



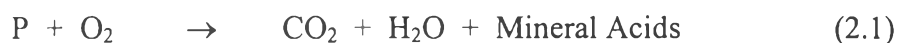
CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Principle of Photocatalysis Reactions

The word “photocatalysis” comes from photochemistry and catalysis. So, the photocatalytic process implies that light and a catalyst are used together to accelerate chemical transformations. The difference between conventional catalysis and photocatalysis is the mode of activation of the catalyst, in which the thermal activation is replaced by a photonic activation (Herrmann, 1999).

The photocatalytic process, part of a process known as Advanced Oxidation Technologies (AOTs), is a promising alternative because this process can oxidize a number of nonbiodegradable organics into less toxic compounds. The products from this process are mostly carbon dioxide, water and other inorganic compounds. The organic compounds containing phosphorus, sulfur and halogen heteroatom may be oxidized quantitatively yielding phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) and halide (X), respectively. The common characteristic of all AOTs is the generation of a very reactive free radical principally hydroxyl radical (Litter, 1999). The overall process for the photocatalysis reaction of waste materials (P), sensitised by semiconductors (SC) is shown (De Lasa *et al.*, 1992).



The basic principle of photocatalysis can be described as follows. A semiconductor (SC) is characterized by an electronic band structure that are occupied valence band (vb) and unoccupied conductance band (cb). These two bands are separated by the energy gap called the “band gap” (E_{bg}). When the semiconductor is illuminated with light that has energy higher or equal to the band gap, an electron from the vb is promoted to the cb with the simultaneous generation of a hole (h^+) in the vb as illustrated in Figure 2.1.

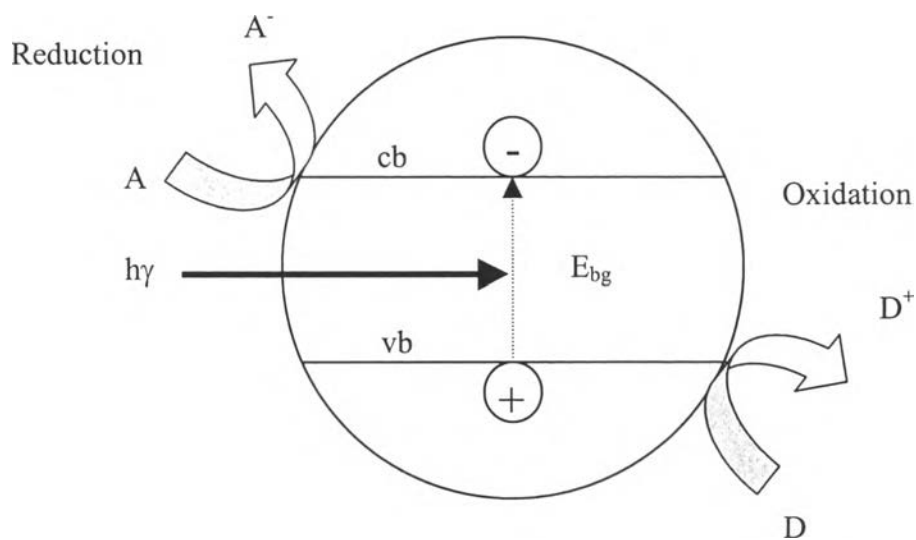


Figure 2.1 Promotion of an electron from the valence band to the conduction band on illumination of a semiconductor (Litter, 1999).

When a solution containing a semiconductor absorbs a photon ($h\nu$) of a suitable wavelength, possible reactions are shown in the following (Robertson, 1996):



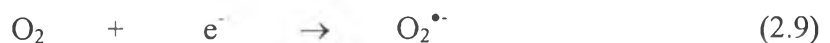
The electron and hole pair may recombine on the surface or in the bulk of the particles in a few nanoseconds resulting in the generation of heat or can be trapped in surface state where they can react with other species that are adsorbed or close to the surface of particles. For example, if an electron donor or species D is adsorbed on the surface, it will react with the hole and the oxidation reaction occurs. On the other hand, if an electron acceptor or species A is adsorbed on the surface, it will receive an electron and the reduction reaction occurs. The energy level at the bottom of the cb is the reduction potential of photoelectron and the energy level at

the top of the vb determines the oxidizing ability of the photohole. From thermodynamic points of view, adsorbed species can be reduced photocatalytically by the cb electrons if they have redox potentials more positive than the flat band of the cb and can be oxidized by vb holes if they have redox potentials more negative than the flat band of the vb (Litter, 1999).

