CHAPTER II
LITERATURE REVIEWS

2.1 Principle of Heterogeneous Photocatalysis

Photocatalytic process is known as an effective treatment system, which can degrade the hazardous polluting materials prior to discharge of the effluent to environment. Because this technique can completely decompose most organic materials to carbon dioxide, water and mineral ion by oxidation reaction or reduction reaction. Equation (2.1) shows the overall reaction for the photo-decomposition of organic materials (P), sensitized by TiO_2 (Roberson, 1996).

$$P + O_2 \xrightarrow{TiO_2/h\upsilon} CO_2 + H_2O + \text{Mineral acids} \tag{2.1}$$

When a semiconductor catalyst (SC) is illuminated with photons ($h\upsilon$) that have energy is equal to or greater than band gap energy (Eg) of a semiconductor, $h\upsilon \geq Eg$, absorption of these photons occurs, an electron from the valence band is promoted to the conduction band, creation of electron-hole pairs, which dissociate into free photoelectrons (e^-) in the conduction band and photoholes (h^+) in the valence band (Herrmann, 1999; Litter, 1999), by following equations (Roberson, 1996): (Figure 2.1)

Light Absorption:	$SC + h\upsilon \rightarrow e^- + h^+$	(2.2)
Oxidation:	$D\,(ads) + h^+ \rightarrow D^{\bullet +}$	(2.3)
Reduction:	$A\,(ads) + e^- \rightarrow A^{\bullet -}$	(2.4)

A and D are species A and species D, respectively.

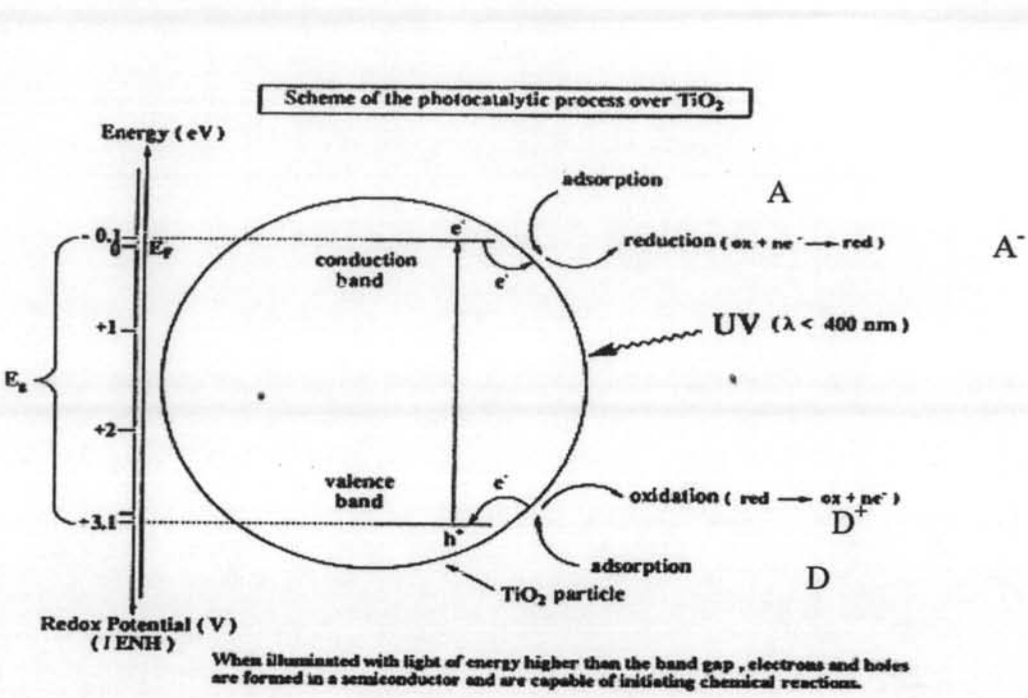

Figure 2.1 Energy band diagram of a spherical titania particle (Herrmann, 1999).

