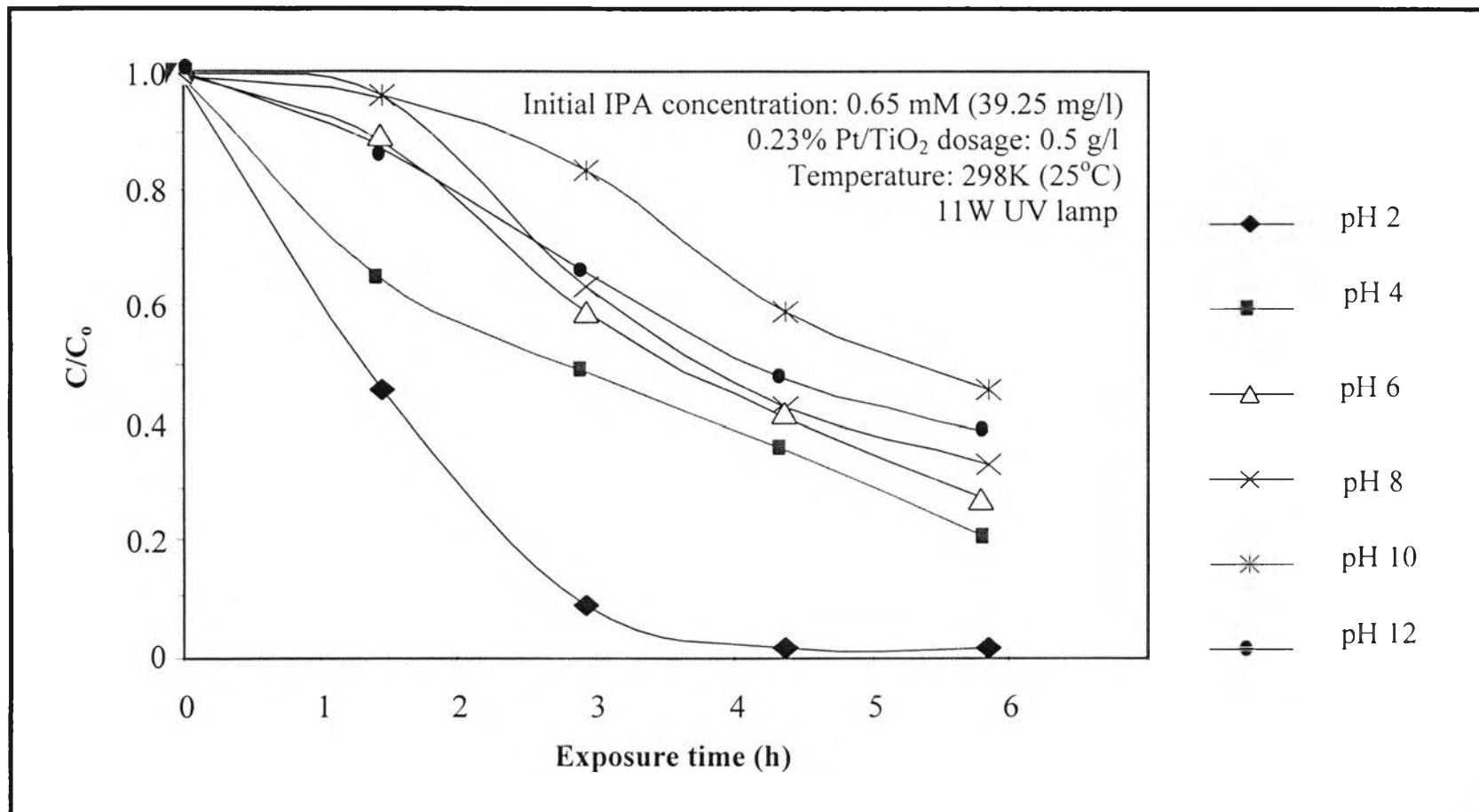


Figure 4.11 IPA concentration ratio as a function of exposure time with different pH values

