# CHAPTER III

# LITERATURE REVIEW

## 3.1 Methane Utilization

Methane, the major component of natural gas, is generally generated along with liquid petroleum processing. Nowadays only a small percentage of the world methane production of around 7% is utilized for production of other more valuable chemicals (Liu *et al.*, 2001). Most of methane is used for heating and power generation, and approximately 4% is flared or vented to atmosphere (Lunsford, 2000). These account for the wastage of the valuable resource and the increase of pollutant emissions, especially carbon dioxide that is the most important greenhouse gas. Furthermore, production of methane rises progressively and rapidly in each year, and this trend is possibly extended into the 21$^{st}$ century (Lunsford, 2000). Consequently, according to environmental awareness and regulation, the technology of methane conversion has been a prominent issue recently.

At the present time, methane is commercially converted to more useful chemicals via indirect route. Synthesis gas that is carbon monoxide and hydrogen is initially produced from methane by reforming reaction by steam or carbon dioxide, or partial oxidation reaction to which the large quantity of heat is essential for supplying. After that, synthesis gas is further processed to other useful chemicals such as $C_1$-compounds (methanol and formaldehyde) and $C_2$-compounds (ethane and ethane). Energy cost and heat management, thus, is the common issue of this route. On the contrary, via direct route, methane is converted straight to $C_1$ and $C_2$-compounds without the need of large amount of energy for synthesis gas production. Accordingly, even through this method is under research and development stage, the direct technology of methane conversion has been investigated intensively, especially the oxidative coupling of methane (OCM) to $C_2$-hydrocarbons (ethane and ethane).

## 3.2 Oxidative Coupling of Methane (OCM)

The oxidative coupling of methane to ethane and ethylene was achieved firstly by Keller and Bhasin in 1982 and then a large number of papers concerning this topic have been increased rapidly. Most researchers have paid attention to the development of the catalysts and reaction mechanisms. The catalytic oxidative coupling of methane may be conducted in two modes of operation: cyclic mode (redox mode) in which methane and oxidant is introduced to the catalyst alternately and co-feed mode in which methane and oxidant is introduced simultaneously. From experimental results, among the OCM catalysts, the irreducible catalysts (stable cationic valence catalyst) containing a rare earth metal or a transition metal showed the best $C_2$-yield in the co-feed mode of operation. Examples of the rare earth metal oxides promoted by alkali earth oxide and halide are $SrO/La_2O_3$ (Mimoun *et al.*, 1990), $SrF/Sm_2O_3$ (Long and Wan, 1997) and $BaF_2/9LaOF$ (Wan *et al.*, 1999), and those of the transition metal oxides promoted by alkali are $MnK_2WO_4/SiO_2$ (Palermo *et al.*, 2000). These catalysts can reach more than 20% $C_2$-yield.

From kinetics studies, it is generally accepted from many experiments (Tsai *et al.*, 1999) that the OCM process consists of complex heterogeneous-homogeneous free radical reactions. A hydrogen atom is abstracted from methane gas on active oxygen species, forming $CH_3 \bullet$ radical. Then two radicals couple together in gas phase to ethane as the primary product. Ethane can, after that, react further to the secondary product, ethylene, by both oxidative dehydrogenation of ethane on the catalyst surface and a free radical hydrogen-transfer reaction in gas phase. Small quantity can be formed by thermal dehydrogenation in gas phase. Oxidation reactions can take place from all hydrocarbons in the system. In addition, it was found that the carbon dioxide gas is mainly occurred from oxidation of ethylene on catalyst surface and of methane in gas phase (Pak, Qiu and Lunsford, 1998). It was suggested that active oxygen species, the $O_2^-$ or $O_2^{2-}$ or $O^-$ species, are responsible for $C_2$ hydrocarbon formation (Au et al., 1998: Au, Liu and Ng, 1998: Sinev, Korchak and Krylov, 1986).

In addition, from kinetics investigation, the order of oxygen in OCM reaction is lower than that in deep oxidation (Lane and Wolf, 1988); hence, operation with the lower oxygen concentration can improve the selectivity of $C_2$-compounds, or applying a membrane reactor to the OCM reaction is a good alternative.

