CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Processes for Hydrogen Production

Hydrogen or a flexible fuel is thought to be the cleanest energy source of 21st century as it can be used in many fields without polluting the environment. As a result, extensive studies are undertaken in academia as well as in industry to develop energy-efficient processes for production of hydrogen with economical methods and transporting of this hydrogen are of the first order of importance. There are three major processes that can be employed to produce hydrogen from e.g. steam reforming, autothermal reforming and partial oxidation process.

2.1.1.1 Steam Reforming (SR)

SR is a process for converting hydrocarbons into syngas in industry. However, this process has many disadvantages; first of all CO_2 is produced along with the syngas so the separation of CO_2 and its disposal are major issues and secondly high energy demand because SRM is a highly endothermic process. The process typically occurs at temperatures of 700 to 850 °C and pressures of 3 to 25 bar. Steam reforming can be described by the irreversible reaction (2.1) combined with the reversible reactions (2.2).

$$C_nH_m + nH_2O \rightarrow nCO + \left(n+\frac{m}{2}\right) H_2 \qquad \Delta H^0_{298}>0 \qquad (2.1)$$

$$CO + nH_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298}= -41.2 \text{ kJ/mol} \qquad (2.2)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H^0_{298}= -206.2 \text{ kJ/mol} \qquad (2.3)$$

Catalytic steam reforming (CSRM) is a two-stage-process. The first stage is highly endothermic reaction (2.1) which requires heat and catalyst. The second stage is water-gas-shift reaction (WGS reaction) (2.2) which usually taken place in another reactor at temperature about 130 ^{0}C.

There also are some side reactions occurring such as methanation (2.3), methane decomposition (2.4), and carbon monoxide disproportionation (Boudouard reaction) (2.5) that be caused of carbon deposition.

$CH_4 \rightarrow C + 2H_2$ $\Delta H^0_{298} = 74.9$ kJ/mol (2.4)

$2CO \rightarrow C + CO_2$ $\Delta H^0_{298} = -172.4$ kJ/mol (2.5)

The carbon deposition on the catalyst occurs in the form of filament and encapsulating carbon leading to the deactivation of catalytic activity as a result of methane decomposition (2.4), and carbon monoxide disproportionation (Boudouard reaction) (2.5).

2.1.1.2 Catalytic Partial Oxidation (CPO)

The catalytic partial oxidation offers the greatest potential for a fast, efficient and economical conversion of methane to synthesis gas, due to the high conversion, high selectivity, suitable H_2/CO ratio, and very short residence time. This process is achieved by passing methane and oxygen (air or pure oxygen) through a suitable catalyst at temperature range of 300-1000 °C at atmospheric pressure. The general reaction can be described by:

$C_xH_y + \frac{x}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2$ $\Delta H^0_{298} < 0$ (2.6)

This process has many advantages that is mild exothermic reaction, requires less energy to operate that makes more energy efficient. Especially, this process provides high methane conversion and desired H_2/CO ratio for methanol and Fischer-Tropsch synthesis. However, this process has some side reactions such as methanation (2.7), water-gas-shift reaction (2.8), methane decomposition (2.9), and also carbon monoxide disproportionation (2.10)

$CO + 3H_2 \rightarrow CH_4 + H_2O$ $\Delta H^0_{298} = -206.2$ kJ/mol (2.7)

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H^0_{298} = -41.1$ kJ/mol (2.8)

$CH_4 \rightarrow C + 2H_2$ $\Delta H^0_{298} = 74.9$ kJ/mol (2.9)

$2CO \rightarrow C + CO_2$ $\Delta H^0_{298} = -172.4$ kJ/mol (2.10)

The partial oxidation of methane is diagrammatic shown in Figure 2.1 and also gave some information below.

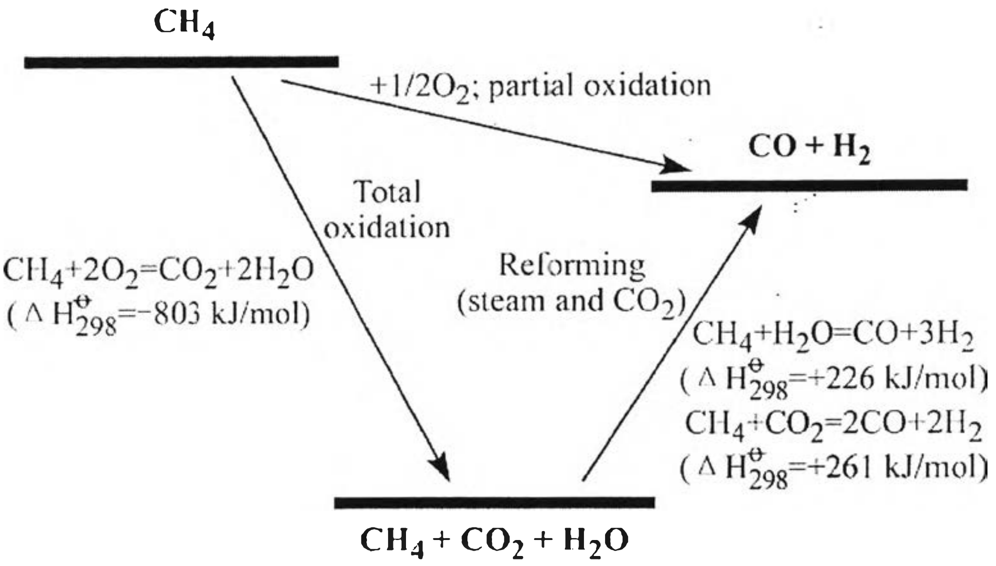


Figure 2.1 Thermodynamic representation of the partial oxidation of methane (Zhu *et al.*, 2004).

