

LANTHANUM PROMOTED COBALT CATALYST FOR METHANE DRY REFORMING

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ABSTRACT

In the present work, different loadings of lanthanum cobalt based catalyst for the dry reforming reaction was studied. The BET specific surface area has declined with the increment of La loading although pore volume increased significantly beyond 1wt% La doping. 5wt% La-Co/MgO catalyst has BET specific surface area of $31.67 \text{ m}^2 \text{ g}^{-1}$ and $0.30 \text{ cm}^3 \text{ g}^{-1}$ of pore volume. From FESEM imaging, an addition of lanthanum promoter has created solid with smaller particle size. This is consistent with XRD analysis where crystallite size significantly dropped when the percentage of La was higher. XRD shows that the peaks representing Co_3O_4 occurred at $2\theta = 36.94^\circ$ and MgO or Co/MgO at $2\theta = 42.94^\circ$; 62.32° ; 74.74° and 78.64° . As lanthanum loading increases, the crystallite size dropped from 24.5nm to 17.9nm at peak $2\theta = 42.94^\circ$ while the crystallite size decreased from 23.5nm to 17.1nm at peak $2\theta = 62.32^\circ$. Reaction studies have found that 5wt% La catalyst gave the highest rate formation of product yield (H_2 and CO) However; the composition of products yield was quite low. It was about 1.6%. It was then employed for further reaction studies. The rate was optimum at $\text{CO}_2:\text{CH}_4$ feed ratio of 0.67. Next, when reforming temperature was increased, the reaction rate also increased. The activation energy obtained was $82.26 \text{ kJ mol}^{-1}$.

ABSTRAK

Kajian ini menyelidik tentang kandungan La yang berlainan dalam jenis Co pemangkin terhadap tindak balas metana dan CO₂. BET kawasan permukaan pemangkin semakin berkurangan apabila kandungan La meningkat walaupun isi padu liang banyak meningkat dengan >1wt% La. 5wt% La-Co/MgO mencapai BET kawasan permukaan pemangkin 31.67 m² g⁻¹ dan isi padu liang 0.30cm³g⁻¹. FESEM menunjukkan bahawa penambahan La promoter menghasilkan pepejal yang berpartikel kecil. Ini konsisten dengan analisis XRD, size kristal menurun apabila kandungan La bertambah. XRD menunjukkan puncak-puncak yang mewakili CO₃O₄ pada 2θ = 36.94 ° dan MgO or Co/MgO pada 2θ = 42.94 °, 62.32 °, 74.74 ° and 78.64 °. Sementara kandungan La bertambah, size kristal pada puncak 2θ = 42.94 ° berturun dari 24.5nm to 17.9nm. Seterusnya, size kristal berturun dari 23.5nm to 17.1nm pada puncak 2θ = 62.32 °. Kajian reaksi melaporkan 5wt% La pemangkin mempunyai kadar formasi produk (H₂ and CO) yang tertinggi. Bagaimanapun, produk komposisi masih rendah dalam 1.6%. Kajian reaksi dijalankan untuk mengaji parameter seperti nisbah feed dan suhu reaksi. Hasil kajian melaporkan kadar optimum adalah pada CO₂:CH₄ 0.67. Selain itu, kadar reaksi meningkat dengan suhu reaksi. Pengaktifan tenaga terdapat ialah 82.26 kJ mol⁻¹.

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LIST OF ABBREVIATIONS

- c : characteristic constant of the adsorbate
 d : inter plane distance of crystal
 d_{spacings} : interplanar distance
 D : crystalline size
 E_a : activation energy
 k_{Sch} : Scherrer constant
 n : order of reflection (integer)
 P : gas pressure
 P_s : saturation pressure of the adsorbate gas
 P/P_o : relative pressure
 r_k : pore radius
 R : gas constant
 T : temperature
 V : volume of gas adsorbed
 V_m : volume of gas adsorbed corresponding to monolayer coverage
 V_m : liquid molar volume
 w_f : final weight of the sample
 w_o : initial weight of the sample
 w_t : residual weight of the sample at the temperature

