

CHAPTER II

LITERATURE SURVEY

Basic principles about plasmas and electric discharges environment, particularly in parts that deal with the chemical reactions of methane, are described within this chapter. Beginning with some basic knowledge about the chemical properties of the methane molecule, a few aspects of the plasmas will then be introduced to eventually describe how the plasma can be generated for activating the methane molecules in order to initiate the direct methane conversion. Along with these, some practical studies on the direct methane conversion process under the different types of the electric discharges will be mentioned so as to be the evidence on the advances of the work in this field. Finally, aspects of the dielectric-barrier discharge reactor saved for the purpose of generating those plasmas for the present work will be discussed in details. It is necessary to point out that the present knowledge and insights about the electrical discharges environment and its plasma chemistry are very complicated, and so much of these information will not be presented here. Some literature (Nassar, 1971) is, however, recommended as good descriptive sources whenever the higher levels of the knowledge on the subjects of the plasmas are necessary.

2.1 Physical and Chemical Properties of Methane

Methane is commercially well known as a very inexpensive and environmentally safe feed stock of fuel supplies. It is, in a chemical point of

view, the smallest molecule in the entire hydrocarbon series, which consists of only one carbon atom surrounded by four hydrogen atoms. The most abundant and unique source of methane is the natural gas reserves, which are located in many different parts of the world. With its low molecular weight and non-polar nature, the boiling point of methane is extremely low ($-164\text{ }^{\circ}\text{C}$) and can only be found in the gaseous state under ambient conditions. This property, coupled with the fact that many natural gas deposits are now located in very remote areas, makes this resource somewhat expensive to transport.

The fact that methane is very flammable when presents in the oxygen atmosphere makes some people confused that methane is one of the very reactive molecules. Indeed, methane is a somewhat unreactive compound by its nature. Tables 2.1 and 2.2 compare the average bond energy of C-H bond inside the methane molecule and its first ionization potential with some of those other common gases.

Based upon these data, although the ionization potential of the methane molecule is in the same order of magnitude with those of other common gases, its bond energy between C-H is markedly high compared to other covalent bonds.

Table 2.1 The average chemical bond energy of some covalent bond (Gillespie et al.,1989)

Bond	Bond Energy (kJ mol^{-1})	Bond	Bond Energy (kJ mol^{-1})
C-H	413	H-H	436
C-C	348	O-H	463
C=C	619	O-O	143
C-O	335	O=O	494

Table 2.2 The first ionization potential of some common gases (Lide,1991)

Gas	Ionization Energy (eV)*	Gas	Ionization Energy (eV)
CH ₄	12.6	O ₂	12.06
H ₂	15.43	CO	14.1
N ₂	15.58	CO ₂	13.77
Li	5.39	Na	5.14
K	4.34	Cu	7.73

* 1 eV = 1.6×10^{-19} J

In almost all cases, methane can be made active only by using very active species such as radicals so the radicals chemistry are among the few effective techniques that have been traditionally applied for reaction with methane. Currently, the oxidation of methane with oxygen is one of the most well-known radicals reaction, which thermally converts the methane molecule into a wide range of products depending upon the reaction conditions used but, thermodynamically, this application favors the production of CO₂, CO and H₂O.

2.2 Gaseous Plasmas for Activating Methane Molecules

Since the gaseous plasma is another good source of active species including the electrons, ions and radicals, then some researches on the methane reactions using such plasma to initiate the reaction have been conducted.

2.2.1 Fundamental properties of plasma

In its simplest definition, gaseous plasma is a mixture of the negatively and positively charged particles in an otherwise neutral gas. The positively charged particles are, in all cases, the cations but the negatively charged particles can be either the electrons or the anions. The neutral species may be the mixture of the free-radical species with the stable neutral gases. Two important properties possessed by the plasma.

(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

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

In general, plasma can occur in all states (Nasser, 1971). The plasma in the solid is called solid-state plasma while the plasmas generated in the liquid and gaseous states do not have any specific names. From this point, only the gaseous plasmas (i.e., shortly called as “plasmas”) will be discussed along with the chemical reactions.

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

2.2.2 Generation of plasma

There are several means of generating charged particles to produce the plasma. The collisions between the cosmic rays and the gases in atmospheric layers can, for example, cause the electrons in those gaseous molecules liberated out and thus produce the charged species. This process of

liberating an electron from a *gas* particle with the creation of positive ion charge is termed *ionization*. On the other hand, the process of liberating 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 to collide with the solid surfaces to emit other electrons. These electrons, in turn, can collide with other gaseous particles to cause ionization. Various common ways of creating the charged particles can be classified as schematically shown in Figure 2.1(Nasser, 1971).

