CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1. Introduction of Synthesis Gas

Synthesis gas or syngas is a mixture of carbon monoxide and hydrogen, which is used in the petrochemical industry. It can be used both pure gas and mixture gas. The mixture gas can be mainly produced as methanol, hydrocarbon and reducing gas for the smelting works. For the pure gas, it can be widely used as the raw material in producing ammonia, liquefied petroleum gas (LPG), dimethyl ether (DME), fuel cell and other derivative chemicals as the important feedstocks in petrochemical industry.

2.1.1. The Manufacture of Synthesis Gas

The synthesis gas is generally produced from hydrocarbon feedstocks, i.e., natural gas, oil and coal by several processes as follows:

1. Reforming of the natural gas or light hydrocarbon with steam or carbon dioxide (or both steam and carbon dioxide)
2. Partial oxidation of heavy oil, POX
3. Gasification of coal or coke

These processes can give different hydrogen to carbon monoxide ratio as illustrated in Table 2.1 [12]. It is found that the ratio of synthesis gas is dependent on the producing processes. The first, if the producing process is the methane steam reforming, the carbon monoxide to hydrogen ratio will be 1:3 with the following reaction:

$$CH_4 + H_2O \xrightarrow[850\ ^{\circ}C,\ 30\ bar]{Ni} CO + 3H_2 \qquad (2.1)$$
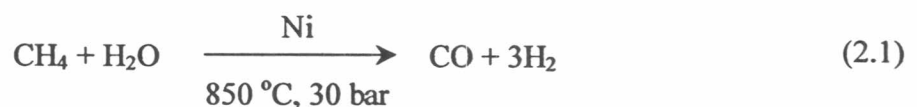
Table 2.1. The ratio of synthesis gas from the producing processes [12].

Source	CO	H_2
1. Methane steam reforming	1	3
2. Toluene steam reforming	1	2
3. Partial oxidation	1	1
4. Coal gasification	2	1

The second, naphtha or toluene is used as the raw material for the synthesis gas production. Then, the carbon monoxide to hydrogen ratio of synthesis gas is 1:2 by the following reaction:

$$PhCH_3 + H_2O \xrightarrow[430\,°C]{Rh/Al_2O_3} PhH + CO + 2H_2 \qquad (2.2)$$

The raw materials for this process are selected to depend on the utilization of synthesis gas in the petrochemical industry. In addition, both naphtha and toluene can be also used as the raw materials for the partial oxidation process. However, the process is widely used as the Shell-Gasification process [13]. The fuel oil can be selected mainly as the raw material for this process because it is not expensive as illustrated in Figure 2.1. The reaction is as follows:

$$C_nH_{2n} + (n/2)O_2 \longrightarrow nCO + nH_2 \qquad (2.3)$$
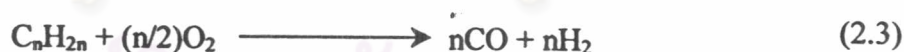
However, the coal is important alternative to produce the synthesis gas at present since crude oil is increasingly expensive. Then, the coal gasification process is widely used and developed in Germany as illustrated in Figure 2.2 [14]. Especially, the Shell-Kopper process is a perfect gasification process, which obtained about 93 to 98 percent of synthesis gas and little by-product [15]. The overall reaction is as follows:

$$C + H_2O \longrightarrow CO + H_2 \qquad (2.4)$$

$$C + \tfrac{1}{2}O_2 \longrightarrow CO \qquad (2.5)$$

The reaction (2.4) and (2.5) are the steam reforming process and the partial oxidation process, respectively.
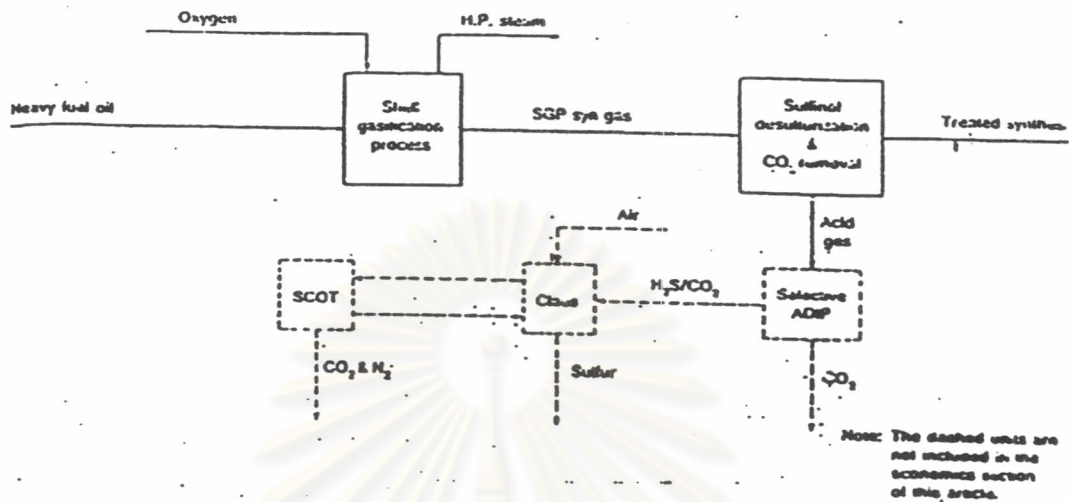
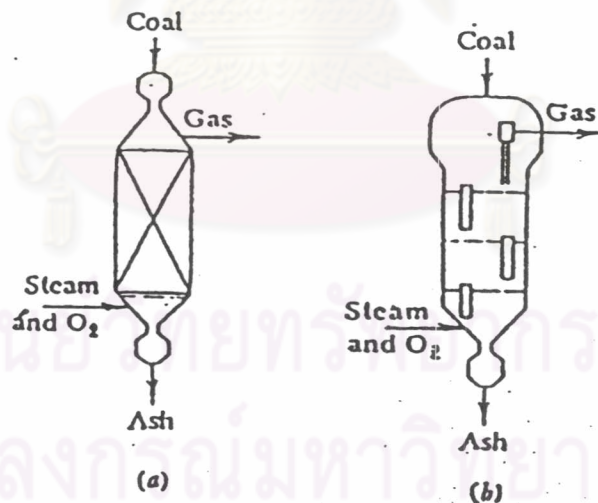

Figure 2.1. Partial oxidation process [13].

Figure 2.2. Coal gasification process [14].

        a) Continuous layer of small-sized coal.

        b) Fluidized-bed of coal.

The synthesis gas can be used as the raw material in several petrochemical industries, which depended on its ratio as illustrated in Table 2.2 [12].

Table 2.2. The utilization of synthesis gas in petrochemical industry [12].

Product	H_2 : CO (Molar)	Wt. retention (%)
Methanol	2 : 1	100
Ethylene glycol	1.5 : 1	100
Acetic acid	1 : 1	100
Acetic anhydride	1 : 1	85
Ethyl acetate	1.5 : 1	71
Vinyl acetate	1.5 : 1	70
Ethanol	2 : 1	72
Ethylene	2 : 1	44
BTX	1.5 : 1	42

The production of methanol from synthesis gas can use 1:2 mole ratio of carbon monoxide to hydrogen. The methane steam reforming process is widely used for the methanol production. In addition, the partial oxidation process is also used for the production of acetic acid or acetic anhydride. Moreover, the production of aldehyde from olefins by hydroformylation process used homogeneous cobalt catalyst at high temperature and pressure as in the following reaction:

$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO \qquad (2.6)$$

The optimum ratio of synthesis gas for the reaction (2.6) should be 1:1 as using from the partial oxidation process. Furthermore, the synthesis gas is also able to change its form as oxygenated compound directly. Its advantage is there is no raw material loss to change to water (56 percent). However, the synthesis gas is mainly produced with the reforming process of natural gas (or light hydrocarbon to naphtha) at present. Although heavy oils and coal are less expensive feedstocks, the capital cost of a POX or coal gasification plant can be two to three times of that of a steam reforming plant as illustrated in Table 2.3 [16]. Steam reforming is the most economic choice based

on a plant starting up in the U.S. in 1987, which is based on a natural gas price of $4.10/million Btu ($3.90/GJ) and an oil price of $3.73/million Btu ($3.50/GJ). Lower current energy costs make steam reforming even more attraction since the capital portion of the product cost increases with lower feedstock costs. In addition, partial oxidation can be attractive if special circumstance exists. For example, if natural gas or other light hydrocarbon is not easily available, POX may be the most economical alternative. If the oil feedstocks were priced at $2.60/million Btu (70 % of base value), POX and steam reforming approximately break even. Then, partial oxidation and coal gasification also become increasingly more attractive as the plant capacity increases. However, at typical capacities and with a choice of feedstocks, reforming of light hydrocarbon is expected to remain the most cost-effective way to generate synthesis gas for at least the next decade and probably until the year 2000.