Greek

- \AA : angstrom
 α : coke conversion
 β_{obs} : observed width at half maximum intensity (degree)
 β_d : angular width
 β_{inst} : instrumental line width by standard (degree).
 (ΔG_r) : Gibbs free energy change of reaction
 λ : wavelength
 γ : surface tension

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
EDX	Energy Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction

1. INTRODUCTION

Synthesis gas is a fuel gas mixture consists of carbon monoxide and hydrogen vital valuable feedstock in the downstream petrochemical industries, production of ammonia, methanol and etc. Furthermore, renewable energy has become a special interest in nowadays society since the demand for energy resources increases rapidly. Synthesis gas plays a significant role in resolving the above mentioned issues. Synthesis gas can be used as an energy source for power plants generation. Besides, a wide range of synthetic products can be produced from the synthesis gas like clothes, solvents and fuels. Thus, it has become a high demand in the industrial area.

Synthesis gas can be produced from natural gas, petroleum and its derivatives, biomass and coal. There are some routes to produce the synthesis gas. One of them is through the dry reforming reaction of methane. It is a process where methane and carbon dioxide is converted into synthesis gas by using a catalyst. Biogas itself is readily for dry reforming process as it is an optimum route to chemically utilize natural gas and mitigate greenhouse emission particularly from the industrial waste (Ding et al., 2001). Dry Reforming method is more preferable as in this process the H_2/CO product ratio is close to 1/1 (Atiyeh & Mehran, 2012). However, one of the major problems encountered in this reaction is the ease of catalyst deactivation due to the carbon deposition and coke formation.

Catalysts play a particular important role in this reaction. Catalyst is comprised of a promoter, active metal and a support. Promoter can strongly affect the physicochemical and catalytic property of the cobalt active site (Chen et al., 2007). Previous studies and reviews have been published on the Ni based with different supported system catalysts used in the methane dry reforming. DRM was studied over Ni catalysts supported on Al_2O_3 and $MgAl_2O_4$ with Ni loadings of 10% and 2% at 943K (Kang et al., 2011). The addition of metal oxides such as CeO_2 and ZrO_2 to Ni/ Al_2O_3 and Ni/ $MgAl_2O_4$ catalysts as promoters has improved catalytic activity and stability. The best performance was obtained for 10 wt% Ni on $MgAl_2O_4$ with the addition of 5 wt% ZrO_2 or CeO, which showed 80% methane conversion and 87% carbon dioxide conversion respectively at

943K and a CH₄/CO₂ molar ratio of 0.91. The promotion of rare earth onto cobalt based catalysts can enhance the dispersion of metallic and increased the amount of active site in the catalyst (Ernst, 1999). Furthermore, studies showed that rare earth promoter indeed improved in the methanation activity (Kok et al., 2011). Therefore, it is to believe that the presence of rare earth promoter may significantly improve the performance of catalyst in dry reforming reaction.

1.1 Problem Statement and Motivation

Fossil fuels hydrocarbon resources are decreasing, thus synthesis gas is playing a growing role in the energy sector and as an alternative fuel source in future. This work aims to produce synthesis gas from the waste of palm oil mill effluent through methane dry reforming reaction. However, catalyst deactivation due to carbon deposition is the major problem that encountered in this reaction. Previous studies primarily investigated the development of catalyst for high catalytic performance and stability. Thus, an optimum conversion of synthesis gas can be achieved. However, previous catalytic researches are mostly limited to nickel based catalysts with alumina support. In fact, cobalt based catalyst are known to be more active than the nickel catalysts even though they are more expensive. An effective way for improving the catalytic performance in this reaction is through the addition of promoter in the catalysts. Moreover, it is worth to explore the possibility of rare earth as catalyst promoter in this study.

1.2 Objective

This research work is carried out to synthesis magnesium oxide supported cobalt catalyst promoted with various loading of lanthanum metal, a rare earth element for reaction study of biogas dry reforming reaction.