For the photocatalytic oxidation of organic molecules in aqueous solution, there are two possible mechanisms when a semiconductor is illuminated with photon energy greater or equal to its band gap energy. There are direct hole oxidation and OH^\bullet oxidation (Ilisz and Dombi, 1999). Normally, the OH^\bullet oxidation tends to be the main mechanism in the photocatalytic oxidation. For the direct hole oxidation, the photohole reacts directly with the adsorbed organic molecules as shown in equation (2.3) while for the OH^\bullet oxidation, the photohole reacts with surface hydroxyl group (OH^-) or adsorbed water to produce hydroxyl radical (OH^\bullet). This hydroxyl radical has high oxidation potential. It can react rapidly and non-selectively with most organic compounds and convert them mostly into carbon dioxide, water and other inorganic compounds (De Lasa *et al.*, 1992). The OH^\bullet oxidation reactions are as follows:



The recombination must be avoided because it inhibits the oxidation reaction. Adding some electron scavengers such as oxygen molecules will delay the recombination since they can trap electrons out from the positive hole and transform into superoxide radical ion ($\text{O}_2^{\bullet-}$) and lead to the additional formation of hydroxyl radical (Litter, 1999).



It has been pointed out that both H₂O and O₂ are essential species in the photocatalytic process. Photocatalytic oxidation of 4-CP does not occur in the absence of either H₂O or O₂ or both (De Lasa *et al.*, 1992).

2.2 Types and Forms of Photocatalysts

2.2.1 Types of Semiconductors

A semiconductor used as photocatalyst should be an oxide or sulfide of metals such as TiO₂, CdS and ZnO. The energy band gap of the photocatalyst should match the energy gained from a light source. The valence band, conductance band, band gap and band gap wavelength of some common semiconductors are shown in Table 2.1.

TiO₂ is a popular photocatalyst because the band gap is considerably high around 3.0 eV. It can be activated in the near ultraviolet light (~ 380 nm). Other types of semiconductors that can be used as photocatalysts such as ZnO or CdS may not be applicable due to their toxicity. Moreover, ZnO is corroded by illumination in aqueous solution and toxic Zn²⁺ is found (De Lasa *et al.*, 1992). CdS also has the toxicity problem due to CdS photocorrosion (Reutergardh and Iangphasuk, 1997). TiO₂ is more stable and insoluble in aqueous solution than ZnO and CdS. It has been shown that TiO₂ does not lose its activity when reused (De Lasa *et al.*, 1992). Apart from its highly corrosive resistance, TiO₂ is considerably inexpensive. Therefore, TiO₂ is suitable for the photocatalytic process. Generally, there are three different forms of TiO₂ namely anatase, brookite and rutile. TiO₂ in the anatase form has been observed to be active and stable over very long irradiation times (Cheng *et al.*, 1995).

Table 2.1 The band positions of some common semiconductor photocatalysts (Robertson,1996).

Semiconductor	Valence band (eV)	Conductance band (eV)	Band gap (eV)	Band gap wavelength (nm)
TiO ₂	+3.1	+0.1	3.0	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

2.2.2 Supported TiO₂

Many investigations have been carried out to observe the effect of a variety of supporting materials for the degradation of organic compounds. In general, it is assumed that good supporting materials for TiO₂ as photocatalyst should have the following attributes: (1) to be transparent to UV radiation, (2) to favor strong surface chemical-physical bonding with the TiO₂ particles without negatively affecting their activity, (3) to offer a high specific surface area, (4) to have a good adsorption capability for the organic compounds to be degraded, (5) to be in a physical configuration which favors the liquid-solid separation, (6) to allow reactor designs that facilitate the mass transfer processes and (7) to be chemically inert (Pozzo *et al.*, 1997).

