



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Basic Principle 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 and/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 negatively charged carriers must be equal to the total density of positively charged 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 liquid or gaseous states does not have any specific names. Only the gaseous plasma is shortly called as “plasma”. There are many differences between plasma and gas. 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 plasma, 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” leading to the electrons leaving the electrode surface. The most interesting phenomena on the electrode surface under an extremely high-electric field is that many electrons can leak from the surface despite

its kinetic energy is too low to overcome the potential barriers. This phenomenon is known as “tunnel effect”. Under a sufficiently high voltage, the plasma is 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 known as the “field” emission process (Eliasson and Kogelschatz, 1991).

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 various ionized gases with excess free electrons. Accordingly, these free 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 once the application of electric field is started. Several active species produced can further initiate various chemical reactions leading to the production of specific chemicals and the destruction of organic pollutants. Table 2.1 shows some important collision mechanisms of plasma chemistry (Eliasson and Kogelschatz, 1991).

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	$A^* + B_2 \longrightarrow AB + B$

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 (Nasser, 1971).

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 (Eliasson and Kogelschatz, 1991; and Grill, 1994). An essential condition for the formation of this plasma is sufficiently high working temperatures. 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 was used in this study.

The basically 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.

2.3 Basic Principle of Photocatalysis

Photocatalysis is a combination of photochemistry and catalysis implying 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 into CO₂, water and inorganic compounds. A semiconductor such as TiO₂ is specified by the electronic band structures, which are occupied valance band (vb) and unoccupied conductance band (cb). When a semiconductor absorbs light, the light energy can

force the electrons at the occupied valance band to move to the unoccupied conductance band that has a higher energy level, and consequently positive holes (h^+) are formed. The difference of both energy levels is called energy band gab. If gases localized by trapping at both energy bands long enough, both reduction and oxidation reactions will occur as shown in Figure 2.1.

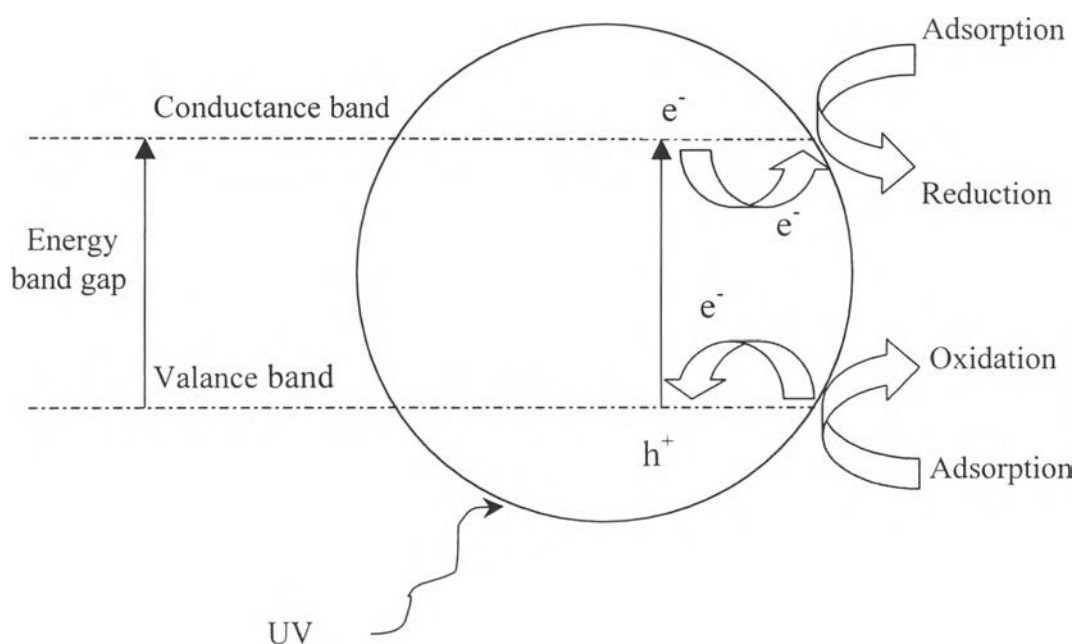


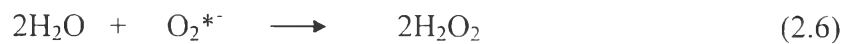
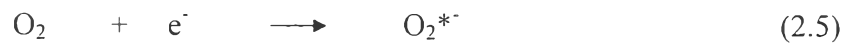
Figure 2.1 The mechanism of photocatalytic process of a semiconductor (Litter, 1999).

