CHAPTER II
BACKGROUND

2.1 Physical and chemical properties of methane

Methane is a colorless, odorless and tasteless gas. It is the major component of natural gas, which is an inexpensive and abundant energy resource. With its low molecular weight and extremely low boiling point (-162°C), it can only be found in the gaseous state under ambient condition. This disadvantage makes this resource difficult to handle due to its difficulties of transportation and storage.

Methane is a somewhat unreactive molecule. Tables 2.1 and 2.2 compare the average bond energy of C-H bond of the methane molecule and its first ionization potential with some other common gases. Although the ionization potential of methane is in the same order of magnitude as those of other common gases, the bond energy between C-H is markedly high compared to other covalent bonds.

In almost all cases, methane can be made reactive only by using very reactive species such as radicals which is one of the few effective techniques that have been traditionally applied for the reaction of methane. At present, the

Table 2.1 Average chemical bond energy of some covalent bonds

Bond	Bond Energy (kJ mol^{-1})	Bond	Bond Energy (kJ mol^{-1})
C-H	463	H-H	436
C-C	344	O-H	463
C=C	615	O-O	142
C-O	350	O=O	539

Table 2.2 The first ionization potential of some common gases

Gas	Ionization Energy (eV)	Gas	Ionization Energy (eV)
CH_4	12.5	O_2	12.2
H_2	15.6	CO	14.1
N_2	15.5	CO_2	14.4
Li	5.39	Na	5.14
K	4.339	Cu	7.7

oxidation of methane with oxygen is one of the most well-known radical reactions which thermally converts the methane molecule into a wide range of products depending upon the reaction conditions used but, thermodynamically, this application favors for the formation of CO_2 and H_2O in the combustion reaction.

2.2 Catalytic system for methanol synthesis

There are many catalytic systems that have been proposed for direct methanol synthesis from methane. Cu/MoO_3 seems to be the best catalyst in this research field. Unfortunately, the conversion and yield per pass of those systems is still not favorable from a commercial viewpoint. The main difficulties of the reaction are the unstableness of the desired product (methanol, which is more reactive than methane) and the catalyst requiring severe operating conditions. The other approach to methanol synthesis is utilization of synthesis gas, CO and H_2. Methanol synthesis from synthesis gas was also intensively examined by many researchers. The first commercialization was in Germany in about 1923 by BASF, using $ZnO-Cr_2O_3$ catalyst. The achievable conversion for the methanol synthesis reaction is greatly limited by thermodynamic equilibrium. Since the reactions are all

exothermic, the maximum equilibrium conversion is achievable at the lowest temperature (Satterfield, 1991), where the reaction rate is the lowest.

2.2.1 High-pressure process

A list of catalysts proposed for methanol synthesis is given in Table 2.3. Zinc oxide alone is a good catalyst for methanol synthesis at high pressure and temperatures above $350^{\circ}C$. However, it is not stable and it losses its activity very quickly. Stabilizers such as chromia probably prevent recrystallization of the zinc oxide and preserve the defect structure, as well as prevent crystal growth and loss of surface area.

Table 2.3 Catalysts proposed or used for industrial methanol synthesis (Satterfield, 1991)

Catalyst composition	Active phase in methanol synthesis	Properties and use
ZnO	ZnO	Original synthesis catalyst. Short life
ZnO/Cr_2O_3	ZnO	Standard high-pressure catalyst
$ZnO/MnO/Cr_2O_3$ + alkali	Alkalized ZnO	Standard high-pressure catalyst
Cu/ZnO Cu/ZnO/Cr_2O_3	Cu	Early low-pressure catalysts, short life
Cu/ZnO/Al_2O_3	Cu	Industrial low-pressure catalyst
Pd/SiO_2 Pd/basic oxides	Pd	Active; poorer selectivity than copper catalyst
Rh/SiO_2 Rh/basic oxides	Rh	Active; poorer selectivity than copper catalyst

2.2.2 Low-pressure process

After introduction of the high-pressure process in 1923, many different elements and compounds as synthesis catalysts were tested. One of these catalysts is copper oxide which, while it appeared to have little synthesis activity itself, was very effective when added to zinc oxide. This catalyst (Cu/ZnO) can have a very high activity at temperatures as low as $300^{\circ}C$. Copper metal is formed from reduction of CuO and is readily sintered at synthesis temperature with consequent loss of activity. ZnO can act as a stabilizer or dispersing agent to separate the active copper crystallites physically. Although the ZnO itself has activity for methanol synthesis, this is much less than that of copper (Twigg, 1989).