1.3 Scopes

In order to achieve the objective of this work, the following scopes have been identified:

i) Catalysts Preparation:

The catalyst was prepared by impregnation method. MgO was used as the catalyst support and doped with solutions containing cobalt (10%) and lanthanum nitrate salts using conventional co-wetness impregnation technique. Promotion with lanthanum was carried out for 0.5%, 1%, 3% and 5wt%. The support after impregnation will be oven dried and then calcined at 1023K for 3 h.

ii) Catalyst Characterisation

The methods applied in this study were BET, XRD, TGA, FESEM and EDX. BET was used to find out the specific surface area, pore volume and pore size distribution sample of catalysts. The crystalline structure and the size of crystallite diameter were determined via XRD. The reduction temperature of sample catalysts can be done by TGA. In addition, TGA also allow the determination of coke location as well. Lastly, the image of coke deposit structure at the sample catalysts can be observed via FESEM while EDX shows the composition of element that contained in the sample catalysts.

iii) Catalyst Reaction:

The catalytic screening was carried out by placing 0.2 g of catalyst into the quartz glass fixed-bed reactor (ID: 10 mm) supported by two layers of quartz wool. The feed comprised of the CH₄ and CO₂ mixture at equal proportion and the reaction temperature was set at 1073 K. CO₂ to CH₄ ratio and temperature were then adjusted to determine the ratio of product produced by the best catalyst.

2. LITERATURE REVIEW

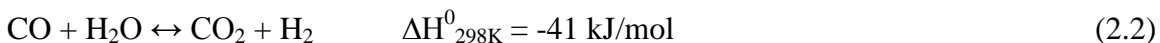
2.1 General Overview

Synthesis gas is a major ingredient for many downstream petrochemical processes. Conventional production of syngas is via natural gas steam reforming. However, fossil hydrocarbons resources are decreasing in the face of growing demand from developing countries; consequently resulting in a spike to energy price. In lieu of this, synthesis gas availability as an alternative fuel source (via Fischer-Tropsch synthesis) in addition to the aforementioned processes is clearly desirable.

In this chapter, previous studies pertaining to the reforming reaction, related catalysts, as well as coke deactivation phenomena are presented.

2.2 Steam reforming reaction process

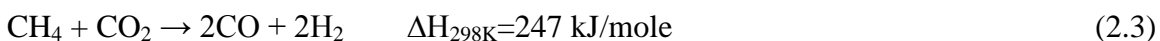
The most established process for syngas production is natural gas/ methane steam reforming. This reaction is endothermic and takes place at temperature above 1173K. The reforming reaction can be represented as:



Methane steam reforming however suffers from the thermodynamic equilibrated steam reforming and water-gas shift reactions.

2.3 Dry reforming reaction process

The methane dry reforming is a highly endothermic reaction and the reaction occurs at 973-1073K⁰C and under atmospheric pressure. Theoretically, the process has a unity molar ratio of H₂/CO. The reforming reaction can be represented as:



However, there are some drawbacks of dry reforming methane, viz. catalyst sintering at high temperature, a possibly lower H₂/CO ratio attributed to the reverse water-gas shift reaction (Oyama et al., 2010) and catalyst deactivation due to carbon deposition from either methane cracking (CH₄ ↔ C + 2H₂) or Boudouard reaction (2CO ↔ C + CO₂). On the other hand, attractive feature by turning greenhouse gases into useful products and the production of high quality synthesis gas suitable for Fischer-Tropsch reaction has become the impetus to carry out the research into this area.

2.4 Reactions in CO₂ reforming of methane

Table 2.1 shows the main reactions which may occur in CO₂ reforming of methane.

