

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogen Production Processes

Hydrogen can be generated in a number of ways, such as electrochemical processes, thermochemical processes, photochemical processes, photocatalytic processes, or photoelectrochemical processes. The main alternative methods of hydrogen production from energy sources are given in Figure 2.1. Hydrogen is commonly produced by steam reforming of methane. Hydrogen is also produced as a byproduct of other processes such as CO₂ from methane steam reforming process. The discovery and development of less expensive processes of hydrogen production is relevant to the establishment of a hydrogen economy.

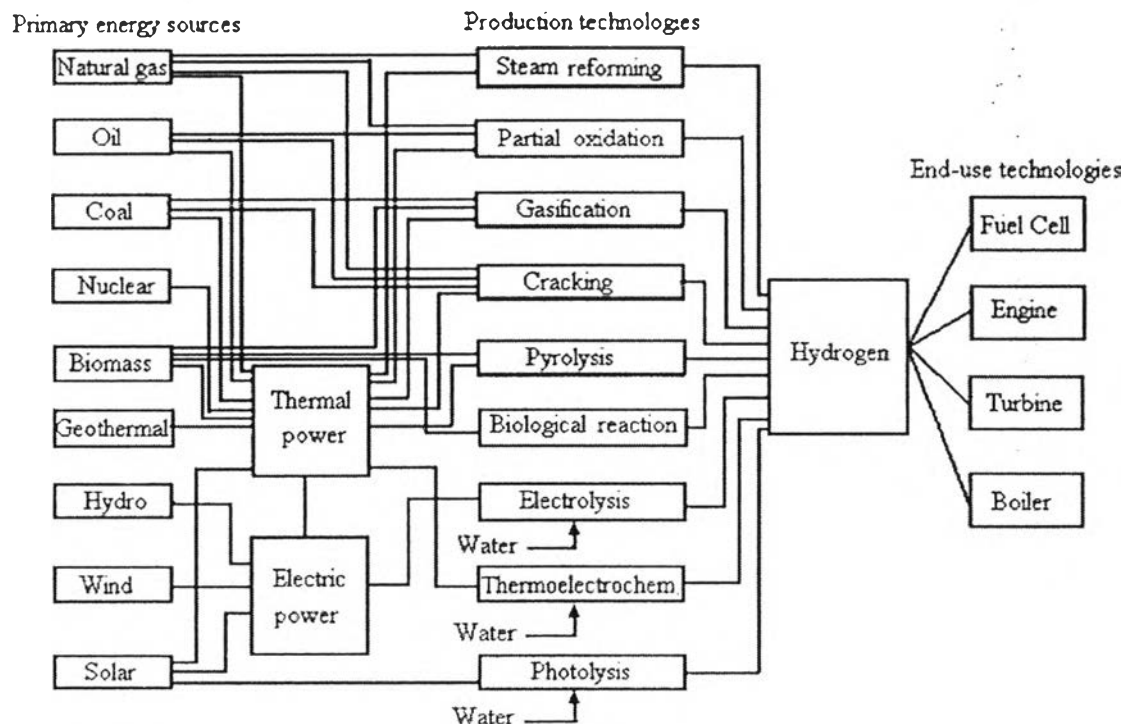


Figure 2.1 The main alternative methods of hydrogen production from energy sources. (Source: Boehm *et al.*, 2003).

2.2 Steam Reforming

Steam reforming (SR) referred as methane steam reforming (MSR). Steam reforming is a well-established process for converting natural gas, mostly is methane, into hydrogen or synthesis gas (a mixture of CO and H₂) in industry. In general, the steam reforming reaction of hydrocarbon can be expressed by two steps:

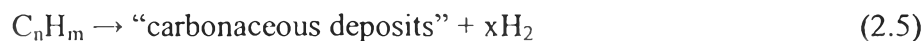
First step, referred to reforming of natural gas, involves methane reacting with steam at 700-800°C to produce a synthesis gas (syngas), a mixture primarily made up of hydrogen (H₂) and carbon monoxide (CO).



