



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Basic Principles of Plasma

Gaseous plasma consists of negatively and positively charged particles in an otherwise neutral gas. The positively charged particles are mostly cations but the negatively charged particles can be either electrons or anions. The neutral species may be the mixture of free radical species with stable neutral gases. Plasma possesses two important properties (Eliasson and Kogieschatz, 1991).

1) Quasi-neutral property

The total density of negative charge carriers must be equal to the total density of positive charge carriers.

2) Interaction with electromagnetic fields

Plasma can have some interactions upon the applying of an electromagnetic field due to the fact that they consist of charged particles.

Normally, plasma can occur in all states (Nasser, 1971). Plasma in solid is called solid-state plasma while plasma generated in the liquid and gaseous states does not have any specific names. Only gaseous plasma is shortly called as “plasma”. There are many differences between plasmas and gases. Their differences include pressure, distributions of charged-particle density in the entire plasma volume and temperature.

2.2 Generation of Plasma

There are several means of generating charged particles to produce plasmas, e.g., collisions between cosmic rays and gases in atmospheric layers. However, in the present study, an externally intense electric field is applied across metal electrodes to cause the reduction in its “potential barrier” and thus the energy that each electron requires for leaving the metal surface. The most interesting phenomena on the metal surface under an extremely high

electric field is that many electrons can leak from the surface despite its less kinetic energy to overcome the potential barriers. This phenomenon is known as “tunnel effect”. And then the plasma was first generated by the collisions between the electrons emitted from the surface of metal electrodes and the neutral molecules. This process of plasma generation is normally known as the “field” emission process.

The electrons liberated from the metal surface will immediately be accelerated to move corresponding to the direction of the electric field and then can collide with any neutral gaseous particles in their vicinity to form the ionized gases with an additional set of electrons. Accordingly, these electrons can further move and collide with other species. As a result, a large quantity of electrons including the excited atoms and molecules, ions and radicals can be formed in the bulk of the gases within a very short period of time after the application of electric field has been started. Many active species can initiate the chemical reactions leading to the production and destruction of the chemical species (Kruapong, 2000). Table 2.1 shows some important collision mechanisms.

The combined steps of the field emission process among these plasma species and the collisions between the species and the electrode surfaces are referred to as “electric discharges” phenomena.

Plasma is divided into two types. The first type is “thermal plasma” or “equilibrium plasma”. In this type, the temperature between gas and electron are approximately equal, which is close to thermodynamic equilibrium (Harndumrongsak, 2002). An essential condition for the formation of this plasma is sufficiently high working pressure. An example of this plasma is arc discharge.

The second type is “non-thermal plasma” or “non-equilibrium plasma”, which is characterized by low gas temperature and high electron temperature. Those typical energetic electrons may have energy ranged from 1 to 10 eV, which corresponds to the temperature of about 10,000 to 100,000 K (Rosacha *et al.*, 1993). This plasma can be classified into several types depending upon their generation mechanism, their pressure range and the

electrode geometry (Eliasson *et al.*, 1987). Examples of this plasma are radio frequency discharge, microwave discharge, glow discharge, dielectric-barrier discharge, and corona discharge, which is used in this study.

The electrode geometry in corona discharge is a pair of wire and plate metal electrodes oriented in a perpendicular direction to each other, Corona discharge can solve the instability of the glow discharge at high pressure.

Table 2.1 Collision mechanisms in the plasma (Nasser, 1971)

Collision	Reaction
Elastic Collision	$e^- + A \longrightarrow e^- + A$
Excitation	$e^- + A \longrightarrow e^- + A^*$
Ionization	$e^- + A \longrightarrow 2e^- + A^+$
Attachment	$e^- + A \longrightarrow A^-$
Dissociative Attachment	$e^- + B_2 \longrightarrow B^- + B$
Recombination	$e^- + B_2^+ \longrightarrow B_2$
Detachment	$e^- + B_2^- \longrightarrow 2e^- + B_2$
Ion Recombination	$A^- + B^+ \longrightarrow AB$
Charge Transfer	$A^\pm + B \longrightarrow A + B^\pm$
Electronic Decomposition	$e^- + AB \longrightarrow e^- + A + B$
Atomic Decomposition	$A^* + B_2 \longrightarrow AB + B$

2.3 Basic Principle of Photocatalysis

Photocatalysis is a combination of photochemistry and catalysis and implies that light and a catalyst usually a semiconductor are necessary to bring or accelerate a chemical transformation (Herrmann, 1999).