Table 2.1: Reactions in CO₂ reforming of methane

Reaction number	Reaction	$\Delta H_{298}(kJ/mol)$
1	$CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2$	247
2	$CO_2 + H_2 \longleftrightarrow CO + H_2O$	41
3	$2CH_4 + CO_2 \longleftrightarrow C_2H_6 + CO + H_2O$	106
4	$2CH_4 + 2CO_2 \longleftrightarrow C_2H_4 + 2CO + 2H_2O$	284
5	$C_2H_6 \longleftrightarrow C_2H_4 + H_2$	136
6	$CO + 2H_2 \longleftrightarrow CH_3OH$	-90.6
7	$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O$	-49.1
8	$CH_4 \longleftrightarrow C + 2H_2$	74.9
9	$2CO \longleftrightarrow C + CO_2$	-172.4
10	$CO_2 + 2H_2 \longleftrightarrow C + 2H_2O$	-90
11	$H_2 + CO \longleftrightarrow H_2O + C$	-131.3
12	$CH_3OCH_3 + CO_2 \longleftrightarrow 3CO + 3H_2$	258.4
13	$3H_2O + CH_3OCH_3 \longleftrightarrow 2CO_2 + 6H_2$	136
14	$CH_3OCH_3 + H_2O \longleftrightarrow 2CO + 4H_2$	204.8
15	$2CH_3OH \longleftrightarrow CH_3OCH_3 + H_2O$	-37
16	$CO_2 + 4H_2 \longleftrightarrow CH_4 + 2H_2O$	-165
17	$CO + 3H_2 \longleftrightarrow CH_4 + H_2O$	-206.2

Figure 2.1 shows the equilibrium constant of reactions involving in $\text{CH}_4 - \text{CO}_2$ reaction at different temperatures and atmospheric pressure.

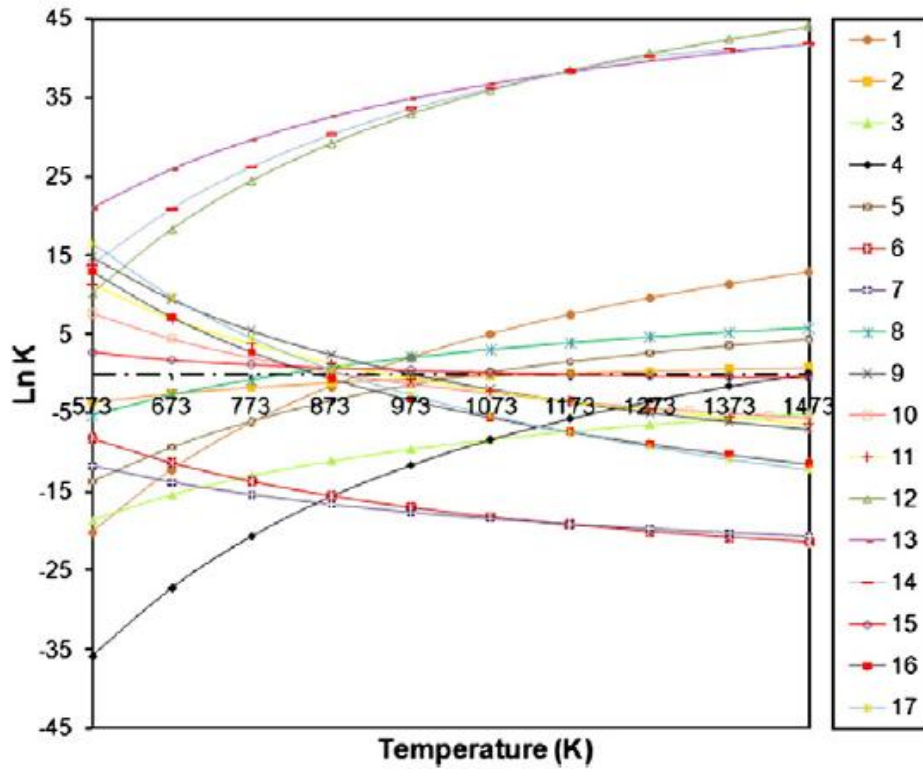


Figure 2.1: Equilibrium constant of reactions involving in $\text{CH}_4 - \text{CO}_2$ reaction at different temperatures and atmospheric pressure

