Hydrogen Production from CO_2 Reforming of Methane over Cobalt-based Catalysts

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ABSTRACT

Increased concerns on anthropogenic greenhouse gas emissions have renewed interest in the CO_2 (dry) reforming process as an alternative to steam reforming for synthesis gas production from natural gas. For hydrocarbon dry reforming, where the product stream H_2:CO ratio is less than 3, synfuel production is more amenable and acceptable for downstream methanol and other oxygenated synthesis. However, dry reforming is highly endothermic, and suffers from carbon-induced catalyst deactivation. This thesis therefore investigates and evaluates the performance of methane dry reforming process at different operation conditions such as reaction temperature and feed composition, and the effects of loaded metals (Mo and Ni) on alumina-supported Co-based catalyst. Runs of the methane dry reforming experiment were conducted in a computer-controlled fixe-bed reactor at different feed compositions and reaction temperature. Both MoO_3 and NiO phases were formed during wetness co-impregnation with a mixture of deionized water and alumina support as measured in X-ray diffraction. Temperature-programmed calcination showed that the transformations from MoO_3 to $CoMoO_4$ phase and NiO to $NiAl_2O_4$ phase were a 2 step process involving the formation of an oxidation intermediate form. Calcination of co-impregnated catalysts at 500 ^{0}C for 5 h appeared to be optimal preparation condition for H_2 selectivity. Al_2O_3 support was the best support to give the highest H_2 to CO ratio. Second metal promotion did not alter reaction rate significantly. However the interaction of loaded metal oxides with the surface carbonaceous species resulted in substantially reduced carbon deposition on Co-based catalyst, with Ni providing the greatest coking resistance compared to Mo. A quantitative relationship between activation energy and feed composition of CO_2:CH_4 (1:1, 2:1 and 3:1) as well as reaction temperatures (923 K, 953 K and 973 K) was obtained over bimetallic 5%Ni-10%Co/Al_2O_3 catalyst which gave the highest value of H_2/CO ratio in the methane dry reforming process. Methane dry reforming activity was stable with time-on-stream for 4 h.

ABSTRAK

Peningkatan tentang kebimbangan ke atas pengeluaran gas rumah hijau antropogenik telah menarik semula minat dalam proses pembaharuan (kering) CO_2 sebagai alternatif kepada pembaharuan stim untuk pelahiran sintesis gas daripada gas asli. Bagi pembaharuan kering hidrokarbon, di mana nisbah aliran produk H_2:CO adalah kurang daripada 3, pengeluaran synfuel adalah lebih sesuai dan diterima untuk hiliran metanol dan sintesis oksigen lain. Walau bagaimanapun, pembaharuan kering adalah proses yang sangat endotermik, dan mengalami karbon yang disebabkan penyahaktifan mangkin. Tesis ini oleh itu akan menyiasat dan menilai prestasi proses pembentukan semula metana kering pada keadaan operasi yang berbeza seperti suhu tindak balas dan komposisi makanan, dan kesan-kesan logam dimuatkan (Mo dan Ni) pada pemangkin alumina yang berasaskan Co. Eksperimen pembaharuan metana kering dijakankan di sebuah reaktor yg dikawal oleh komputer dalam kalangan komposisi bekalan yang berbeza dan suhu yang berlain-lainan. Kedua-dua fasa MoO_3 dan NIO telah dibentuk semasa kelembapan bersama dengan campuran air ternyahion dan alumina seperti bentuk yang diukur dalam pembelauan sinar-X. Pengkalsinan yang berasaskan suhu yang diprogram menunjukkan bahawa perubahan daripada fasa MoO_3 kepada $CoMoO_4$ dan fasa Nio kepada $NiAl_2O_4$ adalah satu proses yang melibatkan 2 langkah pembentukan bentuk perantaraan pengoksidaan. Pengkalsinan pemangkin yang bersama-impregnated dijalankan dehgn suhu yang sebanyak 500 ^{0}C selama 5 jam boleh dikira sebagai keadaan yang optimum bagi penyediaan dalam pemilihan H_2. Al_2O_3 adalah bahan yang terbaik untuk memberikan nisbah H_2 kepada CO yang tertinggi. Promosi logam kedua tidak mengubah kadar tindak balas dengan ketara. Walaubagaimanapun interaksi oksida logam dimuatkan dengan permukaan spesies karbon menyebabkan berlakunya kekurangan pemendapan karbon pada pemangkin berasaskan-Co, dengan Ni membekal rintangan coking yang paling besar berbanding dengan Mo. Hubungan kuantitatif antara tenaga pengaktifan dan komposisi bekalan CO_2: CH_4 (1:1, 2:1 dan 3:1) dan juga suhu yang berlainan (923 K, 953 K and 973 K) telah diperolehi dengan penggunaan pemangkin dwilogam 5%Ni-10%Co / Al_2O_3 yang memberikan nilai yang paling tinggi dalam nisbah H_2/CO bagi proses pembaharuan metana kering. Aktiviti pembaharuan metana kering mencapai kestabilan dengan masa-ke-aliran sebanyak 4 jam.