Generally, there are two possible mechanisms, which are direct hole oxidation and hydroxyl radical oxidation. For the direct hole oxidation, the photohole reacts directly with the adsorbed organic molecules as shown in Equation (2.3), while, for the hydroxyl oxidation, the photohole reacts with surface hydroxyl group (OH^-) or adsorbed water, and hydroxyl radical ($OH^\bullet$) will be formed as shown in the following equations:

$$OH^- + h^+ \rightarrow OH^\bullet \tag{2.5}$$

$$H_2O + h^+ \rightarrow OH^\bullet + H^+ \tag{2.6}$$

The efficiency of the photoreaction can be reduced by the electron-hole recombination with the generation of neutral center (N) and heat (Herrmann, 1999), and this inhibits the oxidation reaction, as shown in Equation (2.7):

$$e^- + h^+ \rightarrow N + \text{heat} \tag{2.7}$$

The way to decrease the possibility of recombination is adding some electron scavengers such as oxygen molecules because they can trap electrons out from the positive holes and transform into super oxide radical ions ($O_2^{\bullet -}$) and lead to the addition formation of the hydroxyl radical ions ($OH^{\bullet}$) (Litter, 1999), by the following equations:

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (2.8)$$

$$2\,H_2O + O_2^{\bullet -} \rightarrow 2H_2O_2 \quad (2.9)$$

$$H_2O_2 \rightarrow 2\,OH^{\bullet} \quad (2.10)$$

The majority of this work will use TiO_2 as a photocatalyst, Table 2.1. This semiconductor has band gap energy about 3.1 eV and therefore absorbs in the near UV light (~ 380 nm). So this material is able to use for oxidizing and reducing materials in a wide range of applications.

Table 2.1 Band positions of some common semiconductor photocatalysts*
(Roberson, 1996)

Semiconductor	**Valence band (eV)**	**Conductance band (eV)**	**Band gap (eV)**	**Band gap wavelength (nm)**
TiO_2	+3.1	+0.1	3.1	380
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	390
ZnS	+1.4	-2.3	3.7	336
WO_3	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	497
CdSe	+1.6	-0.1	1.7	730
GaAs	+1.0	-0.4	1.4	887
GaP	+1.3	-1.0	2.3	540

*in aqueous solution at pH 1

In some situations, modifying the surface of semiconductor, the type of final products generated may be different. Many research works tried to improve the activity of photocatalyst by several techniques such as by metal doping method or by finding better preparation technique that may be able to improve catalytic activity.

Guillard *et al.* (1999) studied the photocatalytic degradation of 4-chlorophenol, (4-CP) using different industrial TiO_2 catalysts: P25 (50 m^2g^{-1}), HombikatUV 100 (250 m^2g^{-1}), TiLCOM HC 120 (120 m^2g^{-1}), and TiONA PC10 (9 m^2g^{-1}). It was concluded that for the degradation of 4-CP, TiONA PC10 gave the highest activity because for lower surface area, there was a decrease in the readsorption rate of intermediate products and consequently in the photodegradation rate. Moreover, it resulted in the lowest rate of degradation of intermediate products because of its low surface area. For the degradation rate of TOC, it was found that TiLCOM HC 120, a moderate surface area, gave the highest rate of TOC degradation. Although, the higher surface area, the higher the efficiency in destroying the intermediate products to CO_2, but, when the particles became too small (very high surface area), there was a blue shift with an increase of ban gap energy, detrimental to the near UV-photon absorption, and an increase of the e^-/h^+ recombination. So HombikatUV 100 had lower rate of TOC degradation than TiLCOM HC 120.

Phuapromyod (1999) studied photocatalytic degradation of isopropyl alcohol (IPA) using Pt, TiO_2 and Pt/TiO_2. Pt or TiO_2 alone showed a low activity but Pt/TiO_2 had a much higher activity for the degradation of IPA.

Tharathonpisuttikul (2001) studied the photocatalytic degradation of 4-chlorophenol (4-CP) using TiO_2, Pt/TiO_2, TiO_2-SiO_2 and Pt/TiO_2-SiO_2 prepared by the sol-gel method. It was found that the addition of a small amount of Pt into TiO_2 improved the activity of catalyst and the highest activity was obtained with 1% Pt/TiO_2. For TiO_2-SiO_2 catalyst, the highest activity was achieved at 10% SiO_2-TiO_2 because of its highest adsorption capacity. For Pt/TiO_2-SiO_2 with 1% Pt and 10% SiO_2, 1% Pt or 10% SiO_2 alone in TiO_2 could improve the catalytic activity but the synergistic effect of adding both 1% Pt and 10% SiO_2 was not observed due to the agglomeration of the catalyst causing lower catalytic activity.

