CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Basic Principles of Plasma

Regarding the principles of physics and chemistry, plasma is an ionized gas and is usually considered to be a distinct phase of matter, as showed in Figure 2.1. The term of "ionized" means that at least, one electron has been removed from a significant fraction of molecules. The free charges make the plasma electrically conductive so that it couples strongly to electromagnetic fields. This fourth state of matter was first identified by Sir William Crookes in 1879 and dubbed "plasma" by Irving Langmuir in 1928.

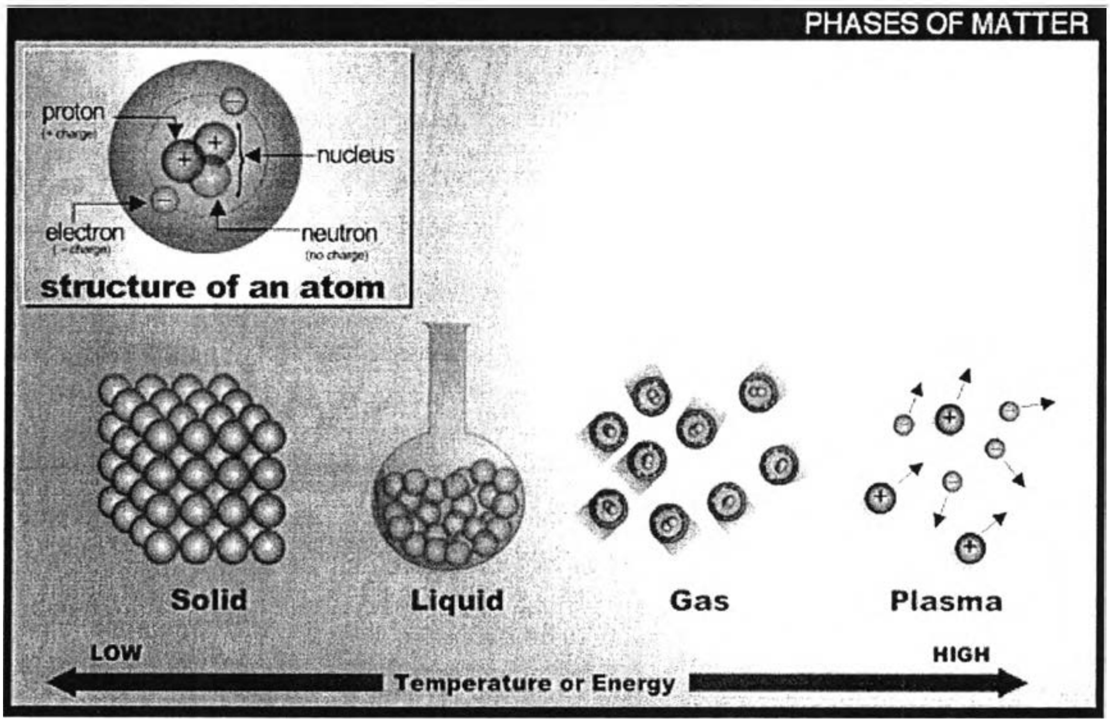

Figure 2.1 Phase of matter consists of solid, liquid, gas and the fourth state named "plasma".

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Since the gaseous plasma is an effective source of active species formation, including electrons, ions and radicals, a number of studies of chemical reactions using such plasma to initiate various reactions have been carried out extensively.

2.1.1 Fundamental Properties of Plasma

In its simplest definition, 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 the following 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.

2.1.2 Generation of Plasma

There are several means of generating charged particles to generate 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 eventually reach 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 are that many electrons can leave the surface despite its less kinetic energy to overcome the potential barriers. This phenomenon is known as “tunnel effect”. Afterward, 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 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 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, as well as 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 of electric field has been applied. Many active species can further initiate several chemical reactions, leading to the production and destruction of the chemical species (Kruapong, 2000). The combined steps of the field emission process among these plasma species and the collision between the species and the electrode surfaces are referred to as “electric discharges” phenomena. Table 2.1 shows all possibilities of reactions occur in the plasma environment.

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

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

Plasma is divided into two types. The first type is "thermal plasma" or "equilibrium plasma". In this type, the temperatures of gas and electrons are approximately equal which are close to thermodynamic equilibrium (Fridman *et a.*, 1999). An example of such plasma is those produced in the arc discharge and plasma torches.