When a semiconductor is irradiated with light at an appropriate wavelength, most often in the ultraviolet spectral range, it generates oxidant species, which can convert most organic materials to CO₂, water and inorganic

compounds. A semiconductor such as TiO_2 is specified by the electronic band structures, which are occupied valance band (vb) and unoccupied conductance band (cb). When a semiconductor absorbs light, it can accelerate electrons from the occupied vb into the unoccupied cb that has a higher energy level, and consequently form positive holes. The difference of both energy levels is called energy band gab. If gases localized by trapping at both energy bands long enough, they will transfer to adsorb electrons to initiate reduction and oxidation reaction shown in Figure 2.1.

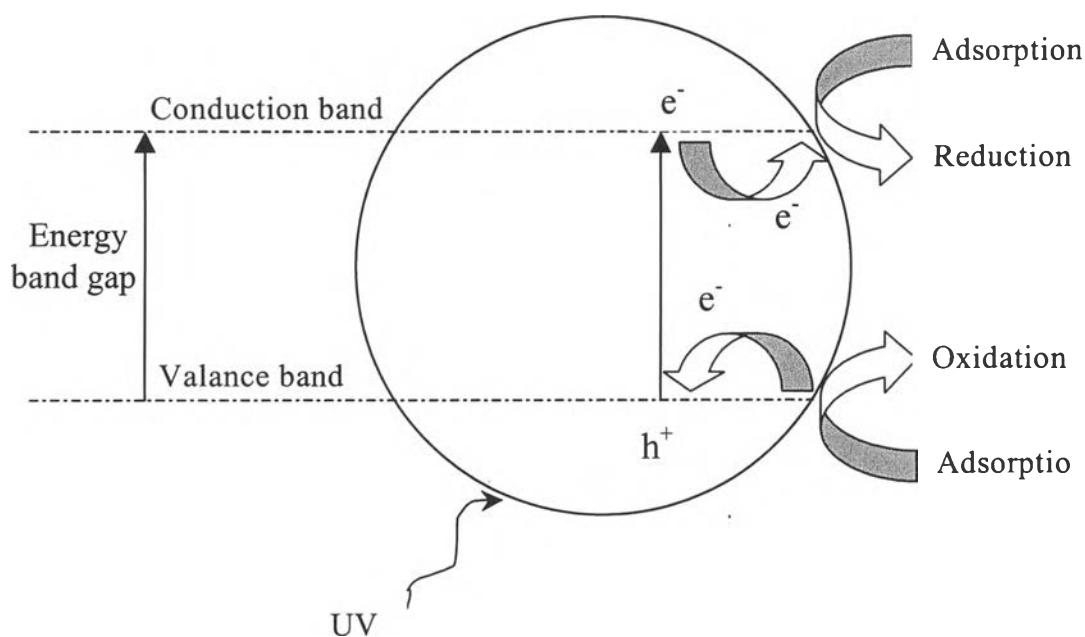
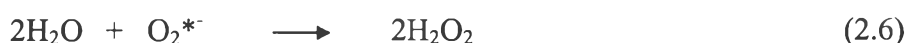


Figure 2.1 Mechanism of photocatalytic process of a semiconductor (Litter, 1999).

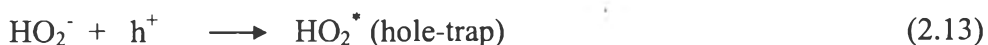
There are possible reactions that can occur when a gas containing a semiconductor absorbs a photon ($h\nu$) of a suitable wavelength (Robertson, 1996).