Table 2.3. The technology of synthesis gas generation [16].

Item	Steam Methane Reforming	Partial Oxidation	Coal Gasification
Feedstock Cost ($/10^6 Btu)	4.10	3.73	1.48
($/10^9 J)	3.90	3.50	1.40
Feedstock Requirement (Btu/std. ft^3)	482	475	562
(10^6 J/kmol)	426	419	496
Capital Cost* (10^6 $)	74	125	496
Product Cost** ($/× 10^3 std. ft^3)	3.00	4.25	14.60
($/kmol)	2.51	3.55	12.21

* Capacity = 75 × 10^6 std. ft^3/d (3,740 kmol/h), 1987 Start-up.

** 1987 Start-up product cost.

2.1.2. The Utilization of Synthesis Gas

2.1.2.1. Synthesis Gas

The primary products are produced from the synthesis gas used as raw material, which illustrated in Figure 2.3. These products can be used as raw material for producing other product in petrochemical industry as illustrated in Figure 2.4 [17].

The synthesis gas is important raw material for producing the organic chemicals, which is used mainly as petrochemicals. In the early 1920s, the German scientist discovered the synthesis gas could be changed to methanol with using zinc-chromium oxide catalyst and also to alkanes and alcohols with using cobalt-iron oxide catalyst. The reaction of changing to alkanes and alcohols was well-known Fischer-Tropsch reaction. The aim of this reaction was the liquid fuel production as high molecular weight alkanes in the World War II. In addition, the liquid fuel could be also used in South Africa [18]. However, the production of methanol from synthesis gas was developed with the Imperial Chemical Industries (ICI) company. This company improved zinc-chromium oxide catalyst to copper-zinc oxide catalyst. As a result, the reaction was achieved at the optimum temperature and pressure. The utilization of methanol can be used as raw material for producing formaldehyde, acetic acid, methyl chloride and so on. In the future, the methanol will be important that it can be used as fuel and produced the single cell protein (SCP). Furthermore, the methanol is also used as additive, methyl tertiary butyl ether (MTBE), in gasoline and source of hydrogen production by the methanol separation to hydrogen and carbon dioxide [19]. Moreover, the synthesis gas still uses as raw material for producing oxo alcohol, which is used for the shampoo and detergent production by the interaction of synthesis gas with olefins, ethylene glycol, phosgene and so on.
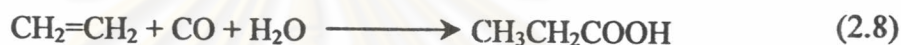
2.1.2.2. Carbon Monoxide

The carbon monoxide is toxic gas, inflammable, colorless and odorless, which is generated from the partial combustion. The carbon monoxide is separated from synthesis gas by the adsorption of carbon monoxide with liquid copper and the cryogenic separation. The carbon monoxide can be used mainly in the carbonylation

and hydroformylation (or oxo reaction) processes. For the olefinic carbonylation process, it is the interaction of olefins with water, alcohol, amine and acetic acid by using metal group VIII as catalyst. For example, the production of acrylic acid by the interaction of acetylene with carbon monoxide and water using $NiCO_4$ catalyst at 150 °C and 30 bar can be obtained 90 percent of acrylic acid the following reaction:

$$HC{=}CH + CO + H_2O \xrightarrow{\text{NiCO}_4} CH_2{=}CHCOOH \qquad (2.7)$$

The production of propionic acid from ethylene by the hydroxycarbonylation process using nickel propionate as catalyst at 270-320 °C and 200-300 bar can be obtained more than 95 percent of propionic acid the following reaction:

$$CH_2{=}CH_2 + CO + H_2O \longrightarrow CH_3CH_2COOH \qquad (2.8)$$

The phosgene can be produced from the interaction of carbon monoxide with chlorine by using activated carbon as catalyst at 500 K. The phosgene is used as raw material for producing toluene diisocyanate. For producing acetic acid, it can be produced from the carbonylation reaction between carbon monoxide and methanol using promoted cobalt with iodide catalyst at extreme condition (220 °C and 474 atm), which can be obtained 60 percent of acetic acid. If the promoted rhodium with iodide is used as catalyst for producing acetic acid, the reaction condition will be at 175-195 °C and 30 atm. Then, the amount of acetic acid, which is based on methanol, will be 99 percent. Moreover, the carbon monoxide can be also used for producing nickel. The nickel can be purified by the interaction of carbon monoxide with nickel. The nickel carbonyl is generated, which is stable at lower than 60 °C, and cracked rapidly to become pure nickel and carbon monoxide at 180 °C. However, the carbon monoxide can be used as raw material in other industries, i.e., the formic acid and propinoic acid production by hydroformylation process or the aldehyde production.

2.1.2.3. Hydrogen

The hydrogen production by using different raw material is illustrated in Figure 2.5 [20]. As a result, the purity and amount of hydrogen are different with several raw materials. In addition, the price and type of raw material are also

important factors for producing hydrogen. For example, the electrolysis of an aqueous solution, i.e., the electrolysis of brine to produce hydrogen of 100 to 500 tons of hydrogen per year. Furthermore, the hydrogen can be produced with passing steam to spongy iron at 650 °C and atmospheric pressure. Nowadays, the hydrogen is also by-product from the nuclear power plant. However, the hydrogen can be produced widely as raw material in petrochemical industry with the reforming process, which illustrated in Table 2.4 [21]. In 2000, the global hydrogen was used for producing ammonia and petroleum refining as illustrated in Table 2.5 [22].

Table 2.4. The hydrogen production with several processes [21].

Method	Temp.	Pressure	Catalyst	Remarks
1. Electrolysis of Brine	-	-	-	This method is employed where 100-500 tons / annum of gas are required
2. Reaction of steam with spongy iron	650 °C	atmospheric pressure	-	
3. Reaction of natural gas with steam	900 °C	-	Ni Catalyst promoted by magnesia or alumina	

The ammonia can be produced widely with Haber process at present. Hydrogen and nitrogen are used as raw materials in this process. This process is achieved with using Fe_2O_4 and other metal oxide as catalyst at low temperature and high pressure. The ammonia from this process can be used as raw material for producing fertilizer to transform as anhydrous ammonia and ammonia compound, i.e., ammonium nitrate, ammonium phosphate, urea and so on. In addition, the hydrogen can be also used in petroleum refining in order to improve the quality of oil and other petrochemicals using the hydrosulfurizing and hydrocracking process. However, the hydrogen still be

important raw material in other industry, i.e., petrochemicals, organic chemicals, food and so on.

Table 2.5. The utilization of global hydrogen in 2000 [22].