Thermal plasma or "hot plasma" is close to thermodynamic equilibrium. It has a uniform temperature for all particles and a very high temperature in the discharge region. An essential condition for the formation of thermal plasma is a sufficiently high working pressure. The large number of collision between particles leads to rapid redistribution of energy so that equilibrium is reached. An example of this plasma is arc discharge.

Thermal plasma technology offers a wide range of advantages over other waste management solutions due to the very high temperatures of thermal plasma, changing the state of wastes to destroy hazardous materials. It is also highly flexible and easy to control, with a low environmental impact of its own. In addition, it enables the production of a valuable vitrified slag that may be used in construction and other applications.

The second type is "non-thermal plasma" or "non-equilibrium plasma", which is characterized by a low gas temperature with a high electron temperature. Typical energetic electrons may have energy ranging from 1 to 10 eV, which corresponds to the temperature range 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.

Non-thermal plasma or "cold plasma", in contrast, is far from thermodynamic equilibrium. Typically, electrons in this plasma have very much higher temperatures than the heavy ions and neutral species particles. Its uses are based chiefly on the reactivity of ions or radicals generated in the plasma for gas phase or surface reaction. This group includes radio frequency, microwave, glow, dielectric-barrier, and corona discharge.

2.1.3 Types of Non-Thermal Plasmas

Non-thermal plasmas can be divided into several types, depending on the mechanisms used for their generation, their pressure range, and the electrode geometry. The general characteristic and applications of each non-thermal plasma type are briefly explained as follows.

2.1.3.1 Glow Discharge

The glow discharge is a stationary and low-pressure discharge, usually generated between the two flat electrodes (Figure 2.2). The glow can be produced by applying a potential difference between two electrodes in a gas. Since the pressure is typically lower than 10 mbar, the reduced field or the electric field divided by the neutral gas density can therefore be quite high, which is a characteristic of non-thermal plasma. One reason for the popularity of glow discharges is the comparatively low voltage and current needed to generate plasma. It has become an important laboratory tool for plasma chemical investigations. There are some practical applications of glow discharge in light industry such as neon tubes (for outdoor advertising) and fluorescent tubes.

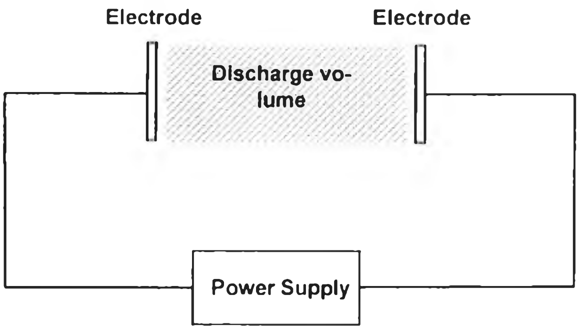


Figure 2.2 The glow discharge-homogeneous electrode can be operated at low pressure (Eliasson *et al.*, 1987).

2.1.3.2 Silent Discharge

The silent discharge is predetermined for applications in volume plasma chemistry. It combines the large volume excitation of the glow discharge with the high pressure of the corona discharge. A characteristic of the silent discharge is that a dielectric layer covers at least one of the electrodes, sometimes both. For this reason, the silent discharge is also referred to as the "dielectric-barrier discharge (DBD)," or simply, "barrier discharge." The dielectric is the key for the proper functioning of the discharge. Once ionization occurs at a location in the discharge gap, the transported charge accumulates on the dielectric. The dielectric serves two functions: (1) it limits the amount of charge transported by a single microdischarge and (2) distributes the microdischarges over the entire electrode area. The silent discharge is an excellent source of filaments containing energetic electrons. In most gases, the reduced field at breakdown corresponds to electron energies of about 1-10 eV. This is the ideal energy range for the excitation of atomic and molecular species and the breaking of chemical bonds.

