

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogen Production

Hydrogen is not only used as raw material in the chemical industry for the manufacture of ammonia, methanol, and variety of organic chemicals, but also widely used in the petroleum industry for refining and upgrading of crude oil. Hydrogen generation technologies can be classified into three general categories: (1) thermal processes including steam reforming, partial oxidation, and autothermal steam reforming, (2) electrolytic processes, and (3) photolytic processes. Each method has limitation and the choice of the best route depends on the economics of the location involved. Hydrogen world production is around 45-50 Mt per year. Most of it derives from methane (48 %) by steam reforming. The rest is gained from oil (30 %) and coal (18 %) by partial oxidation processes. Only 4 % of the hydrogen worldwide is produced by electrolysis, in variably only when high purity is required (Fornasiero and Graziani, 2011).

From hydrogen production technologies, they generally use hydrocarbons and coal as feedstock. However, both of hydrocarbons and coal are the kinds of fossil fuels, which release the huge amount of carbon dioxide emissions during the hydrogen production processes. On the other hand, it is necessary to produce hydrogen from an alternative energy source owing to concerns about the depletion of fossil fuel reserves and the pollution caused by continuously increasingly energy demands. Therefore, the development of the technology utilizing biomass energy resources to produce hydrogen attracts much attention due to the renewable and carbon-neutral features of biomass.

2.2 Pyrolysis of Biomass

Pyrolysis is a thermal decomposition process in which biomass is rapidly heated to high temperature in the absence of oxygen. The products of biomass pyrolysis include bio-char, bio-oil, and gases including methane, hydrogen, carbon

monoxide, and carbon dioxide. The simple flow diagram of biomass conversion via pyrolysis technique is shown in Figure 2.1.

Depending on the type of biomass and the conditions, pyrolysis will yield mainly bio-char at low temperatures (less than 450 °C with the heating rate is quite slow) and mainly gases at high temperatures (greater than 800 °C with a rapid heating rate). At an intermediate temperature and under relatively high heating rates, the main product is bio-oil. Pyrolysis processes can be categorized as slow pyrolysis and fast pyrolysis. Fast pyrolysis is currently the most widely used for pyrolysis systems. Slow pyrolysis takes several hours to complete and results in bio-char as the main product. On the other hand, fast pyrolysis yields 60 % bio-oil and takes seconds for complete pyrolysis. In addition, it gives 20 % bio-char and 20 % synthesis gas.

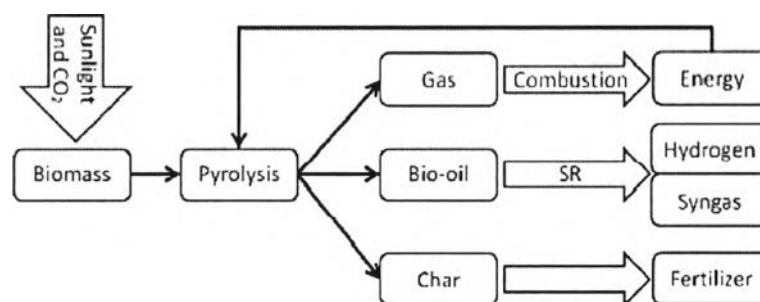


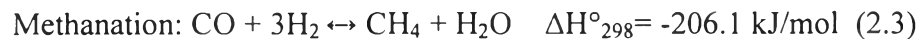
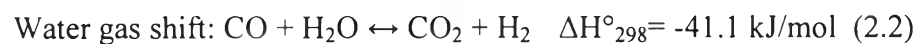
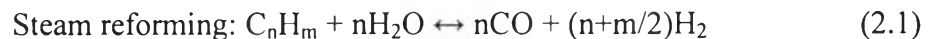
Figure 2.1 Simple flow diagram for the complete path from biomass to synthesis gas via bio-oil steam reforming (Trane *et al.*, 2012).

Bio-oil is a dark brown liquid and has a similar composition to biomass. It has the advantages of the ease of handling and high energy density. Moreover, it is the fact that it can be used for the on-demand hydrogen production for fuel cells directly. The aqueous phase of the bio-oil contains of 20 % organics and 80 % water. Main components of bio-oil belong to the following groups: acids, alcohols, esters, ketones, phenols, furans, and sugars.

2.3 Steam Reforming

2.3.1 Conventional Steam Reforming

Steam reforming is a process that steam and hydrocarbons react together at high temperatures and converted to hydrogen and carbon monoxide. The steam reforming is generally cooperated with the water gas shift and the methanation reactions, as shown below:

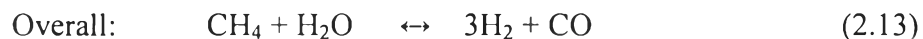


The steam reforming reaction is endothermic reaction while the water gas shift and methanation reactions are exothermic. The reforming equilibrium is favored at high temperature and low pressure while the water gas shift reaction is shifted toward water and carbon monoxide at high temperatures.

About 40 % of the world hydrogen production is gained by methane steam reforming (Equation 2.13). In most industrial application areas, hydrogen is required at the pressure of 20-30 atm and at temperature of about 850-900 °C. High pressures allow for a more compact reactor design, thus increasing the reactor throughput and reducing the cost of materials.