End use	Demand in year 2000			
	United States		Rest of the world	
	Low	High	Low	High
Anhydrous ammonia	2,460	4,490	5,200	12,700
Petroleum refining (e.g. Hydrocracking)	2,340	32,640	8,000	36,000
Other uses	1,450	24,660	2,000	25,000
Total	6,250	61,790	15,200	73,700

Figure 2.3. The production of primary products from synthesis gas [17].
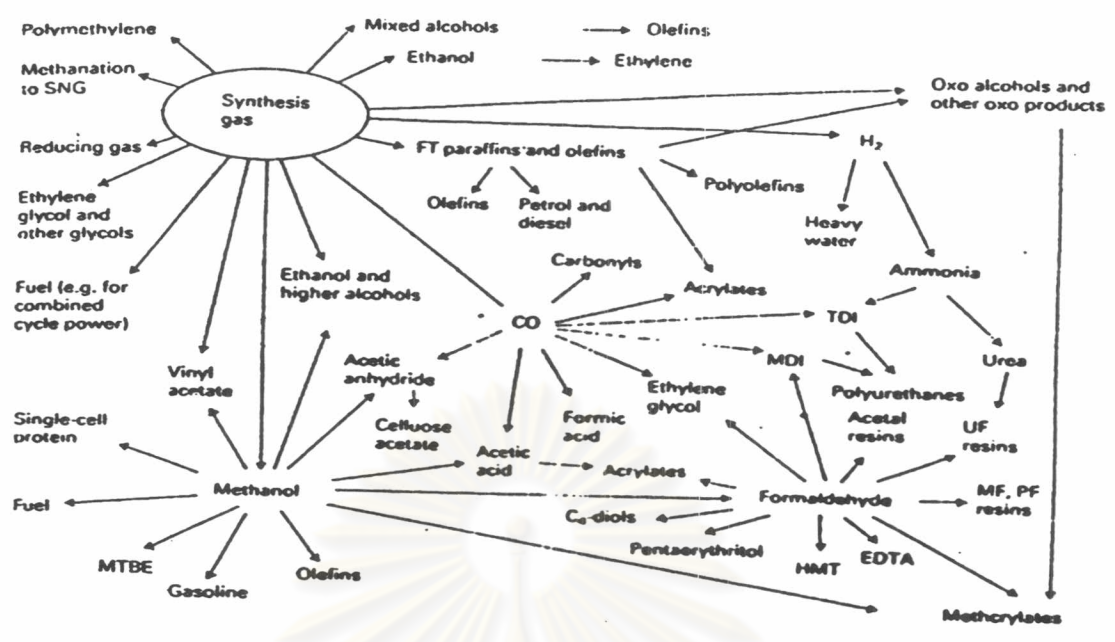
Existing and potential synthesis gas applications (FT = Fischer-Tropsch; TDI = toluene diisocyanate; UF resins = urea formaldehyde resins; MF resins = melamine formaldehyde resins; PF resins = phenol formaldehyde resins; EDTA = ethylene diamine tetra-acetic acid; HMT = hexamethylene tetramine; and MTBE = methyl tertiary butyl ether).

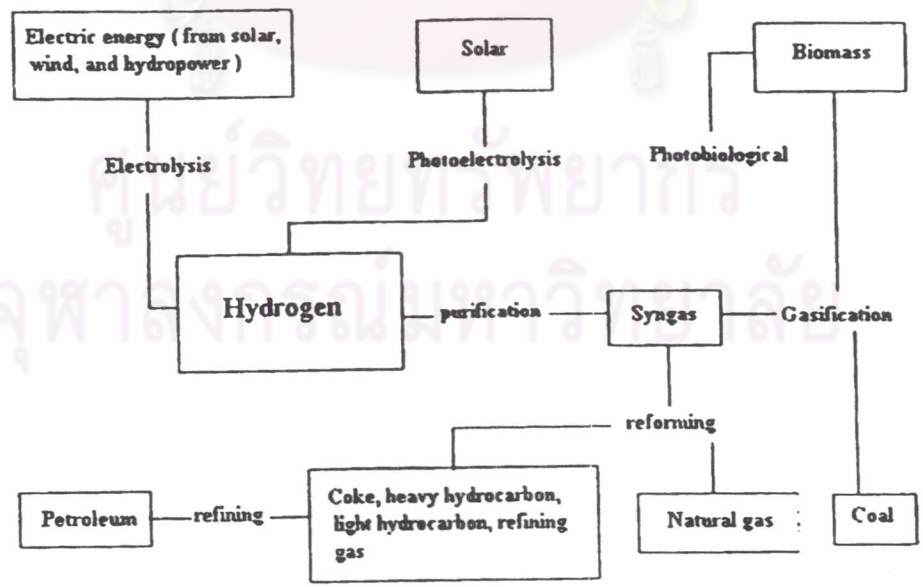**Figure 2.4.** The utilization of primary products [17].

Figure 2.5. Sources of the hydrogen production [20].

2.2. Theory of Reforming Reaction

2.2.1. Raw Material

Hydrocarbon can be widely used as raw material in the reforming reaction. Its properties are as follows:

1. Low molecular weight saturated hydrocarbon is widely used owing to if using high molecular weight type, so partial energy is employed to change its state from liquid to gas. Furthermore, carbon deposition problem is taken place. As a result, the catalyst is deactivated. Unsaturated hydrocarbon is not used because it enables side reaction to occur easily.

2. Hydrocarbon must be pure and not be poisoned with catalyst. For example, if hydrocarbon is contaminated with sulfur or sulfur compound, e.g. hydrogen sulfite, active site of catalyst will decrease due to catalyst deactivation.

2.2.2. Reforming Reaction

The reforming process is hydrocarbon conversion to generate mixed gas of hydrogen, carbon monoxide, carbon dioxide and unconverted hydrocarbon.

The basic reaction of synthesis gas production with using catalyst is the conversion of hydrocarbons by steam over catalyst which is called hydrocarbon steam reforming, as the following reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^\circ_{298} = 206 \text{ kJ/mol}$$
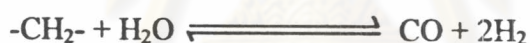$$(49.3 \text{ kcal/mol})$$
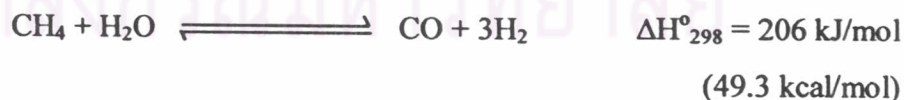
This reaction is strongly endothermic and its equilibrium is shifted to the right only at an elevated temperature as illustrated in Figure 2.6, curve 1. In order to increase the degree of conversion of methane, the process is carried out at 800-900 °C in an excess of steam. At atmospheric pressure, this excess of steam is not large, about 2:1, but an

increase in pressure has an unfavorable effect on the state of equilibrium, and in this case the steam-methane volume ratio has to be about 4:1. Apart from the methane conversion, there also is the conversion of carbon monoxide as the following reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^o_{298} = -41.0 \text{ kJ/mol}$$
$$(-9.8 \text{ kcal/mol})$$
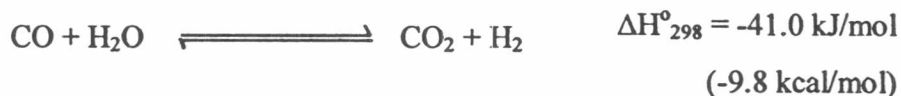
This reaction is exothermic and its equilibrium is shifted to the left at an elevated temperature as illustrated in Figure 2.6, curve 3. The excess steam causes the formation of a larger amount of carbon dioxide. The conversion of carbon monoxide proceeds rapidly and the composition of the converted gas depends on its equilibrium. The conversion of methane by steam yields a gas with a large hydrogen-carbon monoxide ratio, which being 3:1 as a minimum, while for organic synthesis it required synthesis gas with an hydrogen-carbon monoxide ratio of 1:1 to (2-2.3):1. Such a ratio can be achieved by conversion of liquid hydrocarbons as the following reaction:

$$-CH_2- + H_2O \rightleftharpoons CO + 2H_2$$

or by addition of carbon dioxide to steam during the conversion, the carbon dioxide also converts the hydrocarbons as the following reaction:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^o_{298} = 247 \text{ kJ/mol}$$
$$(59.2 \text{ kcal/mol})$$

