

## CHAPTER II

### LITERATURE REVIEWS

Since the pioneering work of Keller and Bhasin [36], the OCM leading to higher hydrocarbons has received much attention. Recently, Lee and Oyama [10] published an excellent review on this reaction which is useful in obtaining information on the methane coupling reported up to early 1987. Almost the OCM reactions are studied relevantly with catalyst systems. Reports of improved catalysts appear at regular intervals. Recently, it is claimed that La and Sm oxides are especially good catalysts for methane coupling. However, it is frequently difficult to assess these claims since the activity and selectivity of catalysts for this reaction are very dependent on the experimental conditions used (temperature, space velocity,  $\text{CH}_4/\text{O}_2$  ratio reactor design, etc.). The catalyst systems concerned for these reactions are as follows:

#### 1. The alkali and alkaline earth metal oxides

Lunsford and his co-worker [15] mentioned that lithium-doped magnesia was an active and selective catalyst for oxidative coupling reaction. The other alkali metals have also been shown to be highly effective in promoting MgO such as Na/MgO, the products of  $\text{C}_2 +$  is up to 22.4 %. The combination of Li and lanthanide (La, Ce, Pr, Nd, or Sm) promoters for MgO give the spectacular selectivity to  $\text{C}_2$  98.4% at methane conversion of 25 % and catalysts are stable. Yamamura et. al. [6] mentioned that NaCl is the most effective promoter among the alkali halides to promote perovskite oxide catalysts.

The alkaline earth metal oxides such as MgO is the most popular compound used as catalyst in the OCM. It is mostly used with lithium oxide or lithium chloride. Ross et. al. [1] found that the catalyst for the OCM reaction increased slightly.

Beryllium oxide itself is not a selective catalyst for C<sub>2</sub>, but when doped with Li show a high selectivity of 63% at a conversion of 24 %. BaO alone give a high C<sub>2</sub> selectivity at low partial pressure of oxygen. Generally the other alkaline earth metal oxides are the effective catalysts when mixed with other groups. Although calcium oxide is less studied compared magnesia, it is an effective catalyst especially when promoted with alkali metals.

A.A. Davydov et.al[25] mentioned the basic sites on the oxide surfaces effect on the methane coupling. The introduction of Sm<sub>2</sub>O<sub>3</sub>, PbO, and Na<sub>2</sub>O admixtures affects greatly the content and strength of basic sites on MgO surface. They have found the mechanical activities also changes the basic sites number. Hence, for MgO the basic sites number increases considerably after mechanical activities providing a higher MgO activity in OCM. According to their data strong basic sites, forming on the surface of active and selective OCM catalysts, indeed participate in methane activation. They have proved this by direct experiments on methane interaction with MgO surface by means of IR and UV spectroscopy .

Therefore, they can explain the reasons for a high catalytic activity of Sm<sub>2</sub>O<sub>3</sub>/MgO systems and design catalysts by varying basic sites strength and number. They can do this (i) by doping catalysts with various admixtures and (ii) by increasing the number of coordinatively unsaturated states on the surface.

Bi Ying-Li et.al [26] studied the OCM on the superionic conductors, they found that the reaction mechanism of the OCM has attracted world wide attention. In this study a series of catalysts modified by Li<sup>+</sup>, Na<sup>+</sup> containing superionic conductors or solid electrolytes have been tested for the OCM. It was observed that the addition of A<sub>2</sub>BO<sub>4</sub> (A = Li<sup>+</sup>, Na<sup>+</sup> ; B = S,W,Mo) compounds to La<sub>2</sub>O<sub>3</sub> and Na<sup>+</sup> containing superionic conductors to CaO enhanced C<sub>2</sub> yield and the C<sub>2</sub> yield of the modified catalysts was intimately related with their conductivities.

E.V. Kondratenko et al [27] studied the OCM over oxides of alkali earth metals using  $N_2O$  as oxidant. Using a  $CH_4 - O_2$  and a  $CH_4 - N_2O$  reaction mixture,  $N_2O$  was shown to be more active and more selective oxidant than  $O_2$ , but  $CH_4$  conversion was similar for both oxidants. The pressure of hydrogen significantly enhances the decomposition of  $N_2O$  and the formation of  $C_2H_6$  over  $SrO$ .