According to thermodynamic principles (Smith, 2005), whenever Gibbs free energy change of reaction (ΔG_r), is negative (larger $\ln(K)$), indicates the reaction is spontaneous. Conversely, for Gibbs free energy change of reaction (ΔG_r), is positive, the reaction is thermodynamically limited. From the figure, dry reforming of methane to form syngas is a favorable reaction particularly at a temperature of higher than 1000K, consistent with the suggested temperature range in the previous studies (Istadi et al., 2005). Reaction 2 which is known as reverse water gas shift is much affected by equilibrium within the entire investigated temperature range. In general, it occurs simultaneously throughout the carbon dioxide reforming of methane. Reaction 3, 4, 5 and 6 are not feasible to occur except at a very high temperature. One of the important aspects that need to be considered in reforming reaction is the coke deposition as this will lower the stability of the catalyst and soon lead to catalyst deactivation during the reaction. Carbon may be

formed via methane decomposition (reaction 8), carbon monoxide disproportionation (reaction 9), hydrogenation of carbon dioxide (reaction 10) and hydrogenation of carbon monoxide (reaction 11). When the equilibrium constant, K is near to 1 or $\ln(K)$ is near to zero, varying the molar ratio of the reactants has considerable influence on the distribution of products (Wang et al., 2009). Therefore, these reactions can be affected by the changing in molar ratio. Methane decomposition (reaction 8) has the tendency to occur at the higher temperature, while the rest of 3 reactions tend to generate carbon at lower temperature ($< 800\text{K}$) and can be influenced by equilibrium limitations at higher temperature. Reaction 12, 13 and 14, however can be improved towards the right hand side within the whole considered temperature range, whereas reaction 15 is easily influenced by equilibrium limitations. Methanation (reaction 16 and 17) occur at lower temperature ($< 800\text{K}$) but restricted at the high temperature (Khoshtinat & Amin, 2010).

2.5 Reforming catalyst

Nickel (Ni) based catalyst is normally employed as a reforming catalyst due to their low cost and high effectiveness at elevated reaction temperatures. Sintering of Ni particles takes place at the reaction temperature of 1073K (Fidalgo, 2010). Using support with ordered structured, for example, a mesoporous molecule sieve, Ni particles can be confined in the channels of the mesoporous material, therefore the sintering of Ni metallic particle can be relieved, in other words, it will not be easily sintered at high temperature soon resulting in improved stability (Yi, 2005). Nanostructured Ni based catalyst reported to be higher stability due to the presence of Ni nanoparticles involved in long term conversion at higher temperature (Francisco, 2005). Nevertheless, cobalt (Co) based catalysts have also been used in reforming reaction since it generally shows better coking resistance and higher stability under the extreme reaction condition. Previous studies showed the effect of the presence of cobalt and nickel on the deactivation behavior of catalysts in dry reforming of methane. The remarkable stability is due to both Ni and Co species produced amorphous and graphitic carbon, being the latter deactivating carbon deposits (Francisco et al., 2012). Additionally, cobalt has good activity for soot oxidation, which help in promote the carbon resistance of that catalyst in reforming reaction (Chen, 2010). Cobalt catalysts supported on TiO_2 , were reported as

stable catalyst at high pressure with a small amount of carbon deposition (Nagaoka, 2002). In terms of cost, Co is pricier compared to Ni. Meanwhile, supported noble metal catalysts such as Rhodium (Rh), Ruthenium (Ru), Iridium (Ir) and Palladium (Pd) are reported to be less sensitive to coking than the Ni based catalysts (Gadalla & Sommer 1988). Nonetheless, they have not received much attention due to involvement of high costs and limited availability of noble metals. Consequently, it is not economically competitive in comparison to the other transition metals, i.e. Ni and Co. Different loading of metal on supported catalyst do affect the conversion of CH₄ and CO₂ in dry reforming. There is an increase in CH₄ and CO₂ conversions with an increase in nickel loading. This is due to higher nickel dispersion and surface area (Atiyeh & Mehran, 2012).

