

CHAPTER II

LITERATURE SURVEY

2.1 Photocatalysis

2.1.1 *Principle of Photocatalytic Reaction*

The word photocatalysis is a combination of photo-chemistry and catalysis and implies that light and a catalyst are necessary to bring about or accelerate a chemical transformation.

The catalyst used in this process is normally a semiconductor. In the photocatalytic process, the valence band and conductance band of the semiconductor are important. The valence band has electrons filled in the band but the conductance band has no electrons. These two bands are separated by an energy distance called an energy band gap. When the molecules of semiconductor catalysts are illuminated by light with the appropriate wavelength, which will have an energy equal to or greater than the energy band gap between the valence band and conductance band, the light will activate the electrons in the valence band which will move to the conductance band and leave positive holes at the valence band. The photocatalytic reaction is initiated by oxidation and reduction respectively with positive hole (h^+) and photoexcited electron produced at the catalyst surface. At the solid-liquid interface, electrons can be transferred from the conductance band to an electron acceptor in the solution, this is known as reduction process. The electrons from electron donor can also be transferred to the hole in the valence band to start the oxidation process as shown in Figure 2.1 (Reutergardh and Iangphasuk, 1997).

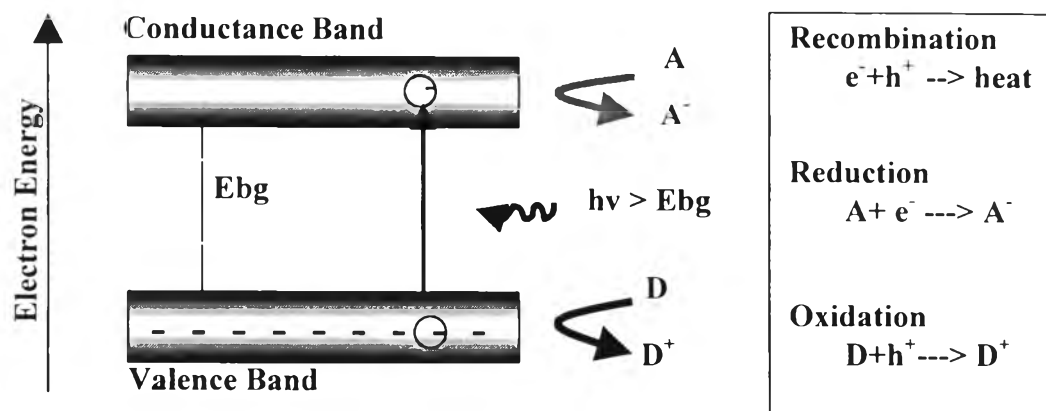


Figure 2.1 Promotion of an electron from the valence band to the conductance band on the illumination of a semiconductor

The separation of these electron-hole pairs can be expected to enhance the reaction rate since the reaction will be inhibited by the recombination of these two charges and generate heat or illuminant. Hence, the recombination process will be avoided by adding some electron scavenger such as oxygen molecule to trap electron out from the positive hole (Stafford *et al.*, 1995).



Normally, the reaction with the organic molecule occurs via the hydroxyl radical, a primary product of the photocatalytic process. Hydroxyl radical is a specie that has a very high oxidation potential and can react with organic molecules rapidly and nonselectively (Haarstrick *et al.*, 1996). This tends to be the main mechanism in photocatalytic oxidation. The hydroxyl radical can be formed by the following reactions.



In addition, direct oxidation can occur by an adsorbed organic substrate at the positive hole of catalyst surface. The environment that serves a good adsorption of organic substrate onto the catalyst surface can enhance the reaction rate.

2.1.2 *Influencing Parameters*

The reaction rate of the photocatalytic process is governed by several parameters such as light intensity, initial concentration of reaction substrate, type of catalyst, amount of catalyst, temperature, pH, dissolved oxygen, and electrolytes. Some parameters have more influence and a small change can have a serious effect on the mechanism and the reaction rate.

i) Light intensity

For the photocatalytic process, the influence of the light intensity can be divided into 2 regions of low and high light intensity. At low intensity, approximately $I_a \leq 5 \cdot 10^{15}$ photons/s, the rate increases proportionally to the light intensity. The reaction can occur efficiently by the absorption of light to form the trapped electron and positive hole pair. At high intensity, approximately $I_a \geq 5 \cdot 10^{15}$ photons/s, the reaction rate is linear dependent on the square root of I_a . Even though the rate of the photocatalysis depends on light absorption, the recombination of the two charges produced from the process is also predominant. However, Preis *et al.* (1997) reported that even though the increasing light intensity will increase the reaction rate, it also lowers the efficiency of the photocatalytic reaction.