Nevertheless, there are several limitations in commercializing the conventional OCM process. The problem on hot-spot temperature within catalyst bed is one of great concern. It is because the OCM reaction occurs at high temperature (above 973 K) and generates a large amount of heat, as well as a great quantity of heat from methane oxidation reaction. Therefore, the temperature within the catalyst bed may be 150-300 K higher than the exterior (Lunsford, 2000). Moreover, the methane conversion is restricted less than 40% since the concentration of oxygen in feed stream must be kept below an explosion value and the catalyst lifetime is also insufficiently lengthy due to volatile promoters. As above limitations, there have been considerable efforts to deal with this engineering problem such as the design of reactor configurations. Membrane reactor has been demonstrated a great potential for the OCM process. By controlled distribution of oxygen to the catalyst bed via a membrane, the heat of reaction released to the catalyst bed can be much more flat throughout the reactor cross section, thereby the hot-spot temperature is less sever. The high conversion of methane can be obtained because the oxygen and methane flow stream does not contact with each other and, consequently, there is no explosion limit in operating with membrane reactor. The application of membrane to OCM reaction does not only show the ability to prevent the hot-spot problem and the explosion limitation, but it is also capable of developing the catalytic performance of reaction through the kinetics aspect of this reaction. From theoretical studies, Reyes et al. (1993) and Cheng and Shuai (1995) reported that the $C_2$-yield could reach 45% in a membrane reactor.

## 3.3 Membrane Reactor for Oxidative Coupling of Methane

The membrane applied to the oxidative coupling of methane process can be classified into three types according to the feature of the transportation of oxygen through membrane: oxygen molecule transportation, oxygen lattice diffusion, and oxygen ion conduction. These corresponding membranes are (1) porous membrane, (2) dense metal and metal oxides membrane, and (3) dense oxygen ionic conducting solid oxide electrolyte membrane, respectively (Liu *et al.*, 2001).

In the porous membrane reactor, membranes frequently used for studies are ceramic and vycor glass, especially alpha-alumima ceramic membrane due to its stability at high temperature. From experimental results, it was found that the $C_2$-yield

from porous membrane is somewhat small since the pore size of the membrane is so board that the permeation rate of oxygen as well as nitrogen when using air as oxidant is quite high, and the hydrocarbons also can transfer through membrane to oxidant side. In a small number of studies in which pure oxygen and pure methane is used as reactants, it was shown that the high $C_2$-yield was achieved (Coronas *et al.*, 1994); however, owing to the high cost of air separation, exploiting pure oxygen is economically unreasonable. Like the porous membrane, the dense membrane fabricated from a metal or a metal oxide gives small $C_2$-yield due to very low diffusion rate of oxygen lattices through the membrane. There are not many studies using this membrane type. An example of this membrane is lead oxide supported on magnesia (PbO/MgO) membrane (Omata *et al.*, 1989) and the silver membrane (Anshits *et al.*, 1990).

According to the above mentioned, many attentions have, therefore, been paid to the last membrane type, dense solid oxide electrolyte membrane that conducts oxygen ion. Through the high temperature of operation in this reactor, the high oxygen transportation rate and the high reaction rate is attainable such that the $C_2$-yield can be improved. Furthermore, this membrane system is able to operate as a fuel cell as well as an oxygen pump, particularly fuel cell operation by which the electric power can be generated as another product.

## 3.4 Solid Oxide Fuel Cell for Oxidative Coupling of Methane

The first application of a fuel cell reactor with a solid oxide electrolyte membrane for production of chemicals was conducted by Vayenas and Farr (1981). They converted amonia to nitrogen oxide in solid electrolyte fuel cell. The concept of simultaneous generation of more valuable chemicals and electric power, after that, was developed considerably, especially the $C_2$-hydrocarbons production by the OCM reaction in a solid oxide fuel cell reactor (SOFC reactor).

Solid oxide fuel cell was, perhaps, firstly applied as a membrane reactor for the co-generations of $C_2$-hydrocarbons and electric power by Pujare and Sammells approximately in 1988 and this system, after that, has been received interest widely at the present day. The reasons are that the SOFC reactor makes it possible to deal with the OCM reaction that needs high operating temperature in order to generate $C_2$-compounds and it can provide the potential oxygen form selective for the OCM

reaction as well. Through the fuel cell principle, this power generator efficiently produces the electricity since the electrical energy is created straight from the chemical energy without thermal energy stage. From the experimental result in the SOFC reactor, the heat of reaction of OCM reaction was converted effectively into electric power with the high $C_2$-yield and this system was regarded as the chemicals energy co-generation system (Tagawa *et al.*, 1999). In addition, the pollutant emissions released from the SOFC reactor is very small. Nonetheless, the high temperature of the SOFC operation restricts the property qualification of each material and sealing the cell is also a serious problem.

Configurations of the SOFC cell that has been developed are tubular type and flat plate type (bipolar type). A most commonly used electrolyte is 8%mol yttria-stabilized zirconia (YSZ), which possesses high oxygen ion conductivity at a wide range of oxygen partial pressure and temperature. Strontium-doped lanthanum manganite (LSM) and doped lanthanum chromite is generally used as the cathode material and the cell connector material, respectively.