Second step, referred to water gas shift reaction, the carbon monoxide produced in the first reaction is reacted with steam over a catalyst to form hydrogen and carbon dioxide (CO₂). This process occurs in two stages, consisting of a high temperature shift at 350°C and a low temperature shift at 190-210°C.



In addition, reactions 2.1 to 2.2 may be attended by following reactions forming carbon:



At high temperature (above 650°C), the hydrocarbons may react in parallel to reaction 2.1 by thermal cracking (called “steam cracking”) into olefins which may easily form coke by reaction 2.5. The risk of carbon formation must be eliminated in operation since carbon causes serious operational troubles such as deactivation of the catalyst and increasing pressure drop. Therefore, addition of excess steam is normally used to avoid coke formation.

Steam reforming of natural gas is widely used in industry today. Hydrogen is produced by the methane steam reforming process in large centralized industrial plants for use in numerous applications, including chemical manufacturing and petroleum refining. Research and development (R&D) programs are currently investigating the development of small-scale methane steam reforming technologies to enable the development of small-scale, distributed hydrogen production and delivery infrastructure.

Steam reforming of natural gas offers an efficient, economical, and widely used process for hydrogen production, and provides near- and mid-term energy security and environmental benefits. The efficiency of the steam reforming process is about 65% to 75%, among the highest of current commercially available production methods. Natural gas is a convenient, easy to handle, hydrogen feedstock with a high hydrogen-to-carbon ratio. It is also widely available from sources in the U.S. and Canada.

The cost of hydrogen produced by methane steam reforming is acutely dependant on natural gas prices and is currently the least expensive among all bulk hydrogen production technologies. A well-developed natural gas infrastructure already exists in the U.S., a key factor that makes hydrogen production from natural gas attractive.

However, the disadvantages of the steam reforming process are high energy consumption, intensive capital cost, and coke deposition problems. Therefore, much research has been focused to investigate reforming catalyst conditions in order to solve these problems and improve reforming efficiencies.

2.3 Catalytic Steam Reforming of Methane

Catalytic steam reforming is used to produce hydrogen by splitting water. Steam reacts with methane to produce hydrogen and carbon monoxide, when heated to very high temperatures and is in the presence of a metal based catalyst.

2.3.1 Preparation Methods

Apart from the chemical composition, also physical properties relating to structure influence the reactivity and stability of catalysts. The preparation method determines these physical properties to a large extent. Although many preparation techniques are practiced, only two common methods will be discussed here.

Probably the most common technique for catalyst preparation is impregnation of a metal salt in an aqueous solution onto a support material, e.g., γ - Al_2O_3 . Another common method of catalyst preparation is co-precipitation. In this procedure, solutions of metal salts are added together, usually at constant pH, and precipitate into the desired product.

The different effects of the impregnation and co-precipitation methods on the catalytic activity are illustrated by the following Wang and Lu (1998b) investigated for nickel catalysts the effects of support phase and preparation technique on the reforming of methane with CO_2 . They found, amongst others, that the impregnated Ni/MgO-catalyst performed better than the co-precipitated one).

Chen *et al.* (2008) reported that im-Ni/CZ-CTAB and pre-Ni/CZ-CTAB catalysts had larger surface area and pore volume than im-Ni/CZ and pre-Ni/CZ. However, Ni^{2+} entered the lattice of the solid solution in the co-precipitated catalysts, which led to a better nickel species dispersion and a stronger interaction between nickel species and solid solution. Whether in the impregnated catalysts or the co-precipitated catalysts, nickel species promoted the reducibility of the solid solution. im-Ni/CZ-CTAB and pre-Ni/CZ-CTAB, especially pre-Ni/CZ-CTAB, showed higher activity than im-Ni/CZ and pre-Ni/CZ in CH_4 - CO_2 reforming. This is mainly attributed to their large surface area and pore volume. The nickel dispersion and the interaction between nickel and the supports were also the important factors influencing the catalyst performance.