ii) Initial concentration of reaction substrate

For this effect, the results from many works showed different trends. Some of the studies showed that the rate of organic degradation increased with

increasing initial concentration. Surprisingly, some studies also that the rate of degradation decreased with increasing initial concentration. Moreover, some reactions showed the initial concentration had no significant effect on the process. Freudenhammer *et al.* (1997) found that the rate of degradation of dichloroacetic acid on fixed TiO₂ was lower at higher initial concentration of reaction substrate while Gupta (1994) showed the rate of PCE degradation increased with increasing initial concentration of PCE. Therefore, the rate or the mechanism of each system is different depending on the reaction substrate, the catalyst used, and also the operational conditions. Hence, the influence of this factor can be observed for each system and indicated by the rate of degradation or production rate.

iii) Type and form of catalyst

The catalyst that is chosen to use in the photocatalytic process should be a semiconductor. The barrier between the valence and conduction energy levels should match the energy gained from the light. Normally, these catalysts would be oxide or sulfide of metals such as TiO₂, CdS, ZnS, and SiO₂. The properties of these types of catalysts are very different from the metals that are widely used as catalysts for other reactions. The metals have an energy band gap narrower than the semiconductor. Eventhough activation of the electron in the valence band of the metal to the conductance band is easier, the recombination process also proceeds easily. This is the reason why the metals are not good photocatalyst.

Besides the type of catalyst, the form and the properties of catalyst are also important. The same catalyst may perform differently because of the different preparation techniques giving different physical and chemical properties such as structure, phase, particle size and surface area (Zeug *et al.*, 1985).

The specific surface area of the catalyst influences on two major processes. One is the reaction of the electron-hole pair with the adsorbed substrate, which increases linearly with surface area so the overall reaction rate should increase. The other is a linear increase of the recombination process with increasing the surface area that will decrease the reaction rate. Thus the reaction rate may be constant, increase or decrease with increasing of surface area, depending on the nature of semiconductor and substrates (Heller *et al.*, 1987).

Based on the previous works, Titanium(IV)oxide was chosen to study in this work. TiO_2 is a popular semiconductor photocatalyst because of its high efficiency in photocatalytic processes and has some advantages: stable, insoluble, corrosion resistant and relatively inexpensive. Some studies showed that TiO_2 did not lose activity when reused so this is another point of benefit (Reutergardh and Iangphasuk, 1997).

The energy band gap of TiO_2 is around 3.0 eV. Therefore, it can be activated by the UV light in the range of 340-350 nm. Generally, there are two different forms of TiO_2 : anatase and rutile. This difference in the form of the catalyst was also studied. The results showed the higher activity was achieved by the use of anatase TiO_2 (Ohtani and Nishimoto, 1993).

iv) Amount of catalyst

Based on several studies including the work done by Matthews (1990), it can be concluded that at a low initial concentration of substrate and a sufficient amount of catalyst, the reaction rate does not increase with increasing the catalyst dosage. However, at a relatively high concentration of substrate and an insufficient amount of catalyst results in low reaction rates. Therefore, an increase in the amount of catalyst will increase the overall reaction rate if the substrate concentration is not limiting. However, increases in the substrate concentration and the catalyst dosage also limit the light

penetration. This will limit the reaction rate due to lower flux protons from the light available to supply the needed energy. Hence, the optimum amount of the catalyst for each system should be determined.

v) Temperature

An increase in temperature can enhance the reaction rate. This may be attributed to the increasing collision frequency of reaction molecules and decreasing reaction activation energy (Serpone and Pelizzetti, 1989).

Normally, the relationship between the temperature and the reaction rate follows the Arrhenius equation:

$$k = A e^{-\frac{Ea}{RT}} \quad (2.6)$$

$$\ln k = -\frac{Ea}{RT} + \ln A \quad (2.7)$$

where

- k = reaction rate constant, min⁻¹
- A = the frequency factor or pre-exponential factor, min⁻¹
- Ea = activation energy, J mole⁻¹
- R = constant = 8.3143 JK⁻¹mole⁻¹
- T = absolute temperature, K

From this relationship, the value of Ea can be determined by plotting the logarithm of rate constant versus the reciprocal of absolute temperature. The slope of the straight line is equal to -Ea/R and the value of Ea can then be calculated.