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LIST OF ABBREVIATIONS

Notation	**Explanation**
a_m	cross-sectional area of adsorbate molecule
A_{sat}	quantity of gas adsorbed at saturation
APS	active particle size
Bi_w	wall Biot number
C_{Ab}	bulk gas-phase concentration of component A
C_{As}	concentration of component A on catalyst surface
C_{pg}	specific heat capacity of gas mixture
d_p	catalyst particle diameter
D_{eff}	effective diffusivity
D_i	density of metal i
E_a	activation energy
F_i	sample weight fraction of metal i
h	heat transfer coefficient
$-\Delta H_{ads,i}$	heat of adsorption for species i
$-\Delta H_d$	heat of desorption
$-\Delta H_{rxn}$	heat of reaction
k_c	mass transfer coefficient
k_d	deactivation coefficient
k_{rxn}	reaction rate constant
K_i	adsorption constant of species i
m_0	initial mass
m_f	final mass
M_a	molecular weight of adsorbate
MW	molecular weight
n^a	amount of gas adsorbed
n_m	monolayer capacity of adsorbate
N_A	Avogadro's number (6.023×10^{23} molecules/mol)
P	system pressure
P_0	saturation pressure of absorbate gas at temperature T
P_i	partial pressure of species i

PD	percent dispersion
Pr	Prandtl number
r_i	rate of reaction for species i
r_k	Kelvin radius
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
$\Delta S_{ads,i}$	change in entropy for adsorption of species i
S_A	surface area of the sample
S_m	metallic surface area
SA_i	specific area of metal i
Sc	Schmidt number
SF_{i}	stoichiometric factor of metal i
t_{ads}	thickness of adsorbed layer
T	temperature
T_b	bulk gas phase temperature
T_s	catalyst surface temperature
T_w	tube wall temperature
T_p	peak temperature
U	superficial gas velocity
v_m	volume of gas adsorbed for monolayer coverage
V_{ads}	volume of gas adsorbed
V_{inj}	volume per injection
V_{liq}	volume of liquid in pores
V_m	molar volume
V_{na}	volume not adsorbed
V_S	volume chemisorbed

Greek	*Explanation*
α	solid state conversion
β	temperature ramping rate
ε	bed voidage
γ_s	surface tension of adsorbate at its boiling point
λ	wavelength
λ_p	thermal conductivity of catalyst particle
θ	diffraction angle
ρ_b	bulk density of catalyst
ρ_g	density of gas

1 INTRODUCTION

1.1 *Motivation and statement of problem*

From the twentieth century till today, world's energy consumption always is a title which attracts attention from population over this world. Undeniably, world population growth and the new out-coming countries' natural desire to achieve a higher level of economic and quality of life are some of the main causes of the restless growth in energy demand and in the concurrent increase in pollution (especially for CO_2). Therefore, finding more secure, clean and sustainable energy sources would be a most prioritize task and successful strategy to reduce the greenhouse gas emissions and meet the world's energy need at the same time. Compared to other alternatives, hydrogen has a large number of advantages.

Hydrogen can be considered as one of the most potential energy in future since it is green, efficient and environmentally-friendly. Therefore, much more attention has been started paid to hydrogen production technology in order to ensure the future energy is stable and sustainable (Fan & Abdullah *et al*., 2011). In their review paper, J. Gao and Z. Hou (2009) stated that hydrogen can be produced via methane by technologies such as steam methane reforming, methane dry reforming and methane partial oxidation. In addition, methane oxidative CO_2 reforming (Oxy-CO_2 reforming) was proposed in recent years as an energy efficient manner to utilize methane resources. However, in our study, methane dry reforming is the only chosen method to be studied for the hydrogen production based on its high H_2/CH_4 molar ratio where the CH_4 can be easily found in Malaysia, less coke formation and low energy consumption. The latter approach can be regarded very useful at remote natural gas fields where containing large amount of CO_2. Compared to reforming with H_2O, utilization of CO_2 is much more attractive because it can be employed in areas where water is not available.