The steam reforming of hydrocarbons occurs through adsorbed species on the catalyst. The steam dissociative adsorbs on the support or on the metal particles forming OH species and the hydrocarbons dissociative adsorb on the metal forming $C_xH_y^*$. The OH^* and $C_xH_y^*$ react at the interface between the support and the metal forming carbon monoxide and hydrogen. The surface reactions in the methane steam reforming are assumed to be (adsorbed species, *):

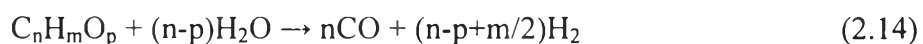




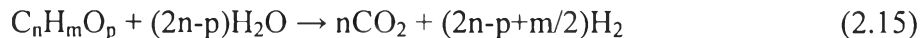
The conventional steam reforming process is catalyzed by group VIII metals and nickel is preferred due to its good activity and lower price, even though noble metal catalysts can be more active and less prone to coke formation. The catalysts used for steam reforming can be deactivated by carbon formation, sintering, or poisoning (Trane *et al.*, 2012).

2.3.2 Steam Reforming of Oxygenates

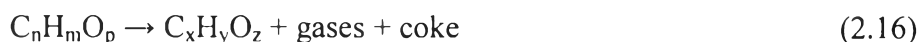
The general stoichiometry for the oxygenated steam reforming is expressed as:



Equation 2.14 in combination with water gas shift reaction (Equation 2.2) fully shifted toward the right is expressed as:



The steam reforming of oxygenated compounds is described by Equation 2.15, although at high temperatures, the water gas shift reaction is shifted to the left and carbon monoxide is present in significant amounts. However, the methanation of carbon monoxide (Equation 2.3) will also influence the product distribution at equilibrium, especially at low temperatures and high pressures as these conditions favor the reaction. For oxygenated compounds, thermal decomposition reaction (Equation 2.16) can also occur due to thermally unstable and this reaction should be minimized because of the coke formation from this reaction.



The steam reforming of oxygenated compounds is endothermic reaction, like the conventional steam reforming, and therefore it is favored at high temperatures and low pressures as predicted by Le Châtelier's principle. The use of high temperatures in the process has two effects; one is that water gas shift reaction is shifted toward carbon monoxide and water, resulting in decreasing the hydrogen yield, and the other one is that the methane is reformed by steam.

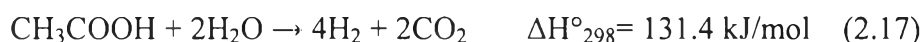
The direct steam reforming of oxygenated compounds always generates by-products and unacceptable levels of carbon deposition, sintering, and sulfur poisoning, leading to rapidly deactivation of catalysts. Developing selective and coke-resistant reforming catalyst is a key challenge for successful application of oxygenated compounds as a resource of hydrogen. The motivation for testing model compounds instead of all bio-oil components is that it is possible to get a better understanding of the reactions, influence of experimental conditions, deactivation, etc. Acetic acid has been extensively performed by other research groups due to it is one of the major components of bio-oil (Koehle and Mhadeshwar, 2013).

2.3.3 Steam Reforming of Acetic Acid

Acetic acid is the one of the major constituents of bio-oil (up to 12 %), which can be easily obtained from biomass by fast pyrolysis or fermentation process. Acetic acid is nonflammable unlike methanol and ethanol; hence, it is a safe hydrogen carrier. In addition, acetic acid also can be easily converted to hydrogen with high selectivity over effective catalysts. For this reason, steam reforming of acetic acid has been widely used as a model compound to study its reaction network by several research groups (Li *et al.*, 2012b).

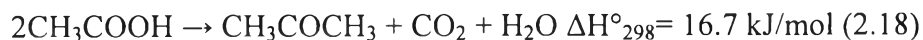
Steam reforming of acetic acid is very complex system because it is not thermally stable. Thus, there is a significant competition between catalytic reforming reactions and thermal decomposition reactions. As a result, there are many pathways for acetic acid conversion, which are summarized in the following stoichiometry (Li *et al.*, 2012a).

The overall steam reforming reaction:



Steam reforming of acetic acid is an endothermic reaction. It is entirely feasible from a thermodynamic point of view and it is favored at high temperatures. Besides, the homogeneous and heterogeneous reactions such as ketonization (Equation 2.18), dehydration (Equation 2.19), and decomposition (Equations 2.20 and 2.21) may occur before reaching or on a catalyst bed. Therefore, undesired organic by-products are generated, which diminishes hydrogen yield.

Ketonization reaction:



Dehydration reaction:



Decomposition reaction:



The primary organic products such as acetone and methane can produce hydrogen via steam reforming of acetone (Equation 2.22) and methane (Equations 2.23 and 2.24). These reactions become significant only when they are thermodynamically favorable, normally at high temperatures.

Steam reforming of acetone:



Steam reforming of methane:



Carbon monoxide is an intermediate and one of the main by-products in steam reforming process. Low reaction temperatures resulted in low efficiency of steam reforming, incomplete process can be occurred and produced carbon monoxide. However, it can also be a secondary product produced from the steam reforming of methane (Equation 2.24) and reverse water gas shift reaction (Equation 2.25) at high reaction temperatures, leading to the large amount of carbon monoxide generation. Conversely, the water gas shift reaction (Equation 2.26) and methanation of carbon monoxide (Equation 2.27) contribute to the elimination of carbon monoxide in mild temperature region. Methanation (Equations 2.27 and 2.28) is thermodynamically favorable in steam reforming due to the high concentration of carbon oxides and hydrogen in product. Methanation consumes a huge amount of hydrogen and generates a large portion of methane formation, but that is just for mild temperatures. At high temperatures, the methanation is not thermodynamically favorable and steam reforming of methane (Equations 2.23 and 2.24) initiates, which converts methane to hydrogen again.