2.3 Gaseous plasma for activating methane molecules

The non-thermal plasma or non-equilibrium plasma can be produced at ambient temperature by using proper technique. A plasma is a good source of active species including electrons, ions and radicals for methane activation. The advantage of this energy saving process is the active molecules can be obtained under mild conditions instead of performing the reaction at high temperature and pressure. The non-equilibrium plasma also compensates for the disadvantages of the catalytic and non-catalytic direct partial oxidation of methane to methanol. Normally, the methanol synthesis process has an equilibrium limitation. The conversion and selectivity per pass are relatively low. Substantial amounts of unreacted gas has to be recycled. Several stages of reactor and cooling facility must be used to achieve the reasonable yield. In a non-thermal plasma, the temperature of active species is much higher than the bulk gas temperature. This can also quench the active reactants inside the reactor and avoid the equilibrium limitation of the reaction so that a better yield of desired product can be achieved.

2.3.1 Fundamental properties of plasma

Plasma is a mixture of the negatively and positivily charged particles in an otherwise neutral gas. The positively charged particles are the cations but the negatively charged particles can be either the electrons or the anions. The neutral species may be a mixture of free-radical species with stable neutral gases. Two important properties are known to be possessed by the plasma.

i) Quasi-Neutral property

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

ii) Interaction with electromagnetic fields

The plasma can have some interactions with an applied electromagnetic field due to the fact that it consists of the charged particles.

In general, plasmas can occur in all states (Nasser, 1971). The plasma in the solid is called a solid-state plasma. The gaseous plasma does not have any specific name. From this point, only the gaseous plasmas (which we now call "plasma") will be discussed along with the chemical reactions.

Unlike gases, plasma differ greatly in many aspects according to which they are usually classified. These aspects include the pressure, the distributions of charged-particle density in the entire plasma volume and the temperature.

2.3.2 Generation of plasma

There are several means of generating charged particles to produce the plasma. The collisions between the cosmic rays and gases in atmospheric layers can, for example, cause the electrons in those gaseous molecules to be liberated and thus produce the charged species. This process of liberating an electron from a gas particle with the creation of positive charge is termed ionization. On the other hand, the process of liberation an

electron from a solid is called electron emission. Both of these processes are of equal importance for the generation of the plasmas. The electrons and charged particles produced in the gaseous boundaries may be induced by the electromagnetic waves colliding with the solid surfaces to emit other electrons. These electrons, in turn, can collide with the solid surfaces to emit additional electrons. Various common ways of creating the charged particles can be classified as schematically shown in Figure 2.1(Nasser, 1971).

Production of Charged Particles

- Electrons plus Positive Ions
  - in Gases
    - Chemical and Nuclear Processes
    - Excited Atoms
    - Thermal Ionization
    - Radiation
    - Electron Collision
    - Positive-Ion Collision
- Electrons
  - on Surfaces
    - Chemical and Nuclear Processes
    - Field Emission
    - Electron Impact
    - Positive-Ion Bombardment
    - Radiation (Photoemission)
    - Thermonic Emission
- Negative Ions
  - in Gases
    - Radiative Attachment
    - Ion-Pair Production
    - Associative Attachment
    - Dissociative Attachment
  - on Surfaces
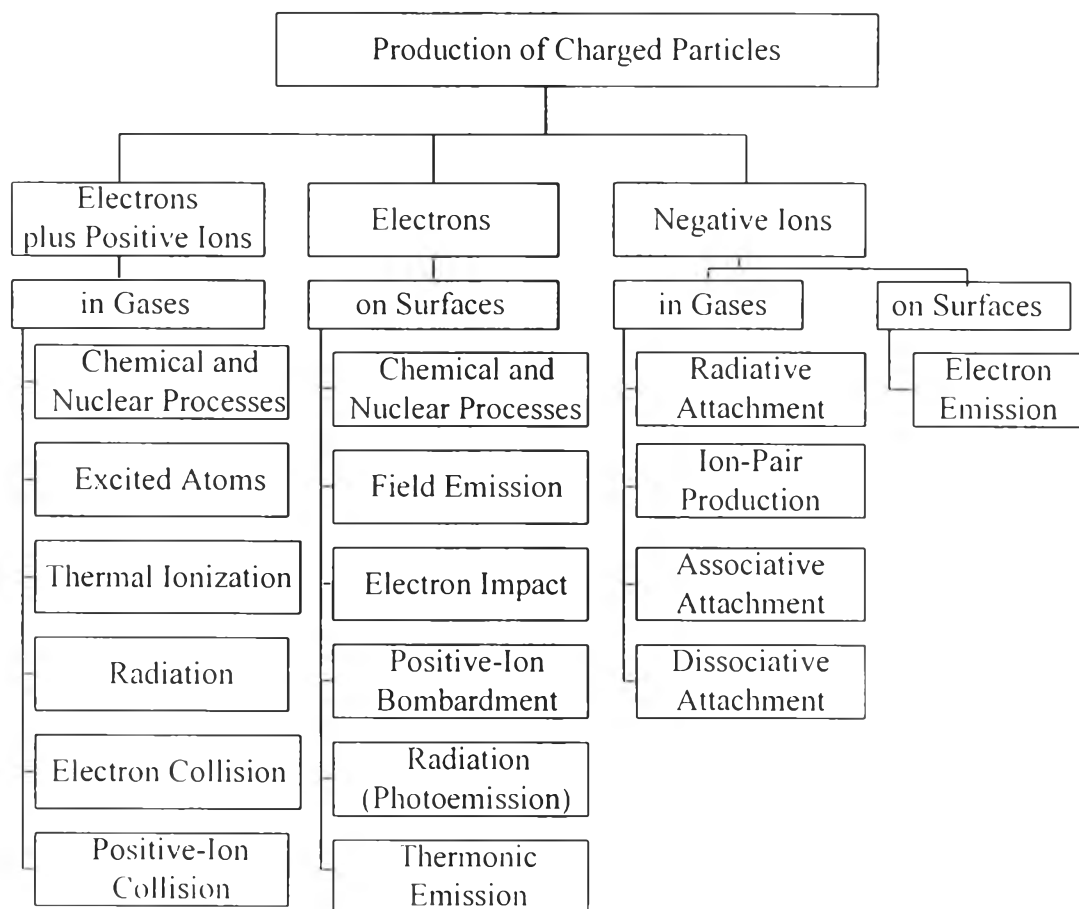   - Electron Emission