The reaction is endothermic and its equilibrium is shifted to the right at a sufficiently high temperature as illustrated in Figure 2.6, curve 2. It proceeds at a slower rate than the methane-steam reaction. In this case, a hydrogen-carbon monoxide ratio will be about 2:2.
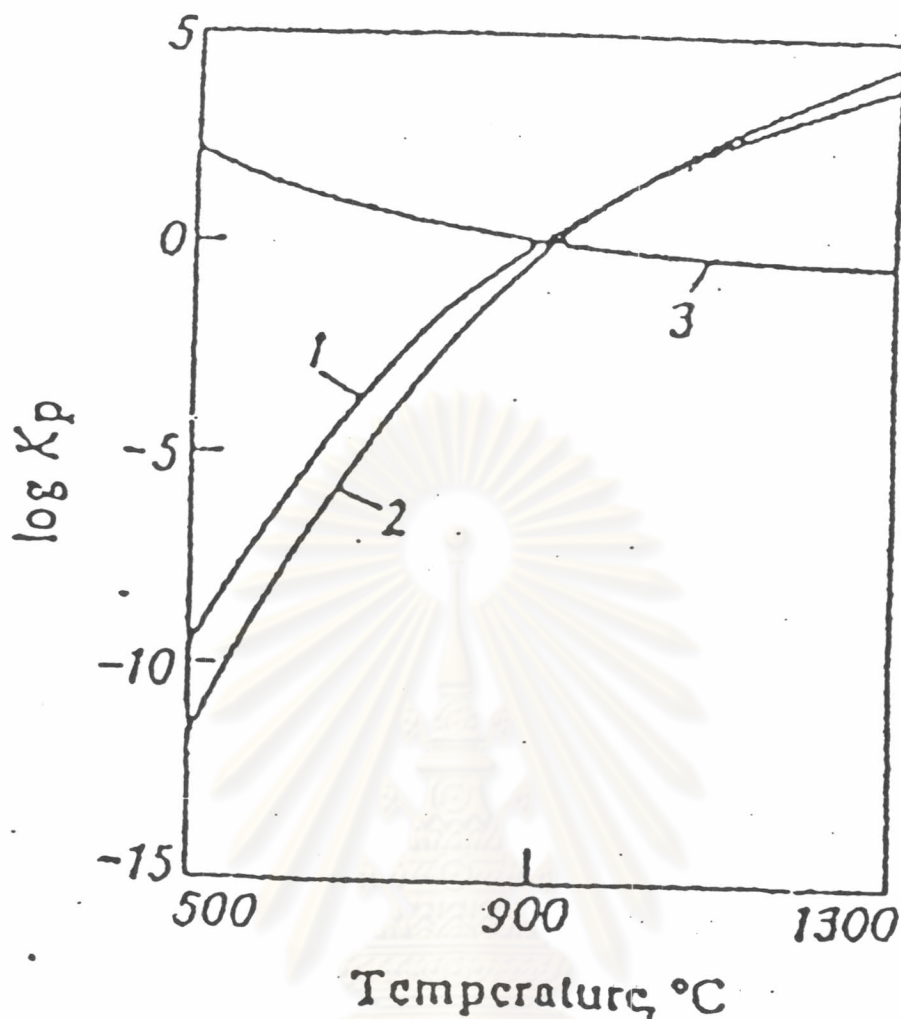
Figure 2.6. Temperature dependence of the equilibrium constants of the conversion reactions [14]:

1. $CH_4 + H_2O \rightleftharpoons CO + 3H_2$
2. $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$
3. $CO + H_2O \rightleftharpoons CO_2 + H_2$
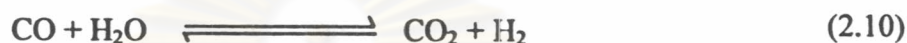
2.2.2.1. Steam Reforming Reaction

Steam reforming is a reaction using steam to react catalytically with natural gas, primarily methane, or with hydrocarbon feedstock such as naphtha to form a mixture of hydrogen and carbon monoxide, which is called synthesis gas (or syngas) [23].

Steam reforming is a mature technology, practiced industrially on large scale for hydrogen production and several reviews of the technology have been published [24-26]. The production of hydrogen and synthesis gas by steam reforming is summarized in Figure 2.7. This process has two main reactions as follows:

1. Reforming reaction

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{2.9}$$
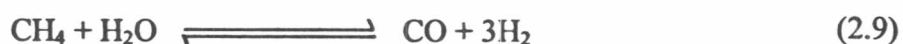
2. Water-gas shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2.10}$$

The reforming reaction is normally carried out over a supported nickel catalyst at elevated temperatures, typically above 500 °C. The heavy hydrocarbons also react with steam in a similar reaction as follows:

$$C_nH_m + nH_2O + heat \rightleftharpoons nCO + (n+m/2)H_2 \tag{2.11}$$

Reactions (2.9) and (2.10) are reversible and normally at equilibrium as the reaction rates are very fast. The composition of the product gas from a conventional reformer reactor is therefore governed by thermodynamics. Steam is normally added in excess of stoichiometric requirement of reaction (2.9) so that equilibrium of reaction (2.10) moves toward more CO_2 produced rather than CO consumed. Steam may be replaced completely or partly by CO_2 as the following reaction:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{2.12}$$

Furthermore, methane may also be converted to a hydrogen rich gas by means of oxygen through partial oxidation as the following reaction:

$$CH_4 + 3/2O_2 \rightleftharpoons CO + 2H_2O \tag{2.13}$$
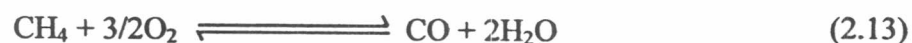
Several metals have been found to catalyze reactions (2.9) to (2.13), but nickel is generally preferred on the cost grounds. In commercial steam reforming catalysts, nickel is supported on a ceramic oxide. The choice of support is governed by the

surface area required, as well as the need for ability in the environmental operation. Various modifications of alumina are frequently used. Corundum or α-alumina is an ideal support for high temperature steam reforming application where a high specific activity is not required because it is the most stable form of alumina. The steam reforming catalysts can be prepared from precipitation method and impregnation method. For the precipitation method, the nickel and alumina are co-precipitated as hydroxy carbonates by addition of alkali to an aqueous solution of their salts. The precipitate is subsequently separated by filtration, washed, dried and then calcined to decompose the precursor to nickel oxide and alumina. Unfortunately this method of preparation leads to the formation of γ-alumina which is thermodynamically less stable than the α-alumina form. Under high pressure of steam at elevated temperatures, such as are present under steam reforming conditions, the γ-alumina converts to α-alumina over period of time. This process is called hydrothermal sintering. It results in a substantial change in the microstructure of the catalyst and leads to degradation of the catalyst activity. For the impregnation method, the nickel can be incorporated by impregnating a performed catalyst support with a solution of a nickel salt, which is subsequently decomposed by heating to the oxide. Impregnated catalysts are widely used because they are generally stronger than precipitated catalysts. Many methods of producing stable supports have been devised over the past 30 years and commercial catalysts frequently contain mixtures of alumina, magnesia, zirconia, and other ceramic oxides. The physical form of steam reforming catalysts has also evolved over the years to maximize the activity and rate of heat transfer within the reformer reactor. The catalyst pellet size is a compromise between ensuring good packing, mechanical stability and low-pressure drop. The pressure drop is in turn governed by the vessel size and mass velocity for which the reactor is designed.
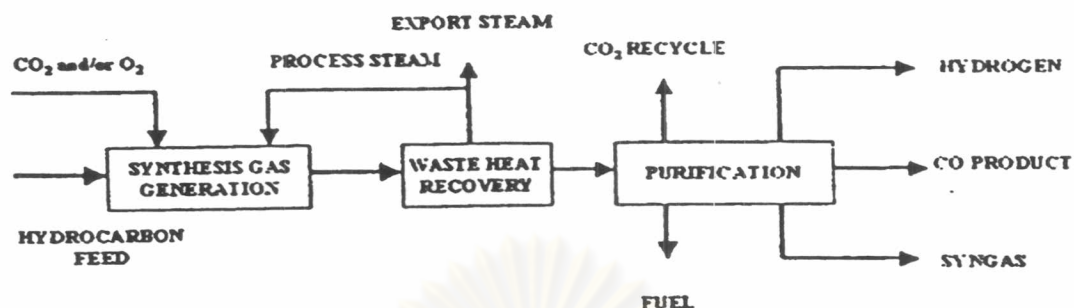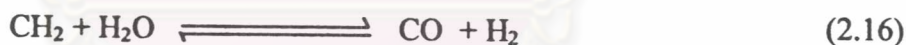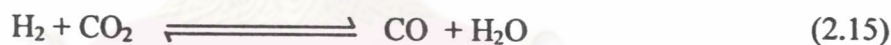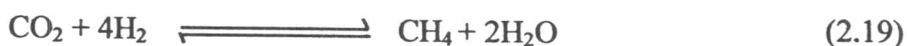
SYNGAS/CO PRODUCTION

Figure 2.7. The diagram of hydrogen and syngas production [25].

