CHAPTER III

LITERATURE REVIEWS

3.1 Oxidative Coupling of Methane

After the pioneer work of Keller and Bhasin in 1982, there has been extensive research and development efforts on the oxidative coupling of methane to C2 hydrocarbons. Effective catalysts are important for oxidative coupling of methane (OCM). Many studies have been focused on the design of catalysts for OCM (Guczi *et al.*, 1996; Gesser and Hunter, 1998; Ji *et al.*, 2003). The methane coupling reaction is shown as follows (Nozaki and Fujimoto, 1994; Cheng and Shuai, 1995; Guo *et al.*, 1997; Choudhary *et al.*, 1997).

$$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O \qquad (3.1)$$

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O \qquad (3.2)$$

The major obstacles of this route are the low C2 products yield and hot spot temperature. The C2 products yield achieved in a conventional packed-bed reactor was limited to about 25% (Wang and Lin, 1995; Lunsford, 2000). This is due to the presence of undesired complete oxidation reactions in the gas phase and partially on the catalyst surface. As found from the OCM kinetics (Wang and Lin, 1995; Guo *et al.*, 1997), the deep oxidation of methane to CO_x is the main problem. A lower oxygen partial pressure is favorable in achieving in higher C2 selectivity. Therefore, distributing the oxygen along the reactor length is an important strategy to improve the performance. A membrane reactor was proposed to control the distribution of oxygen to the catalyst bed. 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 severe. Moreover, because methane does not directly contact with oxygen when using a membrane reactor, methane combustion reaction can be avoided from the explosion problem. In addition, the use of membrane reactor to control the oxygen concentration in a continuous reactor offers a possibility to achieve a much higher C2 selectivity and yield for OCM.

3.2 Membrane Reactor for Oxidative Coupling of Methane

The membranes applied to the oxidative coupling of methane process can be classified into three types according to the feature of the transportation of oxygen through the membrane: oxygen molecule transport in porous pore, 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).

A porous membrane reactor was earlier suggested. Santamaria and co-workers (Lafarga *et al.*, 1994; Coronas *et al.*, 1994a; 1994b) reported a porous ceramic membrane tube reactor for OCM. The membrane reactor gives a considerably better selectivity than the fixed-bed reactor; however, the improvement in C2 yield is usually small. In addition, it is not economical to use pure oxygen when air is to be used in porous membrane reactor, a subsequent separation of product and nitrogen is needed (Liu *et al.*, 2001).

To avoid this problem, the dense metal oxide membrane could be of interest. The dense membrane fabricated from a metal or a metal oxide was formerly suggested. An example of this membrane is lead oxide supported on magnesia (PbO/MgO) membrane (Omata *et al.*, 1989), lead oxide supported on porous tube (PbO/SiO_2-Al_2O_3) (Nozaki and Fujimoto, 1994) and the silver membrane (Anshits *et al.*, 1990). Compared to porous membrane reactors, the dense metal oxide or metal membrane reactors were more successful in terms of attaining high selectivity (Omata *et al.*, 1989; Nozaki and Fujimoto, 1994). However, due to very low diffusion rate of oxygen lattices through the membrane, the reaction rate is very slow (Liu *et al.*, 2001). Another problem is very difficulty in fabricating a pinhole-free PbO film on the porous support material (Nozaki and Fujimoto, 1994). Therefore, there are limited works using this type of membrane for this reaction.

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. Lin and co-workers investigated the performance of OCM reaction in conventional FBR and membrane reactor using dense mixed conducting ceramic membrane packed with Li/MgO catalyst (Kao *et al.*, 1997). The kinetic equation over

Li/MgO were obtained from their previous work (Wang and Lin, 1995). It was found that the use of the dense mixed conducting ceramic membrane significantly improved C2 selectivity and yield. They also studied OCM reaction using a membrane reactor with a catalytically active membrane reactor such as $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) (Akin *et al.*, 2001, 2002; Zeng *et al.*, 2001) and 25 mol% yttria doped bismuth oxide (BY25) (Zeng and Lin, 2000). It was found that the best single-pass C2 yield was achieved in BYS doping with Y and Sm membrane reactor (Akin *et al.*, 2002). C2 yield of 35% and C2 selectivity of 54% at 1173 K could be obtained in their system (Akin *et al.*, 2002).

Among the various inorganic membranes, solid oxide electrolyte membrane has much more attention especially due to their great potential in fuel cell application (Stoukides, 2000; Liu *et al.*, 2001). Some attempts were recently reported on electrochemical selective oxidation of methane to C2 products using the reactors which are similar to the solid oxide fuel cells (Tagawa *et al.*, 1998, 1999; Guo *et al.*, 1999).

3.3 Solid Oxide Fuel Cell Reactor for OCM

Solid oxide fuel cell (SOFC) system has been attracting a lot of attentions as a future energy system which converts the energy of combustion directly into electric power with high efficiency. Among these studies, chemicals and electric power co-generation is one of the outstanding topics. Farr and Vayenas (1980) first demonstrate this mode of operation for the case of NH_3 conversion to NO. For SOFC as a reactor for OCM reaction, a solid electrolyte was used as an oxygen separator and an oxygen distributor to achieve higher C2 selectivity. In this electro-catalytic system, combined effects of activation of oxygen on an anode and permeation of oxygen through the electrolyte control the performance of reactor. Therefore, the activation of adsorbed oxygen on an anode and the oxygen transport through the electrochemical system should be studied. The literature of the characteristics of oxygen species and oxygen permeation through the solid electrolyte are cited as shown in the following paragraphs.