2.1.1.3 Autothermal Reforming (ATR)

Autothermal Reforming (ATR) is a combination of SR and CPO reactions. The method uses exothermic heat of the oxidation reactions to provide the heat required by the endothermic reforming reaction in a single unit to produce hydrogen. The method is useful for small scale hydrogen production because of faster startup, small size, higher efficiency, fuel flexibility and hydrogen purity. The process operates at temperature in the range of 950 °C to 1100 °C and 100 atm of a gas pressure. This reaction can be described by eq. 2.11 and 2.12.

$$2CH_4 + O_2 + CO_2 \rightarrow 3H_2 + 3CO + H_2O + \text{Heat} \qquad (2.11)$$

$$4CH_4 + O_2 + 2H_2O \rightarrow 10H_2 + 4CO \qquad (2.12)$$

Table 2.1 Comparison of technologies for H_2 production from natural gas

Technology	**SMR**	**ATR or POX**
Advantages	High efficiency High cost investment	Smaller capacities Lower cost investment Simple system
Drawbacks	Complex system Sensitive to qualities of natural gas	Lower efficiency

The most challenge of catalytic partial oxidation of methane is the deactivation of catalytic activity due to the carbon deposition from methane decomposition and carbon monoxide disproportionation reaction. Moreover, the sintering of metal catalyst at high temperature is also found. Thus, many studies have been focused on the catalytic partial oxidation of methane so as to modify the catalytic stability. Therefore, many literature surveys of this process are reviewed

2.1.2 Polyol Method

Since the unique properties in optical, electrical, and catalytic applications of the metal nanoparticles, so they have been widely investigated. Especially, in the catalytic applications, the particle size, shape and metal distribution in dispersion medium are the particular factors to control the catalytic properties. The methods were used for metal nanoparticles synthesis such as hydrazine, polyol, borohydried, γ-ray irradiation, etc (Ningthoujam *et al.*, 2009).

Polyol process has often been used for reduction of metal ions to metal particles. The polyol process has been used to prepare elemental Ni, Cu, Co, Ag, Pt, Au, Pd, Fe, and Cd and also bimetallic alloys of AgPd, CoNi, FePt, and AuPt. This process applies a polyalcohol such as ethylene glycol, propylene glycol, diethylene glycol, trimethylene glycol, and butylene glycol (Figure 2.2) as both reducing agent and solvent, and when coupled with a base, it encourages as a perfect medium for the reduction of metal salt precursors (Carroll *et al.*, 2011).

Polyols perform as solvents which are able to dissolve inorganic compounds and offer a wide operating temperature in range from 25 °C to boiling point for preparing inorganic compounds due to their relatively high boiling points. Polyol itself can act as a protective agent to avoid agglomeration. For example, ethylene glycol, when the zero valent metal is nucleated from the bivalent metal ion at the high boiling point of ethylene glycol, metal particles are surrounded with lone pair of electrons of oxygen of butane-2,3-dione derived from ethylene glycol (eq. 2.13, 2.14). The presence of a lone pair of electrons keeps the metal particles separated and therefore, the particle size is regulated and controlled without surfactants (http://shodhganga.inflibnet.ac.in/bitstream/10603/6499/6/06_chapter%201.pdf).

$$HOCH_2CH_2OH \rightarrow CH_3CHO + H_2O \qquad (2.13)$$

$$2M^+ + 2CH_3CHO \rightarrow CH_3COCOCH_3 + 2M + 2H^+ \qquad (2.14)$$

The selection of which polyol is used for the reduction of metal precursors is defined by the reduction potential and the boiling point of the glycol. For example, the easily reducible metals: Pt, Cu, and Pd do not need high heat and can reduced in propylene glycol, which has boiling point about 188 °C, while the less easily reducible metals: Ni, Co, and Fe need higher heat so the trimethylene glycol with boiling point about 327 °C is suitable.

The significant parameters which effect on controlling size, shape and agglomeration of the metal particle are temperature, amount of alkali base, reduction time, and reactant concentration.

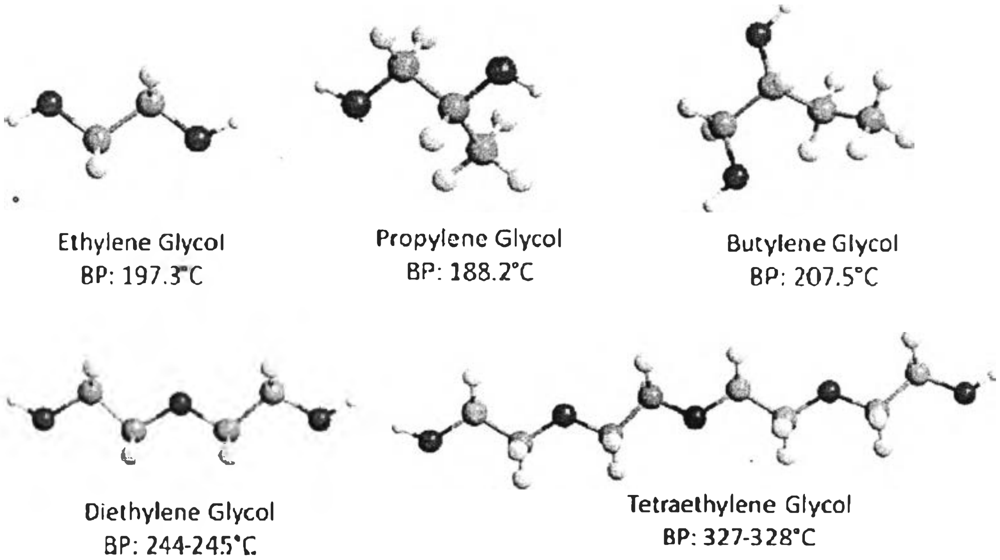


Figure 2.2 Numerous polyalcohol used for the polyol process (Carroll *et al.*, 2011).