2.1.3.3 Radio Frequency Discharge

The radio frequency (RF) discharges are used extensively in the laboratory to produce plasmas for optical emission spectroscopy and for plasma-chemical investigations. The inductively coupled plasma (ICP) operating between 2-60 MHz is especially a widespread laboratory tool for spectroscopic analysis. Very common frequency used in the industrial applications is frequency of 13.56 MHz. One advantage of RF discharges is that the electrodes can be kept outside of the discharge volume, thus avoiding electrode erosion and contamination of the plasma with metal vapor. Since the wavelength of the electric field is much larger than the vessel dimensions, reasonably homogeneous plasmas can be generated. RF discharges work well at low pressure, but are also used at atmospheric pressure. Low-pressure RF discharges for etching purposes have been found widespread applications in semiconductor manufacturing. As long as the collision frequency is higher than the frequency of the applied field, the discharge behaves very much like a dc discharge. This implies that non-thermal conditions can be expected at low pressures, whereas thermal plasmas are generated at about atmospheric pressure. Figure 2.3 shows three typical electrode configurations for RF discharges. While Figures 2.3 (a) and (b) use capacitive coupling and are mainly used at low pressure, the configuration, shown in Figure 2.3 (c), uses inductive coupling by placing the discharge in the magnetic field of an induction coil. This arrangement is typical for RF torches and is used at pressures up to 1 bar.

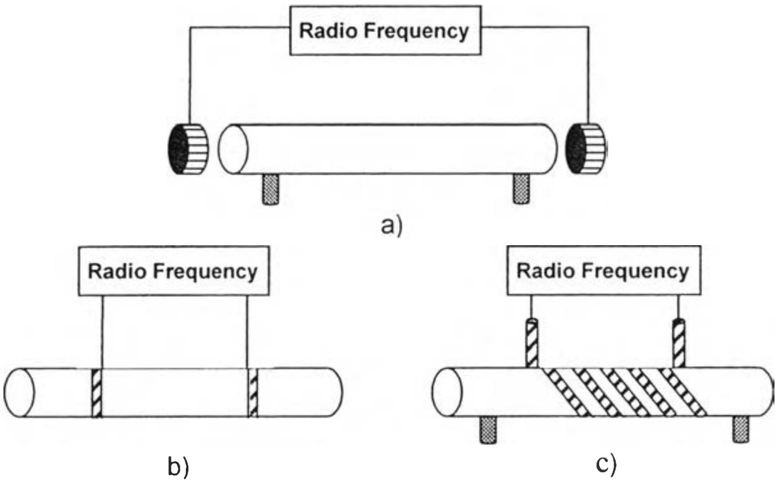


Figure 2.3 Schematic of various types of radio frequency discharge: (a) and (b) contain capacitive coupling, normally used at low pressure, (c) use inductive coupling instead of capacitive coupling, which can be operated at pressure up to 1 bar. (Eliasson and Kogeischatz, 1991)

2.1.3.4 Microwave Discharge

In the microwave region (0.3-10 GHz), the wavelength of the electromagnetic field becomes comparable to the dimensions of the discharge vessel, which necessitates other coupling mechanisms. Most microwave-induced plasmas are produced in a waveguide structure or resonant cavity. As the dimensions of the cavities diminish when the frequency increases, the maximum microwave frequencies used for discharge applications are usually below 3 GHz. A very common frequency is 2.45 GHz, which is also used in microwave ovens. Since at these frequencies only the light electrons can follow the oscillations of the electric field, microwave plasmas are normally far from local thermodynamic thermal state. They can be operated in a wide pressure range, starting from below 1 mbar to about atmospheric pressure. An interesting development is the use of microwaves to induce surface-wave-sustained discharges. They can be operated over a large frequency and pressure range and can produce large-volume non-thermal plasmas of reasonable homogeneity.

The plasma is contained in a dielectric tube of a few centimeters diameter and is sustained by an electromagnetic wave, which requires only the plasma column and the tube as its propagating media. Plasma columns of up to 4 m in length have been thus produced. Due to the large pressure range, under which these discharges can be operated, electron densities between 108 and 1015cm^{-3} have been reported. These surface wave plasmas have many similarities with the positive column of a glow discharge. Applications so far have been limited to elemental analysis and lasing media. The ease of operation and the possibility of imposing a gas flow and influencing plasma parameters make these discharges attractive also for plasma-chemical investigations.

2.1.3.5 Corona Discharge

One type of discharge, which can operate at both extremely low and high pressure. This type of discharge is generally constructed with inhomogeneous electrode geometries; e.g. a pointed electrode and a plane electrode (or pin and plate), as shown in Figure 2.4. The discharge generated by this kind of electrode is called corona discharge.