Reverse water gas shift reaction:



Water gas shift reaction:



Methanation of carbon monoxide:



Methanation of carbon dioxide:



Carbon deposition is one of the major problems in catalytic reforming reactions, which will cause the loss of the effective surface area, pore blockage, and lower heat-transfer rate from catalyst to gas. Carbon formation may take place in several ways, such as Boudouard reaction or disproportionation of carbon monoxide (Equation 2.29), acetic acid decomposition (Equation 2.30), methane decomposition (Equation 2.31), acetone polymerization (Equation 2.32), and the reaction of carbon oxides with hydrogen (Equations 2.33 and 2.34). Under a given conditions, steam and carbon dioxide contribute to the elimination of carbon deposition (Equations 2.35 and 2.36).

Boudouard reaction:



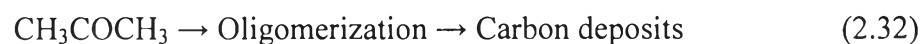
Acetic acid decomposition:



Methane decomposition:



Acetone polymerization:



Reaction of carbon oxides:



Elimination of carbon deposition:



As presented above, there are many routes for conversion of acetic acid. Nevertheless, the main reaction pathway depends on reforming catalyst and the operating parameters.

2.3.4 Catalysts Used in Steam Reforming of Acetic Acid

Basagiannis and Verykios (2007) discussed on the catalytic performance of Pt, Pd, Rh, Ru, and Ni, which were supported on Al_2O_3 , $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Al}_2\text{O}_3$, and $\text{CeO}_2/\text{Al}_2\text{O}_3$ under conditions of acetic acid steam reforming. It was observed that 17%Ni/ Al_2O_3 showed the highest activity, while the other supported metal catalysts exhibited less activity as shown in Figure 2.2, due to the high metal loading and higher intrinsic activity per exposed atom among all catalysts investigated, the rank based on their activity seems to be as the following: Ni > Ru > Rh > Pd > Pt. In the case of addition of basic carrier, such as La_2O_3 or MgO on Al_2O_3 , Ni/MgO/ Al_2O_3 catalyst seems to be much more active than single carrier due to alteration of its surface acidity/basicity characteristics. For the amount of coke formation on each catalyst, it was found that Ni-based and Ru-based showed lower amounts of carbon deposit. However, Ni catalysts were not as stable as Ru catalysts.

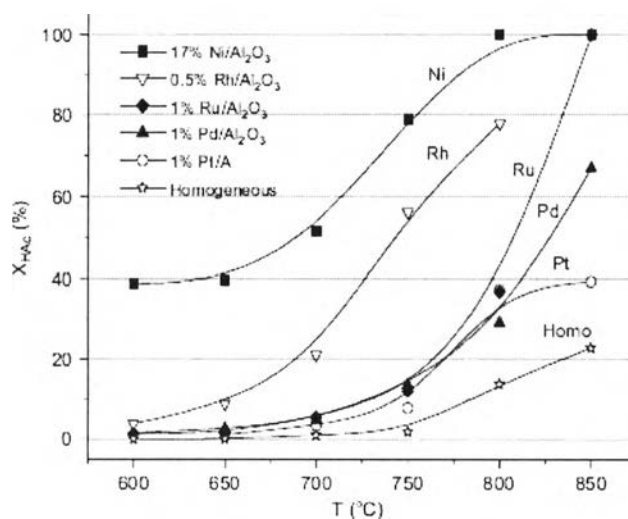


Figure 2.2 Acetic acid conversion as a function of reaction temperature (Basagiannis and Verykios, 2007).

According to Vagia and Lemonidou (2010), they reported the properties of Ni and Rh supported on ceria-zirconia mixed oxide and their performance in steam reforming of acetic acid. The catalysts were tested using steam-to-carbon molar ratio of 3:1 at 550, 650, and 750 °C. It was found that 0.5%Rh/Zr_{0.84}Ce_{0.16}O₂ catalyst was more active than 5%Ni/Zr_{0.84}Ce_{0.16}O₂ catalyst and Zr_{0.84}Ce_{0.16}O₂ by the higher acetic acid conversion and values of hydrogen yield at 550 and 650 °C due to the higher dispersion and intrinsic activity of Rh. Moreover, the addition of metals decreased the rate of coke deposition, which was even lower for the Rh catalyst.

Steam reforming of acetic acid was investigated over Pt/ZrO₂ by Takanabe *et al.* (2004). The results showed that Pt/ZrO₂ exhibited high performance and high hydrogen selectivity at initial time on steam (TOS), indicating that Pt was necessary for steam reforming, while ZrO₂ was essential to extend the catalyst life. However, ZrO₂ was also a precursor for oligomer formation derived from acetic acid or acetone, leading to the catalyst deactivation. In order to develop a durable catalyst, the condensation/oligomerization reactions, which take place on ZrO₂ and block the active site, need to be minimized.

Trane *et al.* (2012) summarized that a variety of catalytic systems have been researched and Ni, Ru, or Rh seem to be the most promising metals. Among the non-noble metal catalysts, nickel-based catalyst is attractive due to its high activity, low cost, and abundance, but in the most cases, the catalysts were not stable over longer time of operation due to coke formation. Support materials including of a mixture of alumina and basic oxides were necessary to get high potential system for low carbon deposition.

Li *et al.* (2012b) studied the effects of nickel loading in the range of 0-23 wt% over ZrO₂ carrier to investigate the performance of acetic acid steam reforming. As a result, 16%Ni/ZrO₂ catalyst showed the highest of both acetic acid conversion and hydrogen selectivity since this ratio possessed enough active sites with appropriate Ni particle size and presented lower activity towards secondary reaction, such as methanation and reverse water gas shift reaction, which produced undesirable by-products. The carbon deposition was decreased with an increase in Ni loading up to 16 wt%.