There are possible reactions that can occur when 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 the electrons and the positive holes because it

inhibits the redox reactions. To solve this problem, electron scavengers such as oxygen molecules are added since it can trap electrons out from the positive hole to form superoxide radical ion ($O_2^{\bullet-}$) leading to the sequential formation of hydroxyl radical (Litter, 1999), which is essential species in the photocatalytic process since the hydroxyl radical is the most powerful oxidant.



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



2.4 Types of Semiconductors

A semiconductor used as photocatalyst should be either oxide or sulfide of metals, such as TiO_2 , CdS, and ZnO. The energy band gap of the semiconductor must be matched with the energy gained from a light source. TiO_2 is a popular one since the band gap is around 3.1 eV, which can be simply activated in the near

ultraviolet light (~380 nm). Other advantages of TiO₂ include more stable and insoluble in aqueous solution, high reactive catalyst, nontoxic and inexpensive catalyst. Furthermore, TiO₂ is corrosion resistant and does not lose activity when reused (De Lasa *et al.*, 1992).

TiO₂ 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 two phases because of its higher surface area. Rutile is a thermally stable form at high temperatures, whereas heating amorphous TiO₂ produces brookite.

Other types of semiconductors such as ZnO or CdS may not be applicable due to their toxicity. Table 2 compiles the common properties of several semiconductors.

Table 2.2 Band positions of some common semiconductor used as 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 effects of oxygen and moisture on trichloroethylene (TCE) decomposition by using a pulsed corona reactor. When nitrogen gas was used as a carrier gas in the dry condition, higher decomposition efficiency of TCE was obtained. 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 process of electron transfer. Negative effect of moisture on TCE decomposition efficiency indicates quenching of high-energy electrons and excited nitrogen and oxygen molecules as an energy transfer agent. Under aerated conditions, triplet oxygen molecules scavenged 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 that under deaerated conditions.

Futamura *et al.* (1999) investigated plasma chemical behavior of hazardous air pollutants (HAP's) (Cl₂C=CCl₂, Cl₂C=CHCl, Cl₃C-CH₃, Cl₂CH-CH₂Cl, CH₃Cl, CH₃Br, and benzene) by using a ferroelectric packed-bed plasma reactor. It was found that oxidation of CO to CO₂ was a slow reaction in plasma, and the formation of CO or CO₂ is mainly resulted from different precursors. An increasing oxygen content did not improve CO₂ yield because of the slow backward reaction of CO₂ to CO in air.

Sano *et al.* (1997) studied the removal of acetaldehyde and skatole by a corona-discharge reactor. They found that under the pure nitrogen atmosphere, methane was produced as a reaction by-product from the removal of acetaldehyde but no reaction by-product was produced from the removal of skatole. It was explained that skatole was removed on the basis of its electron attachment. When oxygen was added, the removal efficiencies of acetaldehyde and skatole increased greatly since ozone (O₃) was produced inside the reactor. It was estimated that the O₃ produced contributed half of the removal efficiency of acetaldehyde. For the mixture of acetaldehyde and skatole under the mixed gas of N₂ and O₂, it was found that the coexisting skatole inhibited the formation of the negative ion clusters of acetaldehyde.

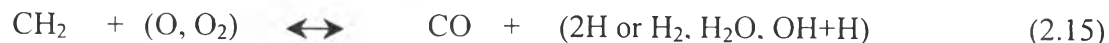
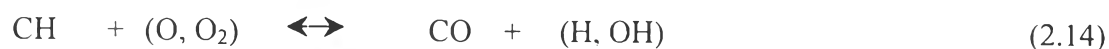
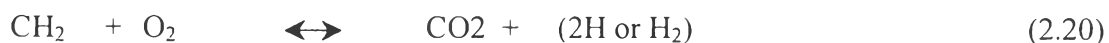
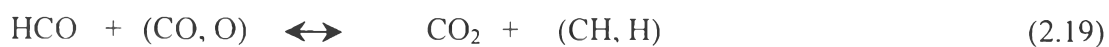
CO₂/CH₄ reforming by glow discharge plasma with and without micro-arc formation using a Y-type reactor was studied by Huange *et al.* (2000). It was

reported that the system with the formation of micro-arcs produced more CO as well as higher energy efficiencies than that without the micro-arc formation. Furthermore, with an increase in the CO₂ to CH₄ ratio, the selectivity to CO increased, and less coke formed.