In terms of support, the active metals are usually dispersed on various oxide systems like Al₂O₃, MgAl₂O₄, CeO₂, ZrO₂ and so on. It has been suggested that a high dispersion of metal species over the support can reduce the coke formation. Oxide support can be used to control the metal particle sizes (Hu & Ruckenstein, 2002). Studies using CaTiO₃ and BaTiO₃ perovskites containing a small amount of Ni in Ti sites as the precursor to obtain highly dispersed and stable nickel metal in situ, the results show high activity and resistant to coking (Hayakawa et al. 1999). In addition, pre reduced La₂NiO₄ catalysts obtained by PC method shows high activity and higher stability (Guo, 2003). Zirconium based mixed oxides were proved to be a good support for nickel catalyst in methane dry reforming (Rezaei et al., 2008).

Addition of promoter into catalysts has often contributed to facilitate the reducibility of metal on the support and create active site, therefore improve the catalysts performance. Promoters can be an alkali earth metal, noble metal or even rare earth metal. The addition of different promoters like rare earth oxides metals and noble metals can enhance the cobalt metal dispersion and the reducibility of CO₃O₄ to metallic cobalt. La³⁺ promotes the formation of new active sites and increases the dispersion of cobalt metal (Vannice et al., 1987). In the early study, the addition of rare earth promoter, cerium enhances the dispersion degree and lowers the reduction temperature of cobalt oxides over the pillared montmorillonite supported cobalt catalysts (Su, 2009). ZrO₂ was also employed as promoter and the Ni/Al₂O₃ promoted with ZrO₂ exhibits a much more stable than the

unpromoted catalyst. Ni is more likely uniformly distributed and positioned close to the ZrO_2 , where oxygen intermediates are dissociated and react with carbon species (Rezaei et al., 2008). Table 2.2 shows the summary of previous research.

Table 2.2: Summary of previous research and its significant result

Catalyst	Significant results	Reference
-barium and lanthanum incorporation to supported Pt and Rh on $\alpha-Al_2O_3$	-La incorporation induces a rate enhancement in conversion of methane to synthesis gas. -Rh is more active than Pt.	(Madani & Pascal, 2012)
-nickel catalysts supported on $CaO.2Al_2O_3$	- Nickel catalyst with different nickel loadings supported on nanocrystalline calcium aluminate employed in methane reforming, show high activity and stability due to the presence of CaO in the support which declined coke deposition in catalysts. -7% Ni loading showed higher activity and lower coke formation.	(Atiyeh & Mehran, 2012)
-nickel catalysts supported on nanocrystalline calcium aluminates with different CaO/ Al_2O_3 ratio	--nanocrystalline calcium oxides with different CaO/ Al_2O_3 ratio are suitable as the support of catalysts in dry reforming process. -calcium aluminate due to its relatively high basicity and small particle size show high activity and stability. -CaO in the catalysts can reduce the carbon formation during the reaction. -CH ₄ and CO ₂ conversion decreased with increasing CaO/ Al_2O_3 ratio, this may be due to the fact that higher ratio have	(Atiyeh & Mehran, 2012)

	lower surface area and thus lower nickel dispersion in catalysts.	
-Promotion of active nickel catalysts by aluminum addition	-The formation of La-Ni-Al solid solution in all proportion has constant local elemental distribution.	(Parvary et al., 2001)
	-The $\text{LaNi}_x\text{Al}_{1-x}\text{O}_3$ systems are efficient catalysts for syngas production from methane dry reforming reaction.	
-Co and Ni supported on CeO_2 as selective bimetallic catalyst	-Bimetallic Co-Ni/ CeO_2 catalysts is more active, selective and thermally stable for the synthesis gas production due to intrinsic property of Co-Ni alloy.	(Igor et al., 2012)
- $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ni}_{0.8}\text{M}_{0.2}\text{O}_3$ perovskite (M=Bi,Co,Cr,Cu,Fe)	--LNS(Cu)O perovskite possessed good performance in initial activity.	(Sutthiumporn et al., 2012)
	-LNS(Fe)O showed high final activity and thermal stability with no carbon formation.	
- Cobalt-magnesia catalyst by oxalate co-precipitation method	-Cobalt-magnesia catalyst prepared by oxalate co-precipitation method (Co-MgO) showed high activity at 1023K, 1atm. -Co-MgO (7 mol% Co) showed more stable activity at high space velocity.	(Omata et al., 2004)
- Nickel and Cobalt catalysts prepared from La-Based Perovskite Precursors.	-Among 4 perovskites type complex oxides(LaNiO_3 , La_2NiO_4 , LaCoO_3 and La_2CoO_4) was prepared using 3 methods: a) 2 solution gel method b) Pechini method c) citric acid complexing method.	(Guo et al., 2003)
	-Ni based catalyst from	