3.3.1 Characteristics of oxygen species

A number of reviews were published on this topic (Eng and Stoukides, 1991; Voskresenskaya *et al.*, 1995; Stoukides, 2000). The use of external potential is also of recent interest. Special attention has been focused on the effect of non-Faradaic electrochemical modification of catalytic activity (NEMCA) (Vayenas *et al.*, 1996; Metcalfe, 2002) observed for a wide range of reactions in the presence of metals such as Pt, Pd, Rh, Au, Ag and Ni, and those of oxides such as IrO_2 and RuO_2. Conventional solid electrolytes used in most studies are O^{2-} conductors like YSZ (Belyave *et al.*, 2000; Tsiplakides *et al.*, 2000) or CeO_2 (Petrolekas *et al.*, 1998).

Temperature-programmed desorption (TPD) technique is usually used to investigate behaviors of oxygen species on the selective oxidation catalyst by detecting gas phase oxygen desorbed from pretreated oxide surface with increasing the temperature of the sample oxide. However, very limited studies on TPD in SOFC reactor are reported. Tsiplakides *et al.* (2000) investigated oxygen TPD on metal electrode (e.g. Pt and Ag) deposited on YSZ. Two oxygen adsorption states, i.e., strongly bonded anionic oxygen and weakly bonded atomic oxygen were generated by applied potential. Baker *et al.* (1995) studied TPD in system of SOFC by using CaO-stabilized zirconia (CSZ) tube as a solid oxide electrolyte and Ag as a cathode. Two anode systems were used, $La_{0.8}Ca_{0.2}Cr_{0.9}Co_{0.1}O_3$ with Au current collector and Au alone. A new low-temperature desorption peak was electrochemically generated (Baker *et al.*, 1995). The formation of new oxygen species, at lower desorption temperature, under electrochemical oxygen pumping conditions were observed in both cases (Tsiplakides *et al.*, 2000; Baker *et al.*, 1995).

As a tool for designing anode catalysts for the oxidative coupling of methane in the SOFC reactor, the conventional TPD technique has been successfully applied (Tagawa *et al.*, 1998). Tagawa *et al.* (1998) using temperature-programmed desorption (TPD) technique to specify the surface oxygen species. Various LnAlO powder samples (Ln = La, Sn, Nd, Dy, Ce, Tb, Pr) were investigated. The results suggested that the lanthanum containing catalyst (LaAlO) was active and oxygen species were capable of moving around at the operating temperature of SOFC. They proposed that the oxygen species desorbed at low temperature (below 1000 K) were active for CO and CO2 formation (oxygenate site) while the oxygen species desorbed at higher temperature (above 1000 K) were active for oxidative coupling of methane to C2-hydrocarbon (coupling site). A novel fuel cell type temperature-programmed desorption (FC-TPD) was proposed and proved to be a very useful tool for characterization of SOFC type reactors (Tagawa *et al.*, 2003). In the same report (Tagawa *et al.*, 2003), the effect of applied potential on reactivity was also investigated. The change in the selectivity with applied potential, when the selective oxidation catalyst was employed as the anode with a pre-mixed feed of air and methane, gave a new aspect to NEMCA phenomena.

3.3.2 Oxygen permeation through solid electrolyte

Several research groups have published their experimental results on the overall oxygen permeation through many oxygen permeable electrolyte membranes such as YSZ (Han *et al.*, 1997), Calcia Stabilized Zirconia (CSZ) (Nigara *et al.*, 1995), mixed ion-electronic conducting materials such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) (Teraoka *et al.*, 2002; Lee *et al.*, 2003) and other perovskite type ceramics, for example, $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) (Akin *et al.*, 2001; Platon *et al.*, 2002), $BaBi_xCo_{0.2}Fe_{0.8-x}O_{3-\delta}$ (Shao *et al.*, 2000), $BaCo_{0.4}Fe_{0.6-x}Zr_xO_{3-\delta}$ (Tong *et al.*, 2000).

Perovskite-type $(A,La)(Co,Fe)O_{3-\delta}$ (where A is alkaline-earth element) are among the known mixed conductors with highest oxygen permeability, but are thermodynamically and/or dimensionally unstable under large oxygen chemical potential gradient typical for membrane reactor operation conditions (Kharton *et al.*, 1999; Shaula *et al.*, 2003). At temperatures below 1000–1070 K, the membrane performance is degraded with time. More over, it has a very high thermal expansion (Kharton *et al.*, 1999; Shaula *et al.*, 2003). The membrane material for membrane reactor, especially OCM reaction, should offer high oxygen permeation flux but the gas phase oxygen should be greatly minimized or eliminated. This can be achieved by selecting a suitable anode catalyst to provide a reasonable reaction rate (ten Elshof *et al.*, 1995; Xu and Thomson, 1997; Zeng and Lin, 2000; Akin and Lin, 2002). The conventional Yttria Stabilized Zirconia (YSZ) electrolyte has been widely used to provide the electrochemical permeation of oxygen for the oxidative coupling of methane (Moe *at al.*, 1998a,b; Tagawa *et al.*, 1998, 1999, 2003; Guo *et al.*, 1997, 1999).