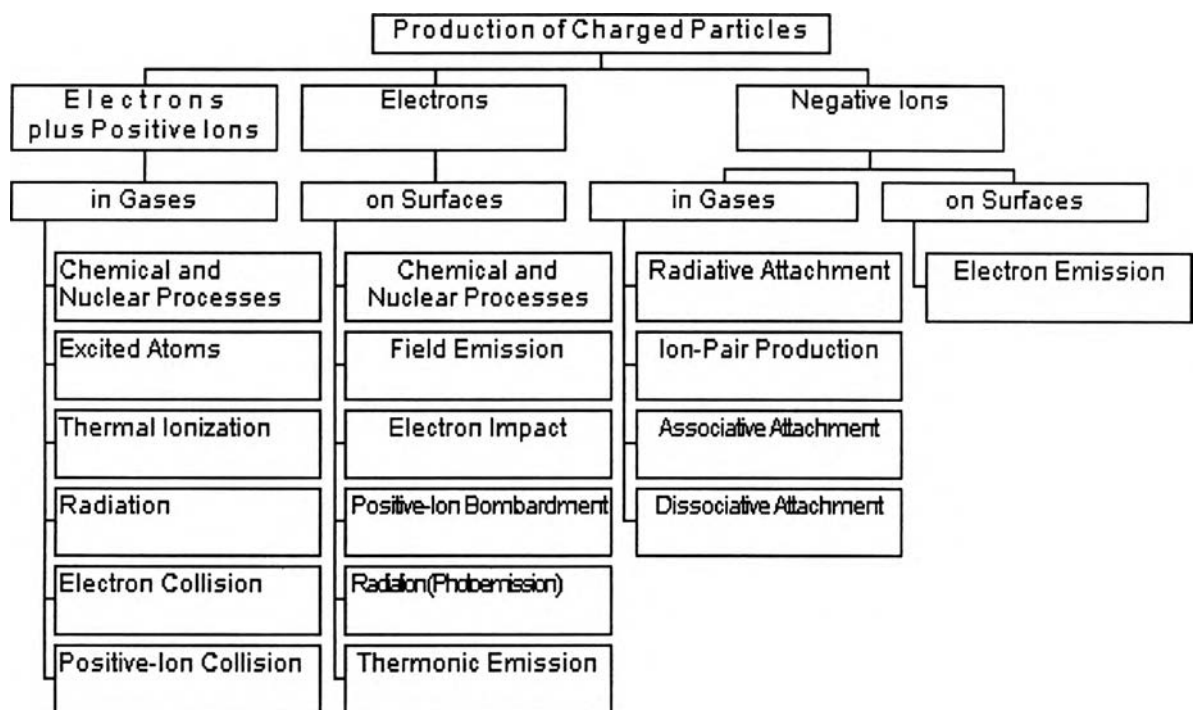


Figure 2.1 The alternative methods of charged particles generation.

From Figure 2.1, the formation of negative ions can take place, when free electrons are available and attach themselves to neutral atoms or molecules, negative ions are formed. Gases with one or two electrons deficient 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 O₂ and thus form the negative charged particles as well.

In the present study, the plasma was first generated by the collisions between the neutral molecules (e.g., methane) 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 externally intense electric field is applied across the metal electrodes to cause the reduction in its “potential barrier” and thus the energy that each electron requires for leaving the metal surface. A most interesting phenomena that occurs on the metal surface under the presence of 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”.

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, 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 has been started. Various numbers of collision mechanisms can be occurred simultaneously in the gaseous space, for which many of those can initiate the chemical reactions leading to the production and destruction of the chemical species. Some important collision mechanisms occurred in the gases are typically shown in Table 2.3.

Table 2.3 The collision mechanisms in the gases (Nesser,1971)

Collisions	
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	$A^\pm + B \longrightarrow B^\pm + A$
Electronic Decomposition	$e + AB \longrightarrow A + B + e$
Atomic Decomposition	$A^* + B_2 \longrightarrow AB + B$

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 discharges” phenomena. And they are applied as the basis for the plasma generation technique used in this present study.