Catalytic activity of the supported TiO₂ is affected by several factors. For example, the change in the TiO₂ energy band structure resulted from the chemical bond with the support. In addition, the alteration of the catalyst crystal structure is resulted from the temperature treatment after loading. The decrease in

the catalyst surface area are caused by catalyst particle agglomeration, catalyst support binding, and catalyst particle trapping inside support pores (Pozzo *et al.*, 1997).

Adderson and Bard (1997) found that the $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst for photocatalytic decomposition of salicylic acid gave improved activity relatively to pure TiO_2 . It was suggested that TiO_2 behaved as the photoactive center, e.g., generating hydroxyl radicals under irradiation while the Al_2O_3 provided better adsorption sites in the vicinity of the TiO_2 .

Jung and Park (2000) studied the effect of adding SiO_2 into TiO_2 prepared by the sol-gel method on the photoactivity of trichloroethylene decomposition. The SiO_2 mole fraction was varied from 0.05 to 0.6. The photoactivity of $\text{SiO}_2/\text{TiO}_2$ increased with increasing SiO_2 content and reached the maximum level at 30 mol% of SiO_2 in TiO_2 . This highest activity was five times higher than Degussa P25. The addition of SiO_2 helps increasing the thermal stability of TiO_2 which, in turn, suppresses the phase transformation of anatase to rutile when the calcination temperature increases. The surface area of $\text{SiO}_2/\text{TiO}_2$ increased with increasing the silica content. However, the average pore size and pore volume had the maximum values at 30 mol% of SiO_2 . It was suggested that the high porosity and large pore size of $\text{SiO}_2/\text{TiO}_2$ facilitate the mass transfer of reactants leading to the significant improvement of the catalytic activity as compared to pure TiO_2 . The photoactivity of $\text{SiO}_2/\text{TiO}_2$ was also improved simultaneously with increasing both the surface area and the crystallinity.

Chun *et al.* (2001) studied the photocatalytic degradation of azo dyes using $\text{TiO}_2/\text{SiO}_2$ prepared by the impregnation method. For $\text{TiO}_2/\text{SiO}_2$, the catalyst with a small particle size of SiO_2 had a higher photoactivity than that of the catalyst with a large particle size of SiO_2 . The optimum composition of the $\text{TiO}_2/\text{SiO}_2$ catalyst was 30 wt% $\text{TiO}_2/\text{SiO}_2$. The reaction rate of 30 wt% $\text{TiO}_2/\text{SiO}_2$ was lower than that of Degussa P25, but three times higher than that of B- TiO_2 (predominantly anatase, Beijing Chemical Factory). However, 30 wt% $\text{TiO}_2/\text{SiO}_2$ had an advantage over Degussa P25 by enhancing the precipitation rate.

2.2.3 Metal- Loaded TiO₂

Brezova *et al.* (1997) studied the phenol decomposition using different metal-loaded TiO₂ photocatalysts prepared on glass fibers by the sol-gel method. The metals used in this study were Li⁺, Zn²⁺, Cd²⁺, Ce³⁺, Cr³⁺, Co³⁺, Fe³⁺, Al³⁺, Mn²⁺ and Pt⁰ and all metals were loaded at 5 mol%. The presence of metals such as Li⁺, Zn²⁺, Cd²⁺ and Pt⁰ improved the photoactivity of the TiO₂ layer. On the other hand, the presence of Ce³⁺, Cr³⁺, Co³⁺, Fe³⁺, Al³⁺ and Mn²⁺ in the TiO₂ layer supported on glass fibers had a detrimental effect on the photoactivity of phenol decomposition.

Blazkova *et al.* (1998) studied the photocatalytic decomposition of phenol by varying % Pt loading on TiO₂. The platinum loading was varied from 0.5-5.0 mol% Pt⁰: Ti⁴⁺. The best results were obtained from TiO₂ with 1.25 mol% Pt. For the concentration of Pt ≥ 5 mol%, Pt has a detrimental effect on the photocatalyst activity. The major role of Pt on TiO₂ is to accelerate the superoxide radical anion O₂^{•-} formation and consequently decreases the recombination. The increase in Pt loading to a certain level causes a decrease in the electron transfer of photoelectron from the semiconductor to metal particles resulting in increasing recombination and lowers the photocatalytic activity for the phenol decomposition.