2.2 Literature Review

2.2.1 Partial Oxidation of Methane

Methane is a chemical compound which be main component of natural gas. Methane is used for LNG products, power gas, and syngas. Especially, Syngas or synthesis gas is a gas mixture of hydrogen, carbon monoxide, and some carbon dioxide. Possible pathways via which methane is converted are shown in Figure 2.3 Syngas is used as feedstock for chemical production, such as olefins and synthetic oil via Fischer–Tropsch process. Steam reforming, partial oxidation, and autothermal reforming are main process which use for syngas production. Obviously, partial oxidation of methane (POM) is the interested process to produce syngas because this process is high conversion, high selectivity, suitable H_2/CO ratio, and very short residence time. Normally, the partial oxidation of methane operate at temperature in range of 300 to 1000 °C so many researchers has studied and has sought for a catalyst which be stable at operating condition, give both high conversion and selectivity, can reduce the operating temperature and reduce carbon formation.

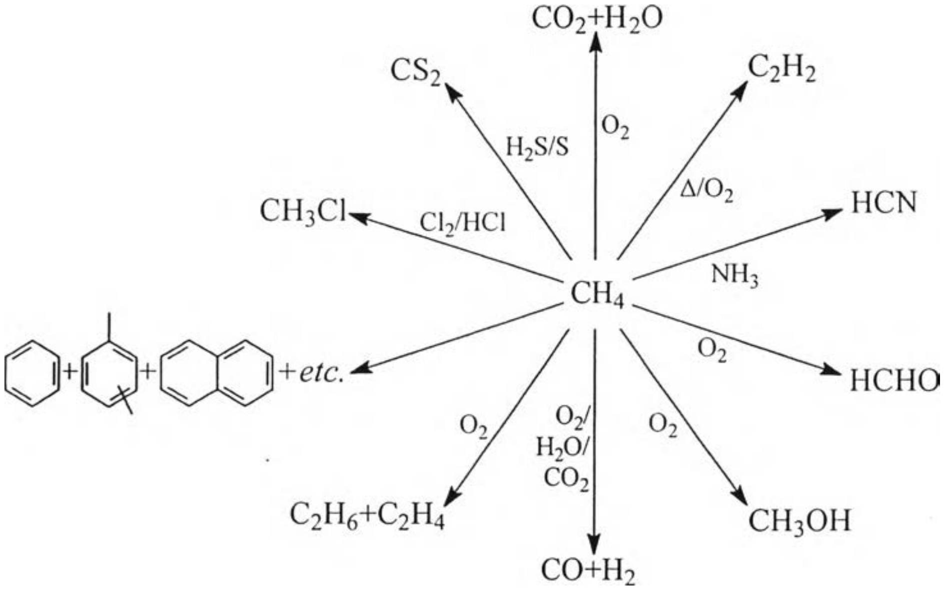


Figure 2.3 Possible route for methane conversion (Zhu *et al.*, 2004).

2.2.2 Catalysts for Partial Oxidation of Methane to Syngas

2.2.2.1 Noble Metal Catalyst

The noble metal catalyst is well-known as a high activity and outstanding stability in catalytic partial oxidation of methane. Many catalysts containing group of noble metals such as Pt, Ru, Pd, and Rh are investigated by many researches for catalytic partial oxidation of methane.

In 2011, Nematollahi *et al.* used noble metal catalysts such as Ru, Pt, Pd, and Ir supported on alumina-stabilized magnesia for CO_2 reforming of methane combined with partial oxidation of methane to syngas. The results indicated that the Rh and Ru catalysts showed the highest activity and high catalytic stability without any decrease in methane conversion prolonged reaction time in both the partial oxidation and dry reforming, and combined reforming of methane. The following order of activity was observed for different catalysts: Rh~Ru > Ir > Pt > Pd respectively.

Ru/TiO_2 supported catalysts exhibited high selectivity to synthesis gas (>65%) in the low methane conversion range (oxygen conversion < 100%) for partial oxidation of methane (Boucouvalas *et al.*, 1996). For Rh/ZrO_2

catalysts which used in methane partial oxidation, when Ce was dopped to ZrO_2 support, it led to increase both methane conversion and syngas selectivity. This as result of the high Rh dispersion on ZrO_2 support due to the presence of ceria prevents thermal sintering of the Rh particles (Eriksson *et al.,* 2007). Moreover, Rh catalysts showed a higher methane conversion and also higher H2 and CO selectivities than Pt catalysts for methane partial oxidation (Eriksson *et al.*, 2007).

Furthermore, Tanaka *et al.,* (2010) modified Rh/MgO with Fe, Co, and Ni and used for the catalytic partial oxidation of methane. The results showed that the reduction of the Fe, Co, and Ni on MgO was promoted by the presence of Rh, and the reducibility was Fe > Co >Ni. The additives (Fe, Co, and Ni) affected Rh/MgO catalysts. The addition of Ni to Rh/MgO gave the higher metal dispersion the Rh/MgO. On the other hand, the addition of Fe to Rh/MgO aggregated the metal particles. Moreover, the addition of Co to Rh/MgO did not affect the size of metal particles.