From a number of experiments with a variety of catalysts, it was revealed that the low methane conversion and electrical current was a major problem, even if the high $C_2$-selectivity could be achieved. The $C_2$-yield could not reach more than 4% (Eng, 1980; Guo *et al.*, 1999; Tagawa *et al.*, 1999). Eng (1980) prepared silver anode catalyst on a tubular 1.8 mm-thicked YSZ. The best result showed the $C_2$-selectivity of 53.6%, the $C_2$-yield of less than 3% and the electrical current of 153 mA. After that, Guo *et al.* (1999) studied the silver electrode that was catalyzed by $Sr/La_2O_3$-$Bi_2O_3$ on the tubular 1.0 mm-ticked YSZ. It was shown that the high $C_2$-selectivity of 90-94%, the $C_2$-yield about 0.2-1% and the electrical current of 20-40 mA was obtained. Furthermore, from their mathematical model, it was found that the increase in the methane conversion and electrical current caused the decrease in the $C_2$-selectivity, and the experimental results were consistent with this model. These problems are caused intensively by the insufficient activity of the anode catalyst and the insufficient oxygen transport rate through the solid oxide electrolyte. Hence, the development of a superior anode catalyst and a solid oxide electrolyte with high ionic conductivity are very essential. The other improvements that are crucial for success are, for example, development of catalyst preparation method and fabrication of thin solid electrolyte.

To select an anode catalyst, many requirements of OCM catalyst as an anode catalyst in a SOFC reactor must be considered. As the activity and selectivity of the catalyst for $C_2$-compounds depends markedly on the appropriate control of oxygen species adsorbed on the catalyst surface and the $O^-$, $O_2^-$, $O_2^{2-}$ and $O_3^-$ species are responsible for the formation of the $C_2$-compounds. These species can be controlled by the type and composition of the metal in the catalyst. It was recommended that the catalyst surface should exhibit high basic characteristic (Choudhary et al., 1997). The metal oxides of alkali, alkali earth and rare earth metal are capable of serving this quality. Besides the catalytic activity, an anode catalyst should be a high electronic conductor (Singhal, Park et al., 2000) because whereas occurring the OCM reaction on anode side, electrons, that transfer from the oxygen ions on electrolyte to the anode catalyst to form the adsorbed oxygen species and that are produced by taking place the reaction between the adsorbed oxygen species and methane, must move out to external circuit through the anode catalyst. It was also proposed that the anode catalyst should be a p-type semiconductor (Gellings and Bouwmeester, 2000). Furthermore, the catalyst should be able to resist severe condition both thermal and chemical in the SOFC reactor.

It was found that the preparation method of the anode catalyst considerably influenced the catalytic activity of OCM reaction. Tagawa et al. (1998) compared the activity of the LaAlO anode catalyst prepared by the nebulizer method and that prepared by the paste method. They found that the formation rate of $C_2$-compounds obtained by nebulizer method was four times more than that obtained by paste method. It was explained that the nebulizer method could provide the surface structure that was active for the $C_2$-compounds formation and could give a strong interaction between the catalyst and the YSZ plate, which resulted in the stability of active structure after the reaction, thereby improving the catalytic activity. An effective way to improve the methane conversion, which is impeded by the transportation of oxygen ion through electrolyte membrane, is the use of a thin solid oxide electrolyte. Tagawa et al. (1999) studied the influence of the YSZ electrolyte thickness on the catalytic activity. The results showed that the thickness of YSZ affected strongly on the methane conversion; the reduction of the thickness from 2.0 mm to 1.5 mm caused the methane conversion to increase around 14 times at 1223 K. Another way to increase the transportation rate of oxygen ion through membrane is the application of electromotive force to the SOFC reactor in order to accelerate the

oxygen ion movement, being termed the electrochemical oxygen pump. From the experimental results, the enhancement of activity by applying the electromotive force to the cell was dependent on the anode catalyst. In the $La_{1.8}Al_{0.2}O_3$/YSZ/LSM SOFC reactor, the increase of oxygen ion transportation by supplying the positive potential (oxygen pumping) promoted the formation rate of carbon oxides whereas affected insignificantly on that of the $C_2$-compounds (Tagawa *et al.*, 1999, 2002). Alternatively, when applying the negative potential, the formation rates of carbon oxides were suppressed while that of the $C_2$-compounds was stable (Tagawa *et al.*, 2002). For the $Bi_2O_3$-Ag system, the electrochemical oxygen pumping could improve the activity and selectivity of the reaction (Otsuka *et al.*, 1985).

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