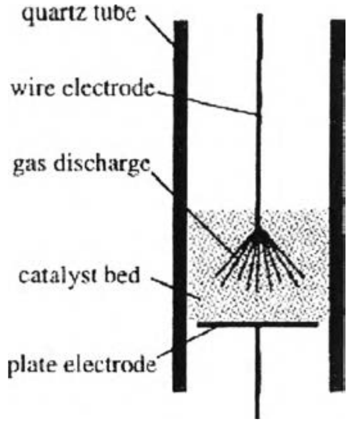


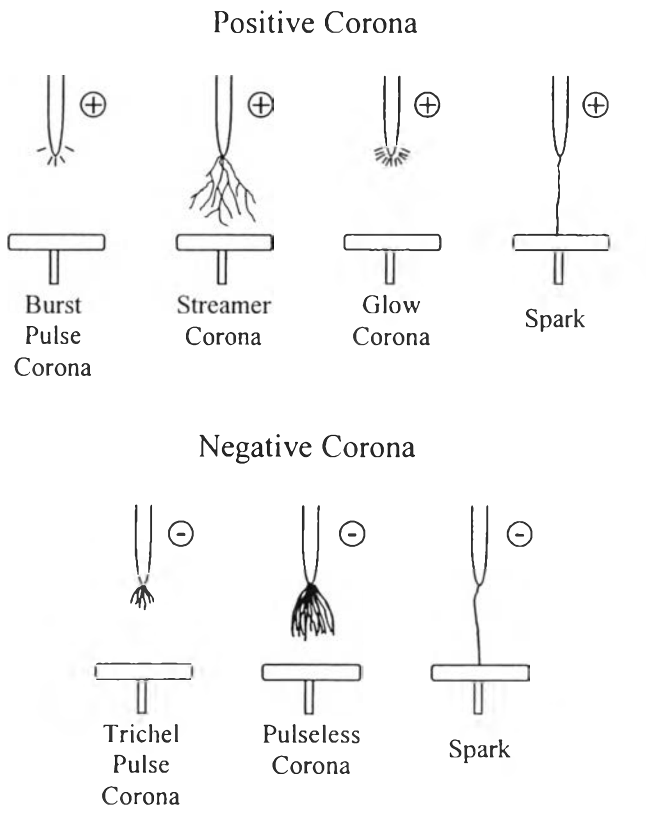
Figure 2.4 Schematic of pin and plate corona charge (Amin, 2006).

Types of Corona Discharge:

Corona discharges exist in several forms, depending on the polarity of the field and the electrode geometrical configurations.

a) Positive Corona

For positive corona in the pin-plate electrode configuration, there is a corona inception voltage, which depends on the radius of the point and the gap spacing. Discharges start with burst pulse corona, and when the voltage is increased, streamers are produced, leading to the typical corona phenomenon named streamer corona followed by glow corona. By increasing the voltage further, breakdown occurs, and a spark bridges the gap, as depicted in Figure 2.6. Unlike Hermstein's positive sheath (Hermstein, 1960) or Hermstein's glow, the positive streamer corona is a discharge confined to a narrow channel, which originates at the electrode. It produces an unsteady current (because the streamer is repetitive), is quite noisy, and is the direct precursor to a spark.



Positive Corona

Negative Corona

Figure 2.5 Schematic of various forms of corona discharge depending upon applied voltage at constant electrode geometrical configuration (Chang, 1991).

Positive corona depends more on photoionization for its propagation. The positive streamer, for example, may advance at as much as one percent of the speed of light. In either case, the ultraviolet photon flux from ion-electron recombination is quite large (Chang, 1991).

b) Negative Corona

For negative corona in the same geometry, once voltage is increased, the so-called Trichel pulses are generated. Short current pulse or pulseless corona is observed with a frequency proportional to the applied voltage, and also depends on the radius of the point. As the voltage is increased further, a glow develops before complete breakdown occurs.

Negative corona generally propagates by impact ionization of the gas molecules, which is in slightly different manner from positive corona. Due to space-charge phenomena in the neighborhood of the point, the negative corona is less sensitive to the radius of curvature of the point than the positive corona. It is the small radius of curvature of the point that leads to the high fields necessary for ionizing the neutral molecules. The field drops rapidly as one move away from the point toward the other electrode. It is very important that the applied voltage is not too high; otherwise the corona might bridge the gap, produce a spark, and finally break down. In this sense, the corona discharge can be considered a partial breakdown.

The characteristic of corona discharge is that the generated-plasma volume excited is nearly smaller than the total discharge volume. This tends to be not suitable for large quantities of chemical species production. There are, however, applications where only very small concentrations of excited or charged species are needed. The outstanding example is electrostatic precipitators, which are operated at industrial scales for collecting the particulate emissions in the utility, steel, paper manufacturing, and cement and ore-processing industries.