Phuaphromyod (1999) studied the photocatalytic degradation of isopropyl alcohol using Pt, TiO₂, and Pt/TiO₂. Pt or TiO₂ alone showed a low activity but Pt/TiO₂ had a much higher activity for the degradation of isopropyl alcohol.

Tharathonpisutthikul (2000) studied photocatalytic degradation of 4-CP by using TiO₂, Pt/TiO₂, TiO₂-SiO₂ and Pt/TiO₂-SiO₂ prepared by the sol-gel method. It was found that addition of small amount of Pt into TiO₂ improved the catalyst activity and the highest activity was obtained with 1% Pt/TiO₂. For TiO₂-SiO₂ catalyst, the highest activity was achieved at 10% SiO₂-TiO₂ because of its highest adsorption capacity. For Pt/TiO₂-SiO₂ with 1 % Pt and 10 %SiO₂, although 1 % Pt or 10 % SiO₂ alone in TiO₂ could improve the catalyst activity, the synergistic effect of adding both 1 % Pt and 10 % Si was not observed due to the agglomeration of the catalyst, which, in turn, lowered the catalytic activity.

2.3 Parameters Influencing the Rate of Organic Degradation

2.3.1 Light Source

For the photocatalytic process, effect of light intensity can be divided into 3 regions. At low intensity, the degradation rate is first order with respect to light intensity. At intermediate intensity, the reaction rate increases with the square root of intensity. An increase in intensity always increases the reaction rate until the reaction is mass transfer limited. Therefore, at high intensity, the reaction rate is constant due to limitation of mass transfer (De Lasa *et al.*, 1992).

Stafford *et al.* (1997) investigated the effect of light wavelength on the rate of photocatalytic degradation of 4-CP. In this experiment, two lamps, a 450 W medium pressure mercury lamp ($\lambda > 340$ nm) and an 8 W black light lamp ($\lambda_{\text{max}} = 350$ nm), were used. The other parameters were kept constant. With the 8 W black light lamp, the rates were slower and the maximum concentration of intermediates was lower because of the lower light intensity. It was reported that when a lamp with lower intensity was used, subsequent reactions of intermediates occurred at relatively faster rates than that of the degradation of 4-CP. Therefore, the rate of mineralization was more rapid. This enhancement rate of mineralization at the lower light intensity may occur because the slower rate of hole production allows the other species in solution to come into adsorption equilibrium with TiO_2 . The other reason is that when the lower wavelength is used, electrons adsorb more energetic photons and the higher energy electrons are less likely to recombine. Therefore, the photoactivity increases with decreasing light wavelength.

Blazkova *et al.* (1998) studied the effect of light sources on the phenol degradation using Pt/TiO_2 immobilized on glass fibers. The four standard emission lamps were used as the irradiation sources with maximum intensities at 320, 350, 410 nm and white lamp resembling the solar spectrum. The highest photoactivity was obtained for the source with the maximum intensity at 320 nm. This experiment was consistent with the results published by Stafford *et al.* (1997). The photocatalytic activity significantly increased with decreasing wavelength. Although the white lamp resembling the solar spectra had lower efficiency, it showed that the prepared Pt/TiO_2 catalysts may be used for solar applications.

Herrmann *et al.* (1999) studied the photocatalytic degradation of 4-CP using the synergistic effect between TiO₂ and activated carbon (AC) in aqueous suspension. The light source in this study was solar light. 4-CP adsorption had been performed at 20 °C on Degussa P25 (50 mg), on activated carbon (10 mg) and on a suspended mixture of them with the same respective masses. The adsorption isotherms were determined assuming a Langmuir isotherm. The amount of 4-CP adsorbed on TiO₂-AC was slightly smaller than on pure AC. There was no addition of the adsorption capacities of both solids when they were mixed together. The addition of AC to TiO₂ obviously created a kinetic synergistic effect in the 4-CP disappearance, with an increase of the rate constant by a factor of 2.4. The synergistic effect was ascribed to an extended adsorption of 4-CP on AC followed by a transfer to TiO₂ where it was photocatalytically degraded. The beneficial synergistic effect due to the addition of AC to TiO₂ also decreased the release of intermediate products in the solution.