2.2.2.2. Carbon Dioxide Reforming Reaction

Sigov, S.A. and Abdullaeva, U.A. [27] studied the reaction mechanism of methane reforming with carbon dioxide by using nickel catalyst at 700-800 °C. They found that the reactions were as follows:

$$CH_4 \rightleftharpoons CH_2 + H_2 \qquad (2.14)$$

$$H_2 + CO_2 \rightleftharpoons CO + H_2O \qquad (2.15)$$

$$CH_2 + H_2O \rightleftharpoons CO + H_2 \qquad (2.16)$$

Kunugita et al. [28] studied the methane reforming with carbon dioxide. They found that little water was generated in reaction and also took place little coke at high temperature and carbon dioxide-methane ratio, which was negligible. Besides, at low temperature occurred little methane. Then, the residual gas composition was CO_2, CH_4, CO, H_2 and H_2O only. The reactions of this study were as follows:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad (2.17)$$

$$H_2 + CO_2 \rightleftharpoons CO + H_2O \qquad (2.18)$$

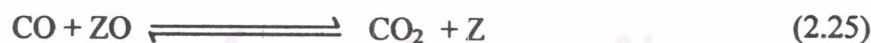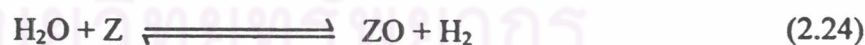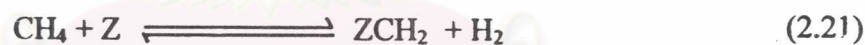$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad (2.19)$$

From the experiment at higher than 650 °C, the reaction (2.19) was negligible. Thus, only reactions (2.17) and (2.18) could take place in this study.

Satayaprasert, C. [29] studied the methane reforming with carbon dioxide on nickel/alumina catalyst at 600-850 °C. The reaction of this study was as follows:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{2.20}$$

2.2.3. Reaction Mechanism of Methane Steam Reforming

For the reaction of methane reforming with steam, methane is cracked to form CH_2 on the surface of catalyst. Thereafter CH_2 and steam are interacted to form carbon monoxide on the surface of catalyst and then desorbed from surface of catalyst. Besides, partial steam is cracked to form oxygen atom on the catalyst surface and thence oxygen atom is reacted with carbon monoxide to form carbon dioxide [30]. These reactions are as follows:

$$CH_4 + Z \rightleftharpoons ZCH_2 + H_2 \tag{2.21}$$

$$ZCH_2 + H_2O \rightleftharpoons ZCO + 2H_2 \tag{2.22}$$

$$ZCO \rightleftharpoons Z + CO \tag{2.23}$$

$$H_2O + Z \rightleftharpoons ZO + H_2 \tag{2.24}$$

$$CO + ZO \rightleftharpoons CO_2 + Z \tag{2.25}$$

Notes:

Z = Active sites of catalyst, which can adsorb reactants.

ZCH_2 = Active site of catalyst, which can adsorb CH_2.

ZCO = Active site of catalyst, which can adsorb CO.

ZO = Active site of catalyst, which can adsorb oxygen atom.

In addition, Ross, J.R.H. and Steel, M.C.F. [31] studied the reaction mechanism of methane steam reforming over nickel/alumina catalyst at 500-680 °C. They could describe the reaction mechanism that methane was cracked to form CH_3 and H and thereupon CH_3 was continuously cracked to form CH_2, CH or C on the catalyst surface. Thereafter these free radicals and OH group, which was taken place from cracking of steam, were interacted to form oxygenated species and then cracked as carbon monoxide, which illustrated in Figure 2.8.
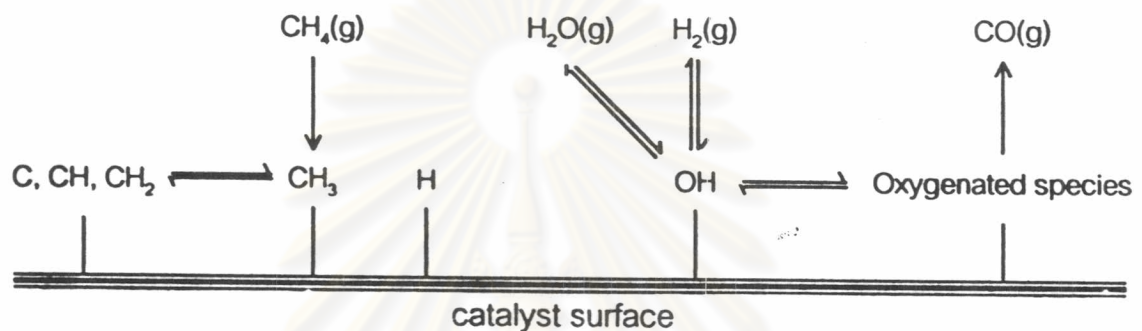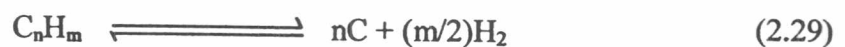

Figure 2.8. The reaction mechanism of methane steam reforming [31].

### 2.2.4. Formation of Carbon Deposition

Formation of carbon or coke is a major problem in the operation of an industrial steam reformer, not only because of catalyst deactivation, but also because of the severe consequences of maldistribution of heat and the damage. Failure of tube metal due to overheat caused by formation of hot spots, hot band or hot tubes.

The high temperatures associated with steam reforming to produce hydrogen also favor the formation of carbon. Four reactions may be involved [32]:

$$2CO \rightleftharpoons CO_2 + C \qquad (2.26)$$

$$CO + H_2 \rightleftharpoons C + H_2O \qquad (2.27)$$

$$CH_4 \rightleftharpoons C + 2H_2 \qquad (2.28)$$

$$C_nH_m \rightleftharpoons nC + (m/2)H_2 \qquad (2.29)$$

For a given steam to carbon ratio, it is possible to predict thermodynamics of carbon deposition via reaction (2.26) from equilibrium gas mixtures containing carbon oxides, hydrogen, steam and methane. However, it has been well established that the minimum steam to carbon ratio for carbon formation over nickel catalysts via reaction (2.26) is lower than predicted from the thermodynamic data for graphite formation. It has been fairly well established that the key reactions occur over a surface layer of nickel atoms. If a layer is allowed to build up, a filament or whisker of carbon, because of the low steam partial pressure can start to grow and attach to a nickel crystallite. Carbon filaments can generate massive force within catalyst pellets and once started can lead to rapid catalyst break down, and the blocking of reactor tubes. Carbon may also be formed by thermal cracking of hydrocarbons in the absence of air. Reactions (2.28) and (2.29) tend to lead to a surface, pyrolitic carbon, which in a catalyst can encapsulate the nickel particles, again causing deactivation. Reaction (2.28) and (2.29) have the greatest risk of occurring at the inlet to a reformer, where there is almost no hydrogen present. At this point the likelihood of carbon deposition is governed not so much by equilibrium considerations as by the relative kinetics of carbon formation reaction and the carbon removal reaction. Higher hydrocarbons have a greater propensity for carbon deposition than methane. Thermal or steam cracking of hydrocarbons can occur above 600-650 °C even in the absence of nickel catalysts. The cracking leads to olefins and then to a carbonaceous polymer, which can dehydrogenate to produce coke. There are two explanations for the carbon-induced reaction of the activity of nickel catalysts. The first is encapsulations of nickel crystallites by the layers of inactive carbonaceous material, and the second is the formation of inactive as bulk nickel carbide phases. As a result, it leads to the catalyst deactivation due to coke formation as illustrated in Figure 2.9 [33]. The active metal is blocked and the pores in a support are plugged. For the solution of this problem, there are several ways to solve the coke formation, which is the one of main problems in steam reforming catalysts. Type of catalyst is the one of solution. This study selected the nickel magnesia solid solution catalyst for methane steam reforming because it could inhibit carbon deposition and also obtain the highest yield, which showed its high activity and stability.
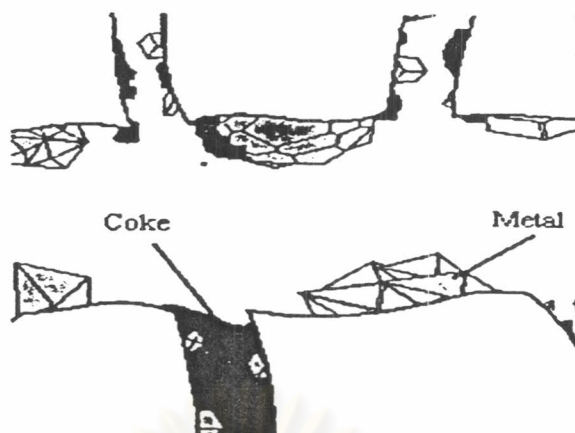
Figure 2.9. The deactivation by coke formation in a supported metal catalyst [33].