The electron-hole pairs can recombine either directly or indirectly by radiative and nonradiative processes in a few nanoseconds. The problem of photocatalysis is a recombination reaction between electrons and positive holes because it inhibits the oxidation reaction. To solve this problem, electron scavengers such as oxygen molecules are added since it can trap electron out from the positive hole and transform into superoxide radical ion (O_2^{*-}) and lead to the additional formation of hydroxyl radicals, which are essential species in the photocatalytic process (Litter, 1999).



Water is a major source of hydroxyl group as the primary oxidant, which is generated by dissociative adsorption. So, in the absence of water vapor, the photocatalytic oxidation of organic is seriously retarded and total mineralization to CO_2 does not occur. The hydroxyl radical has high oxidation potential. It can react rapidly and non-selectively with most organic compounds and oxidize them into carbon dioxide, water and other inorganic compounds (De Lasa *et al.*, 1992). A mechanism involving hydroxyl ions as photo hole traps is illustrated below (Peral *et al.*, 1997).



2.4 Types of Semiconductors

A semiconductor used as a photocatalyst should be oxide or sulfide of metals, such as TiO_2 , CdS, and ZnO. The energy band gap of the photocatalyst should match the energy gained from a light source. TiO_2 is a popular one since the band gap is around 3.1 eV, and that can be activated in the near ultraviolet light (~ 380 nm). Other advantages of TiO_2 include its stability and insolubility in aqueous solution, high reactive catalyst, nontoxic and inexpensive catalyst. Furthermore, TiO_2 is corrosion resistant and does not lose activity when reused (De Lasa *et al.*, 1992).

TiO_2 is classified into three different phases, which are anatase, rutile and brookite. In the anatase phase, it has been observed that it is more active and stable than the other phases because of its higher surface area. Rutile is a thermally stable form at all high temperature, whereas heating amorphous TiO_2 produces brookite.

Other types of semiconductor such as ZnO or CdS may not be applicable due to their toxicity. Table 2.2 illustrates the common properties of several semiconductors.

Table 2.2 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	3.1	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

2.5 Related Research Works

2.5.1 Plasma

Futamura and Yamamoto (1997) studied the effect of oxygen and moisture on trichloroethylene (TCE) decomposition by using a pulsed corona reactor. When nitrogen gas was used as a carrier gas in dry condition, higher decomposition efficiency of TCE was reported. They suggested that active oxygen species in air were not responsible for the initial processes of halogenated olefin because oxygen competed with TCE in the processes of electron transfer. Negative effect of moisture on the TCE decomposition efficiency indicates quenching of high-energy electrons and excited nitrogen and oxygen molecules as energy transfer agent. Under aerated conditions, triplet oxygen molecules scavenge intermediate carbon radicals derived from the TCE decomposition to finally give CO and CO₂ resulting in much lower

by-product yields below their threshold limit values than under deaerated conditions.

Futamura *et al.* (1999) investigated plasma chemical behavior of hazardous air pollutants (HAP's) ($\text{Cl}_2\text{C}=\text{CCl}_2$, $\text{Cl}_2\text{C}=\text{CHCl}$, $\text{Cl}_3\text{C}-\text{CH}_3$, $\text{Cl}_2\text{CH}-\text{CH}_2\text{Cl}$, CH_3Cl , CH_3Br , and benzene) by using a ferroelectric packed-bed plasma reactor. It was found that oxidation of CO to CO_2 was a slow reaction in plasma, and that CO and CO_2 mainly result from different precursors. An oxygen content increase did not improve CO_2 yield because of the slow backward reaction of CO_2 to CO in air.

In 1999, Malik and Malik investigated the effect of combining cold plasma with catalysis of VOC decomposition. They found that the addition of suitable catalysts, particularly supported noble metal catalysts, such as platinum, palladium, rhodium and ruthenium, could activate CH_4 at relatively low temperatures, at faster rates and could further improve the efficiency as well as the selectivity of the desired products. Noble metal electrodes had the best results for the conversion of CH_4 to C_2 hydrocarbons in a pulsed corona discharge. Results for the electrodes were in the following order: Platinum > Palladium > Copper.