Hong *et al.* (2003) studied the preparation of TiO_2 by the microemulsion technique using PDMAEMA-*b*-PFOMA surfactants and its photocatalytic activity for the decomposition of *p*-nitrophenol. It was found that TiO_2 showed higher activity than the bulk TiO_2 because the bulk TiO_2 had a larger particle size than the TiO_2 particle prepared by the microemulsion method. This result suggested that the photocatalytic activity of the degradation of *p*-nitrophenol depended on the particle size, and increased with a decrease in the particle size.

Moonsiri *et al.* (2004) studied the photocatalytic degradation of 4-chlorophenol, (4-CP) using TiO_2 (Degussa P25), TiO_2 by sol-gel methods, Pt/TiO_2 and Ag/TiO_2. For TiO_2 prepared by the sol-gel methods, the decrease of 4-CP concentration was much faster than that with TiO_2 (Degussa P25) because of their higher surface areas. But the reduction rate of total organic compounds (TOC) with TiO_2 (Degussa P25) was higher than those with TiO_2 prepared by sol-gel methods because of its higher crystallinity. The addition of a small amount of either Pt or Ag could improve the catalyst activity. It was found that the presence of Ag did not significantly affect the degradation of 4-CP but had the effect on the intermediate products and TOC reduction: 0.5 mol% Ag showed the highest activity. It was suggested that a small amount of Ag on TiO_2 increased the rate of superoxide radical anion formation resulting in decreasing the recombination process and Ag also increased the rate of direct hole oxidation pathway leading to the photocatalytic activity improvement.

Thangsatjatham (2004) studied the photocatalytic degradation of 4-CP using Ag/TiO_2 (Degussa P25), Au/TiO_2 (Degussa P25) and temperature treated TiO_2 (Degussa P25) and tested in suspension systems. It was found that adding a small amount of Ag and Au could improve the activity of TiO_2 and the highest activity was observed with 0.1% Ag and 0.1% Au. It was suggested that the small amount of Ag and Au accelerated super oxide radical anion, $O_2^{\bullet-}$, formation and it also decreased the recombination. On the contrary, the addition of Ag or Au could also block the active site exposed to the UV light. For the temperature treated TiO_2, it was found that the TOC degradation rate slightly decreased with increasing the calcination temperature because of the sintering of the catalyst and its transformation from anatase to rutile with increasing temperature.

Jung *et al.* (2005) studied the effect of TiO_2 prepared by low-pressure metal-organic chemical vapor deposition (LPMOCVD) method on its properties and its activity on the photocatalytic degradation of methylene blue. It was found that the thickness of TiO_2 film increased with the increase in the deposition time. When the deposition time was short, very fine particles were observed. As the deposition time increased, the size of the TiO_2 particles increased and the film became dense. For the photocatalytic activity, it indicated that the photocatalytic activity strongly depended on the deposition time or on film thickness in a nonlinear fashion. Catalytic activity increased drastically between 1-5 μm of the film thickness. However, increasing the film thickness higher than 5 μm, the photocatalytic activity was not increased.

Hu *et al.* (2005) studied the preparation of TiO_2 thin films at low temperature from anatase TiO_2 sols and tested its photocatalytic activity on X-3B in an aqueous solution as a model of pollutant. At room temperature and in ambient atmosphere, crystalline TiO_2 thin films were deposited by the dip-coating method from the anatase TiO_2 sol. It was found that the higher acidic condition (the lower pH), the smaller and well-dispersed TiO_2 particles. For the photocatalytic degradation rate of X-3B, it was found that the reaction rate constants increased with increasing the dip-coating cycles because the increase in the amount of TiO_2 that can be illuminated with photon.