2.3.2 Active Metals

Numerous supported metal catalysts have been tested for methane reforming. Among those, nickel-based catalysts and noble metal supported catalysts (Rh, Ru, Pd, Pt, Ir) were found to have promising performance in terms of catalytic activity and selectivity. The activity trend of methane reforming is $\text{Ru, Rh} > \text{Ir} > \text{Ni}$,

Pt, Pd, and the catalyst based on noble metals were reported to be less sensitive to coking than Ni based catalyst (Rostrup-Nielsen and Hansen, 1993). However considering the aspect of high cost that limit the availability of noble metals, it is more desirable, from an industrial point of view, to develop Ni based catalyst which are resistant to carbon deposition and exhibit more stable more stable operation for a long period of time.

Kusakabe *et al.* (2004) investigated the methane steam reforming over Ce-ZrO₂-supported Ni and noble metal catalyst at low temperature. They found that the highest activity was obtained for the Rh/Ce_{0.15}Zr_{0.85}O₂ catalyst for which methane conversion was 28.1% at 500°C. And among the structure of Ce_{1-x}Zr_xO₂ support with a 10 wt.% Ni loading, the Ce_{0.15}Zr_{0.85}O₂ showed the highest CH₄ conversion at 500–600°C and a high H₂/CO ratio due to the oxidation of CO via the water–gas shift reaction.

2.3.2.1 Noble Metal Catalysts

Liguras *et al.* (2003) studied the catalytic performance of supported noble metal catalysts for the steam reforming of ethanol in the temperature range of 600-850°C with respect to the nature of the active metallic phase, the nature of the support and the metal loading. They observed that Pt is not as active as Rh, which is significantly more active and selective for hydrogen formation compared to Ru and Pd.

Ru-added Ni catalysts supported on Al₂O₃ or MgAl₂O₄ were prepared by Jeong *et al.* (2005) for methane steam reforming to investigate Ru-induced effects on the catalytic activity.

Ishihara *et al.* (2005) studied the effect of the addition of ruthenium on nickel steam reforming catalysts supported by MgO, La₂O₃, and Al₂O₃. Using m-cresol as fuel, they discovered that the presence of ruthenium enhances the catalytic performance of the Ni based catalyst when the loading of ruthenium was increased up to 15 wt%. In addition, did a study of loading Ni up to 15% onto a Ru-based catalyst, and found that it too enhanced the catalytic activity of the catalyst. Further, they developed a bimetallic catalyst consisting of 2 wt% Ru – 15 wt% Ni and found a reasonably high resistance to carbon deposition.

2.3.2.2 Transition Metal Catalysts

Nickel based catalysts are attractive for this reaction due to their high activity and low cost. Hegarty *et al.* (1998) studied steam reforming and partial oxidation of methane over Cu, Co, Fe and Ni supported on ZrO₂ catalysts at the temperature from 400 to 800°C. The result showed that the activity of the catalysts were found to decrease in the order Ni>Cu>Co>Fe.

Rakass *et al.* (2006) studied steam reforming of methane over unsupported nickel powder catalysts as a catalyst in internal or external reforming of solid oxide fuel cell systems. The unsupported Ni catalyst (Inco Ni 255) is a pure nickel powder with a BET surface area of 0.44 m²g⁻¹. The catalytic activity was conducted in a seven-cell differential reactor system. The partial pressure of water in the gas was used to regulate the CH₄:H₂O ratio. It was observed that CH₄ conversion increased and coke deposition decreases significantly with a decrease of CH₄:H₂O ratio. Thermodynamic equilibrium was achieved at a CH₄:H₂O ratio of 1:2. CH₄ conversion of 98±2 % was achieved at 700°C and no coke was generated. This compares favorably with supported Ni catalyst systems. In conclusion, a ratio of 1:2 of fuel to water showed that unsupported Ni catalyst exhibited high catalytic activity and stability during the reforming of methane at low-mid temperature range.

The activity of a catalyst is related to the metal surface area (i.e., the number of active sites). This implies that, generally, the catalytic activity benefits from a high dispersion of the metal particles. Common dispersions for Ni catalysts are of 2–5%, with metal particles of 20–50 nm (Rostrup-Nielsen, 1984). There is an optimum beyond which an increase in Ni-content does not produce any increase in activity, usually around 15–20 wt% (depending on support structure and surface). Although the nickel surface area is generally increased with higher loadings, the dispersion or utilization of the nickel tends to decrease with increasing nickel content. Hence, the activity will not increase any further.