Steam reforming of acetic acid was examined over Ni-Co (0.25:1), Ni-Co/CeO₂-ZrO₂ (15:60:10:15 wt%), and Ni/La₂O₃/Al₂O₃ (17:15:68 wt%) by Pant *et al.* (2013). The influence of several parameters were examined, including reaction temperature, space time, and feed concentration. The results indicated that Ni-Co without support was more effective when compared with the others by the higher of activity and hydrogen yield.

Thaicharoensutcharittham *et al.* (2011) investigated the effect of the supports (Ce_{0.75}Zr_{0.25}O₂, Al₂O₃, and MgO) and Ni content on steam reforming catalytic activity and stability of acetic acid. It was observed that 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst exhibited an excellent activity and stability in terms of C-C breakage conversion and hydrogen yield. Besides, Ce_{0.75}Zr_{0.25}O₂ support provided better redox properties and oxygen mobility than the Al₂O₃ and MgO support, leading to lower coke formation even at low steam-to-carbon ratios as shown in Figure 2.3.

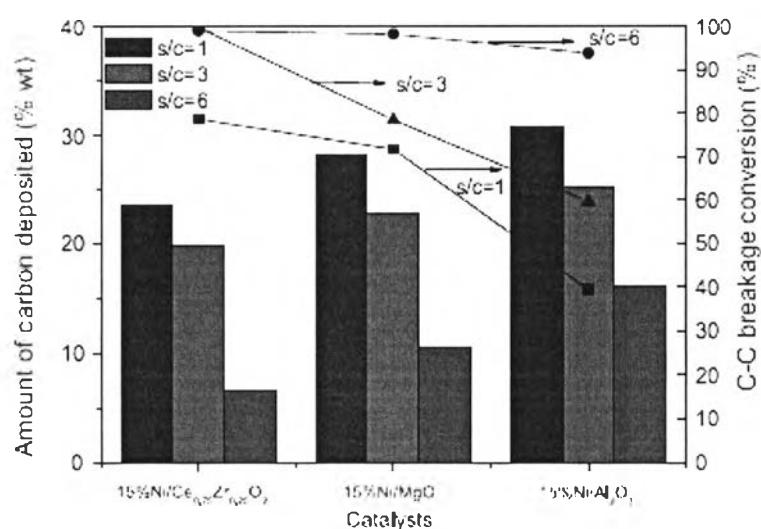


Figure 2.3 Total amount of carbon deposited on catalysts and C-C breakage conversion at 650 °C, S/C ratios of 1-6 (Thaicharoensutcharittham *et al.*, 2011).

2.4 Partial Oxidation

2.4.1 Catalytic Partial Oxidation of Methane

Catalytic partial oxidation of methane (Equation 2.37) is an alternative process to generate synthesis gas by passing oxygen (pure oxygen or air) and methane through a suitable catalyst at temperature range of 700-1000 °C at atmospheric pressure.



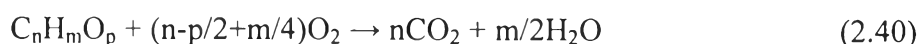
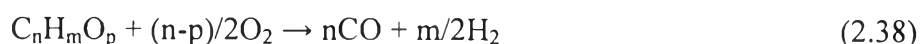
This process is mildly exothermic reaction, so it requires less energy to operate the reaction that causes this process more energy efficient. Moreover, this process provides high conversion of methane and also desired hydrogen to carbon monoxide product ratio of two that can be used directly for Fischer-Tropsch synthesis. Besides these benefits, catalytic partial oxidation of methane is considered more rapidly than the catalytic steam reforming of methane process.

Like a steam reforming process, the catalytic partial oxidation counters with some side reactions such as methanation (Equation 2.3), carbon monoxide disproportionation (Equation 2.29), and also water-gas-shift reaction (Equation 2.2).

The most challenge of catalytic partial oxidation of methane is the deactivation of catalytic activity due to the coke deposition from carbon monoxide disproportionation and decomposition reaction. Furthermore, the sintering of metal catalyst at high temperature is also occurred. Therefore, several studies have been concentrated on the catalytic partial oxidation of methane so as to modify the catalytic stability.

2.4.2 Partial Oxidation of Oxygenates

The partial oxidation reactions of oxygenates is described by Equations 2.38-2.40, which may include several reactions depending on the process conditions.



2.4.3 Catalysts Used in Partial Oxidation of Methane

The catalysts that have been used in this reaction can be widely classified into two types which are the non-noble metal catalysts such as Ni, Co, and Fe and the noble metal catalysts such as Rh, Ru, Pd, and Pt. Due to the high cost and rareness of noble metal catalysts, several researches change to the non-noble metal catalysts such as nickel, iron, cobalt, and copper in order to use as the catalyst in the catalytic partial oxidation of methane.

Slagtern *et al.* (1998) reported the iron-, cobalt-, and nickel-based catalysts for partial oxidation of methane to synthesis gas. The results showed that nickel-based catalyst exhibited the highest activity than the other catalysts whereas iron-based catalyst exhibited poor activity. They suggested that the metallic form of metal was an active form for partial oxidation of methane reaction while the oxide form was favor for total combustion reaction. In addition, they proposed the order of reducibility of these metals in the following order: Ni>Co>Fe.

Among the non-noble metal catalysts, nickel-based catalyst is attractive due to its high activity, low cost, and abundance. However, nickel-based catalyst is suffered from the deactivation caused by carbon deposition and metal sintering at reaction temperature. So, a number of researches have been focused on modifying nickel-based catalyst stability. Most studies deal with the support and the introduction of some promoters in order to improve the stability, as well as catalytic performance.