The plasma produced by these discharge phenomena can be divided into two types. The first type is “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 plasma in equilibrium. Typical examples of such plasma are those produced in the arcs and plasma torches. The second type of plasma is termed “low-temperature” or “non-thermal” (cold-) 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 that have much higher energy than the neutral gas particles. 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).

The first implementation of the electric discharges generation technique as a tool for activating the chemical reaction can be tracked back to Siemens's experiments (Siemens, 1857) with the "silent discharge" (presently known as dielectric-barrier discharge) for the ozone generation in 1857. Even though large installations of such ozone generating systems for drinking water treatment plants have been settled in many countries since the early of this century, some extensive studies on the plasma application for the ozone production have still been continued to the last decades (Morinaga and Suzuki, 1961; Morinaga, 1962; Eliasson, 1987 and Nomoto et al, 1995).

At present, the process dealing with the plasma chemistry of electric discharges may be classified into two types, namely, the volume chemistry process; e.g., the ozone production in the so-called dielectric-barrier discharge, and the surface chemistry process; e.g., etching, deposition, or surface modification. The important application of methane plasma in volume chemistry process is the use of ionized methane as the ion source of the mass spectrometers. And the only application of methane plasma in the industrial surface chemistry process is the preparation of diamond coatings and ceramic materials.

Only the non-equilibrium, volume chemistry plasma in the space filled with electric discharge will be treated in connection with the present study.

2.3 Type of Non-Equilibrium Plasma

When the potential difference is applied across the plasma, the electric field will exert upon 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 extremely higher velocities than those 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 partly the ions will, on the 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 “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, 1991).

2.3.1 Radio frequency (RF) 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 plasmas. Since the wavelength of the electric field is much larger than the vessel dimensions, the homogeneous plasmas is formed. RF discharges work very well at low pressure but are also used at atmospheric pressure in which the thermal plasmas can sometimes occur.

Gogolides et al. (1995) conducted a study on the RF plasmas in methane. They focused their interest on the application of RF plasmas for the deposition of the diamond-like carbon films. Even though, no any results could

be exactly related to the study of the direct methane upgrading process, their published paper showed another good qualitative and quantitative discussion on the subject of methane plasma.

2.3.2 Microwave discharge

This is another type of high frequency discharge that can be practiced presently. The microwave discharge induced by the microwave (0.3-10 GHz) radiation source 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. Some experimental work in the area of direct methane conversion under the influence of the microwave discharge were conducted by Zerger et al. (1992) and Huang et al. (1994).

Zerger et al. (1992) investigated the combined effects of microwave plasma and several types of heterogeneous catalysts on the oxidation of methane and oxygen at low pressures (3-500 torr). The microwave frequency of 2.45 GHz was used to generate the free-radical species, which resulted in the subsequent reactions over the catalysts that were placed downstream from the plasma zone. They found that, with the constant CH_4/O_2 of about 2.22, the activation of microwave plasmas could lead to the formation of various gas-phase radicals, which then recombined over the catalyst surfaces. Many kinds of products could be obtained including ethane, ethylene, C_3 compounds, formaldehyde and methanol. The influence of the different catalysts was also reported. Typical catalysts used for thermal activation of methane such as Li/MgO and related systems were not very active or selective in plasma reactions. The methane conversion ranged from 4-55 % could be obtained for different catalysts. Ethane was the primary product with the highest selectivity

of 73 % while the ethylene was found to be the secondary product with the highest selectivity of 27 %. The Pt catalysts could promote the total oxidation pathway to CO₂ as has been found with methane catalysts promoted thermally. While the MoO₃ was observed to be effective in maximizing the ratio of ethane to ethylene, the highest C₃ compounds were found with the Pt catalysts. They concluded from their work that the major reaction pathway for the formation of ethane and ethylene were due to the coupling of two similar radicals; i.e., CH₃[•] and CH₂[•], respectively.

In the latter work (Huang et al, 1994), they focused on several designs of the microwave plasmas reactors for the oxidation of methane to produce methanol. With their specially designed reactors, they had proposed new techniques to control the generation of free radicals. Without the introduction of any catalysts into the reaction systems, one of the most interesting conclusions was that the methane dimerization products (C₂ hydrocarbons) could be eliminated by introducing CH₄ downstream from the plasma zone to react with the plasma generated from the O₂. However, the highest selectivity obtained was only about 4.4 %. The attempt of varying the power and the CH₄/O₂ ratio to increase the methane conversion (from 2.7-97 %) mostly produced carbon oxides from the reactions. Furthermore, the reactions had to be carried out under vacuum conditions (15-101 torr).