For Pd/SiO_2 catalysts prepared by impregnation method exhibited high methane conversion above 90% with H_2 yield higher than 80% in partial oxidation of methane (Li *et al.*, 2013). Futhermore, Pd on MgO-supported catalysts were more active for steam reforming reaction the same as Pt on MgO-supported catalysts and more than Ni. And metal such as Fe and Co were very inactive in this reaction (Nielsen *et al.,* 1975). In case of noble metal Pt, Pt/CeO_2 catalysts active for methane partial oxidation and further increase with increasing of amount of Pt doped (Tang *et al.,* 2010). Moreover, $Pt/CeZrO_2/Al_2O_3$ catalysts were investigated for the same reaction. The result showed that the Pt dispersion significantly increased with decreasing of Pt loading and the best performance catalysts for methane partial oxidation was 1.5Pt/CeZr/Al, and regardless Pt content, Pt/CeZr/Al catalysts were more stable than the Pt/Al catalysts on partial oxidation of methane (Silva *et al.*, 2009).

Ruckenstein and wang, (2000) studied the effect of precursor of MgO on the partial oxidation of methane over the MgO-supported Rh catalysts. They prepared magnesium oxides from five magnesium-containing precursors (magnesium nitrate hexahydrate (MgO-1), magnesium hydroxide (MgO-2), magnesium peroxide (MgO-3), magnesium carbonate (MgO-4), and magnesium citrate (MgO-5) respectively) with 1 wt% Rh loading. They found that the precursor affected to dominant extents the dispersion of rhodium that relative to surface area of support, the larger the surface area of support, the higher the Rh dispersion of the catalyst. The Rh dispersion decreased in the sequence: MgO-2 > MgO-5 > MgO-4 > MgO-1 > MgO-3. The results in partial oxidation reaction showed that the precursor of MgO had no notable effect on the methane conversion. The methane conversion is nearly equal for each supports because the reaction is diffusion limited or even because the number of metallic sites was in each of the catalysts sufficiently large for thermodynamic equilibrium to be achieved at its exit. Furthermore, the resistance to carbon deposition was strongly dependent on the magnesium oxide used. The magnesium oxide with larger surface area was more resistant to the decomposition of the CH_4 than magnesium oxide with small surface area.

2.2.2.2 Transition Metal Catalyst

Although noble metals based catalysts exhibited high selectivity and activity with good stability but they are costly. So many researches interested to seek alternative catalysts, the transition metal has been investigated for partial oxidation of methane such as Ni, Cu, Fe, and Co.

Noble metals like Co, Cu, Fe, Ni, Pd, and Pt (1wt%) were supported on ZrO_2 and used for steam reforming and partial oxidation of methane at temperature in rage of 400 °C to 800 °C. The resulted indicated that the activities of the catalysts decreased in order Pt, Pd > Ni >> Cu, Co and Fe. In addition, only Pt catalyst showed the stable catalyst prolonged reaction time at high temperature ~800 °C (Hegarty *et al.*, 1998).

Generally, Ni-based catalysts were widely used for partial oxidation of methane. Ni catalysts based on alumina, hexaaliminate-type, and perovskite-type differently active for this reaction. The Ni/Al_2O_3 and $BaNiAl_{11}O_{19-\alpha}$ catalysts showed the highest activity. Contrary, $LaA_{15/6}Ni_{1/6}O_3$ showed the lowest activity (Utaka *et al.*, 2003). Likewise, 10%Ni on Alumina-supported exhibited the best performance to CH4 conversion (>95%) and and H_2 selectivity (100%) (Vella et al., 2011).

In 2012, Yu et al. added Sr as promoter to Co/Al_2O_3 and investigated performance of catalysts for partial oxidation of methane. The result showed that addition of Sr to Co/Al_2O_3 could be improved the stability and activity of catalysts for partial oxidation of methane. They found that 2wt% loading of Sr is the suitable quantities that exhibited better activity and stability than lower and above 2 wt% loading, related to surface area of catalysts.

2.2.2.3 Methane Partial Oxidation Mechanisms

The catalytic partial oxidation (CPOX) is an attractive process to produce synthesis gas (H_2 and CO) from hydrocarbon fuels such as methane that mainly found in natural gas. This process has the advantage that was mentioned above.

Prettre *et al.*, (1946), who was the first to study the partial oxidation of methane over a nickel catalyst. They found that this process consists of two steps, those are exothermic and endothermic oxidation of CH_4 to CO_2 and H_2O ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$ and $CH_4 + H_2O \rightarrow CO + 3H_2$).

The mechanisms of Methane partial oxidation was rather complex process. In general, the Methane partial oxidation to synthesis gas was provided as for two mechanisms, direct and indirect mechanisms. In the direct mechanism, methane is decomposed to carbon and hydrogen elements. Then, the oxygen reacts with carbon element on the surface of catalyst to form CO and desorb H_2 and CO from the surface to yield synthesis gas. For indirect mechanism or combustion and reforming reaction, the product presented in two zones of the reactor. First, methane reacts with oxygen to form combustion products as CO_2 and H_2. Second, remaining methane occurred SR and CO_2 reforming reaction to get CO and H_2 products.