Since the rise of hydrogen production techniques, the research and development of the synthesized catalysts have been paid much more attention today, especially in the performance and characterization. Therefore, a number of different types of catalysts have been proposed for the production of hydrogen. Awadallah, Aboul-Enein & Aboul-Gheit *et al*. (2014) reported that catalytic activities are mostly dependent on their origins, structures and surface areas and found that the disordered forms of carbon are more catalytically active than the ordered ones after studied methane decomposition over 30 different forms of carbon catalysts.

Ni-based catalysts are generally used toward hydrogen production owing to their high reaction activity. However, the Ni-based catalysts are very sensitive to H_2S as it could cause a serious poisoning of the catalysts (Baowei & Yuqin *et al.*, 2014). JL Oliphant & RW Fowler (1978) illustrated that Ni-based catalysts are limited to less than 0.1 ppm of H_2S content for an ideal performance which is very strict requirement to the feed gas or desulfided samples. Other than that, carbon deposition will be occurred and formed seriously when the ratio of H_2/CO is less than 3, causing deactivation of Ni-based catalysts (CH Bartholomew, 1980). Thus, all these obstacles have burden and confine the development of Ni-based catalysts.

Co-based catalysts are widely used in catalytic industry compared to Ni-based catalysts, such as in the processes of hydrotreating and hydrodesulphurization (HDS), and in the synthesis of alcohols (Pecoraro & Chianelli, 1981). In 1960s-1970s, Co-based catalysts were used to improve the heat value of coal gas. Co-based catalysts can be used directly in the dry reforming reaction without desulfurization. Meanwhile, Mo-based catalyst still can be used and functioning well with a H_2/CO ratio as low as 3 (Baowei & Yuqin *et al.*, 2014). These advantages suggest that Co-based catalyst owns a good prospect of application compared to Ni-based catalyst.

According to Al-Zeghayer & Sunderland (2005), a deep study on Co, Ni bimetallic component catalysts were carried out. It has been found that Ni addition can change the structure of Co on the catalyst surface and increase its resistance to sintering and improve its reaction activity. In contrast, the current study aims to discover the effect of the different synthesized bimetallic Co-Ni/Al_2O_3 catalyst towards the hydrogen production result.

1.2 Objectives

The objectives of this research are given below:

- To synthesize and evaluate the physicochemical properties of monometallic 10%Co/Al_2O_3 catalyst, bimetallic 5%Ni-10%Co/Al_2O_3 catalyst and 5%Mo-10%Co/Al_2O_3 catalyst.
- To evaluate the performance of methane dry reforming reaction at different operation conditions such as reaction temperature and feed composition.

1.3 Scope of this research

The scopes of this research are summarized as follows:

i) To fabricate the bimetallic catalysts, 5%Ni-10%Co/Al_2O_3 from $Co(NO_3)_2$ and $Ni(NO_3)_2.6H_2O$ precursors using wet impregnation method.

ii) To characterize the synthesized catalysts by using the following advanced techniques namely; X-ray Diffraction Measurement (XRD), Brunauer-Emmett-Teller (BET) surface area measurement, temperature-programmed oxidation (TPO), temperature-programmed reduction (TPR) and scanning electron microscopy (SEM).

iii) To optimize the operation variable such as CO_2/CH_4 ratio and temperature for CO_2 (or dry) reforming reaction in order to locate the ideal process settings for highest performance.