2.1.3.6 Dielectric Barrier Discharge

Dielectric-barrier discharges (DBD) comprise a specific class of high-voltage, AC, and gaseous discharges that typically operate in the near-atmospheric pressure range. Their defining feature is the presence of dielectric layers that make it impossible for charges generated in the gas to reach the conducting electrode surfaces. With each half-cycle of the driving oscillation, the voltage applied across the gas exceeds that required for breakdown, and the formation of narrow discharge filaments initiates the conduction of electrons toward the more positive electrode. As charge accumulates on the dielectric layer at the end of filament, the voltage drop across the filament is reduced until it falls below the discharge-sustaining level, whereupon the discharge is extinguished. The low charge mobility on the dielectric not only contributes to this self-arresting of filaments but also limits the lateral region, over which the gap voltage is diminished, thereby allowing parallel filaments to form in close proximity to one another. Thus, the entire gas-filled space between parallel electrodes can become, on average, uniformly covered by transient discharge filaments, each roughly 0.1 mm in diameter and lasting only about 10 ns.

The DBD unique combination of non-equilibrium and quasi-continuous behavior has provided the basis for a broad range of applications and fundamental studies. Its use in industrial ozone reactors has generated interest in optimizing conditions for specific chemical reactions. Several groups have modeled single-filament dynamics in order to account for many two- and three-body reactions involving electrons, ions, neutral atoms, and photons. These efforts have been moderately successful in explaining and predicting the chemical and radiative properties of various DBD systems. On another research front, it has been seen that the transverse spatial distribution of discharge filaments in 2D parallel-plate DBD can take the form of stable and large-scale patterns reminiscent of those associated with magnetic domains or Rayleigh-Bénard convection. These patterns have been modeled with some success using methods that apply generally to pattern formation in nonlinear dynamical systems. Thus, the dynamical interactions between filaments, as well as the chemical and electronic interactions within filaments, have proven interesting. The schematic diagram for dielectric barrier discharge reactor is shown in Figure 2.5.

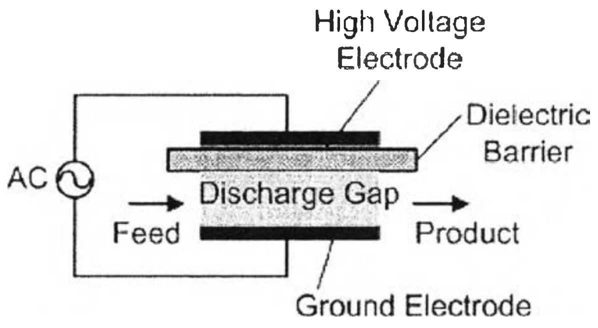


Figure 2.6 Schematic for dielectric barrier discharge reactor (Amin, 2006).

2.2 Non-Thermal Plasma for Chemical Reactions

The non-thermal plasma is widely used in many industrial applications. The first use for chemical synthesis via silent discharge is ozone generation by Siemen (Horvath, 1980). Main areas of applications are the generation of reactive species, isomerizations, eliminations, cyclizations, condensations, and multistep reactions (Suhr, 1983). For the industrial production of epoxides, ethylene oxide, which is the most important epoxides in industrial processes, is made by conventional methods using catalysts. There are also some studies on plasma organic syntheses such as oxidations of aromatic, liquids hydrocarbons, and olefins using oxygen plasma (Suhr *et* al., 1984; Tezuka and Yajima, 1996; Suhr *et al.*, 1988; Patiño *et al.*, 1995). Furthermore, the product selectivity is far superior to plasma oxidations in the gas phase, making these techniques attractive for preparative chemistry (Suhr *et al.*, 1984).

The previous studies on plasma oxidation at low pressure suggested that the most important species in the plasma partial oxidation was O(^{3}P) (Suhr, 1983; Suhr *et al.*, 1988; Patiño *et al.*, 1995; Patiño *et al.*, 1999; and Suga and Sekiguchi, 2005). The following reaction proposed for the epoxidation of the carbon double bond:

In addition, Jeong *et al.* (2000) reported that the concentration of O(^{3}P) decreased significantly with increasing distance between the tip and the tube in discharge reactor, which is in good accordance with the previous work of Suga and Sekiguchi (2005).