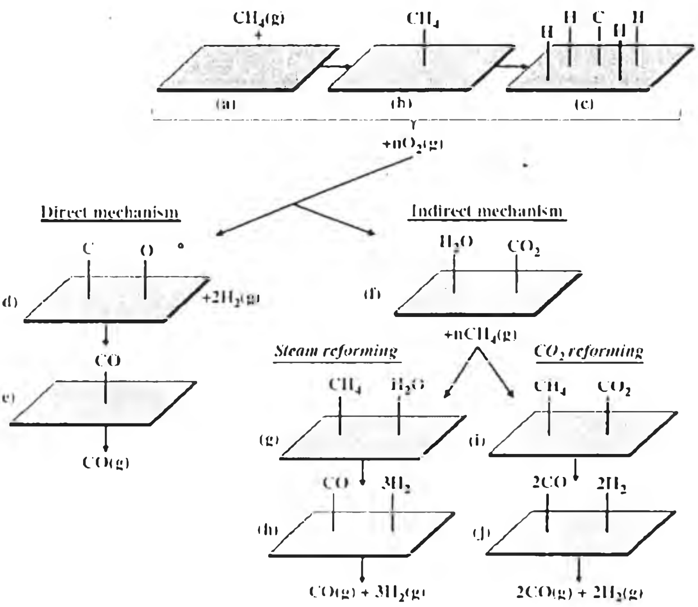
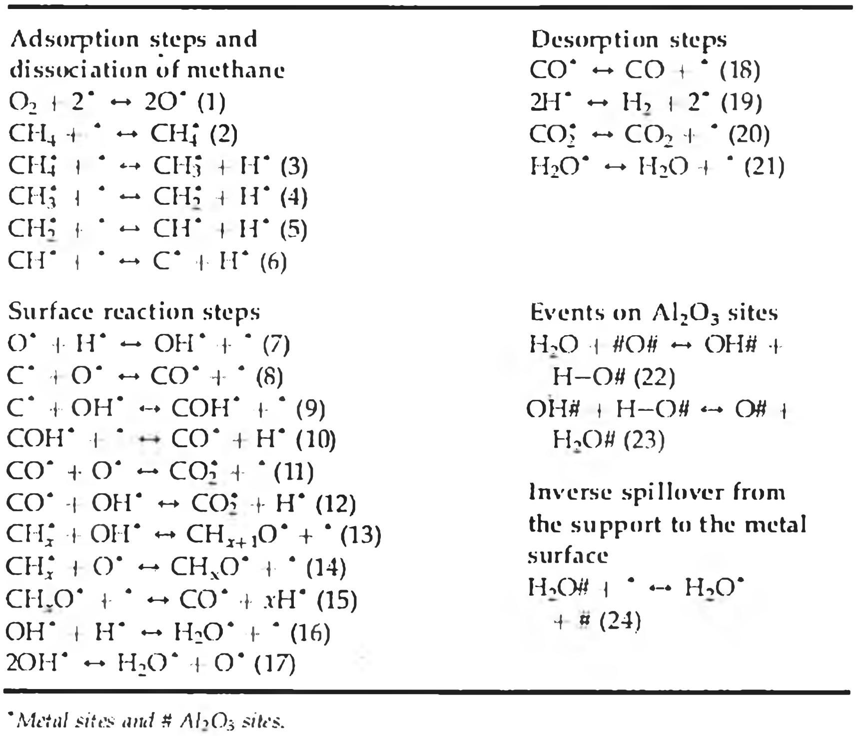


Figure 2.4 The direct and indirect mechanism for catalytic partial oxidation of methane (Smith and Shekhawat, 2011).

From Figure 2.4, the first three steps (a-c) are the adsorption and decomposition of methane to carbon and hydrogen element on the surface. For direct mechanism (Figure 2.4d and e), the dissociative adsorption of oxygen follows, which oxidizes carbon to CO on the surface and then desorbed into the bulk gas.

Moreover, Wang *et al.*, (1996) studied the direct mechanism of methane partial oxidation over Rh/Al_2O_3. They reported that a mechanism consisted of 24 steps divided into five classes: (1) adsorption and dissociation of methane, (2) surface reactions, (3) desorption, (4) events on Al_2O_3 sites, and (5) inverse spill-over from the support to metal surface. These steps are showed in Table 2.2

Table 2.2 Mechanism of methane catalytic partial oxidation (Wang *et al.*, 1996)



Adsorption steps and dissociation of methane

$O_2 + 2^* \leftrightarrow 2O^*$ (1)
$CH_4 + {}^* \leftrightarrow CH_4^*$ (2)
$CH_4^* + {}^* \leftrightarrow CH_3^* + H^*$ (3)
$CH_3^* + {}^* \leftrightarrow CH_2^* + H^*$ (4)
$CH_2^* + {}^* \leftrightarrow CH^* + H^*$ (5)
$CH^* + {}^* \leftrightarrow C^* + H^*$ (6)

Surface reaction steps

$O^* + H^* \leftrightarrow OH^* + {}^*$ (7)
$C^* + O^* \leftrightarrow CO^* + {}^*$ (8)
$C^* + OH^* \leftrightarrow COH^* + {}^*$ (9)
$COH^* + {}^* \leftrightarrow CO^* + H^*$ (10)
$CO^* + O^* \leftrightarrow CO_2^* + {}^*$ (11)
$CO^* + OH^* \leftrightarrow CO_2^* + H^*$ (12)
$CH_x^* + OH^* \leftrightarrow CH_{x+1}O^* + {}^*$ (13)
$CH_x^* + O^* \leftrightarrow CH_xO^* + {}^*$ (14)
$CH_xO^* + {}^* \leftrightarrow CO^* + xH^*$ (15)
$OH^* + H^* \leftrightarrow H_2O^* + {}^*$ (16)
$2OH^* \leftrightarrow H_2O^* + O^*$ (17)

Desorption steps

$CO^* \leftrightarrow CO + {}^*$ (18)
$2H^* \leftrightarrow H_2 + 2^*$ (19)
$CO_2^* \leftrightarrow CO_2 + {}^*$ (20)
$H_2O^* \leftrightarrow H_2O + {}^*$ (21)