Several studies focused on the steady state oxygen permeation in membrane reactors for oxidation reactions, for example, partial oxidation of methane (Ishihara et al., 2002) and oxidative coupling of methane (Zeng and Lin, 2000; Akin *et al.*, 2001). However, very limited studies on oxygen permeation in SOFC reactors have been reported. In addition, no modeling work was reported with focus on examining the effects of reaction side conditions on oxygen permeation through the oxygen ion conductor membrane.

3.3.3 Anode catalyst development

Concerning the anode catalyst selection, White *et al.* (1992) suggested that the design of anode for partial oxidation of methane required the development of insight into appropriate electrocatalysis strategy favoring this oxidation path compared with complete oxidation of methane. They have referred to basic knowledge of heterogeneous gas-phase catalysis in designing the anode catalysts and suggested several perovskite oxides as an anode catalyst. Pujare and Sammells (1988) suggested $Sm^{3+}O^{-}$ type active site designed on $Pt/Sm_2O_3/LaSrMnO$ anode. However, only 0.2 % maximum yield was obtained. Selection of the characteristic basicity of rare earth metal oxides (Imai and Tagawa, 1986, 1990; Wada *et al.*, 1989) and control of crystal structure by the mist decomposition method (Imai *et al.*, 1987) enabled to adjust the activity of surface oxygen species to the desired reaction (Imai *et al.*, 1990). One of the active and selective catalysts for OCM was amorphous $Ln_{1-x}Al_xO_3$ catalyst (Ln = rare earth metal) (Imai *et al.*, 1990; Spinicci *et al.*, 2001).

As mentioned above, LaAlO was the best active anode catalyst in their experiments and oxygen species were capable of moving around at the operating temperature of SOFC (Tagawa *et al.*, 1998), the nebulizer method was suggested for prepared the LaAlO anode catalyst on an YSZ plate electrolyte for SOFC reactor. The nebulizer method gives more adhesive property and also higher catalytic activity while using less amount of catalyst than conventional paste method. They studied the OCM in SOFC (LSM/YSZ/LaAlO as cathode, electrolyte and anode) reactor. In their experiment, a plate type cell unit of 7.0 cm^2 with a thickness of 0.3 mm. was placed between two ceramic tubes tightened with a Pyrex seal. Platinum wire was connected to platinum mesh placed on both electrodes to serve as a current collector. The 96.5% of C2 selectivity while 4% of CH_4 conversion can be obtained. Methane was converted to C2 (ethene and ethane) without producing CO_2 and the energy of the oxidation reaction was converted into an electric power. Thus, the reaction system can be regarded as CO_2-free combustion as well as chemical energy co-generation.

The catalyst preparation method was improved later by Moe *et al.* (1998). The ultrasonic mist pyrolysis was applied to prepare the catalyst for the same SOFC configuration as mentioned above. Among several preparation methods, i.e., ultrasonic mist pyrolysis, paste method and nebulizer method; the ultrasonic mist pyrolysis was the most effective for the activity of anode catalyst. The periodic operation for catalyst preparation was suggested to obtain better adhesive properties and to control morphological characteristics.

This system was applied with a tube type cell unit later (Tagawa *et al.*, 1999). The effect of membrane thickness was determined. At 1223 K, the reaction rate with 1.5 mm YSZ is about 14 times higher than that of 2.0 mm. The amount of oxygen atom used for oxidation of methane corresponding well with oxygen atom calculated from electric current by Faraday's law. At 1223 K, maximum of 4% yield with 180 mA of electric current can be obtained. However, comparing with YSZ plate type of their previous work, the YSZ tube gives lower C2 selectivity.

Apart from the effort to decrease of YSZ electrolyte thickness, another way to increase the transportation rate of oxygen ion through membrane is the application of electromotive force to SOFC reactor in order to accelerate the oxygen ion movement, being termed the electrochemical oxygen pump (EOP). From the experimental results, the enhancement of activity by applying the electromotive force to the cell was dependent on the anode catalyst. In $La_{1.8}Al_{0.2}O_3$/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, 2003). 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.*, 2003).

3.3.4 Modeling of SOFC reactor

Regarding the mathematical modeling, very few investigators studied the modeling of OCM reaction in SOFC reactors. Guo *et al.* (1999) studied OCM reaction in SOFC tube type reactor with a YSZ electrolyte of 1 mm thickness. Ag and 1 wt% Sr/La_2O_3-Bi_2O_3 were used as cathode and anode catalyst, respectively. A maximum of 2% yield with 33 mA of electric current can be obtained at 1003 K. A mathematical model based on well-mixed and plug flow with the complex kinetic expressions was proposed. Although good agreement between their simulation and experimental results were observed, some parameters in the model are unclear.