In recent work, there was an extensive attempt to oxidize carbon double bond into epoxide by exposing a liquid 1-decene in atmospheric pressure glow plasma (APGP) where oxygen diluted with argon was used as a plasma gas. The results showed that the yields of all products (1,2-epoxydecane, 1-decanal, 1-nonanal, and 2-decanone) increased linearly with increasing reaction time and shortening the tip of the tube and the liquid surface, and the highest yield of epoxide could be obtained by optimizing plasma reaction parameters (Suga and Sekiguchi, 2005).

2.3 Catalytic Plasma Processing

The plasma properties have an influence on catalytic performance, for example, providing the heating for catalysts which results in desorbing of surface species (Kraus, 2001). On the other hand, the plasma properties can be also influenced by catalysts in plasma zone. The applied catalysts can change the reaction products due to the conductive surfaces, which directly affect surface reaction. The synergism between catalysts and plasma is achieved if this combination can improve reactant conversions and increase product selectivities as compared to the sole plasma or catalyst technique.

The gas temperature is basically the most important factor, indicating the occurrence of most catalytic reactions. However, at low temperatures where catalysts are not active, the plasma influence is observed (Liu *et al.*, 1997). Heintze *et al.* (2004), investigated the performance of DBD with $Ni/\alpha\text{-}Al_2O_3$ for the partial oxidation of methane. At low temperatures, this combined catalyst-plasma system showed influence on both the conversion and product selectivity and the plasma showed the dominant role. At higher temperatures, however, the catalyst promoted the oxidation of CO to CO_2.

Malik and Malik (1999) investigated a combined system of cold plasma and a catalyst for VOC decomposition. They found that the addition of a suitable catalyst, particularly supported noble metal catalysts, such as platinum, palladium, rhodium and ruthenium, could activate CH_4 at relatively low temperatures with faster rates and could further improve the efficiency, as well as the selectivity for the desired products. Noble metal electrodes showed the best results for the conversion of CH_4 to C_2 hydrocarbons in a pulsed corona discharge with the following order: platinum > palladium > copper.

Suttiruangwong (1999) studied the conversion of methane for partial oxidation of methane (POM) in a packed-bed reactor under AC corona discharge without and with a Cu/ZnO catalyst. It was found that the sole plasma system gave much higher CH_4 conversion than the sole catalytic system, and the products mainly consisted of C_2 hydrocarbons. Methane conversion and product selectivity increased with decreasing total flow rate and increasing applied voltage. In the absence catalyst, it gave the feasibility of methane conversion at atmospheric conditions, but the amount of methanol produced was still low. Synthesis gas was also found mainly in the product stream.

Viriyasiripongkul (2000) investigated the oxidative coupling of methane to produce higher hydrocarbons by using AC electric discharge without and with zeolite catalyst at ambient conditions. The plasma system with the Pt/KL zeolite catalyst enhanced the oxygen conversion and the selectivity for ethylene. Moreover, hydrogen and carbon monoxide were the main products. For the plasma system without catalyst, it was found that methane, oxygen, and ethane conversions, as well as yields of C_2 hydrocarbons (ethylene and acetylene) increased with increasing applied voltage and decreasing either frequency or total flow rate.

Saktrakool (2003) developed a combined plasma and photocatalytic system for oxidation of ethylene as a model of VOC removal. Higher applied voltage and stage number of plasma reactors enhanced C_2H_4 conversion and CO_2 selectivity, which were in contrast with the effects of higher input frequency and feed flow rate. The commercial TiO_2 (Degussa P25), TiO_2, and 1%Pt/TiO_2 prepared by sol-gel method were used as photocatalysts. The presence of all studied photocatalysts increased both the C_2H_4 and O_2 conversions, as well as CO_2 selectivity, in the following order: 1%Pt/TiO_2 > TiO_2 > Degussa P25. The synergistic effect of the photocatalysts and the plasma environment results from the activation of TiO_2 by the UV light generated from the plasma.