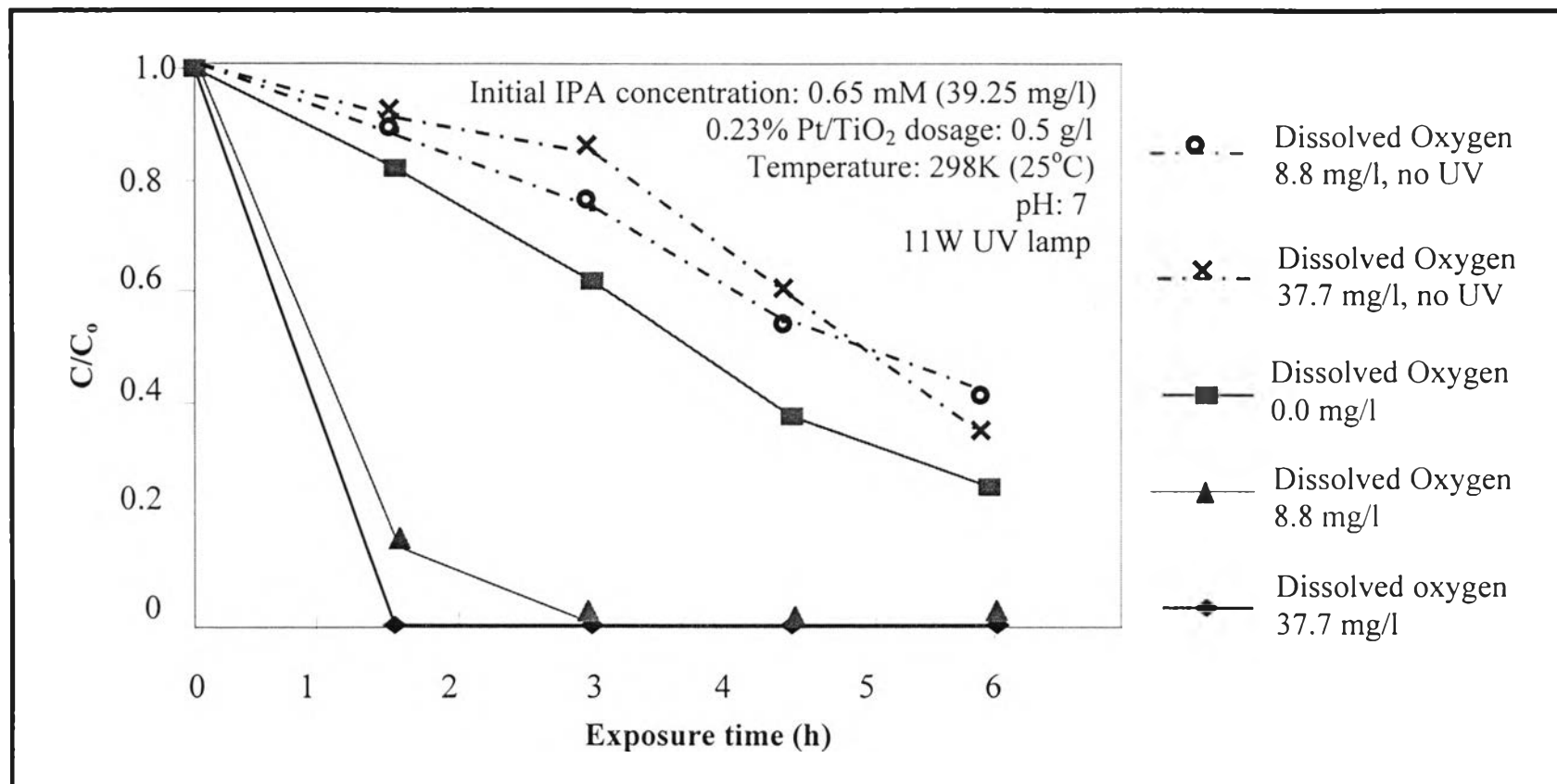


Figure 4.12 IPA concentration ratio as a function of exposure time at different dissolved oxygen levels

IPA concentration. It can be concluded that the dissolved oxygen has a significant role in the photocatalytic degradation of IPA since the oxygen molecule can act as an electron scavenger to trap and separate electron ( $e^-$ ) out from the positive hole ( $h^+$ ) that will reduce the chance of electron-hole pair recombination. Hence, the photocatalytic process can proceed effectively. The oxygen is also a starting molecule to produce a very strong oxidant, hydroxyl radical (OH). The values of oxidation potentials of some oxidants are compared in Table 2.1. The most possible reactions start with an oxygen molecule traps  $e^-$  as shown in Equation (2.1) and then react with the molecule of water to give hydrogen peroxide ( $H_2O_2$ ) that can break to be hydroxyl radical (OH) by UV irradiation as shown in Equation (2.4) and (2.5), respectively. Furthermore, the oxygen molecule can be transformed to an atomic oxygen on Pt which is a strong oxidant so it can react with the reaction substrate directly to enhance the overall reaction rate as illustrated by the dotted line in Figure 4.12 which shows the IPA degradation on Pt/TiO<sub>2</sub> catalyst in the cooperation of oxygen molecule without UV illumination.