Miao *et al.* (1997) studied the effect of alkali metal oxide (Li, Na, K) and rare-earth metal oxide (La, Ce, Y, Sm) addition on the stability and performance of NiO/Al₂O₃ catalyst during the partial oxidation of methane to synthesis gas. They indicated that addition of alkali metal oxide improved the dispersion of active component nickel and the activity for the partial oxidation of methane reaction over the nickel-based catalysts. Besides, these alkali metal oxide and rare-earth metal oxide also improved thermal stability during high temperature reaction and resistivity to coke formation over the nickel-based catalysts during the partial oxidation of methane reaction.

Zhu and Flytzani-Stephanopoulos (2001) investigated the partial oxidation of methane to synthesis gas over Ni-CeO₂ catalysts with various nickel

loading (5, 10, and 20 wt%). It was observed that all catalysts exhibited high performance and selectivity for partial oxidation of methane to synthesis gas at temperature higher than 550 °C but only 5 wt% loading of nickel catalyst showed excellent resistance to carbon deposition and had a high stability under reaction condition. They believed that the high stability of this catalyst was caused by the transfer of oxygen from ceria to the nickel interface, effectively oxidizing carbon species produced from methane dissociation on nickel.

Among various supports of nickel-based catalysts, cerium oxide (CeO_2) is a promising one due to its unique redox properties and high oxygen storage capacity. However, it has a disadvantage of its poor thermal stability at high temperatures. Therefore, many studies have been focused on improving its properties by adding some additives such as zirconia as well as other promoters. Additionally, the prevention of coke formation has also been studied.

Takeguchi *et al.* (2001) studied the performance of $\text{Ni/CeO}_2\text{-ZrO}_2$ catalysts for the partial oxidation of methane to synthesis gas. They found that the catalytic activities of the $\text{Ni/CeO}_2\text{-ZrO}_2$ catalysts for the partial oxidation reaction of methane increased with increasing oxygen storage capacity of the $\text{CeO}_2\text{-ZrO}_2$ solid solution resulting that this process proceeded by means of the redox mechanism. Besides, they also reported that Ni particles that having weak interaction with the support showed huge amount of coke whereas the nickel particles having a strong interaction showed small amount of coke.

Otsuka *et al.* (1999) studied a series of $\text{CeO}_2\text{-ZrO}_2$ composite oxide ($\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$) for the gas-solid reaction with CH_4 in the absence of gaseous oxidant. They reported that at Zr content below 50 wt%, the $\text{CeO}_2\text{-ZrO}_2$ solid solution still showed the fluorite structure and no change in degree of reducibility. $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ provided synthesis gas with a hydrogen to carbon monoxide ratio of two and higher in producing rate and lower activation energy than CeO_2 due to the incorporation of ZrO_2 into CeO_2 this caused the mobility of lattice oxygen to increase. Moreover, they reported the presence of Pt helped enhance the reaction rate.

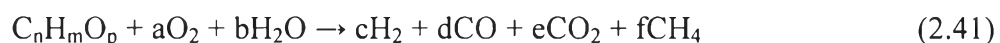
The studies of Ni/Ce-ZrO_2 in oxy-reforming of methane were further investigated by Dong *et al.* (2002). They studied the effect of nickel content of Ni/CeZrO_2 catalysts on the performance of catalyst in oxy-reforming of methane

(ORM) to synthesis gas. They reported that Ni/Ce-ZrO₂ catalyst with 15 wt% Ni loading exhibited highest catalytic activity, selectivity, as well as stability. They suggested that Ni incorporation into Ce-ZrO₂ caused ceria more reducible which helped to produce mobile oxygen during the reforming reaction. Thus, decoking activity would likely be enhanced through the participation of the lattice oxygen. Furthermore, they believed that the high performance of 15%Ni/CeZrO₂ was resulted from the well balance between two kind of active sites which one for the activation of methane and the other one for the steam or oxygen.

Pengpanich *et al.* (2004) studied methane partial oxidation (MPO) to synthesis gas over Ni/CeZrO₂ by varying the Ce to Zr ratio, nickel loading, and also studied the effect of preparation method. They reported that the catalyst prepared by impregnation method were more active than those prepared by gel impregnation method due to the higher degree of metal dispersion and reducibility. The 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst exhibited the best performance and stability to carbon deposition due to its high degree of metal dispersion and surface oxygen mobility. They also suggested that the carbon deposition on this catalyst was mainly from the methane decomposition.

2.5 Autothermal Steam Reforming

The previous two processes for hydrogen production are reforming either steam (steam reforming) or oxygen (partial oxidation). Another reforming option is to use both technologies in parallel to reform the hydrocarbon fuel into a hydrogen-rich fuel. This combination is known as autothermal steam reforming or oxidative steam reforming and can be expressed generally as shown in Equation 2.41.



Autothermal steam reforming offers many advantages from technical and economic point of view. In this case, oxygen and steam are fed together into the process, partial oxidation acts as an internal heat source that supplied thermal energy to the endothermic steam reforming rendering the overall reaction thermoneutral. Thus, the autothermal steam reforming reaction can start quickly and continue without additional or external heat supply. Additionally, this process can develop the

reactor temperature control and reduce the formation of hot spot, avoiding catalytic deactivation by carbon deposition or sintering (Haynes and Shekhawat, 2011). The space of operation for hydrogen production is presented in Figure 2.4.