Chavadej *et al.* (2008) studied the epoxidation of ethylene in a low-temperature corona discharge system in the presence of different catalysts, including Ag/low-surface-area(LSA)α-Al_2O_3, Ag/high-surface-area(HSA)γ-Al_2O_3, Au-Ag/(HSA)γ-Al_2O_3, and Au/TiO_2. The results showed that Ag/(LSA)α-Al_2O_3 offered the highest selectivity for ethylene oxide, as well as the lowest selectivities for carbon monoxide and carbon dioxide. The selectivity for ethylene oxide increased with increasing applied voltage, but remained unchanged when frequency was varied within 300 to 500 Hz, and eventually decreased with the frequency over 500 Hz. The optimum Ag loading on (LSA)α-Al_2O_3 was found to be 12.5 wt.% with ethylene oxide selectivity of 12.98% at input voltage and frequency of 15 kV and 500 Hz, respectively.

2.4 Catalysts Used in Epoxidation of Ethylene

The ethylene epoxidation in a dielectric barrier discharge system was investigated by Sreethawong *et al.* (2008) to find the optimum operating conditions. The results showed that the highest ethylene oxide yield of 5.62% was obtained at an input frequency of 500 Hz and an applied voltage of 19 kV, an O_2/C_2H_4 molar ratio of 1/1, a feed flow rate of 50 cm^3/min, and an electrode gap distance of 10 mm. When comparing with the corona discharge system with 0.2 wt.% Au-12.5 wt.%Ag/(low-surface-area)α-Al_2O_3 catalyst exhibiting comparative good epoxidation performance, the DBD system still provided the better performance in terms of C_2H_4 conversion, C_2H_4O yield, and power consumption per C_2H_4O molecule produced.

Ethylene can be catalytically converted into ethylene oxide with high selectivity over supported silver catalysts. The first commercial ethylene oxide production can be traced back to the Lefort's process in 1937 (Satterfield, 1991). Typically, a unique support for silver catalysts is alpha-alumina (α-Al_2O_3). Low-surface-area (LSA) α-Al_2O_3, possessing the surface area less than 1 m^2/g, was commercially widely used as silver catalyst support. Unfortunately, this support showed poor silver dispersion, which provided relatively low yield of ethylene oxide (Matar *et al.*, 1989). Interestingly, the addition of few ppms of chloride to gaseous reactant as the moderator in the form of chlorine-containing hydrocarbon species, such as dichloroethane ($C_2H_4Cl_2$) and vinyl chloride (C_2H_3Cl), has been reported to significantly increase the selectivity for ethylene oxide by 15-20%, but at the same time, to decrease the rates of ethylene oxide and carbon dioxide formation (Law *et al.*, 1942; Campbell *et at.*, 1984; Tan *et al.*, 1987; and Yeung *et al.*, 1998). The mechanism of chloride moderator is still in question that it has been attributed to geometric (Campbell *et al.*, 1984; Campbell *et al.*, 1985; and Campbell *et al.*, 1986), electronic (Tan *et al.*, 1987), or both effects. Moreover, some previous researches reported that the alkali and transition metals, such as Cs and Cu, also provided the improvement of the selectivity for ethylene oxide (Iwakura, 1985; and Bhasin, 1988). Recently, it was confirmed that copper-silver bimetallic catalysts could offer selectivity improvement compared with bare silver catalysts in the ethylene epoxidation (Jankowiak and Barteau, 2005).

The role of cesium was proposed that the presence of cesium could reduce the acidic sites on the support, resulting in suppressing the isomerization of ethylene oxide to acetaldehyde (Mao and Vannice, 1995; and Epling *et al.*, 1997). At the same time, cesium could, however, promote the direct combustion. The mechanism was proposed that cesium can provide additional electrons to silver lattice, transferring to adsorbed oxygen. As a result, the adsorbed oxygen possesses excess highly electron density, benefiting the total oxidation of ethylene. Moreover, cesium addition can decrease the concentration of nucleophilic oxygen, which is responsible for carbon dioxide formation (Goncharova *et al.*, 1995). Therefore, in the presence of cesium added, the selectivity for ethylene oxide is enhanced by the suppression of the rate of ethylene oxide oxidation, resulting in the decrease in the rate of direct combustion. It, however, has been investigated for adding cesium in high-surface-area(HSA) α-Al_2O_3 that the selectivity for ethylene oxide was not enhanced, but the turnover frequency of ethylene oxidation, as well as the rates of ethylene oxide and acetaldehyde oxidation, were increased (Mao and Vannice, 1995).