Events on Al_2O_3 sites

$H_2O + \#O\# \leftrightarrow OH\# + H{-}O\#$ (22)
$OH\# + H{-}O\# \leftrightarrow O\# + H_2O\#$ (23)

Inverse spillover from the support to the metal surface

$H_2O\# + {}^* \leftrightarrow H_2O^* + \#$ (24)

**Metal sites and # Al_2O_3 sites.*

From Table 2.2, step 1 shows the dissociative adsorption of oxygen. Step 2-6 show a more detailed step-by-step of the adsorption and dissociation of methane. Step 8 shows the reaction of surface oxygen and carbon to form CO. Step 7, 9, 10, and 13 show the formation of hydroxyl groups and their role in oxidizing surface carbon species to CO through the formation of –COH. Step 11, 12, 16, and 17 show the formation of combustion products (CO_2 and H_2O) Step 22-24 show how the support can play a role in the formation of hydroxyl and the combination of these hydroxyl group to form water on the support surface.

For indirect mechanism, in Figure 4f presented the combustion products CO_2 and H_2O which are formed from the adsorbed oxygen. This resulted of the rate of oxidation of CO species is faster than the rate of CO desorption. In addition, the indirect mechanism can occurred two parallel pathways to convert the remaining methane by steam reforming (Figure 2.4g and f) and CO_2 reforming (Figure 1i and j). Both reactions are highly endothermic and dominate once all the oxygen fed with the methane is consumed in the first part of the bed. The indirect mechanism along a typical catalyst bed can be represented by Figure 2.5.

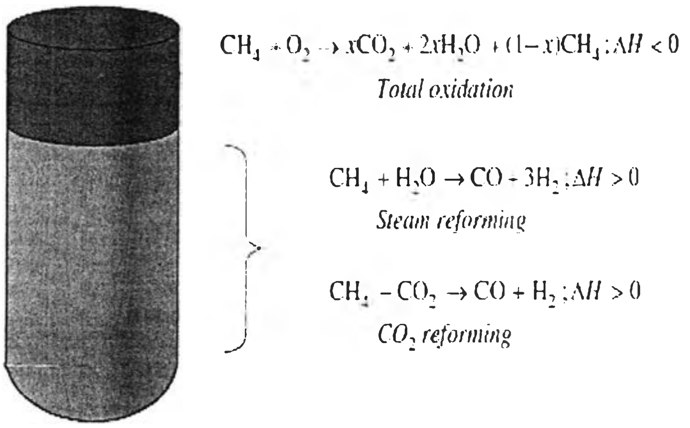


Figure 2.5 Methane partial oxidation reactor with indirect mechanism (Smith and Shekhawat, 2011).

The top of reactor about 10% of total bed, a portion of the methane in the feed reacts with all oxygen for the exothermic reaction. The bottom portion of the catalyst bed, the remaining methane is converted through endothermic secondary reforming reactions with the methane and water produced in the first region.

Horn *et al.*, (2006-2007) studied results supporting the indirect mechanism for the catalytic partial oxidation of methane over Rh catalyst. They found that oxygen conversion is complete within the first 2 mm of the catalyst bed, where some H_2 and CO are formed.

2.2.2.4 Ni-based Catalyst and Carbon Deposition

Ni-based catalysts are attractive for partial oxidation reaction because of its excellent catalytic activity and low cost when compared to noble metal catalysts.

$Ni/Ce_{0.75}Zr_{0.25}O_2$ and $Ni/\beta''-Al_2O_3$ catalysts were used for Partial oxidation of iso-octane for hydrogen production. The result showed that $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts are more active for partial oxidation reaction than $Ni/\beta''-Al_2O_3$ catalysts. As the C/O feed ratios ≤ 1.0, amount of carbon deposition on the $Ni/\beta''-Al_2O_3$ catalysts lower than $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts but the amount of carbon deposition over the Ni/β''-Al_2O_3 catalysts was increased by increasing C/O ratios>10. This indicated that the Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalysts are more stable under rich conditions than the Ni/β''-Al_2O_3 catalysts due to its good redox properties. The addition of steam promotes a water-gas shift reaction resulting in a larger amount of hydrogen production and less amount of coke formation (Pengpanich *et al.*, 2006).

Ni/MgO catalysts preparing via wetness impregnation exhibited high activity and stability for partial oxidation of methane. The amount of Ni loading has positive effect on the catalytic activity, 15%Ni/MgO offered the highest CH_4 conversion. Moreover, reaction temperature, CH_4/O_2 ratio and gas hourly space velocity (GHSV) are significant effected on catalytic activity (Meshkani *et al.*, 2013). Ni/La_2O_3 also exhibited highly active for partial oxidation of methane, but less than Ni/MgO catalysts due to the formation of a cubic MgO and NiO solid solution in which the Ni^{2+} ions are highly stable against reduction at high temperature (Requies *et al.*, 2005).

Ni/SiO-Sph which prepared via sol-gel method, Ni/SiO-Sph and Ni/SiO-commercial that prepared via impregnation method were used for partial oxidation of methane. The result showed that Ni/SiO-Sph catalysts exhibited highest catalytic activity, stability and resistance of carbon deposition because the Ni/SiO-Sph presented the smaller in Ni particles size, stronger interaction between metal and support, and greater the active site dispersion than Ni/SiO-Sph and Ni/SiO-commercial catalysts (Sheng Xia *et al.*, 2012).