2.3.2 Initial Concentration

The results from several works showed different trends of the effect of initial concentration on organic degradation. Some of the studies showed that the rate of organic degradation increased with increasing initial concentration. Surprisingly, some studies reported that the rate of degradation decreased with increasing initial concentration. Moreover, some reactions showed that the initial concentration had no significant effect on the process. Freudenhammer *et al.* (1997) found that the rate of dichloroacetic acid on fixed TiO₂ was lower with a higher initial concentration of reaction substrate while Theurich *et al.* (1996) showed the rate of 4-CP degradation increased with increasing initial concentration of 4-CP. Besides, Reutergardh *et al.* (1997) found that as the reactive black 5 (RB5) concentration increased, the quantities of intermediates increased as well. For competing through side reactions with the parent dye decomposition, an increase in dye concentration affected the light penetration into the solution. Therefore, at high initial dye concentrations, the optical density in the solution was lower and fewer photons reached the catalyst's surface.

Theurich *et al.* (1996) studied the photocatalytic degradation of 4-CP in Degussa P25 suspensions. The concentration of 4-CP was varied from 0.2 to 10 mM. The degradation rate was found to be a function of the initial 4-CP concentration, at least in a certain range, when the other parameters were kept constant. The degradation rate was the function of 4-CP concentration increasing up to 5 mM and remaining constant for the higher 4-CP concentration. One possible explanation for this behavior was given that the adsorption of the substrate molecule was rate limiting. This adsorption was described by the Langmuir-Hinsherwood (L-H) equation,

$$\frac{-d[4-CP]}{dt} = \frac{kK[4-CP]}{1 + K[4-CP]} \quad (2.12)$$

where $d[4-CP]/dt$ is the rate of 4-CP degradation, k is the reaction rate constant, K is the adsorption coefficient of 4-CP and $[4-CP]$ is the concentration of 4-CP. For a high concentration of the pollutant, where saturation coverage of the TiO_2 surface is achieved ($K [4-CP] \gg 1$), the L-H equation simplifies to a zero-order rate equation.

$$\frac{-d[4-CP]}{dt} = k \quad (2.13)$$

For a very low concentration of 4-chlorophenol ($K [4-CP] \ll 1$), the L-H equation changes into a pseudo first-order kinetic law.

$$\frac{-d[4-CP]}{dt} = k'[4-CP] \quad (2.14)$$

with $k' = kK$ being the pseudo first order rate constant. Therefore, at a high initial concentration, the 4-CP degradation obeys the zero order kinetics while the degradation kinetics at the low concentration can be interpreted as an example of the first order kinetics.

2.3.3 Amount of Catalyst

Based on several studies including the work carried out by Matthews (1990), it can be concluded that at a low initial concentration of a substrate and a

sufficient amount of a catalyst, the reaction rate does not increase with increasing the catalyst dosage. However, at a relatively high concentration of the substrate and an insufficient amount of a catalyst results in low reaction rates. Therefore, an increase in the amount of catalyst increases the overall reaction rate if the substrate concentration is not limiting. In addition, Herrmann (1999) found that the concentration of intermediates decreased with increasing the amount of TiO₂. Reutergardh *et al.* (1997) suggested that the reaction rate was enhanced due to the increase of active sites. Limiting factors here were light scattering and reduction in light penetration through the solution caused by the increase in the suspended catalyst. For applications, this optimum mass of catalyst has to be chosen in order to avoid excess of catalyst and to ensure a total absorption of efficient photons.

Stafford *et al.* (1997) studied the photocatalytic degradation of 4-CP by varying the amount of TiO₂ in the solution. Photocatalytic degradation of 250 μ M of 4-CP was carried out with 0.05 – 1.00 g/l Degussa P25 under UV irradiation. The initial rate of 4-CP removal increased slightly with increasing TiO₂. It was explained that at a lower catalyst loading, much of the light was transmitted through the slurry while at a higher catalyst loading, most photons were adsorbed. The decrease in the rate of 4-CP decomposition at the lower catalyst loading was explained by the fact that more light was transmitted through the reactor and the transmitted light was not fully utilized in the reaction. An increase in the TiO₂ loading reduced the concentration of the intermediates and increased the rate of the oxygen consumption. The results indicated that there was more rapid mineralization at the higher TiO₂ loading. But the rate of 4-CP degradation did not always increase with increasing the amount of the catalyst in the slurry photocatalytic processes. The optimum catalyst dosage was reported to be in the range from 0.15 to 8 g/l for different photocatalytic systems and photoreactors. Even for the same catalyst (Degussa P25), a significant difference in the optimal catalyst dosage in the range from 0.15-2.5 g/l was reported (Chen and Ray, 1999).