2.3.3 Catalytic Support

The influence of the support on the steam-reforming reaction can hardly be overrated. It not only determines the dispersion of the catalytically active metal particles or the catalyst's resistance to sintering, it also affects the reactivity and coke resistance of the metal particles, and may even participate in the catalytic reaction itself. In other words, the support is a fundamental part of the catalyst and cannot be considered separately.

For amorphous CeO_2 as a support for Pd catalysts, a strong metal-support interaction leads to partial encapsulation of Pd particles, resulting in significantly reduced catalytic activity for steam reforming (Craciun, 2002). For more complex supports, synergetic effects can emerge. For instance, Ni supported on MgO–CaO showed high basicity and lower coke forming ability attributed to the addition of CaO (Yamazaki, 1992). Al_2O_3 – CeO_2 is known for its catalytic stability and coking resistance, whereas CeO_2 itself may lead to significantly reduced catalytic activity (Wang, 1998a). In the case of the combined Al_2O_3 – CeO_2 support, the beneficial effects (i.e., high porosity and increased stability) of both supports are utilized (Craciun, 2002; Wang, 1998d) – at least, when crystalline (i.e., oxidized) instead of amorphous (i.e., reduced) CeO_2 is used, as mentioned above. In fact, CeO_2 is actually contributing the reaction mechanism itself.

Thammachart *et al.* (2001) found that $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ solid solution gave the highest activity among the mixed oxide catalysts studied. It might be postulated that the cubic phase fluorite structure of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ found mainly in the case where x is less than 0.5 could be reduced easily than the tetragonal phase. It is evident that $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ contains a mixed phase between cubic and tetragonal phases, which might result in a decrease in the degree of reducibility. The presence of tetragonal phase was also noticed in the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, but not to a great extent. This might be the reason why the catalytic activity of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ is lower than that of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. It might be speculated that a solid solution of ceria–zirconia in a cubic phase is a good catalyst for CO oxidation. The presence of tetragonal phase should be avoided in order to achieve high catalytic activities.

2.3.4 Modification of Supported Catalyst

Longya *et al.* (2000) found that the promotion of Mn to Fe/Si-2 catalyst lies not only in increasing C₂H₄ selectivity but also in improving the catalytic stability greatly. The rate of coke deposition on Fe–Mn/silicalite-2 is much less than that on Fe/silicalite-2, due to the modification of Mn to the Fe/silicalite-2 catalyst. The promotion of Mn to the improvement of the catalytic stability of the Fe/silicalite-2 catalyst results from the great prohibition of coke formation on Fe–Mn/silicalite-2 catalyst surfaces.

Xiaodong *et al.* (2006) investigated Effect of Manganese Doping on Oxygen Storage Capacity of Ceria- Zirconia Mixed Oxides. They found that the introduction of Mn to CeO₂-ZrO₂ mixed oxides improves the OSC (oxygen storage capacity) performances including OSCC (oxygen storage complete capacity) and dynamic OSC. It may be attributed to the synergetic effect of incorporated Mn^{x+} in the ceria lattice and segregated manganese oxide on the surface. The doping amount of Mn and its solubility in the CeO₂ lattice affect the OSC performance of the mixed oxides under different measurement conditions.

Bampenrat *et al.* (2010) investigated the Naphthalene steam reforming over Mn-doped CeO₂-ZrO₂ supported nickel catalysts. The results showed that nickel supported on Ce_{0.75}Zr_{0.25-x}Mn_xO₂ mixed oxide catalysts exhibit good activity for naphthalene steam reforming. It was found that the amount of carbon deposition reduced substantially when Mn was introduced to the CeO₂-ZrO₂ mixed oxide. This might be due to the fact that the incorporation of manganese ions into the ceria lattice would improve the oxygen storage capacity and the oxygen mobility on the surface of mixed oxides, resulting in enhancing the gasification of the deposited carbon.