Figure 2.1 Production of charged particles

From this figure, it may be seen that the formation of negative ions can form when free electrons are available and attach themselves to neutral atoms or molecules. Gases deficient in one or two electrons in their outer shell tend to easily attach one electron, thereby filling the outer shell of the atom and forming a charged negative ion. These gases, such as oxygen, are usually known as electronegative gases. However, the electrons do not attach only to atoms but they can also attach to the molecules of two (or more) atoms, such as oxygen and thus form the negative charged particles as well.

$$e^- + O_2 \rightarrow 2O + e^- \rightarrow O^- + O \qquad (2.1)$$

$$e- + O_2 \rightarrow O_2^- \qquad (2.2)$$

The plasma can be generated by the collisions between the reactant gases and the electrons emitted from the surface of metal electrodes. This process of plasma generation is commonly known as the field emission process and is also shown in Figure 2.1. In this type of process, an intense electric field is applied across the metal electrodes to cause the reduction in its potential barrier providing the energy that each electron requires for leaving the metal surface. A most interesting phenomena that occurs on the metal surface when applying an extremely high electric field is that many electrons can leak from the surface despite its lower kinetic energy to overcome the potential barriers. This phenomena is known as the tunnel effect.

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 gases particles in their vicinity to form the ionized gases with an additional set of electrons. Accordingly, all of these electrons can further move and collide with other species. As a result, a large quantity of electrons and plasma 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. Various collision mechanisms can be occurring simultaneously in the gaseous space for which many of those can initiate the reacting chemical species. Some important collision mechanisms which occur in the gases are summarized in Table 2.1

The combined steps of the field emission process, collisions among these plasma species and the collisions between the species and the electrode surfaces are referred to as electric discharge phenomena. It was applied as the basis for the plasma generation technique used in this present study.

Table 2.4 Collision mechanisms in the gases

Collisions	
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	$e^- + AB \rightarrow A + B + e^-$
Atomic Decomposition	$A^* + B_2 \rightarrow AB + B$

The plasma produced by this discharge phenomena can be divided into two types. The first type is a thermal plasma, which is characterized by a high gas temperature and an approximately equal gas and

electron temperature. This type of plasma can also be referred to as a plasma in equilibrium. Typical examples of such plasma are those produced in arcs and plasma torches. The second type of plasma is termed a low-temperature or non-thermal or non-equilibrium plasma. This type of plasma is characterized by low gas temperature and high electron temperature. In other words, the non-equilibrium plasma consists of the electrons which have a much higher energy than the neutral gas particles. These energetic electrons may have energies ranging from 1 to 10 eV which will correspond to the temperature of about 10,000 to 100,000 K (Rosacha *et al.*, 1993)

2.4 Types of non-equilibrium plasmas

When the potential difference is applied across the plasma, the electric field will exert itself the charged particles and impart energy to them. The neutral species in the bulk of the plasma are not directly influenced by the field. The electrons, due to their light mass, are immediately accelerated to much higher velocities than those of heavier ions in the time available between collisions. The energy they lose through the collisions is taken up by their collision partners. If the pressure is small enough or the field is high enough, the electrons and some of the ions will, on average, have a kinetic energy which is much higher than the energy corresponding to the random motion of the molecules. This plasma type is again called a non-thermal or non-equilibrium plasma and can be classified into several types depending upon their generation mechanisms, their pressure range and the electrode geometry (Eliasson *et al.*, 1987).