2.3.3 Glow discharge

This is, in common, the stationary low-pressure discharge usually occurring between the flat electrodes encapsulated in a tube. The typical pressure involved is normally well below 10 mbar and, therefore, need only 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.

2.3.4 Corona discharge

When the pressure is increased in 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 high-current arc discharge, which is rarely controllable. The use of in-homogeneous electrode geometry; e.g., a pair of pointed and plane metal electrodes oriented in perpendicular direction from each other is another method using for stabilizing the high-pressure discharge. The discharge generated from this kind of electrode configuration is termed “corona” discharges. The behavior of this type of discharge is not only differed from that of the glow discharge but also depends significantly upon the type of electrodes used, either negative or positive types. Due to small active volume occurred only around the point, the corona discharge is not very well applicable for the industrial chemical reactions dealing with the large quantities of gases. However, the principles of this discharge type are still satisfied by most manufacturers of the electrostatic precipitators.

A previous work on the application of the corona discharge with the oxidative coupling of methane could also be cited. An irreducible metal oxide, i.e., Sr/La₂O₃, was used as the catalyst coupled with the wire-plane electrode configuration for the production of either negative or positive electric discharges. In all cases, the inlet gaseous components consisted of the mixture of methane and oxygen. From the results, the great enhance in both the methane conversion and C₂ selectivity could be observed when the electric discharges and catalysts were present simultaneously into the reactions. They also found a saturation condition of the discharge current at which beyond that

point increases in the voltage caused nearly unchanged methane conversion. (Thanyachotpaiboon,1995)

2.3.5 The Dielectric-barrier discharge (DBD)

This type of the electric discharges is defined by the discharge generated within the gases-filled gap between a pair of metal electrodes of homogeneous geometry; e.g., the gap between two planar electrodes or in annular space between two concentric cylinders. Either one or both electrodes are covered by the dielectric layer, which is commonly made of glass. Many previous literature 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.

The dielectric is the key for proper functioning of the discharge, in which it can enable the system to be operated under atmospheric pressure up to high pressure range. With this dielectric type and the usual application of alternating high voltages (50 or 60 Hz power frequency to several kHz), substantial quantities of plasma are created by a large number of the so-called “micro-discharges” in the gas, which are statistically spread in space and time over the entire electrode area. Once ionization takes place at a location in the discharge gap, the transported charge moves and accumulates on the surface of the dielectric creating the opposite field to the applied electric field, which acts across the gap. After a few nanoseconds, the magnitude of this opposite field will counterbalance the external applied field and then the small current or, in other words, the continuous flow of energetic electrons within the micro-discharges across the gap is interrupted. Throughout the course of applying the sinusoidal high voltage, the formation of the micro-discharges will be started again and again, once the high enough field is reached in the gap during the successive power cycle. As a summary, the dielectric serves two functions.

The first function is to limit the amount of charge transported by a single micro-discharge and thereby minimize the chance of arc formation. The other task is to distribute the micro-discharges over the entire electrode area to maximize the chance for each gaseous particle to meet the energetic electrons and is, hence, converted into other species.

Apart from the only present commercial utilization of this DBD principle for the generation of ozone, some recent works on the dielectric-barrier discharge applications for the destruction of the toxic species, such as NO_x , SO_x from the flue gases, H_2S , NH_3 and volatile organic compounds were also subjected into studies (Rosacha et al, 1993; Penetrante et al, 1995; Li et al, 1995 and Chang et al, 1996). Their purpose was to monitor the feasibility of using this type of plasma reaction for treating and controlling the air pollution. Though no any commercially-promising results have been approved from those works, those studies of dielectric-barrier-discharges chemical reactions show, however, the encouraging number of interests on the attempt of applying this DBD to process the reactions.

Some recent studies of the partial oxidation of methane to methanol under the dielectric-barrier discharges environment are also reviewed here. The published work of 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. The mixture of 76 % methane and 24 % oxygen at 68 °C were used with the reaction residence time of about 12.5 s. The results concluded that the oxygen conversion could be increased almost linearly with the 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 from that point was that the methane active species, rather than oxygen species, participated directly in the reaction.