2.3. Chemical Reaction Rate [34-37]

For the kinetics of reaction, the aim of this study is to observe rate of reaction that it is fast or slow. The result leads to the prediction of reaction mechanism. Thus, the reaction involving this study can be classified into two categories:

1. Homogeneous reaction is the reaction that all substances are in the same phase such as gas-gas or solution-solution.

2. Heterogeneous reaction is the reaction that each substance is in the different phase such as gas-solution or solution-solid.

2.3.1. Rate Law

$$A + B \longrightarrow C \qquad (2.30)$$

From the reaction (2.30), A and B are interacted to form C. During the reaction, concentration of A and B are continuously decreased but concentration of C is continuously increased. Plot concentration of reactant and product versus time is illustrated in Figure 2.10 by giving a_o as initial concentration of reactant.
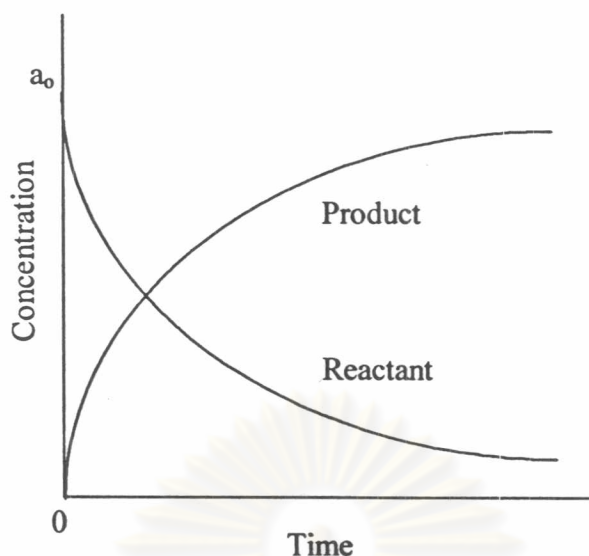
Figure 2.10. Concentration of reactant and product at several times.

The rate of reaction is mainly given in term of concentration of reactant or product at anytime. In case of giving rate of reaction between A and B in term of changing concentration of product, C in a unit of time can be written as follows:

$$\text{Rate of reaction} = \frac{\text{Change of concentration of C}}{\text{Change of time}}$$

$$= d[C]/dt \qquad (2.31)$$

Or in term of changing concentration of reactants, A and B

$$\text{Rate of reaction} = -d[A]/dt = -d[B]/dt \qquad (2.32)$$

The rate of reaction at anytime can be also given in term of slope of graph at anytime in Figure 2.10. In addition, the rate of reaction still means the net rate, which is both forward and backward rate of reaction. Whenever the forward rate of reaction is equal to the backward rate of reaction so the net rate will be equal to zero, which means the reaction to be at equilibrium. From in Figure 2.10, initial rate of reaction is high and continuously reduced as the rate of reaction depend on initial concentration of reactant can be written as follows:

$$\text{Rate of reaction} \ \alpha \ [A] \ [B] \qquad (2.33)$$

From the equation (2.31), (2.32) and (2.33), they can be arranged as follows:

$$\text{Rate of reaction} = -d[A]/dt = -d[B]/dt = d[C]/dt \; \alpha \; [A] \; [B]$$

Thus,
$$-d[A]/dt = k \; [A] \; [B] \tag{2.34}$$

Equation (2.34) can be called rate law or rate equation by giving k as specific reaction rate constant.
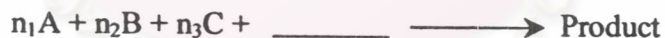
2.3.2. Order of Reaction

From reaction (2.30), it is found that rate of reaction is dependent on concentration of reactant A and B with equation (2.34), order of reaction being 2, which is classified as the same reactant or different reactant the following reaction:

$$2A \longrightarrow \text{Product}$$

and
$$A + B \longrightarrow \text{Product}$$

Thus,
$$\text{Rate of reaction} = -d[A]/dt = k \; [A]^2$$

Or
$$= k \; [A] \; [B]$$

The reaction in general can be written as follows:

$$n_1 A + n_2 B + n_3 C + \underline{\hspace{1.5cm}} \longrightarrow \text{Product}$$

Thus,
$$\text{Rate of reaction} = -d[A]/dt = k \; [A]^a \; [B]^b \; [C]^c \underline{\hspace{1cm}} \tag{2.35}$$
$$\text{Order of reaction} = a + b + c + \underline{\hspace{1cm}}$$

In summary, order of reaction is defined to the sum of the power in term of concentration of rate equation and must be result from the experiment only.

2.3.3. Rate Constant

Rate constant can be widely used as a measure for rate of reaction at various temperatures as it is only a constant for specific reaction and temperature, which means the rate constant is only dependent on reaction and temperature. In addition,

unit of rate constant still also depends on order of reaction. For example, the reaction giving order of reaction being 1 can be written as follows:

$$-d[A]/dt = k [A] \tag{2.36}$$

Or concentration / time = k (concentration)

Thus, Unit of k = $(time)^{-1}$

If unit of rate constant is equal to $(time)^{-1}$, the order of reaction will be 1.
For the reaction giving order of reaction being n:

$$-d[A]/dt = k [A]^n \tag{2.37}$$

Unit of k = $(concentration)^{n-1} (time)^{-1}$

2.3.4. The Measurement of Reaction Rate by Differential Method

This method was studied by Van't Hoff that it was the measurement of concentration at several times and then plotted graph as in Figure 2.10 and thereafter calculated rate of reaction at several times from slope of graph. For example, the reaction is as follows:

$$A \longrightarrow B$$

Rate of reaction can be written in the relationship of concentration of reactant as in equation (2.34), which is differential form, called differential rate equation or differential rate law as follows:

$$-d[A]/dt = r = k C_a^n \tag{2.38}$$

Where r = rate of reaction

k = rate constant
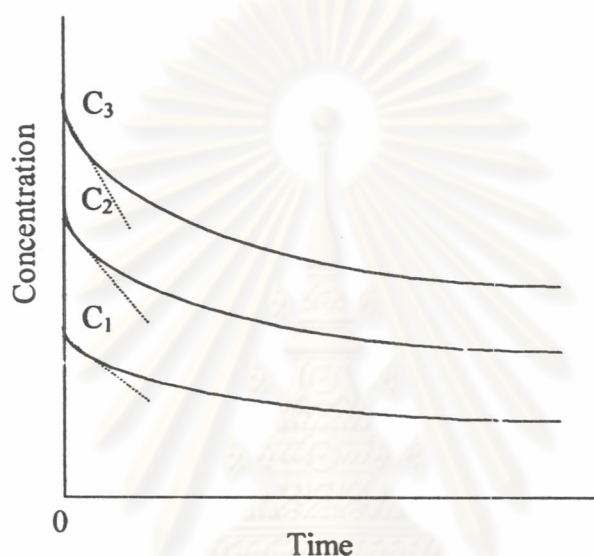
C_a = concentration of reactant

And n = order of reaction

Take "log" into equation (2.38):

$$\log r = \log k + n \log C_a \tag{2.39}$$

Concentrations of reactant are assumed as C_1, C_2 and C_3, respectively and then plotted graph to calculate rate of reaction at time of zero, which is called initial rate of reaction, from slope of graph as illustrated in Figure 2.11.