2.4.1 Radio frequency discharge

These high frequency discharges are used extensively to produce plasmas for optical emission spectroscopy. The electrodes are normally kept outside the discharge volume whereas the plasmas are generated

inside by the induction technique. This can help avoid electrode erosion and contamination by the plasma. Since the wavelength of the electric field is much larger than the vessel dimensions, a homogeneous plasma is formed. RF discharges work very well at low pressure, but are also used at atmospheric pressure in which a thermal plasma can sometimes occur.

2.4.2 Microwave discharge

Another type of high frequency discharge that can be practiced presently is the microwave discharge, induced by a microwave (0.3-10 GHz) radiation source that must be guided or directed into the gaseous vessel by using a wave guide 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 3GHz.

2.4.3 Glow discharge

This is the stationary low-pressure discharge usually occurring between flat electrodes encapsulated in a tube. The typical pressure involved is normally well below 10 mbar and, therefore, needs only a comparatively low electrical potential difference (i.e., voltage) and current to run. Due to its low operating pressure and the resulting low mass flow, the discharge type only finds its best application in the manufacture of fluorescent and neon tubes and is not well suited for the industrial production of chemicals.

2.4.4 Corona discharge

When the pressure is increased in the case of the glow discharge, the operating electric field will have to be increased accordingly. This, unfortunately, makes the glow discharge becomes very unstable and

usually turns into a high-current arc discharge which is rarely controllable. The use of an in-homogeneous electrode geometry; e.g., a pair of pointed and plane metal electrodes oriented in a perpendicular direction to each other, is another method used for stabilizing the high-pressure discharge. The discharge generated from this kind of electrode configuration is termed a corona discharge. The behavior of this type of discharge is not only different from that of the glow discharge, but also depends significantly upon the type of electrodes used, either negative or positive types.

2.4.5 Dielectric-barrier discharge

This type of electric discharge is defined by the discharge generated within the gas-filled gap between a pair of metal electrodes of homogeneous geometry; e.g., the gap between two planar electrodes or in the annular space between two concentric cylinders. Either one or both electrodes are covered by a dielectric layer that is commonly made of glass. Many previous works referred to this kind of discharge as the silent electric discharge in which it has long been known to use in many studies on the plasma chemical reactions (Thanyachotpaiboon *et al.*,1998).

2.5 Non-catalytic direct partial oxidation of methane

Walsh *et al.* (1992) conducted a study of direct oxidative methane conversion at elevated pressure and moderate temperature. 3.8 volume percent of O_2 in the feed, 6.2 MPa, 465°C and 0.7 second of residence time, they achieved a methanol selectivity of 34.9%, methane conversion equal to 2.9% and 80% oxygen conversion. Methane conversion was limited to less than 3.0% and oxygen consumption was incomplete. Under these conditions, products were rapidly removed from the reactor (less than 1 second residence time). The further increase in methanol selectivity to about 35% at this low conversion and residence time and the absence of any other non-CO_x carbon-

containing products indicate that methanol is formed as an initial oxidation product under these conditions.

Casey *et al.* (1994) obtained the methanol yield of 1.8 mol%. This work was carried out in the temperature range of 300-500°C and at pressures of 3-6 MPa. The most important parameters controlling selectivities and yields were identified as the temperature in the reaction zone and the reactor geometry.

Under elevated pressure (3 and 50 bar); gas phase oxidations gave a maximum yield per pass at 3 bar and 475°C that was 1.7%, which is too low to make practical separation of the product. The main reason for low methanol yield is the low product stability under conditions of methane partial oxidation (Sokolovskii *et al.*, 1998).