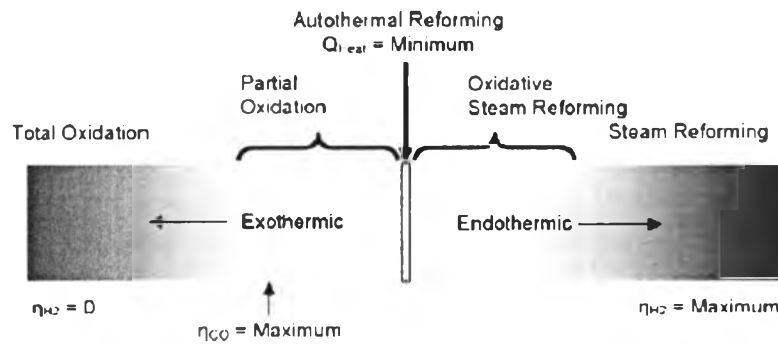
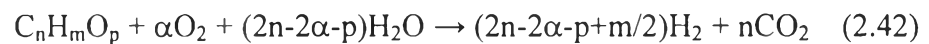


Figure 2.4 Different operating conditions for hydrogen production (Rabenstein and Hacker, 2008).

2.5.1 Autothermal Steam Reforming Operation

Feed compositions under autothermal operation are generally selected based on the overall carbon number as well as the structure of the fuel. The following method developed by Ahmed and Krumpelt (2001) which can be used to estimate the oxygen to carbon (O/C) ratio and steam to carbon (S/C) ratio. The maximum amount of hydrogen can be gained if it is assumed that a stoichiometric amount of steam is present to convert all carbon species to carbon dioxide as shown in Equation 2.42.



Based on reaction stoichiometric, the maximum amount of hydrogen formed is $(2n-2\alpha-p+m/2)$. The reaction enthalpy corresponding to the stoichiometric reaction shown by Equation 2.42 is then

$$\begin{aligned} \Delta H_r &= n\Delta H_{f,CO_2} - (2n - 2\alpha - p) \\ &= \Delta H_{f,H_2O} - \Delta H_{f,fuel} \end{aligned} \quad (2.43)$$

At the autothermal steam reforming, $\Delta H_r = 0$, Rearranging Equation 2.43 to obtain the thermoneutral stoichiometric oxygen coefficient, α , gives

$$\alpha_0 = n - \frac{p}{2} + \frac{1}{2} \left[\frac{\Delta H_{f,fuel} - n\Delta H_{f,CO_2}}{\Delta H_{f,H_2O}} \right] \quad (2.44)$$

2.5.2 Autothermal Steam Reforming Mechanism

The reaction mechanism is depending on the catalyst, the fuel type, and the reaction conditions applied. The autothermal steam reforming reaction has been mainly described by combustion-reforming mechanism.

Combustion-reforming mechanism under autothermal steam reforming conditions, the hydrocarbon conversion takes place in the following two steps. First, part of the fuel undergoes combustion with forming mainly H₂O and CO₂ as products. A very small section of the catalyst bed is utilized during this step, due to the fast kinetics of combustion. If the reaction takes place according to the stoichiometry, 25 % of the fuel is converted during this process by the oxygen. The remaining unconverted fuel fragments are then converted into synthesis gas primarily through endothermic steam reactions down the rest of the catalyst bed. After the initial combustion zone, the equilibrium of the WGS/RWGS also takes place in this region (Ruiz *et al.*, 2008). The combustion-reforming reactions of methane are shown in Equations 2.45-2.47.

Combustion reaction of methane:



Methane reforming and water-gas shift reaction:

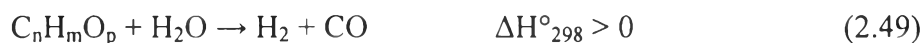


For the combustion-reforming mechanism of higher hydrocarbons can be simplified by similar reactions as shown in Equations 2.48-2.51.

Combustion reaction:



Reforming reactions:



On the study of autothermal steam reforming reaction from combustion-reforming mechanism of n-C₄H₁₀ by varying the contact time (Sato *et al.*, 2009), running at short contact times (0.15 ms) had high selectivity to CO₂ and low fuel conversion (20 %) at O/C=1.0, S/C=1.0, and 450 °C using a Ni/MgO

catalyst. Increasing the contact time from 0.15 to 1 ms resulted in a decrease in CO₂ selectivity, while improving the selectivity of both H₂ and CO, and also conversion (95 %). Collectively these results suggest that the first step in autothermal steam reforming is a highly exothermic combustion reaction, which is then followed by reforming reactions to produce synthesis gas. Also, CO selectivity decreased with increasing the contact time to 10 ms due likely to the water-gas shift and methanation reactions.

These reports also conformed to the temperature profile investigation along the catalysts bed in the autothermal steam reforming condition (Tomishige *et al.*, 2004; Simeone *et al.*, 2008a; Simeone *et al.*, 2008b). They found that the temperature profile along Ni-based catalysts bed showed a high temperature peak at the catalyst bed inlet followed by plateau lower temperature as the flow progressed down the length of the reactor. This indicated that the reaction zones exist separately.