Two successive works in this field were performed in 1993. Bhatnagar et al. (1993) made the extensive analysis on the effect of several parameters including the voltage, residence time, methane to oxygen feed ratio and the individual partial pressure on the change reaction behaviors, i.e., the change in methane conversion and product selectivity. Several conclusions were established including the decrease of methane conversion from 4.07 to 1.73 % and the degree of deep oxidation reactions (CO_2 selectivity falling from 57.71 to 48.62 %) with the increasing CH_4/O_2 feed ratio from 3 to 20 under 9 kV and total flow rate of 500 cc/min. This degree of deep oxidation reaction, however, increased only slightly with the increasing residence time, and it was found to be nearly independent with the increasing voltages. With the methane/oxygen feed ratio of 3 and total flow rate of 500 cc/min, the highest methane conversion (5.72 %) and methanol selectivity (17.76 %) could be obtained at the highest operating voltage of 18 kV. Although methane conversion higher than 5.72 % could be obtained by decreasing the methane/oxygen feed ratio, but the selectivity of the desired products was dramatically low since most of the methane was converted into the carbon oxides products. The chemical pathways leading to the formation of each product were also been studied. From the results, a parallel pathway was found to be existed between the production of methanol and ethane. The pathways leading to the carbon monoxide might also be paralleled to the first two paths. The successively undesired pathways leading to the formation of carbon oxides from alcohol and ethane could also be observed. Upon the increasing voltage, it was found that the decomposition of large molecules like ethane could be occurred while this increased the methanol selectivity. Some preliminary kinetic studies had also been subjected to investigate in this work.

While the former focused their attentions on a lot of factors as previously mentioned, the other workers (Shepelev et al, 1993) had tried to

introduce ethane into the oxidation reaction. In this work, the small dielectric-barrier discharge (silent electric discharge) reactor with the active plasma zone of 1.6 ml was used. Some similar results to the aforementioned work could be observed. For example, the increasing voltage led to an increase in carbon oxides selectivity. Oxygen conversion dropped significantly with an increase in the reaction mixture flow rate. The methanol selectivity rose with the decreasing residence time suggesting that this desired product could be further oxidized to carbon oxides upon the lower flow rates. Some formation of ethylene and formaldehyde were also detected in this work. When only ethane and oxygen were simultaneously fed into the reactor, the oxygen consumption was also found to be increased at higher voltages. Dramatic rises in acetaldehyde and ethylene selectivities were obtained as the voltage was decreased. When the oxygen concentration was lower while maintaining the inlet flow rate and voltage, it was found that the lower selectivities of carbon oxides along with the higher selectivities of ethylene and higher hydrocarbon products could be achieved.

Thanyachotpaiboon (1996) introduced pure methane into a dielectric-barrier discharge plate-reactor with an active plasma zone of about 231-ml. The results were similar to the oxidative reaction system, such as increasing the voltage or residence time led to increasing methane conversion and products selectivities. According to the results of methane conversion, it was concluded that helium was not only a diluent but also enhanced methane to be more active. In this work, the products consisted of several hydrocarbons and ethane had the highest selectivity. It was found that when ethane or propane was introduced with methane into the reactor, the selectivities of C_3^+ hydrocarbon products increased significantly.

Recently, Poonphatanapricha (1997) studied the effect of ethane and propane that were introduced as pure reactant and also with methane in the

system. The products that occurred in the system were C₁ to C₄ hydrocarbons. It was discovered that methane conversion was increased with increases in the voltage or residence time. It was concluded that hydrogen abstraction was the most common initiate reaction that occurred in the system resulting in ethane, ethylene and propylene as the main products in the pure methane, ethane and propane system, respectively. Under the presence of ethane or propane with methane in the system, more ethane gave higher methane conversion but in contrast, propane acted like an inhibitor for methane reaction instead.

Moreover, the global warming problem caused by CO₂ emission has been pointed out for more than ten years. Several attempts of studies have been proposed and developed in order to reduce its atmospheric emissions. Nishiyama and Aika (1990) studied mechanism of the oxidative coupling of methane using CO₂ as an oxidant over PbO-MgO. The mechanism was studied by using isotope techniques. It was found that ¹³CO₂ and ¹²CD₄ produced exclusively ¹³CO and ¹²C₂ hydrocarbons and that no ¹²CO was produced under the low W/F (weight of catalyst/total flow rate) condition of the title reaction over 15 mol % PbO-MgO at 1073 K. The oxidative coupling of methane was assisted by the reverse shift reaction of CO₂, and one of the oxygen atoms of CO₂ was used for the methane coupling reaction. It was also found that products at C₂ hydrocarbons reacted with oxygen from carbon dioxide under high conversion or high temperature.