vi) Initial pH

The acidity and alkalinity have an effect on the degradation of organic molecules since the efficiency of photocatalytic process depends on the adsorption of the substrate on the surface of the catalyst and also the concentration of the hydroxyl radical (OH). pH influences the surface charge

of the catalyst and the form of the substrate consequently, the adsorption of substrate onto the catalyst surface will change with pH. Hence, the trend of this effect depends directly on the nature of the catalyst and substrate. Besides the adsorption capacity, pH also has an effect on the energy band gap of the catalyst by 0.059mV/pH unit (Stafford *et al.*, 1995). For alkaline region, the reaction rate will be enhanced by increasing the hydroxy ion (OH⁻) concentration that will transform to become the hydroxyl radical (OH[•]) (Tanaka and Saha, 1994).

vii) Dissolved oxygen

The dissolved oxygen is another factor that is considered as a rate enhancing parameter since oxygen plays an important role in the separation of e⁻/h⁺ pair. The oxygen will be an electron scavenger that traps electron (e⁻) out from the positive hole (h⁺) to prevent the recombination process. Based on several previous works, it has been concluded that the reaction rate can be enhanced when the dissolved oxygen in the system increases. Besides the above reason, the oxygen itself can act as a strong oxidant to react directly in the system (Ku and Ho, 1990). Table 2.1 shows the values of oxidation potentials of some oxidants including oxygen molecule and hydroxyl radical.

Table 2.1 Oxidation potentials of some oxidants (US EPA, 1993)

Oxidant	Oxidation potential (Volt)	Relative oxidation potential
Chlorine	1.36	1.00
Perhydroxyl radical	1.70	1.25
Hydrogen peroxide	1.78	1.31
Ozone	2.07	1.52
Oxygen	2.42	1.78
Hydroxyl radical	2.80	2.06

However, for some reactions, the oxygen may decrease the rate of degradation because the intermediate from the oxidation process will compete and inhibit the reaction. Ku and Ho (1990) reported that the removal of phenol decreased slightly with increasing the dissolved oxygen due to the formation of peroxide free radicals which compete with phenols for UV irradiation in order to carry out further reaction.

2.2 Catalyst Preparation by Microemulsion Technique

Ultrafine particles of various metals have a number of advantages in industrial applications such as catalysis, photographic emulsions and precursors of ceramics. Semiconductor ultrafine particles are especially important because of their optical functionality. For example, nanometer-sized semiconductor particles have a larger band gap than bulk semiconductor owing to quantum size effects (Brus, 1984).

Several techniques have been developed for the synthesis of various types of nanoparticles. These include i) gas-phase techniques such as gas evaporation, laser vaporization and laser pyrolysis ii) vacuum synthesis techniques of sputtering, laser ablation and ionized beam deposition iii) liquid-phase techniques of precipitation from homogenous solution, sol-gel processing, and freeze drying (Pillai and Shah, 1997).

Microemulsion technique is a novel method to prepare ultrafine particles because of the ability to control the size of particle formed and prevent the aggregation (Pileni, 1993). Microemulsion is the term referring to a suspension of liquid droplets in another liquid. If the aqueous solution or polar substance is added to an oil phase containing a surfactant, aqueous solution can then be solubilized in an oil phase. A microemulsion may be defined as a thermodynamically stable isotropic dispersion of two immiscible

liquids consisting of microdomains of one or both liquids in the others, stabilized by an interfacial film of surface-active molecules. For water in oil microemulsion, the aqueous phase is dispersed as nanosize droplets (typically 5 to 25 nm. in diameter) surrounded by a monolayer of surfactant molecules in the continuous hydrocarbon phase. These aqueous droplets collide, coalesce and break apart continuously resulting in continuous exchange of solute content. The reaction to produce particles occurs in the aqueous droplet that the size and the shape of particles synthesized can be controlled.

The procedure to prepare the ultrafine particles by microemulsion technique starts with two identical W/O microemulsions. One system dissolves reactant A, the other one dissolves reactant B in the aqueous core. After mixing of these two microemulsion systems, reactant A and B come to react each other due to collision and coalescence of the droplets and the particles are produced. This process is illustrated in Figure 2.2. However, the way to achieve this preparation process can be done by another well-known procedure. That is the method of adding of a reducing agent or precipitating agent into the microemulsion contained the reactant in the water core. This was first reported in the synthesis of Pd, Rh, and Pt by reducing the corresponding salts in the water core of W/O microemulsion with hydrazine or hydrogen gas (Pillai and Shah, 1997).