Tharathonpisutthikul (2000) found that the amount of the catalyst had little effect on the 4-CP degradation rate especially at the first 30 minutes. On the contrary, the TOC reduction rate increased significantly with increasing the amount of TiO₂ and the optimum amount of TiO₂ catalyst was 0.7 g/l.

2.3.4 pH of Solution

As we know that the efficiency of photocatalytic processes depends on the adsorption capacity of the pollutant on the surface of the catalyst and also the concentration of the hydroxyl radical (OH^\bullet). The pH generally influences a semiconductor in an electrochemical system by shifting the valence and conduction bands. Additionally, the charge of the semiconductor surface is governed by the solution pH resulting in affecting the adsorption capacity of the pollutant. Since in photocatalysis the adsorption of a pollutant is necessary for its degradation, a change in pH can lead to a change of the degradation rate and of the amount and concentration of intermediates (Theurich *et al.*, 1997).

The solution pH affects not only the surface properties of TiO_2 but also the formation of hydroxyl radicals. Improvement of the reaction rate under alkaline condition can be attributed to the increase of hydroxyl ions, which induces more hydroxyl radical formation. Under acidic condition, the perhydroxyl radical HO_2^\bullet is formed by the protonation of the superoxide radical, equation (2.15). Consequently, the perhydroxyl radical can form hydrogen peroxide, equation (2.16), which in turn gives rise to the hydroxyl radical equations (2.17)–(2.18) (De Lasa *et al.*, 1992). Furthermore, under both acidic and basic conditions, the oxidation of surface bound OH^- and H_2O by h^+ to form the hydroxyl radical was thermodynamically possible (Reutergardh *et al.*, 1997).



Theurich *et al.* (1996) studied the effect of pH on the photocatalytic degradation of 4-CP. From this study, the pH of the solution was varied from 3-11. In each experiment, the pH was maintained constantly throughout the irradiation. It was obvious that the 4-CP degradation rate was hardly influenced by the pH but a larger amount and higher concentration of intermediates were found at a higher pH.

The number and concentrations of intermediates were reached a maximum at pH 9. The results presented in this study showed that it was very important to select the optimum pH for the photocatalytic degradation process to combine a high efficiency with the suppression of the formation of toxic intermediates. However, Tharathonpisutthikul (2000) found that the initial pH of 4-CP solution did not have a significant effect on both the degradation and TOC decreasing rates.

2.3.5 Dissolved Oxygen

Blazkova *et al.* (1998) observed the effect of oxygen on the degradation of phenol using Pt/TiO₂ immobilized on glass fibers. It was found that the phenol half-life decreased linearly with increasing the oxygen flow in the photocatalytic degradation of phenol. However, the oxygen flow higher than 5 dm³/min under the given conditions damaged the photocatalyst quality.

Phuaphromyod (1999) studied the effect of dissolved oxygen on the photocatalytic degradation of isopropanol. The experiments were carried out by flowing nitrogen, air and oxygen into the isopropanol solution to obtain different levels of dissolved oxygen 0, 8.8 and 37.7 mg/l, respectively. For the saturated dissolved oxygen of 37.7 mg/l, isopropanol was degraded rapidly and completely within 1.5 hours. The same results were observed with 8.8 mg/l of dissolved oxygen. When nitrogen was bubbled into the solution to obtain zero dissolved oxygen, the results showed a slight decrease in the isopropanol concentration. It was suggested that the dissolved oxygen had an important role in the photocatalytic degradation of isopropanol since the oxygen molecule can act as an electron trap. The trap separated electrons from the hole and the recombination process was reduced. Hence, the photocatalytic activity increases with increasing the dissolved oxygen. In addition, the oxygen flow served as the stirring medium to enhance the mass transfer rates in the irradiated system.