M. Yamamura et al [3] mentioned that sodium-doped oxide ( $Na/CaO$ ) catalysts prepared by the sol-gel method (SGM) show relatively high performance for the OCM compared with that prepared by impregnation method (IM). The difference between the performance of these catalysts for the OCM seems to come from the difference in morphology and TPD profiles of these catalysts.

## 2. Lanthanide and actinide metal oxides

The oxides of lanthanides,  $M_xO_y$ ,  $CeO_2$  is unusual in that it catalysis nonselective oxidation. However, the ion-conducting characteristics of  $SrCeO_3$  and Ce-Yb mixed oxides impart effectiveness and selectivity for methane coupling at high conversion (25-53%). The selectivity to  $C_2$  over  $La_2O_3$  is very high at low partial pressure of oxygen, but decreases with increasing oxygen/methane ratio. High selectivity to ethylene is attainable at low conversion of methane for some catalyst systems. La, Ce, Nd, and Sm are excellent promoters for  $Li/MgO$ , giving  $C_2$  selectivities to 98.4% at significant conversion. Promotion of  $La_2O_3$  with alkali, or especially alkaline earth metals improves selectivity to  $C_2$ .  $Pr_2O_3$  and  $Pr_6O_{11}$  are of the modest effectiveness for coupling to  $C_2$ , the latter promoted with and alkali metal is highly effective. For the other lanthanide metal gave high selectivities, but low conversion, except for  $Sm_2O_3$ . The basicity (or amphotericity) of  $Sm_2O_3$  apparently makes it the most effective oxide of lanthanide series. Promotion of  $Sm_2O_3$  by lithium salts, especially  $LiCl$ , further enhances the utility of the catalyst. Tang Cailin et al [2]

studied the roles of oxygen and carbon dioxide on methane oxidative coupling over CaO and  $\text{Sm}_2\text{O}_3$  found that in the reaction zone, the rate of methane conversion remain constant over  $\text{Sm}_3\text{O}_3$  catalyst at 837 K. No inhibition of the catalyst activity by carbon dioxide was observed over  $\text{Sm}_2\text{O}_3$  catalyst.

The promoted lanthanide oxides seem to be the most promising catalysts so far for methane coupling. Not only the activity and selectivity, but also the catalyst life is a very important asset for the coupling catalysts under the severe reaction conditions employed.

Z.R. Ismagilov et al [32] mentioned that methane dimerization occurs at 650-850 °C, and catalysts which operate under fluidized bed conditions should have the high mechanical strength and thermal stability to comply with severe conditions of this process. It is evident that these properties of catalysts depend mainly on the support properties. They used impregnated alumina with aqueous solution of the salts. In some experiments a special impregnation method was used: the spherical granules of hydroxide were impregnated with aqueous solution of salts. Solution  $\text{SiO}_2$  was added to aluminium hydroxides before hydrocarbon-ammonia moulding. Some method they used lanthanum adding to silica oxide. The results were obtained to conclude that alumina promotion with lanthanum and cerium give the increase of thermal stability, and thermal stability depends on the method of introduction, type of alumina and amount of additives.

S.N. Vereshchagin and J.R.H. Ross [33] studied the kinetic of the OCM on samarium oxide. The conclusion of kinetic study are: (1) formation of carbon monoxide and carbon dioxide occurs via different reaction routes, rates of formation of  $\text{CO}_2$  and  $\text{C}_2$  are different for cubic and monoclinic modification of  $\text{Sm}_2\text{O}_3$  whereas rate of CO formation is independent of the type of structure. [2] The reaction pathway for formation of CO possibly includes gas phase or decomposition of oxygen containing species such as  $\text{CH}_3\text{O}$  or  $\text{CH}_2\text{O}$ . [3] Rate of  $\text{CO}_2$  formation at high  $\text{CH}_4/\text{O}_2$  ratio is limited by  $\text{CO}_2$  desorption from the  $\text{Sm}_2\text{O}_3$  surface.