1.4 Main contribution of this work

Carbon dioxide (CO_2) has been identified as the most significant greenhouse gas arising from anthropogenic activities. It is of great importance to reduce anthropogenic CO_2 emissions in order to counteract global warming. One such method, which is presently being extensively investigated, is the sequestration of CO_2 produced by concentrated sources (such as industrial plants and power stations). However, no one can be sure of the potential influence of CO_2 buried on the ecosystem in the long term. Conversion of CO_2 instead of its sequestration is presently being explored as one potential alternative solution. Production of useful value-added products (chemicals products, fuels …) by dry reforming of methane appears to be an interesting method. The dry reforming of methane produces an equimolar synthesis gas (syngas) which is a mixture of hydrogen (H_2) and carbon monoxide (CO), from carbon dioxide and methane (CH_4), according to equation below.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{1.1}$$

Undeniably, dry reforming can be viably used as a method of CO_2 mitigation for the production of hydrogen or of synthetic fuels. This work assesses whether monometallic catalyst can be replaced by bimetallic catalyst and used in dry reforming reaction to give a promising conversion of syngas from CO_2 utilisation. First, a comparison between the monometallic catalystt and bimetallic catalyst is performed as well as a study of the production of hydrogen from the dry reforming of methane. Furthermore, a thermodynamic analysis is carried out by the method of equilibrium constants defining the thermodynamic limit and the optimum conditions.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the applications of catalytic steam reforming, CO_2 reforming and catalytic partial oxidation. A general description on the flow characteristics of the system, as well as the advantages and disadvantages are presented. This chapter also provides a brief discussion of different types of catalyst, mentioning their applications and limitations for reforming process as well as the catalyst deactivation. A summary of the previous experimental work of CO_2 reforming is also presented.

Chapter 3 gives a flow chart of preparing the monometallic catalyst and bimetallic catalyst by using wetness impregnation method, followed by mixing slurry and lastly drying and calcination process. In the preparation of bimetallic catalyst section, multiple impregnation technique is selected instead of co-impregnation in order to ensure the desired compositions of metals are loaded on the alumina support respectively. The other sections give detailed explanations about the preparation procedures and precautions.

Chapter 4 is devoted to preliminary work has been done within this semester. In this chapter, the detailed descriptions about the result of characterization by using advanced technologies are discussed.

2 LITERATURE REVIEW

2.1 Overview

This chapter summarizes a detailed description of current technologies for producing syngas. The advantages, disadvantages and the challenges for these processes are also discussed. Furthermore, a detailed literature survey about the physicochemical properties and performance of noble and non-noble catalysts for methane dry reforming is provide in this chapter.

2.2 Introduction

Today’s energy, which is mainly depends on fossil energy carriers, can in no way be evaluated as sustainable. Regarding to the progressive industrialization of developing nations and growth in the world’s population from time to time, especially those countries in Asia as well as South America, the global demand for energy is expected to continue to escalate in the coming decades – by more than 50% until 2030, according to the International Energy Agency (IEA) – with fossil fuels continuing to dominate global energy use (Ball & Wietschel, 2009). At the same time, a growing number of global consensus that greenhouse gas (GHG) emissions, which continue to rise, an effective management is required to prevent dangerous anthropogenic interference with the climate system. Hence, security of supply and climate change represent two major concerns about the future of the energy sector which give rise to the challenge of finding the best way to rein in emissions while also providing the energy required to sustain economies. Concerns about security of energy supply, climate change and local air pollution and rising prices of energy services are giving a growing influence on the policy making over the world. Subsequently, syngas production technologies are starting to attract the world’s attentions based on the requirements mentioned.

Synthesis gas or called as syngas is a mixture of hydrogen and carbon monoxide, which plays an important role in chemical industries as a key intermediate. It usually used as a feedstock for gas-to-liquids (GTL) Fisher-Tropsch synthesis to produce liquid hydrocarbon fuels. Undeniably, the reserves of petroleum and crude oil are depleting from time to time and now becoming a crisis towards the human being over the world (Hussain & Mazhar *et al*., 2009).

The value chain of the syngas market includes feedstock suppliers, syngas technology licensors, syngas & derivatives manufacturers, and the end consumers. The feedstock suppliers are the companies that supply coal, natural gas, petroleum byproducts (heavy oils or petcoke), or biomass/waste. The syngas technology licensors include companies such as L'Air Liquide (France), Haldor Topsoe (Denmark), Air Products & Chemicals (U.S.), KBR (U.S.), Siemens (Germany), MHI (Japan), and Foster Wheeler (Switzerland) among several others. The actual syngas and derivatives manufacturers are Methanex (Canada), Shell (The Netherlands), Sasol (South Africa), and several others producing syngas and its derivatives such as methanol, ammonia, liquid fuels, gaseous fuels, and electricity. The end-users are such as a fertilizer industry for ammonia.