However, Ni is deactivated easily by metal sintering and/or coke formation. Generally, the carbon deposition on a support Ni catalysts mainly comes from methane decomposition ($CH_4 \rightarrow C + 2H_2$) and CO disproportionation reaction at high temperature ($2CO \rightarrow C + CO_2$). The carbon deposition on nickel catalysts was found in the filar form. It is believed that the mechanism of carbon species is involved with the diffusion of carbon atom decomposing from adsorbed hydrocarbon on the active site through nickel particles to form an intermediate carbide phase. Accordingly, many researches have been to modify the surface properties of Ni-based catalysts to prevent this intermediate.

Sn is well known to reduce carbon deposition in many processes namely dehydrogenation and aromatization of paraffins, steam reforming,

CO_2 reforming, and partial oxidation of hydrocarbon (Ferreira *et al.*, 2003). Addition small amount of Sn to Ni supported on α-Al_2O_3 was effective in decreasing the amount of carbon deposition during CO_2 reforming of methane by improving the dispersion of Ni and retarding the sintering of active Ni particles during reaction (Hou *et al.*, 2004). On the contrary, addition different amounts of Sn (<0.5 wt.%) to Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst did not modify the reducibility of support and decreased the amount of carbon deposition, while maintain most of the catalytic activity for iso-Octane partial oxidation (Pengpanich *et al.*, 2008).

In the other way, addition Nb to 5 wt% Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst which prepared via urea hydrolysis and incipient wetness impregnation. The result showed that addition of Nb decreased Ni dispersion and increased the surface area with increased Nb loading, due to partial blockage of Ni surface atom by Nb. From catalytic activity test for partial oxidation of methane, the results showed that the CH_4 conversion decreased as the Nb loading increase, meanwhile, both CO and H_2 product selectivities remained unchanged. This could indicated that the dissociative adsorption of CH_4 to form a carbonaceous intermediate appears over Ni surfaces, some Ni particles would form Ni-Nb alloys, which would leads to a reduction of Ni active sites and depresses their activity. Moreover, the amount of carbon deposition was increased with an increasing amount of Nb loading. This due to the inhibition of surface oxygen reduction of $Ce_{0.75}Zr_{0.25}O_2$ by Nb loading and the strong interaction with Ni and Nb-modified support (Pengpanich *et al.*, 2007).

To overcome the carbon deposition, apart from adding other metal with active Ni particle. The introduction of triplecharged ions can improve the oxygen vacancy number and the mobility of ceria-based mixed oxides, and result in the reduction of carbon formation on such mixed oxides.

Ni supported on $Ce_{0.75}Zr_{0.25}$-xMn_xO_2 mixed oxide catalysts that prepared by urea hydrolysis and incipient wetness impregnation are rather highly active and stable for the steam reforming of naphthalene. The synergetic effect of an ease of reducibility and a good oxidation ability of the $Ce_{0.75}Zr_{0.25}$-xMn_xO_2 supports appears to play a role in promoting the oxidation of carbon precursors on the nickel surface. The addition, Ni supported on $Ce_{0.75}Zr_{0.25}$-xMn_xO_2 possess much lower amounts of carbon formation than Ni supported on $Ce_{0.75}Zr_{0.25}O_2$ mixed oxide that without Mn droped. The results from the TPO profile for spent catalysts divided two types of carbon formation. The first is carbidic carbon at ca. 325 °C and another is filamentous carbon at higher temperature of ca. 680 °C (Bampenrat *et al.*, 2010).

2.2.2.5 CeO_2-ZrO_2 Supported

Ceria catalysts are one of all catalysts which is attended as oxidation catalysts because it has unique redox properties and high oxygen storage capacity. Since pure Ceria has low thermal stability namely, it losses in surface area at high temperature. Therefore, many researchers interest to improve its stability. Hori *et al.*,(1998), Terribile *et al.*, (1998) and Putna *et al.*, (1999) reported that the addition of ZrO_2 to CeO_2 results in improvement in ceria's oxygen storage capacity, redox property, good catalytic activity at low temperature and thermal resistance.

CeO_2-ZrO_2 mixed oxide catalysts which prepared via sol-gel method for CO oxidation were showed the results that $Ce_{0.75}Zr_{0.25}O_2$ solid solution exhibited the highest activity for CO oxidation and CO oxidation activity depended on Ce/Zr ratio, which involved with degree of reducibility that resulted of $Ce_{0.75}Zr_{0.25}O_2$ structure, which is a cubic phase which is easiest reducible catalyst (Thammachart *et al.*, 2001). Moreover, Ni/CeO_2-ZrO_2 mixed oxide solid solution catalysts which prepared by impregnation are more activity for methane partial oxidation reaction than gel impregnated catalysts. The 15%Ni/ $Ce_{0.75}Zr_{0.25}O_2$ catalyst showed the highest metal dispersion with the smallest particle size revealed the highest catalytic performance in terms of C-C breakage conversion and hydrogen yield with less carbon deposition (Thaicharoensutcharittham et al., 2011). To comparison the supports, the Ni over $Ce_{0.75}Zr_{0.25}O_2$ support showed the higher methane conversion, CO and H_2 selectivities, and lower carbon deposition than CeO_2 and ZrO_2 respectively (Pengpanich *et al.*, 2004).

In case of 5%Ni/ $Ce_{0.75}Zr_{0.25}O_2$ catalysts which were prepared by co-precipitation showed the highest activity and stability for partial oxidation of methane with low carbon deposition after prolonged reaction time (Larimi and Alavi, 2012).