Yoo *et al.* (2005) studied the synthesis of anatase TiO_2 particles by modified sol-gel method using water immiscible ionic liquid (IL) as a template and compared its photocatalytic degradation of 4-CP with TiO_2 prepared by the conventional sol-gel method. For the characterization of TiO_2 particles, it was found that with IL, TiO_2 had higher thermal stability than that prepared without IL. It was suggested that this method could use to prepare TiO_2 particles under low temperature. For the degradation of 4-CP, it was observed that the TiO_2 particles prepared with IL at the low calcination temperature showed better degradation of 4-CP than that prepared without IL because it had better formation of anatase phase. However, at the high calcination temperature, TiO_2 prepared with IL showed lower photocatalytic activity than TiO_2 prepared without IL because their crystallinity was lower.

2.2 Effect of Dissolved Oxygen

Phuaphromyod (1999) studied the effect of dissolved oxygen on the photocatalytic degradation of IPA. The experiments were carried out by flowing nitrogen, air and pure oxygen into the IPA solution to obtain different levels of dissolved oxygen of 0, 8.8 and 37.7 mg/l, respectively. For 37.7 mg/l dissolved oxygen, IPA was degraded rapidly and completely within 1.5 hr. The same results were observed with 8.8 mg/l dissolved oxygen. For the absence of dissolved oxygen, the result showed a slight decrease in the IPA concentration. It was suggested that the dissolved oxygen played an important role in the photocatalytic degradation of IPA since the oxygen molecule can act as an electron scavenger to trap and separate electron from the positive hole that can reduce the e^-/h^+ recombination. Additionally, the oxygen flow serves as the stirring medium to increase the mass transfer in the irradiated systems.

Moonsiri *et al.* (2004) studied the effect of dissolved oxygen on the 4-CP degradation rate and on the intermediate products, with 0.5 g/l sol-gel TiO_2. The solution was aerated with nitrogen in case of without dissolved oxygen, while other experiments were carried out at a very high dissolved oxygen level. It was found that in the absence of dissolved oxygen, the main intermediate products generated during the photocatalytic reaction were hydroquinone (HQ), benzoquinone (BQ) and hydroxyhydroquinone (HHQ). But in the presence of dissolved oxygen, BQ was not generated during the 4-CP degradation. Furthermore, the degradation rate of 4-CP and TOC were much higher than those of the system without dissolved oxygen.

2.3 Immobilization of Photocatalyst

Suspended catalyst reactors may be a more efficient design with respect to quantum yield, and volume efficiency but the separation of the catalyst from reaction mixture presents difficulties. The immobilization system has been investigated because it eliminates the separation problem that always occurs in the suspension system. Immobilization is a process that adheres fine particles of a catalyst on a support such as quartz, glass, and stainless steel by different methods (Byrne *et al.*, 1998) (Table 2.2).

Thangsatjatham (2004) studied the photocatalytic degradation of 4-CP using a multi-stage reactor system, which was 4 connected CSTRs, with titania immobilized on a cylindrical stainless steel mesh by dip-coating technique. For the effect of stage number, the 4-CP degradation increased with the increasing in the number of stage in both cases, with and without TiO_2. The TOC degradation was not significantly affected by the stage of without TiO_2. It could be explained that 4-CP is mainly degraded by the UV-C radiation. For the intermediate degradation, TiO_2 enhanced the intermediate degradation. For the effect of feed flow rate, the 4-CP and TOC degradation increased with decreasing in the feed flow rate because an increase in the feed flow rate corresponded to the decrease in the resident time. In addition, the TOC degradation increased significantly when TiO_2 was added in the system. For the durability of TiO_2 on stainless steel, it was found that the activity of TiO_2 coated on stainless steel was still high after the regeneration.

Balasubramanian *et al.* (2004) studied the activities of immobilized TiO_2 powder films for the photocatalytic degradation of 4-chlorobenzoic acid (4-CBA). The experiments were divided into two parts. First was the comparison of the photocatalytic activity of coatings on stainless steel substrates from different sol-gel methods: the conventional alkoxide sol-gel and the Degussa P25 enriched (PE) alkoxide sol-gel method. It was found that TiO_2 film obtained from the PE sol was more active than the film obtained from the conventional alkoxide sol because the fraction of the rutile phase in the PE alkoxide sol-gel method might enhance the activity of photocatalytic degradation of 4-CBA. The second part was the comparison of the photocatalytic activity of three different catalyst coatings: the glass beads coated with conventional alkoxide sol-gel and PE alkoxide sol-gel, and the commercially Ishihara ST-B01 anatase coated beads. It was found that the activity of the PE alkoxide sol-gel coated beads was much higher than that of the conventional alkoxide sol-gel coated beads because of the same reason above. However, the activity of the PE alkoxide sol-gel coated beads was still lower than that of the Ishihara ST-B01 beads. This could be explained that the attrition of the ST-B01 catalyst during the experiment made catalyst formed a fine suspension in the bulk solution that increased the available surface area and created a pseudo-slurry effect. On the other hand, the PE alkoxide sol-gel that had higher attrition resistance than the ST-B01 catatalyst could only use the surface of the coating on the glass beads to generate the electron and radical, not in the bulk solution.