Syngas can be used for production of various chemicals such as methanol, ammonia, oxo chemicals, and their individual derivatives such as formaldehyde, urea, butanol, dimethyl ether (DME), and others. Simultaneously, Fisher Tropsch synthesis (FT–synthesis) can be used for the production of hydrocarbon fuels such as diesel and gasoline. Power generation can be achieved through coupling the syngas plant with an IGCC (Integrated Gasification Combined Cycle). Two or more derivatives can also be produced at the same time, which enables polygeneration. Hence, chemicals, fuels, or power can be produced depending upon the requirement as well as changes in the domestic energy markets or global economic conditions.

The major opportunity in the syngas market is removing dependency on conventional natural resources for the production of chemicals and fuels. Undeniably, gradual depletion of the world's oil reserves enable a growing recognition of the potential of world natural gas reserves have led to an increased interest in more efficient utilization of methane (CH_4), especially in Malaysia where rich in natural gas reserves and production. Figure 2-1 shows that the Malaysia's dry natural gas production and consumption from year 2000 to 2011 (Eia.gov, 2014).

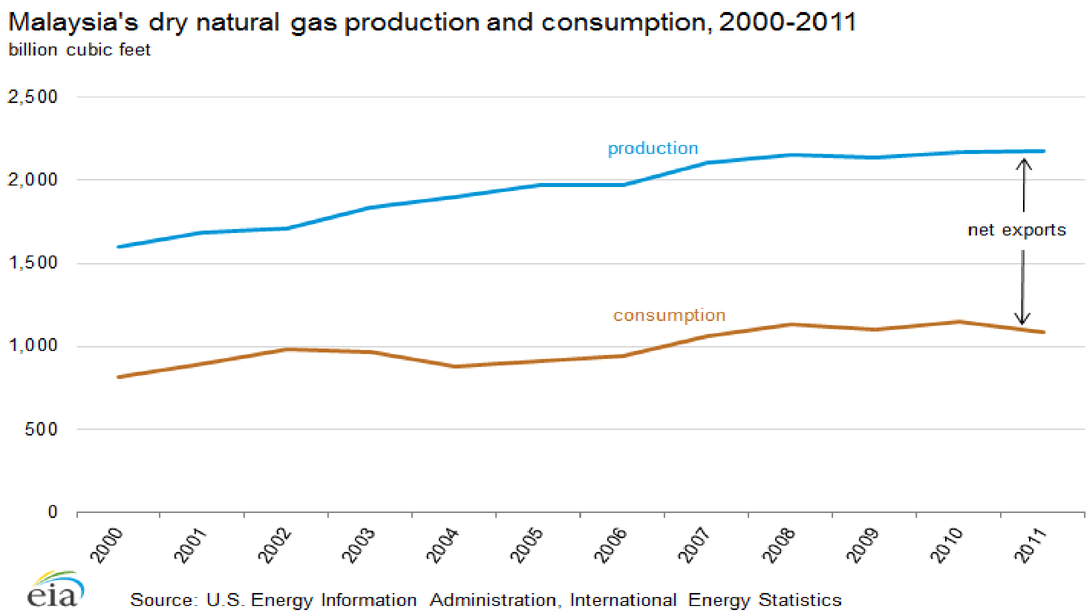

Figure 2-1: Malaysia's dry natural gas production and consumption from year 2000 to 2011.

Natural gas is a fossil fuel, basically a mixture of light hydrocarbons, found in the basement of gas accumulations that occur in porous rocks, and may or may not be associated to oil. Natural gas consists of saturated hydrocarbons, predominantly methane, propane and butane in lower quantities, among other substances, like inorganic gases as well as some low levels of contaminants such as nitrogen, carbon dioxide, water and sulfur compounds (Thomas, 2004). Natural gas currently is one of the best alternatives for the supply of energy and therefore urgent strategic efforts are necessary to develop alternative sources and solutions for the frequent energy shortages currently being reported (Schmal, 2005). Today natural gas is the preferred source for production of syngas, a mixture of hydrogen and carbon monoxide, from which purified hydrogen can be obtained. There are several different catalytic processes for producing syngas from natural gas (Armor, 2005).