Furthermore, Pt/$Ce_xZr_{1-x}O_2$ catalysts exhibited higher active, stable and selective on methane partial oxidation than Pt/CeO_2 and Pt/ZrO_2 due to the higher oxygen storage capacity of support. The highest performance for methane partial oxidation is Pt/$Ce_{0.75}Zr_{0.25}O_2$ (B. Passos *et al.*, 2005).

2.2.2.6 *Catalyst Preparation*

The catalyst preparation methods are significant. That affects shape, active metal particle size, and metal distribution or dispersion over the support. In addition, the catalysts preparation effects in carbon formation during operation. Generally, there are many catalyst preparation methods such as precipitation, impregnation and poly method. Amongst these methods, the polyol method has attracted much recent attention in many researches.

The polyol process has been widely used for catalyst preparation of mono-dispersed metal powders. This process is related to a redox reaction between a metallic precursor and a liquid polyol such as ethylene glycol which is used as both solvent and reducing agent. The advantages of this method are large quantity of the sample prepared, it involves very simple and inexpensive operation condition and the shape and size of the nanoparticles are easily controlled by adjusting temperature, pH, reaction time, and concentration of the protective agent (PVP) in this process.

Awais Naeem *et al.*, (2014), they prepared nano nickel catalysts supported over nano sized oxide such as CeO_2, ZrO_2, and Al_2O_3 by polyol and impregnation method. They found that Ni-Zr impregnated catalyst presented bimodal pore size distribution, while Ni-Zr polyol catalyst presented the unimodal pore size distribution which is a better dispersion of Ni species over support. Moreover, polyol catalysts indicated long term stability, very high activity without any significant reduce in methane conversion and reduce the tendency of carbon deposition. Moreover, addition of PVP during preparation of nanosized Al_2O_3 supported Ni catalysts improved activity for partial oxidation of methane. The result showed that the catalyst with a weight ratio of PVP/Ni as 5:1 exhibited the highest activity that related to the smallest crystalline size of the Ni particles in support. Namely, the PVP influence the particle size of Ni and the catalytic performance. Be said that this process used to prevent the agglomeration of the particles and give homogeneous metal nano particles (Bayrakdar *et al.*, 2013).

In addition, the type of polycol also significantly effected on crystal morphology. The preparation of Cu and Ni nanoparticles via the polyol process with various polycol; ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), tetraethylene glycol (TEG), and butylene glycol (BG). The result showed that Cu nanoparticles, the crystallites were a face-centered cubic (fcc) structure. The TEM analysis analyzed that altering the polycol from a small molecule (EG) to a big molecule (TEG) diversified the particle shape from spherical to rodlike, respectively and the majority of particles are not polycrystalline. Meanwhile, the Ni particles are the stable face-centered cubic (fcc) structure and the nanoparticles are polycrystalline. Moreover the type of polycol effected on the nucleation and growth rates of the Cu and Ni crystals, the bigger molecules of polycol like TEG performed the a slower growth rate of the metal than the smaller molecule of polycol (Carroll *et al.,* 2011). In case of the nanoparticles of Cobalt (Co) that used 1,2-propanediol as reducing agent showed Co crystals are face-centered cubic (fcc) structure with the particle size of 5-35 nm (Biao *et al.,* 2005).

Ikeda *et al.,* (2012) studied synthesis of Rh nanoparticles by polyol method. They reported that pH of ethylene glycol and temperature of reaction during synthesis influenced size of Rh nanoparticles. The particle size can be controlled from 1.7 to 6.7 nm by adjusting the ethylene glycol. The smaller nanoparticles appear at higher pH due to encouragement of the larger ΔE°, resulting in a faster nucleation rate of particles. While, a slower nucleation rate occurred at lower pH and led to the bigger nanoparticles. Moreover, they found that the combination of high pH condition with low temperature (below boiling point of ethylene glycol) was also effective in the monodispersion of small Rh nanoparticles.

Sarkar *et al.,* (2012) studied Ni nanoparticles supported on mesoporous ZSM-5 which prepared by polyol and impregnation methods for methane reforming. The results from temperature program reduction (TPR) showed that the polyol catalysts presented Ni nanoparticles both outside and inside the mesopore of ZSM-5 support, but not found in case of impregnated catalysts. It indicated that the polyol catalysts have higher metal-support interaction than impregnated catalysts. In addition, the Ni/ZSM-5 prepared polyol method showed methane conversion up to 96.2%, but in case of Ni/ZSM-5 prepared impregnation method did not mention. In addition, type of nickel precursors effected on Ni nanoparticles size via reduction polyol reduction method. Ningthougam *et al.*, (2009) reported that using $NiCl_2.6H_2O$, NiO powder, $[Ni(NH_3)_6]Cl_2$ as precursor and used ethylene glycol as reducing agent gave the particle size in range of ~20 to ~38 nm. The Ni nanoparticles which prepared from $[Ni(NH_3)_6]Cl_2$ have a size of ~12 nm and the Ni nanoparticle sizes synthesized from NiO powder and $NiCl_2.6H_2O$ were found to be the same size as 35 nm (Ningthougam *et al.*, 2009).

In 2014, Tientong *et al.* prepared Ni and $Ni(OH)_2$ nanopowders with hydrazine hydrate by chemical reduction. The resulted showed the particle size of nanopowders as in ranging from 7-14 nm. The Ni nanopowder with adding of PVP gave the smallest particle size as 7 nm due to the PVP can avoid agglomeration in the aqueous solution during synthesis, while Ni nanopowder without adding of PVP gave particle size as 12 nm. The $Ni(OH)_2$ powder without PVP has the largest particle size as 14 nm, indicated more agglomerated during synthesis.