Figure 2.11. Concentration of reactant versus time at several concentrations.

From Figure 2.11, it is found that initial rate of reaction is varied with concentration of reactant, which can be observed from slope of graph that slope at C_3 is more than at C_2 and C_1, respectively since C_3 is higher than C_2 and C_1, respectively. As a result, initial rate of reaction at C_3 is the highest but at C_1 is the lowest. In Figure 2.12, plotting between $\log r$ and $\log C_a$ from equation (2.39) by using 3 values of C_a, which are C_1, C_2 and C_3, and then giving graph as linear line where intercept being $\log k$ and slope being n to determine rate constant and order of reaction, respectively. This method can be called the initial rate method.
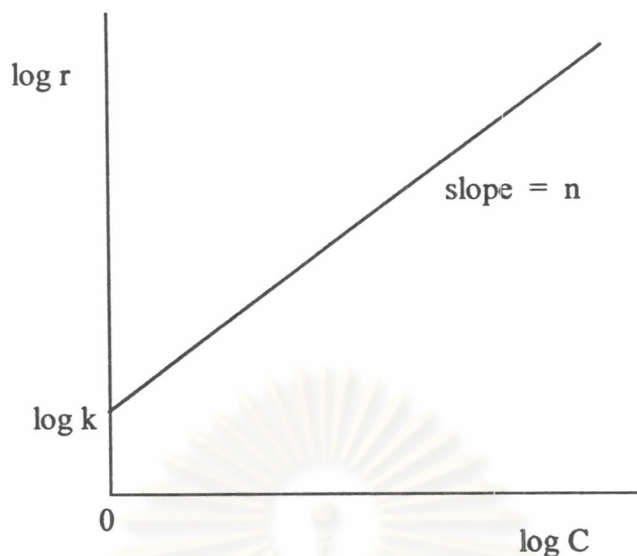
Figure 2.12. Plot between log C and log r.

2.3.5. The Effect of Factors on Rate of Reaction

1. Concentration is the concentration of reactant or partial pressure in case of gas, which largely effects on rate of reaction, and if concentration or partial pressure is high, rate of reaction will be occurred rapidly.

2. Temperature, high temperature will affect on rate of reaction than at low temperature and rate of reaction will be generally increased being two times if elevated temperature of $10\ ^\circ C$.

3. Catalyst or inhibitor can be properly selected to employ with rate of reaction, for example, catalyst can be used if rate of reaction is occurred slowly but if it is too rapid, inhibitor will be selected.

4. Nature of reactant can also effect on rate of reaction, for example, iron is slowly reacted with oxygen but white phosphorus can be ignited in air immediately.

5. Nature of solvent can also effect on rate of reaction in case of reaction in solution, such as viscosity, induction and so on.

6. Particle size in heterogeneous reaction can also effect on rate of reaction because the reaction occurs only at surface of particle therefore, rate of reaction will depend on surface area, for example, small particle size enables rate of reaction to occur rapidly by increasing of surface area.

2.4. Catalyst [38-40]

Catalyst is added to speed up the reaction. The physical and chemical structures of catalyst were not affected after termination of reaction. In summary, the utilization of catalyst can be given as follows:

1. Enhancement of reaction rate
2. Acquirement of desired product from direct reaction
3. Elimination of undesirable side reaction
4. Initiation of novel reaction

2.4.1. Classification of Catalysts

The catalysts can be classified into two categories as follows:

1. Homogeneous catalyst is the catalyst that it can be in the same phase as reactant and product, which is generally in liquid state.

2. Heterogeneous catalyst is the catalyst that it can be in the different phase from reactant and product, which is mainly in solid state but reactant and product are mainly in gaseous or liquid state.

Heterogeneous catalysts can be mainly used in several industries due to their thermal, chemical and mechanical stability. Furthermore, their maintenance and application are easier than homogeneous catalysts since no solvent is used and they can be easily separated from product to reduce cost.

2.4.2. Heterogeneous Catalysis

Learning of heterogeneous catalyst involves in surface chemistry because surface reaction is mainly effect on rate of reaction, for example, if surface of catalyst is increase so rate of reaction will be increasing too. Then, the heterogeneous catalytic reaction is interested to study the effect of structure of catalyst on mechanism of reaction.

2.4.2.1. The Mechanism of Heterogeneous Catalytic Reaction

The reaction using heterogeneous catalyst is mainly occurred on surface of catalyst. Owing to surface of catalyst effects on rate of reaction so if increasing surface area is required, the surface area per volume of catalyst should be high by making as foil or coat on support at high porosity. The coated catalyst on support at high porosity, which is generally called supporter. The mechanism of heterogeneous catalytic reaction consists of seven steps as follows:

1. External mass transfer from bulk to catalyst external surface
2. Diffusion into pores
3. Adsorption
4. Surface reaction
5. Desorption
6. Diffusion out of pores
7. Mass transfer from external surface to bulk fluid phase

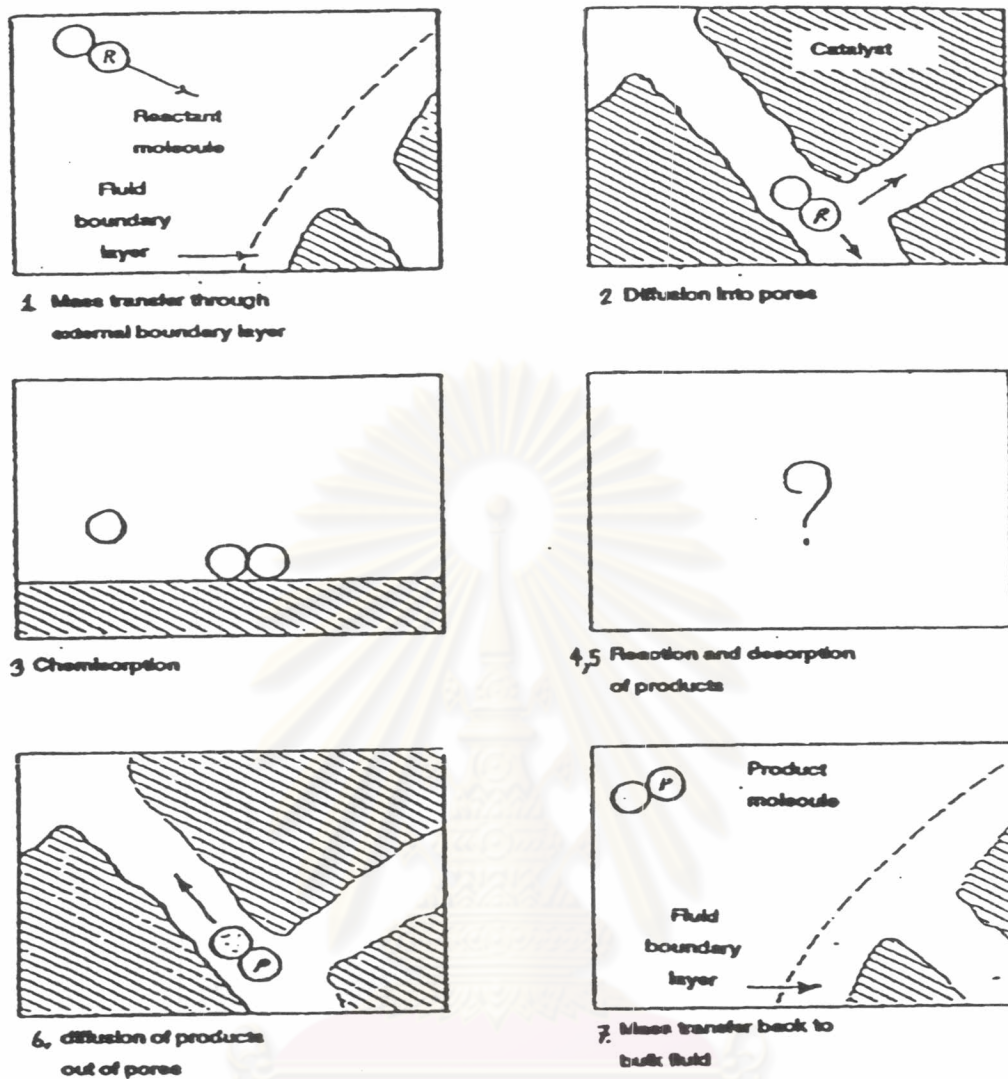All steps of reaction mechanism are illustrated in Figure 2.13.