In fact, the conventional method to produce syngas can be major classified into two, steam reforming of natural gas and the CO_2 (or dry) reforming process. Indeed, CO_2 (or dry) reforming process has attracted significant interest due to increased interest in the effective utilization of CO_2 from the environmental perspective compared to the steam reforming technology. Actually, many natural gas fields contain copious amounts of CO_2, natural gas dry reforming may be readily carried out without pre-separation of CO_2 from the natural gas. In some situation, combination of steam and CO_2 reforming may be advantageous. Undeniably, utilization of the CO_2-CH_4 reforming reaction is already employed in some industrial processes. However, there is always a question whether transformation of CH_4 and CO_2 into other chemicals could have a significant impact on the concentration of these gases in the atmosphere.

Particularly, the major reactions involved in this chapter are shown in reaction (2.1), accompany together with some significant side reactions shown in reactions (2.2) to (2.5):

Dry reforming of CH_4

$$CH_4 + CO_2 \longrightarrow 2\,CO + 2H_2 \tag{2.1}$$

Steam reforming of CH_4

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \tag{2.2}$$

Reverse water-gas shift reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{2.3}$$

CH_4 *dehydration*

$$CH_4 \rightleftharpoons C + 2H_2 \tag{2.4}$$

Boudourad reaction

$$2CO \rightleftharpoons C + CO_2 \tag{2.5}$$

The heats of reaction for reactions (2.1) to (2.5) at temperature, T, may be obtained from equations (2.6) and (2.7):

$$\Delta H\ (T) = \Delta H_{298} + \int_{298}^{T} \Delta C_p dT \tag{2.6}$$

Integration expression:

$$\Delta H(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 - a_4 T^4 \tag{2.7}$$

The constants in equations (2.6) and (2.7) for reactions (2.1) to (2.5) are shown in Table 2.2 below.

Table 2-1. Standard heats of reactions and constants to calculate ΔH(T) for reactions (2.1) to (2.5) from equations (2.6) and (2.7), (Foo, 2012).

Reaction	$\Delta H_{298} x\ 10^{-3}$ (J mol^{-1})	$a_0 x\ 10^{-3}$ (J mol^{-1})	a_1 (J $mol^{-1}K^{-1}$)	$a_2 x\ 10^{3}$ (J $mol^{-1}K^{-1}$)	$a_3 x\ 10^{6}$ (J $mol^{-1}K^{-1}$)	$a_4 x\ 10^{-5}$ (J $mol^{-1}K^{-1}$)
2.1	247.0	238.3	50.64	-33.95	5.997	10.48
2.2	205.8	189.4	66.11	-36.2	5.997	0.806
2.3	41.17	48.8	-15.46	2.25	0	9.677
2.4	74.52	55.13	62.10	-23.36	5.997	-8.339
2.5	-172.4	-91.57	5.728	5.296	0	-9.411

2.3 Catalytic Steam Reforming

Catalytic steam reforming of natural gas is one of the most energy efficient ways to produce hydrogen and carbon monoxide. It does not require the mixing of air in the reaction mixture and therefore produces higher H_2 concentration in the reformed product. Besides that, the elimination of oxygen from the initial fuel mixture improves the overall system efficiency by minimizing energy losses from catalytic combustion.

The process of steam reforming of methane produces syngas (H_2 + CO) with a ratio $H_2/CO = 3$. In this catalytic process, methane reacts with water steam in the presence of a catalyst. The product is called as syngas (Neiva & Gama, 2010). The scheme of the reaction of steam reforming of methane is shown in reaction equation 2.3.

Since the process of steam reforming of methane leads to the production of syngas with the highest H_2/CO ratio, this type of reforming process is considered ideal to obtain high-purity gaseous hydrogen.

Since the overall reaction is endothermic, it is necessary to supply the needed heat to the reaction throughout the whole process. In steam reforming, this is accomplished by combustion of a part of the fuel in a direct-fired or indirectly fired furnace. According to Le Chatelier's principle, equilibrium concentrations for reaction are shifted to the right at high temperature and low pressure. In order to achieve a highly conversion of the methane, a very high temperature and long residence time at this high temperature is required, meaning that an overall energy loss and a huge size for the methane reforming reactor. Nevertheless, by using catalysts it is possible to reduce the temperature necessary for total conversion of the methane to below 1000 ℃ within considerable short residence time. In Table 2-2, the advantages and disadvantages of steam reforming are listed.

Table 2-2 Advantages and Disadvantages of Steam Reforming.