Malik and Malik (1999) investigated a combined system of cold plasma and a catalyst for VOC destruction. They found that the addition of a suitable catalyst particularly a supported noble metal catalysts such as platinum, palladium, rhodium and ruthenium, could activate CH₄ at relatively low temperatures with faster rates and could further improve the efficiency as well as the selectivity of the desired products. The use of noble metal electrodes was formed to enhance the conversion of CH₄ to C₂ hydrocarbons in a pulsed corona discharge with the following order: Platinum > Palladium > Copper.

Thanyachotpaiboon *et al.* (1998) studied the conversion of CH₄ to higher hydrocarbons in AC non-equilibrium plasma. It was shown that CH₄ conversion initially increased with increasing voltage and residence time above the breakdown voltage because a higher density of the electrons gives a higher probability of a CH₄ molecule interacting with electrons to form active species. CH₄ conversion also increased when He and C₂H₆ were added in the feed stream. He and C₂H₆ both appeared to be more easily activated than CH₄ and enhanced CH₄ conversion.

Tsai *et al.* (2001) studied the product distribution of methanethiol (CH₃SH) decomposition in a RF plasma reactor. In the absence of oxygen, over 83.7 % of the total sulfur input was converted to carbon disulfide (CS₂) at 60 W. When oxygen was added, the main product of sulfur was shifted to SO₂ due to the thermodynamic stability. Oxygen was believed to play an important role for inhibiting dihydrogen sulfide (H₂S), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) formation. The mole fractions of methane, ethylene, and acetylene were rapidly decreased as the O₂/CH₃SH ratio increased from 0 to 3, and did not change when the O₂/CH₃SH ratio was further increased to 4.5. At a higher O₂/CH₃SH ratio and increasing input power, CO could be converted to CO₂ by reacting with O, OH, O₂, HCO, and H₂O. The mechanism of the formation and decomposition of CO and CO₂ are shown below.

CO formation and decomposition**CO₂ formation**

Kruapong (2000) determined the effects of voltage, frequency, and flow rate on CH₄ conversion in corona discharge. Higher voltage, lower frequency, and lower flow rate of CH₄ gave higher conversion of CH₄ and O₂ and higher selectivity to CO₂, and H₂.

Suttiruangwong (1999) performed experiments with and without catalysts and found that the non-catalytic system gave much higher CH₄ conversion than the catalytic system and products mainly consisted of C₂ hydrocarbons.

Although the nonthermal plasma technology shows high performance for the removal of VOCs, a major disadvantage of this technique is the formation of some unexpected toxic products such as NO_x, phosgene, etc.

2.5.2 Photocatalysis

Einaga *et al.* (2001) examined benzene conversion by using platinized titania. Without Pt, benzene was converted into CO and CO₂ but CO could not be further oxidized to CO₂. On the other hand, as the amount of Pt loaded on TiO₂ was increased, the rate of the CO photooxidation was increased while the rate of benzene removal was almost unchanged. Moreover, it was found that complete oxidation of benzene to CO₂ could be achieved by using the hybrid catalysts comprising pure TiO₂ and platinized TiO₂.

Obuchi *et al.* (1999) studied the photocatalytic decomposition of acetaldehyde over TiO₂/SiO₂ and Pt-TiO₂/SiO₂. They found that the unplatnized

catalyst gave a conversion of acetaldehyde and a yield of CO₂ about 10 % less than the platinum loaded one. That is because platinum may help increasing the adsorption of the reactant, which was confirmed by calculation based on Langmuir-Hinshelwood. Platinum did not only enhance the rate of the reaction, but also help complete the catalyst regeneration at the lower temperature. Moreover, the FT-IR results showed the band of carbonic acid, suggesting the existence of acetic acid and/or formic acid as an intermediate adsorbed on the catalyst.

Nakamura *et al.* (2000) studied the photocatalytic activity of plasma-treated TiO₂ and raw TiO₂ powder for eliminating NO. They reported that the NO removal by both photocatalysts increased with decreasing wavelength. In the case of plasma-treated TiO₂ catalyst, the reaction occurred above 450 nm due to the change in the electronic state of TiO₂ caused by the reduction. The oxygen vacancies were formed in the crystal lattice of TiO₂ by the plasma treatment, maintaining the anatase structure. Furthermore, it was explained that the oxygen vacancy state between the valence and conductance bands were newly formed and then react with O₂ or O-species to produce reactive oxygen species such as O⁻ and atomic oxygen

Zhang *et al.* (2001) investigated the effect of TiO₂ on the decomposition of NO. The rate of NO conversion decreased with a decrease in the intensity of the incident UV light. Moreover, it was found that the reaction efficiency was high at the beginning of the reaction, and then gradually decreased with the reaction time.