Ilisz and Dombi (1999) investigated the photodegradation of phenol by focusing on the influence of charge-trapping species (O², Ag⁺, and H₂O₂). It was found that in the presence of dissolved oxygen, the OH[•] oxidation dominated and catechol, hydroquinone and 1,2,4, trihydroxybenzene were formed. In the presence of Ag⁺, the direct oxidation dominated and only p-benzoquinone was identified,

while with H₂O₂, both OH[•] and direct oxidation dominated. Moreover, the authors reported that in the dissolved oxygen concentration range of 2.1x10⁻⁶-1.25x10⁻³ mol/dm³, the oxygen had no effect on the product distribution.

2.3.6 Temperature

The overall process of the photocatalytic degradation is usually not very temperature sensitive. The dependence of the degradation rate on temperature is reflected by the low activation energy compared with the ordinary thermal reactions. For example, the activation energy of photocatalytic oxidation of acetone over Pt/TiO₂ is 10-13 kJ/mol while the activation energy of thermal acetone oxidation is 84 kJ/mol (Vorontsov *et al.*, 2000). The influence of temperature is not significant because of the low thermal energy ($kT = 0.026$ eV at room temperature) that has almost no contribution to the activation of TiO₂, which has a high band gap energy (3.2 eV). Therefore, there is no need to heat the system and so it makes the photocatalytic process is very attractive for all aqueous media, especially for water purification, because there is no need to waste energy in heating water, which has a high heat capacity (Chen and Ray, 1999).

2.4 The Sol-Gel Method

TiO₂ can be synthesized by several different methods: (1) inert gas condensation, (2) flame synthesis by TiCl₄ oxidation, (3) oxidation-hydrothermal synthesis of metallic Ti, and (4) hydrolysis precipitation of titanium alkoxides or chlorides. The sol-gel process provides excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures. Besides, it is capable of producing photocatalysts with a high surface area. It involves the formation of a metal-oxo-polymer network from molecular precursors such as metal alkoxides or metal salts. The sol-gel process consists of the hydrolysis of metal alkoxides and subsequent polycondensation as follows:





Where M = Si, Ti, Zr, Al, and R = alkyl group. The relative rates of hydrolysis and polycondensation strongly influence the structure and properties of the resulting metal oxides. Typically, sol-gel-derived precipitates are amorphous in nature, requiring further heat treatment to induce crystallization. The calcination process frequently gives rise to particle agglomeration and grain growth and may induce phase transformation (Wang and Ying, 1999).

Factors affecting the sol-gel process include the reactivity of metal alkoxides, pH of the reaction medium, water to alkoxide ratio, reaction temperature, and nature of solvent and additive. The water to alkoxide ratio governs the sol-gel chemistry and the structural characteristics of the hydrolyzed gel. High water to alkoxide ratios in the reaction medium ensure a more complete hydrolysis of alkoxides, favoring nucleation versus particle growth. In addition, an increase in water to alkoxide ratio leads to reduce the crystallite size in the calcined catalyst. An alternative approach to control the sol-gel reaction rates involves the use of acid or base catalysts. It was reported that for a system with the water to alkoxide ratio of 165, the addition of HCl resulted in the reduction of the crystallite size from 20 to 14 nm for materials calcined at 450 °C. Besides, a finer grain size and a narrower pore size distribution with a smaller average pore diameter were also attained for the sample synthesized with HCl (Wang and Ying, 1999). The size of alkoxy groups in alkoxides also plays an important role in controlling the particle size. The titanium alkoxide contains bulky alkoxy groups such as titanium amiloxide reduces the hydrolysis rate, which is advantageous for the preparation of fine colloidal particles (Murakami *et al.*, 1999).

Piscopo *et al.* (2001) compared the activity between the commercial TiO₂/P25 manufactured by frame hydrolysis and a synthetic photocatalyst, TiO₂/SG prepared by the sol-gel method. It was found that the TOC evolution of the benzamide solution during the photodegradation was different between both photocatalysts. There was a slower decrease of TOC in the case of TiO₂/SG since

the adsorption capacity was lower in the case of TiO₂/SG. Furthermore, the TOC variation depended on the intermediate degradation rate but not on the benzamide.