In the preparation techniques, there are several factors affecting the particle size formed such as type of surfactant, organic substance, water content, and operating conditions. The dependency of the particle size on the water content is a difficult problem. In case the particle size is formed by the instantaneous reaction initiated by the rapid mixing of two reverse micellar solution, e.g. CdS and ZnS, the particle size increases with the size of micelles. In other case, the metallic particles prepared by the addition of reducing agent shows different behavior. With increasing water content, the particle size decreases and then increases through a minimum size. Further,

some particle such as SiO_2 and Au grow much larger than the size of micelles but their size depends on the water content. Therefore, the use of small water content solution is an effective method to obtain small particles but it does not apply to some particles (Hirai *et al.*, 1993).

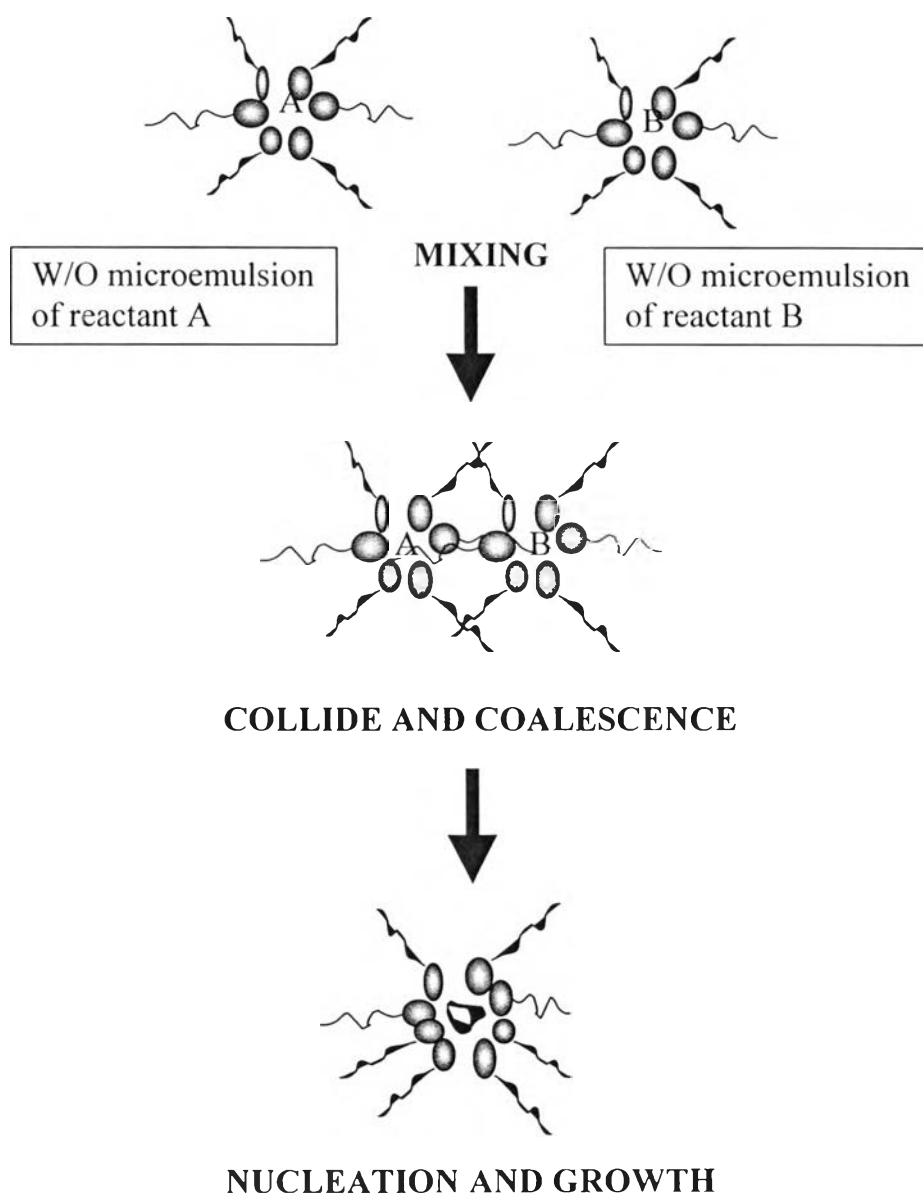


Figure 2.2 Schematic representing the formation of ultrafine particle by microemulsion technique (Lopez-Quintela *et al.*, 1997)