### 3. Transition metal and the others

The oxide of the transition metals are normally effective alone only as catalysts for nonselective oxidation. However, when supported, or promoted, especially with alkali metal halides, significant activity for coupling of methane has been achieved. For example,  $\text{TiO}_2$  promoted with  $\text{LiCl}$  gave selectivity to  $\text{C}_2$  about 80% and predominantly to ethylene. Under cyclic condition or low oxygen/methane ratio,  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  are effective for coupling, but at ratios close to 0.5. However, promotion of  $\text{MnO}_x$  with  $\text{NaCl}$  or  $\text{LiCl}$  gave  $\text{C}_{2+}$  selectivities up to 62.5% at 1023 K and for oxygen/methane ratios close to 0.5.  $\text{LiCl}$  was especially effective as a promoter for generation of ethylene. A.M. Efstathiou et al [5] studied kinetics of methane oxidative coupling on zinc-doped titanium oxide found that the zinc oxide concentration had a large effect on the activation energy of  $\text{C}_2$  hydrocarbon formation and  $\text{CO}_x$  formation. The relationship between the rates of methane conversion,  $\text{C}_2$  hydrocarbon and  $\text{CO}_x$  formation and oxygen pressure in the range 650 to 750 °C was found to depend strongly on the  $\text{ZnO}$  dopant concentration. Temperature and oxygen pressure were found to affect strongly the relationship between the selectivity of  $\text{C}_2$  hydrocarbons formation and  $\text{ZnO}$  dopant concentration.

M.C. Góng et al [29] have studied the effect of additives on  $\text{TiO}_2$ -based catalytic performance. The effect of Li, La, Mn and W added to  $\text{TiO}_2$  on the catalytic performance for the OCM revealed that these system exhibited high activity and  $\text{C}_2$  hydrocarbon selectivity at 770 °C with a GHSV of 14400  $\text{h}^{-1}$ . The following data were obtained: methane conversion 41.65%,  $\text{C}_2$  selectivity 61.7% and  $\text{C}_2$  yield 25.6%.

E.N. Voskresenskaya et al [30] studied  $\text{O}_2$  and  $\text{N}_2\text{O}$  as oxidant for the OCM over the Bi-containing oxide catalysts. The comparative study has been carried out over  $\text{Bi}_2\text{O}_3$ , 20 wt%  $\text{Er/Bi}_2\text{O}_3$ , and 0.2 wt%  $\text{Li/Bi}_2\text{O}_3$  using  $\text{O}_2$  and  $\text{N}_2\text{O}$  as oxidants. It was shown that the rate of  $\text{C}_2$  for undoped and Er-doped  $\text{Bi}_2\text{O}_3$  catalyst at the same level of methane conversion. For  $\text{Li/Bi}_2\text{O}_3$ , the rates of  $\text{C}_2$  production were similar for both

oxidants. Different mechanisms for  $N_2O$  decomposition were suggested over doped and undoped  $Bi_2O_3$ .

A.G. Anshits et al [31] studied the role of the defect structure of oxide catalysts for the oxidative coupling of methane. They mentioned the oxygen defect (anion vacancies for SrO and Li/ $Bi_2O_3$  0.1 wt%) and impurity defects (transition metal ions for Li/CaO, Na/CaO) play the important role for the process of  $N_2O$  activation in OCM. The addition of  $O_2$  in  $CH_4$ - $N_2O$  reaction mixture decreased the rate of  $N_2O$  decomposition over SrO and Li/ $Bi_2O_3$  while for M/CaO catalysts such effect was not observed. It was explained by the fact that the activation of  $O_2$  and  $N_2O$  in OCM process occurs on the same centers for the first group of catalysts and different centers for the second group catalysts. Two temperature ranges of proceeding OCM reaction over SrO were established. The mechanism in which  $CO_2$  is a poison for active oxygen species was



It is clearly seen that not only the catalysts, but also temperature, pressure, partial pressure of oxygen and methane and other variables effect on conversion selectivity in the OCM reaction. For example, Cailin [2] found that the conversion of methane increased sharply to a maximum at the entrance of the bed and then slowly dropped with increasing bed height due to carbon dioxide formation. The curve of rate distribution displays a sharp drop at the point where the concentration of oxygen reaches zero. When adding carbon dioxide to  $Li_2O$ -promoted system, the yield was drastically reduced. Then carbon dioxide occurs in some reactions can inhibit the conversion and selectivities of methane and  $C_2$  respectively.