2.5.3 Catalysts Used in Autothermal Steam Reforming

De Lima *et al.* (2008) studied the performances of Pt/CeZrO₂ catalyst over steam reforming, partial oxidation, and oxidative steam reforming of ethanol. It was observed that addition of oxygen to the feed improved the catalyst stability, but it also adversely affected hydrogen selectivity, as a significant fraction of the hydrogen product formed was oxidized to water. As the same catalyst, Ruiz *et al.* (2008) investigated the performance of supported platinum catalysts on the autothermal reforming of methane by used various supported, such as Al₂O₃, CeO₂, ZrO₂, Ce_{0.14}Zr_{0.86}O₂, Ce_{0.50}Zr_{0.50}O₂, Ce_{0.75}Zr_{0.25}O₂, and Ce_{0.75}Zr_{0.25}O₂. It was found that the Pt/Ce_{0.75}Zr_{0.25}O₂ catalyst exhibited the best stability on the autothermal reforming of methane at 800 °C, using WHSV = 260 h⁻¹, H₂O/CH₄ = 0.6, O₂/CH₄ = 0.5, and H₂/CO ratio = 2. The higher reducibility and oxygen storage/release capacity of Pt/Ce_{0.75}Zr_{0.25}O₂ catalyst promoted the mechanism of continuous removal of carbonaceous deposits from the active sites. Other noble metal catalyst, such as Rh was investigated over autothermal reforming of ethanol on zirconia supported by Gutierrez *et al.* (2011). The Rh-containing catalysts showed the highest selectivity for hydrogen production and were stable in 24 h experiments. The coke formation

was lower on the noble metal catalysts when compared with non-noble metal catalysts.

On noble metal catalysts, such as Rh, Ru, Pd, and Pt, are well-known as a high activity and dominant stability but the rareness and high cost of this type catalysts so several researches change to use non-noble catalyst which is lower cost. However, type of catalytic metal will influence the mechanisms along the catalyst bed. As mentioned by Tomishige *et al.* (2004), Ni catalyst bed showed noticeable high-temperature at the front, which then decrease at the longer catalyst bed. Under O_2 atmospheres as ATR, Ni metallic form had a strong tendency to be converted into NiO. It should be noted that the oxidized form of Ni was known to be active for combustion reactions, but not for reforming reactions. Therefore, Ni at the bed inlet was readily oxidized by the feed gas to NiO, which promoted exothermic reactions and produced a substantial temperature raised in that region.

Ni/CeZrO₂-based catalysts were investigated in autothermal methane reforming by Dantas *et al.* (2007). Addition of alumina provided a higher surface area, which favored the formation of smaller nickel oxide, and metallic nickel particles. The results showed that the catalytic performance of Ni/CeZrO₂/Al₂O₃ was better than the other samples, which may be correlated to the higher reducibility and better redox properties. In 2012, Dantas *et al.* also improved their previous research by used more and complex carriers (Al₂O₃, CeO₂/Al₂O₃, Ce_{0.5}Zr_{0.5}O₂/Al₂O₃, and Ce_{0.5}Zr_{0.5}O₂). The results related to the previous work, as was already mentioned above. Srisiriwat *et al.* (2009) also reported the activity of Ni/Al₂O₃ supports with and without promoted CeO₂, ZrO₂ and CeO₂-ZrO₂. It apparent in the same results that the presence of CeO₂ and/or ZrO₂ improved the catalyst's properties by enhancing Ni dispersion and reducing Ni particle size, especially CeO₂-ZrO₂, improved catalytic activity by increasing the hydrogen yield and the carbon dioxide/carbon monoxide and the hydrogen/carbon monoxide values at higher temperature and higher oxygen to ethanol ratio.

Thermodynamic analysis of hydrogen production via autothermal steam reforming was investigated (Vagia and Lemonidou, 2008; Grascinsky *et al.*, 2012). Equilibrium calculations employing Gibbs free energy minimization were performed for acetone, acetic acid, and ethylene glycol in a broad range of

temperature (130-1030 °C), steam to fuel ratio (1-9) and pressure (1-20 atm) values. The optimal oxygen to fuel ratio to achieve thermoneutral conditions was calculated under all operating conditions. Hydrogen-rich gas is produced at temperature higher than 430 °C with the maximum yield attained at 630 °C. The ratio of steam to fuel and the pressure determine to a great extent the equilibrium hydrogen concentration. The heat demand of the reformer, as expressed by the required amount of oxygen, varies with temperature, steam to fuel ratio, and pressure, as well as the type of oxygenate compound used. The results indicated that when the required oxygen enters the system at the reforming temperature, autothermal steam reforming results in hydrogen yield around 20 % lower than the yield by steam reforming because part of the organic feed is consumed in the combustion reaction.

2.6 Carbon Formation

Coke formation and metal sintering are known as the main reasons for deactivation. The high temperatures associated with thermal processes to produce hydrogen also favor the formation of carbon. The routes for coke formation are complicated and may be involved Equations 2.28-2.33. Because of the high temperatures of reaction, coking may result from gas phase reactions leading to carbonaceous intermediates which condense on a surface. The reactions involve free radical polymerizations and the addition of diluents such as steam reduces their importance. Nonetheless, gas phase coke can accumulate on the catalyst particularly with heavier hydrocarbon feedstock.

As mentioned beforehand, nickel-based catalyst is attractive but it is suffered from the deactivation caused by carbon deposition and metal sintering at reaction temperature. Therefore, several researches have been focused on modifying nickel-based catalyst stability. Most studies (Vagia and Lemonidou, 2010; Thaicharoensutcharittham *et al.*, 2011) deal with the support and the introduction of some promoters in order to improve the stability, as well as catalytic performance. They observed that Ni-based $\text{CeO}_2\text{-ZrO}_2$ catalysts exhibited a better activity with less coke formation as compared to commercial catalysts as Ni-based on MgO and Al_2O_3 supports due to the synergetic effect of an ease of reducibility and a good oxidation

ability of the $\text{CeO}_2\text{-ZrO}_2$ mixed oxide could promote the oxidation of carbon precursors on the nickel surface leaving the surface of the catalyst clean. In addition, the effect of nickel loading on coke formation over Ni/ZrO_2 catalysts under steam reforming of acetic acid was investigated by Li *et al.* (2012b), they found that the lowest of coke formation was around 16%Ni/ ZrO_2 catalyst, which polymerization of acetone was the main route over 2%Ni/ ZrO_2 to 13%Ni/ ZrO_2 catalysts whereas methane decomposition and CO disproportion were the two main routes over 20%Ni/ ZrO_2 to 23%Ni/ ZrO_2 catalysts.