Figure 2.13. Steps of heterogeneous catalytic reaction mechanism [38].

2.4.2.2. Supported Metal Catalyst

Factors influencing on catalyst activity are surface area, porosity, geometric surface feature and resistibility of catalyst deactivation. These factors also effect on selection of catalyst to use in reaction. For example, although metal catalyst shows excellent performance in some reactions, it is not worthwhile to invest so the supporter will be considered. The advantages of supported metal catalyst are as follows:

1. Catalyst can be easily prepared and is safe.
2. Catalyst can be used with several reactors and recycled to use again by filtration if medium in reactor is liquid.
3. Metal particle can be easily separated with sintering filtration.

In addition, other advantages are dependent on specific properties of catalyst, such as nature of metal and type of supporter. The properties of supporter are as follows:

a) Economical aspect
  1. Reduction of capital cost of catalyst, which is expensive.
b) Mechanical aspect
  1. The increase of mechanical strength.
  2. Optimization of bulk density.
  3. Use as thermal source.
  4. Reduction of excess catalyst activity.
c) Geometrical aspect
  1. The increase of catalyst surface area.
  2. The increase of catalyst porosity.
  3. Optimize size of particle and crystallite.
  4. Optimize properly catalyst status in reaction.
d) Chemical aspect
  1. Interaction of catalyst with supporter increases specific activity of reaction and decreases sintering process.
  2. Admission of chemical possibility in reaction mechanism.
e) Deactivation aspect
  1. Thermal stability of catalyst to inhibit sintering process.
  2. Reduction of poison.

However, supporter can be used with its properties, which depends on type of supporter. Types of supporter using widely in several industries consist of alumina, silica and activated carbon. Moreover, the most significance of supporter is sintering resistibility.

2.5. Literature Reviews

Hawk et al. [41] studied reforming of methane with steam in tubular reactor and passed hot air to heat. It was found that optimum condition for the best methane conversion with fewer side reactions at temperature range between 900 and 1200 °C.

Akers and Camp [42] studied kinetics of the methane steam reforming on nickel catalyst at 337 to 637 °C. They found that reaction rate of methane was expressed in first order of partial pressure of methane and temperature effected on reaction with Arrhenius equation.

Rostrup-Nielsen [43] studied the influence of structure of catalyst surface on ethane steam reforming by using supported nickel catalyst that supporters were different. It was found that reaction would be occurred slowly if using zirconia or carbon as supporter due to low activity of nickel. But, if alumina-silica or titanium was used as supporter, reaction would be occurred rapidly because of high activity of nickel.

Murray and Synder [44] studied kinetics of the methane reforming with steam. They found that rate equation of reaction was expressed in order of 1 for methane and proposed mathematical model from software in computer to compare with the experimental data, which gave the best results.

Yamazaki et al. [45] studied steam reforming of methane in a steam to carbon ratio of 1.0 on nickel magnesia solid solution catalyst, which was reduced with hydrogen at high temperature (> 1073 K). This reduced catalyst showed higher activity and more excellent stability than a commercial reforming catalyst (Ni/Al_2O_3-MgO). The catalyst kept its activity for 60 h or more at 1123 K, 0.1 MPa and a steam to carbon ratio of 1.0 by giving little coke on the catalyst (< 1 wt. %). Whereas, the commercial steam reforming catalyst lost its activity at 20 h because of severe coking under the same reaction conditions. However, the rate equation was quite similar for both catalysts.

Besenbacher et al. [46] studied reforming of butane with steam by using supported alloy catalyst, which was mixed metal between nickel and gold with high surface area and using magnesium aluminate as supporter. The gold effected on surface chemical properties of nickel, and as a result, supported alloy catalyst could inhibit more coking on the catalyst than nickel catalyst and also giving higher butane conversion.

Tomishige et al. [47] studied reforming of methane with carbon dioxide and steam reforming on nickel magnesia solid solution catalyst with low nickel content under low steam to methane ratio at 1123 K and 0.1 MPa. This catalyst had shown excellent methane conversion, high stability and no carbon deposition on the catalyst. Moreover, it was found that small nickel particles formed on this catalyst had high ability for inhibiting carbon deposition.

Trimm [48] studied the control of coking during steam reforming of light hydrocarbons, which had various methods. The metals such as Sn, Pb, As, Sb, Bi and Ag could interact with Ni to prevent nickel carbide formation, an essential intermediate for coke formation, on the catalyst surface, and especially, small amounts of Sn could reduce coking very significantly. Furthermore, using rare earth oxides as supporters could also reduce coking. The another possibility for coke minimisation was acceleration of coke gasification.

Roh et al. [49] studied methane reforming reactions, such as oxy-reforming, steam reforming and oxy-steam reforming, over stable $Ni/\theta-Al_2O_3$ catalysts. The catalysts with various Ni loading up to 12 wt. % were found to show not only the highest catalytic activity and selectivity but also remarkable stability due to a good balance between stable complex NiO_x species, which occurred from strong interaction between Ni and $\theta-Al_2O_3$, and free NiO. If below 3 wt. % Ni loading, the catalysts would be transformed into inactive $NiAl_2O_4$ during reforming reactions. Metallic Ni sites formed from the reduction of both free NiO weakly interacting with the support and complex NiO_x species strongly interacting with the support were active sites for methane reforming reactions. Even though free NiO species were prerequisite for high activity, the increase of NiO population in high Ni loading favorably promoted Ni

sintering resulting in low catalytic performance. In addition, oxy-steam reforming reaction could be considered as alternative reforming reaction due to the enhanced methane conversion, safe operating condition and high energy-efficiency.

Hou and Hughes [50] studied the kinetics of methane steam reforming over a Ni/α-Al$_2$O$_3$ catalyst in an integral reactor under conditions of no diffusion limitation. Temperature and ratio of steam to methane had a large effect on the product distribution and no noticeable effect of pressure on it. The experimental results indicated that high ratio of steam to methane and low temperature were favorable to the production of hydrogen and synthesis gas that both carbon monoxide and carbon dioxide formed as primary products. The rate of carbon dioxide formation was much faster than that of carbon monoxide at low temperature whereas the rate of methane conversion was proportional to the contact time and the partial pressure of methane at low product concentrations. The effect of total pressure on initial reaction rates indicated that the rate controlling steps of steam reforming were surface reactions of adsorbed species.

Thaneerat [51] studied the kinetics of methane reforming with steam and carbon dioxide on nickel/alumina catalyst in fixed bed reactor. The experimental results demonstrated that rate of methane reforming reaction was expressed in order of 1.119 for methane, 0.385 for steam and -1.311 for carbon dioxide. The rate equation was as follows:

$$-r_{CH4} = k \, [CH_4]^{1.119} \, [H_2O]^{0.385} \, [CO_2]^{-1.311}$$

Where $\qquad$ k = 55.23 EXP (-15,149/RT) $\quad$ mole$^{0.807}$ (m^3)$^{0.193}$ kg^{-1} s^{-1}