Oda *et al.* (1999) studied the decomposition of TCE by nonthermal plasma with a catalyst; zeolite and vanadium oxide, in the bolt type reactor. With zeolite as a catalyst, they found that the initial decomposition efficiency of TCE was about 80% which did not depend on the discharge power. That was caused by the adsorption only. The saturation time of the adsorption was about 40 min, which was easily observed from the zero discharge curve. The total decomposition performance of TCE was not so good even at rather high electric discharge plasma because the plasma decomposition was mixed with the decomposition effect. On the other hand, in the case of vanadium oxide, the initial adsorption was rather small, about 50% at no discharge. The saturation time of that was about 8 min, which was much smaller than that with zeolite. Fortunately, the reactor containing vanadium oxide had excellent TCE decomposition performance and the decomposition

efficiency increased to 99% only at the small discharge input of 0.27 W. This value was the minimum energy to decompose 1000 ppm TCE more than 99%.

The decomposition of the aromatics benzene (C_6H_6), toluene ($C_6H_5CH_3$), and o-xylene ($C_6H_5(CH_3)_2$) in a plasma reactor packed with $BaTiO_3$ pellets in the presence of various background gas was studied by Ogata *et al.* (2002). It was found that the order of decomposition efficiency was $C_6H_6 < C_6H_5CH_3 < C_6H_5(CH_3)_2$, irrespective of the background gas. Decomposition was suppressed when water vapor (H_2O) was added to the reactant gas; the extent of the suppressions was in the order $C_6H_6 > C_6H_5CH_3 > C_6H_5(CH_3)_2$. They concluded that these behaviors were brought about by the migration of reactant molecules to the solid surface. The decomposition efficiency of C_6H_6 was suppressed in the $C_6H_6 + C_6H_5CH_3 + C_6H_5(CH_3)_2$ mixture, whereas the decomposition efficiencies for $C_6H_5CH_3$ and $C_6H_5(CH_3)_2$ were enhanced in the mixture compared to those for the single-component condition. It seems that inelastic collisions of aromatics with fast electrons and activated oxygen species were affected by the molecular sizes of the targeted substances.

2.5.2 Photocatalysis

Einaga *et al.* (2001) examined benzene conversion by using platinized titania. Without Pt, benzene was converted into CO and CO_2 but it cannot further oxidize CO into CO_2 . On the other hand, as the amount of Pt loaded on TiO_2 was increased, the rate of the CO photooxidation was increased, while that of benzene photooxidation was almost unchanged. Moreover, it was found that complete oxidation of benzene to CO_2 could be achieved by using the hybrid catalysts comprising pure TiO_2 and platinized TiO_2 .

In 2002, Li *et al.* investigated the decomposition of toluene by streamer corona discharge with photocatalyst (TiO_2). They showed the performance of the reactor when the catalyst was packed between the needle electrode and plane mesh electrode. The reactor required low power consumption; the energy efficiency of toluene decomposition was 7.2 g

[toluene]/KWh at the decomposition rate of 76%. The toluene decomposition rate increased with increasing applied voltage or input power. Consequently, the decomposition of toluene could be improved by using combination plasma with the catalyst.

The decomposition of toluene using an atmospheric pressure plasma/TiO₂ catalyst system was studied by Kang *et al.* (2002). They used TiO₂ obtained by an improved sol-gel method, and coated on supports. Toluene of 40% was decomposed at the pulse voltage of 13 KV in the O₂ plasma condition without TiO₂. Furthermore, the conversion enhanced remarkably in the TiO₂/O₂ plasma system, and it reached 70% at the pulse voltage of 13 KV after 120 min. They reported that 80% of toluene decomposition could be achieved by TiO₂ coated on γ -alumina in the O₂ plasma condition.