It is well known that coke formation over different reactions does not show the same behavior in term of qualitative and quantitative. As shown in Figure 2.5, the different characteristic peaks of coke formation from XPS analysis are observed due to the different reactions. Rabenstein and Hacker (2008) studied a thermodynamic analysis for H_2 production from ethanol by different processes. They concluded that the amount coke was formed in the following order: partial oxidation > steam reforming > autothermal steam reforming. Furthermore, De lima *et al.* (2008) also conformed these results and gave the reason that adding both of water and O_2 to the feed improved catalyst stability and promoted the elimination of coke.

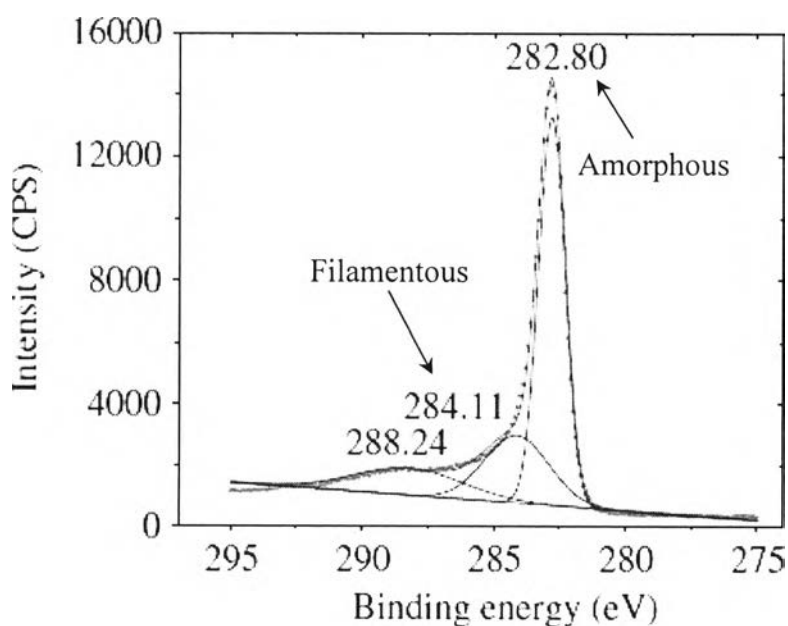


Figure 2.5 XPS profiles of the spent 12%Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (An *et al.*, 2011).

As shown in Figure 2.6, type of coke formation also discussed in several researches (Trimm, 1977; Wang *et al.*, 2008; Wu and Liu, 2010; Vagia and Lemonidou, 2010; An *et al.*, 2011). They found that carbon species deposited over different catalysts and reaction conditions had different structure. For Ni-based catalyst, filamentous carbon or graphitic carbon (hard coke) was unique to metallic Ni because the carbon atoms were soluble in the metal lattice and its nucleation into grapheme layers at the metal-support interface. Then the Ni particle was forced to break away from the catalyst main body. Finally, a carbon nanotube formed. Nonetheless, the formation of filamentous carbon could lead to build up of pressure in the catalyst bed as a result of catalyst fragmentation. Moreover, the thermal processes of oxygenated compound as acetic acid always generated carbonaceous compounds on catalyst surface or amorphous carbon as known as soft coke which easily gasified by steam or transformed to filamentous carbon at the lower temperature. Meanwhile, filamentous carbon would be degraded at the higher temperature.

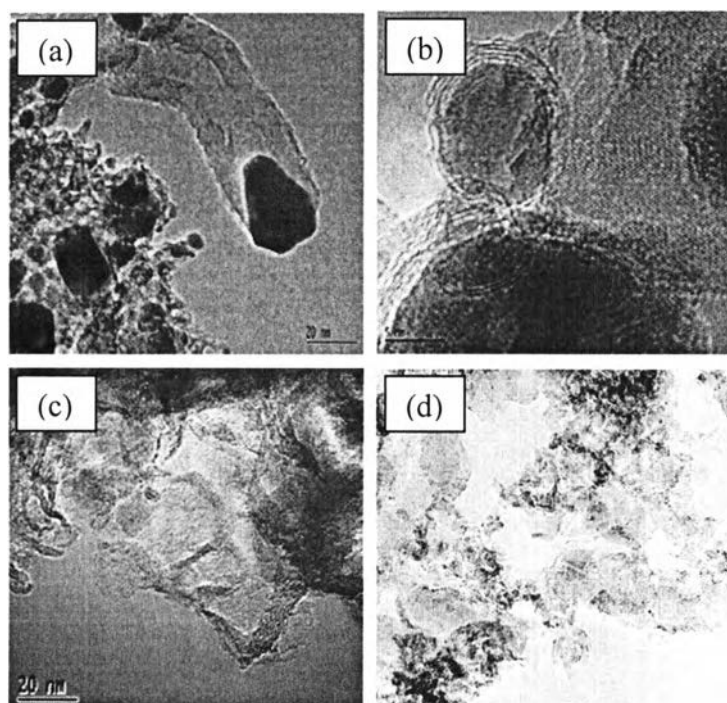


Figure 2.6 TEM images illustrating the different carbon morphologies over Ni-based catalysts of a) filamentous, b) encapsulating, c) pyrolytic and, d) amorphous.