In a previous work (Rojluechai *et al.*, 2006), nominal 1 wt.% Au/TiO_2 catalyst provided the highest selectivity for ethylene oxide with relatively low ethylene conversion. Moreover, the catalytic activity of Au catalysts was found to depend upon the size of Au particles and also catalyst preparation methods. However, ethylene conversion over all studied catalysts: Ag/(HSA)γ-Al_2O_3, Au/TiO_2, and bimetallic Au-Ag/(HSA)γ-Al_2O_3, could not be detected at any temperature below 493 K. Even though the reaction temperature was raised up to 543 K, ethylene conversion was still low in the range of 1-4%. Consequently, this limitation results in high energy consumption for catalyst activation at high temperatures, which is a disadvantage for industrial application. Non-traditional catalysis techniques are, therefore, expected to overcome this constraint. One of potential techniques is to combine the selective traditional catalysis and non-thermal plasma.

With the roles of gold in ethylene epoxidation, there are relatively confused points of view for existing literatures. The effects of alloying silver with gold on the oxygen adsorption properties of Ag over a set of 15 wt.% bimetallic Ag-Au/α-Al_2O_3 were studied (Kondaries and Verykios, 1996). The results showed that the presence of Au influenced the population and the activation energy of adsorbed oxygen species. Especially, when Au content increased, the molecular oxygen was more favorable in adsorption on Ag than atomic oxygen, indicated by its lower activation energy of adsorption. Based on the molecular oxygen theory, this adsorbed specie played a vital role for ethylene oxide formation, whereas atomic oxygen was considered to be an unselective oxidant for partial oxidation (Kilty *et al.*, 1973). While other research group reported in the different way that the selectivity for ethylene oxide was observed at a constant value up to approximately 10 wt.% Au content on the surface and decreased continuously at higher Au contents (Tories and Verikios, 1987). In a previous study (Rojluechai *et al.*, 2006), the effect of alloying Ag with Au supported on (HSA) γ-Al_2O_3 on the activity was investigated. It had been found that the addition of small amount of Au could create the Au-Ag bimetallic particles, which enhanced the ethylene epoxidation, whereas at a higher Au loading, the Au-Ag alloy appeared, leading to complete combustion. For this study, the optimum Ag to Au ratio was 13.18 to 0.63 wt.% at the temperature range of 510-520 K. The ethylene conversion and selectivity for ethylene oxide were enhanced because of the existence of the bimetallic Au-Ag, which increases the new favorable molecular oxygen sites.

As mentioned about the poorly dispersed silver on (LSA) α-Al_2O_3, that is why many researchers have attempted to find other alternative supports to provide better dispersion for silver particles and to enhance the activity of the ethylene epoxidation. Seyedmonir *et al.*, (1989) studied the activity and selectivity for ethylene oxide over well-dispersed Ag/SiO_2, Ag/η-Al_2O_3, and Ag/TiO_2 in the presence and absence of $C_2H_4Cl_2$ (EDC) compared with those of poorly dispersed Ag/α-Al_2O_3. In the presence of 0.5 ppm EDC, the well-dispersed catalyst exhibited the selectivity for ethylene oxide less than the poorly dispersed catalyst, except Ag/SiO_2, due to the presence of secondary oxidation reaction occurring on these reactive supports. In contrast, the ethylene oxide selectivities of 17 and 55% were obtained over 4.4 and 7.6 nm Ag crystallites on SiO_2, respectively, compared with 23% over 1 μm Ag crystallites on α-Al_2O_3 in the absence of EDC and CO_2 at 523 K.

Due to well-dispersed silver over (HSA) α-Al_2O_3 support (approximately 78-104 m^2/g), it has also been used as support for ethylene epoxidation, but it is a poor support for this reaction, and only complete oxidation is obtained. The absence of ethylene oxide was induced by this support containing a certain amount of acidity, leading to secondary oxidation of ethylene oxide, oxidation of ethylene, and isomerization of ethylene oxide to acetaldehyde (Mao and Vannice, 1995).

TiO_2 also has some special properties, which are believed to enhance the catalytic activity of ethylene oxidation reaction. It has been known that titanium dioxide exhibits a strong metal-support interaction effect with group VIII noble metals and possesses the ability for oxygen migration from reduced support particles onto the surfaces of the metallic particles of the catalysts, which, in turn, promotes oxidative reactions (Holgado *et al.*, 1998). However, it was reported that silver supported on TiO_2 showed zero ethylene oxide selectivity due to the isomerization of ethylene oxide to acetaldehyde on the support followed by the complete combustion (Seyedmonir *et al.*, 1989; Yong *et al.*, 1991).