Because methanol can be subsequently oxidized to CO, CO_2, and H_2O, it is desirable to remove methanol continuously from the reactor zone to increase selectivity. Liu *et al.* (1996) performed a modeling study of a non-permiselective membrane with a non-isothermal reactor. The membrane provided a uniform flow distribution and separated the hot reactor wall from a cooling tube located in the center of the reactor. The cold region in the reactor rapidly quenched further reaction. The selectivity for methanol formation at 4.6% conversion increased from 34 to 52% when quenching was used. The highest yield obtained was 3.8% at 55 MPa and 800 K. Methanol selectivity increased with increasing pressure and decreased with increasing temperature, residence time and O_2 concentration.

2.6 Catalytic direct partial oxidation of methane

Catalysis is the other approach for methane partial oxidation. The role of the catalyst is to selectively convert methane to methanol and also lower the operating conditions. Taylor *et al.* (1998) conducted a study on a series of impregnated MoO_3 and WO_3 catalysts at about 450°C and 15 bar. The

Cu/MoO$_3$ and Ga/MoO$_3$ showed the best methanol per pass yield. However, it still was very low (less than 1%). Comparison with the homogeneous gas phase reaction in a quartz packed reactor showed that the Cu/MoO$_3$ catalyst had a selectivity advantage for methanol production at 450°C and the combined selectivity to methanol and formaldehyde was greater than the homogeneous reaction in an empty reactor tube.

Walker *et al.* (1994) investigated the catalyst MoO$_3$:UO$_2$ patented by ICI, and Fe/sodalite in a novel bypass reactor, patented by Sun Chemical Company. For the ICI catalyst, the experimental conditions were 543°C, 5.4 MPa and 0.2 seconds contact time. The maximum selectivity to methanol was 43% at 2.2% methane conversion. Passing the reactants through a reactor with Fe/sodalite coating the reactor lining showed the selectivity to methanol of 23%.

In a catalytic membrane reactor, both catalytic reaction and separation processes are involved and the chemical equilibrium is shifted by removing the product through the membrane. Consequently, the catalytic membrane reactor may have advantages over other reactors. By using a Mo-Co-O/SiO$_2$ microporous membrane, the oxidation of methane to methanol by air was performed at atmospheric pressure and at 500-700°C. Under these conditions, 1.0% methane conversion and methanol selectivity of 11.2% were obtained (Lu *et al.*, 1996).

2.7 Plasma promoted partial oxidation of methane

Mallinson *et al.* (1987) revealed that when methane and oxygen were premixed and then passed through the AC electric field at atmospheric pressure, 5-10% methane conversion and 7-9% methanol selectivity could be achieved. For the mixture of 76% methane and 24% oxygen at 68°C and the reaction residence time of about 12.5 seconds, the oxygen conversion could be increased almost linearly with increasing voltage ranged from 5-8 kV. In

addition, no reactions were observed when only oxygen was passed through the reactor and mixed immediately with methane. A conclusion can be drawn that the methane active species participates directly in the reaction.

Bhatnagar (1993) performed the experiment in the annular discharge reactor to determine the effect of voltage, residence time and methane to oxygen feed ratio. The methane conversion and degree of deep oxidation decreased slightly as an increase of methane to oxygen feed ratio. The maximal methanol selectivity and methane conversion, 5.7% and 17.8% respectively, were obtained at methane to oxygen feed ratio equals to 3, the total flow rate of 500 cc/min and the applied voltage of 18 kV. A parallel pathway was found to exist between the production of methanol and ethane. The undesired pathways leading to the formation of carbon oxides from alcohol and ethane were also observed.

The recent work in this field, direct conversion of methane to methanol under non-equilibrium, squared-pulsed, silent discharge plasma at atmospheric pressure and temperature of $100^{\circ}C$ was done by Okazaki *et al.* (1997). The pulse frequency and voltage range were 250 Hz and 3-17 kV, respectively. High values of 2.4% and 32.6% of methanol yield and selectivity, respectively, were successfully obtained in a single-path experiment. They also concluded that oxygen atom or ions are the most important radical species that controls the reaction processes and selectivity for methanol synthesis. For a higher oxygen concentration, the selectivity of CO_2 becomes larger than that of methanol. The partial oxidation of methane to methanol requires a low concentration of oxygen in the source gas mixture. The sharp rise of the square pulse voltage itself plays an important role in the formation of essential radical species and is responsible for the observed high performance in the direct conversion of methane to methanol.

The methanol synthesis from methane and oxygen was examined using the plasma chemical process at room temperature. The methanol

selectivity increased with an increase in the gas residence time, but decreased with increasing input power. The gas mixture ratio of 96:4 ($CH_4/O2$) appeared to give the optimum performance for methanol production. High methanol yield (about 0.7%) was observed at 9kV, 5 kHz pulse frequency and 6.7 seconds gas residence time (Okumoto *et al.*, 1997).