Characteristic	Advantage	Disadvantage
Hydrogen Yield	Generally higher than 50% at T > 600°C.	Potential high level of carbonaceous material formation.
Heat Requirement	Heat generated from combustion can be used to drive steam reforming reaction with overall higher system efficiency.	External heat transfer device is required, therefore results in system complexity and potential higher cost.
Startup / transients	Relative stable during transition operation.	Still needs external igniter to start up although the catalyst bed can be used for catalyst combustion tentatively. Heat transfer efficiency and higher volume makes the start-up slow

2.4 CO_2 Reforming

The dry reforming is a process whereby methane reacts with carbon dioxide in the presence of a catalyst, and syngas at a $H_2/CO < 1$ ratio is obtained (Lercher et al., 1999). The scheme of the dry reforming of methane reaction is shown in reaction equation 2.1.

Since the value of the H_2/CO ratio obtained in the dry reforming of methane, this process is considered the ideal type of reforming process when it comes to involve utilisation of the syngas produced as a raw material for the synthesis of important fuel liquids which require H_2 and CO as raw materials. However, this type of reforming process is very expensive because it is an endothermic process, meaning it consumes a great amount of energy. The main disadvantage of dry reforming of methane is the significant production of by-products, typically coke, a phenomena of catalyst deactivation, that are subsequently deposited on the surface of the catalyst, impairing its activity in the reaction directly. The occurrence of coking towards a catalyst contributes to the reduction of its useful life. The large formation of coke occurred in this process is explained by the presence of CO_2 as a reagent. Thus, dry reforming is the unique process of methane reforming that is affected by two reagents that contain carbon (CH_4 and CO_2) (Cheng *et al*., 2001; Lercher *et al*., 1999). Edwards and Maitra (2000) reported that there is a greater potential for carbon formation, primarily due to the lower H/C ratio in the dry reforming of methane. Furthermore, the lower H_2/CO ratio is a preferable feedstock of Fischer-Tropsch synthesis for long chain hydrocarbon production in petrochemical industries.

The main challenge for the industrial application of dry reforming of methane is most related towards the development of active catalytic materials. In order to prolong the lifetime of catalyst, a very low coke formation rate is needed to be achieved, either on the catalysts or reactor's cold zones. According to Stagg *et al*. (1998), carbon formation can be controlled by using a support that favours the dissociation of CO_2 into CO and O whilst, the last species are responsible for the cleaning of the metallic surface.

2.5 Catalytic Partial Oxidation

The successful results obtained by steam reforming after 1902 was first summarized in 1924 by Neumann and Jacob and since then the steam reforming become the state-of-art technology for synthesis gas and hydrogen production (Christian Enger, Lodeng & Holmen, 2008). In 1929, Liander *et al.* was the first person suggested that catalytic partial oxidation of methane in production of synthesis gas.

The partial oxidation of methane is a catalytic process whereby methane reacts directly with oxygen in the presence of a catalyst, and the product of this reaction is syngas with a good H_2/CO ratio (Fathi *et al*., 2000). The scheme of the partial oxidation of methane is shown in reaction equation 2.2.

The partial oxidation of methane is an exothermic process and, thus from economic perspective, it can be considered more economic than the processes of steam reforming or dry reforming, because, being an exothermic reaction, it requires a lower amount of thermal energy compared to others. On the other hand, partial oxidation is considered as an expensive process due to requirement of pure oxygen flow. Generally, reaction times are very short (in milliseconds) and occur at high temperatures of 850 to 1200 ^{0}C. The product mixtures have a lower H_2: CO ratio of 2, which is ideal for the Fischer-Tropsch synthesis from synthesis gas (Foo, 2012). The advantages and disadvantages of catalytic partial oxidation are listed in Table 2-3 below.

Table 2-3 Advantages and Disadvantages of Catalytic Partial Oxidation

Characteristic	Advantage	Disadvantage
Hydrogen Yield	None.	Relatively low yield can be tuned by improving catalyst and convert some CO back to H_2.
Heat Requirement	No external heat required. The system is exothermic.	The heat generated from the reaction needs to removed or utilized in the system.
Startup / transients	Startup is fast. Transient test is relatively easy to control.	High temperature startup/shutdowns may cause catalyst degradation.

2.6 Autothermal Reforming

The autothermal reforming of methane is a combination of procedures of steam reforming and partial oxidation. Hence, in the steam reforming there is contact with a flow of gaseous oxygen