Table 2.2 Different methods for the immobilization of TiO_2 on solid substrates (Byrne *et al.*, 1998)

Methods of immobilization	**Substrate coated**
Dip coating from suspension	Glass beads, glass rubbing, glass plate, glass fibers, tin oxide coated, glass, siliga gel, sand.
Sol gel related methods	Quartz, optical fibers, glass beads, siliga gel, glass plate, tin oxide coated, glass, N/A (formation of stable gel).
Oxidation of parent metal	
Electrochemical	Titanium
Thermal	Titanium, titanium alloy
Anodisation of $TiCl_3$	Tin oxide coated, glass, Ti, Pt and Au
Electrophoretic coating	Stainless steel
Plasma spray	Titanium alloy
Aerosol powder coating	Hollow glass beads
Sputtering	Glass, quartz
Liquid phase deposition	Glass plate

2.4 Electrospinning Method

He *et al.* (2003) studied the photocatalytic degradation of solid phase polyvinyl alcohol (PVA) by using PVA-Pt/TiO_2 composite nanofiber prepared by electrospinning technique. It was found that the PVA-Pt/TiO_2 composite nanosize fiber prepared by the electrospinning method had diameter about 150-350 nm and the PVA in the fiber could be degraded by photocatalytic oxidation under UV irradiation. The effectiveness of photocatalytic degradation for composite nanofiber was much greater than that for composite film under the same conditions. It was suggested that the degradation became diffusion-limited when the oxidation used up the oxygen faster than it can be supplied by diffusion from the surrounding air in case of composite film.

Madhugiri *et al.* (2004) studied the preparation of TiO_2 fibers by the electrospinning method and its photodecomposition of phenol and formic acid. It was found that the average diameter of the fiber was 600-700 nm before the calcination and it slightly decreased after the calcination at 400°C. Furthermore, the increase in the calcination temperature resulted in the reduction in the surface area. However, after the calcination at 600°C, the fibers were still in the anatase form. The photocatalytic degradation of phenol and formic acid by using TiO_2 fibers calcined at 600°C was compared with TiO_2 (Degussa P25) and TiO_2 (Hombikat UV 100, HK). P25 was the most active catalyst because of its synergistic effect of the rutile/anatase forms that can enhance the activity. The TiO_2 fibers had less activity than that of the HK catalyst because of its bigger size increasing the recombination rate of e^-/h^+ pair.

Viswanathamurthi *et al.* (2004) studied the surface morphology and crystallinity of the fibers of ruthenium doped TiO_2/polyvinylacetate (PVAC) prepared by the electrospinning technique. It was found that the diameter of the fibers was slightly increased by the addition of Ru, but there was no change in the fiber diameter with the increase in the Ru content. With the increase in the calcination temperature, the phase transformation from anatase to rutile occured at the calcination temperature of 1,000°C.

Watthanaarun (2005) studied the effect of the preparation conditions and silicon secondary metal dopant on TiO_2/polyvinylpyrrolidone (PVP) composite nanofibers prepared by the electrospinning technique. For the effects of spinning conditions, increasing the PVP concentration led to an increase in the fiber diameter with broader distribution because of the increase in the viscosity of the spinning solution. With increasing the electrostatic field strength, the fibers appeared to be smaller in diameter with narrower distribution. For the fibers properties, it showed amorphous form before the calcination, and the crystallization and shrinkage occurred during the calcination. It was found that the higher the calcination temperature, the greater the shrinkage. For the effect of Si doping, it can be concluded that the addition of Si as the second metal dopant enhanced the thermal stability of the titania nanofibers during the calcination.