	<p>La₂NiO₄ is the most active and stable catalysts prepared by Pechini method due to its well defined structure and lower reducibility.</p>	
-Nickel catalyst supported on (Al ₂ O ₃ , CeO ₂ , La ₂ O ₃ , ZrO ₂)	<p>-The catalyst supported on ZrO₂ showed the highest stable activity.</p> <p>- The catalyst supported on CeO₂ has a relatively good activity but showed sign of deactivation after certain reaction time.</p>	(Maria & Adolfo, 2010)
-Manganese as promoter on SCo-Ce-Zr-O _x nano crystal	<p>-Adding of Mn enhanced the catalytic activity and stability of Co-Ce-Zr-O_x catalyst.</p> <p>-molar ratio of 10% Mn/(Ce+Zr+Mn) achieved high catalytic activity and stability.</p> <p>-In Co-Ce-Zr-O_x catalyst, the migration of bulk lattice oxygen species become easier and the content of surface oxygen species is higher results in improved catalytic behavior.</p>	(Wang et al., 2011)
-Strontium carbonate supported cobalt catalyst	<p>-Co-SrCO₃ showed high tolerance to oxidative atmosphere under 1MPa, 1023K.</p>	(Omata et al., 2004)
-Ni/BaTiO ₃ -Al ₂ O ₃	<p>-Ni/BaTiO₃ showed poor stability and severe coke formation.</p> <p>-Ni/BaTiO₃-Al₂O₃ has a higher dispersion of nickel and Ni/32.4% BaTiO₃-Al₂O₃ exhibited a high catalytic activity and excellent stability for lower temperature in dry reforming.</p>	(Xiancai et al., 2012)
-Lanthanum promoted Co-	<p>-Carbon deposition rate decreased with temperature</p>	(Say Yei et al., 2012)

Ni/Al ₂ O ₃	range 923K-1023K. -Lanthanide promotion resulted in lower coke formation due to interaction of the rare earth oxide with the more reactive surface carbonaceous matter in redox reaction.	
-Y ₂ O ₃ -ZrO ₂ supported on nickel catalyst	-The formation of surface oxygen vacancies in Y ₂ O ₃ -ZrO ₂ system increase in the interaction between nickel species and the surface oxygen vacancies, thus improve the methane conversion. -The best performance achieved by 5Ni8YZ catalyst, with Y ₂ O ₃ load of 8% mol.	(Jorge & Elisabete, 2009)
-Alumina supported on Pt, Ni and PtNi alloy	-The alloy formation is associated with higher activity and lower production of carbonaceous materials. -PtNi catalyst which is enriched at the surface by Pt has smaller metal crystal size than the monometallic Pt and Ni.	(Monica et al., 2010)
CaO promoted Ni/ZrO ₂	-CaO-ZrO ₂ solid solution support suffers the influence of surface oxygen vacancies on their reduction behavior. -The best performance achieved by 5Ni8CZ with CaO 8 mol% in support. Beyond this concentration, the dry reforming reaction fell strongly.	(Jorge et al., 2009)
Ni/SiO ₂ and Ni/Li-SiO ₂	-The Li addition on the SiO ₂ support increase coke resistance. - Ni/SiO ₂ has a higher capacity of chemisorptions and metallic surface.	(Francisco et al., 2005)
Potassium promoted Ni/Al ₂ O ₃	-The addition of low amount of potassium (0.2% K ₂ O) increase	(Juan et al., 2006)

	catalytic activity(over 63% methane conversion) and a low coke deposition (< 30mg C/g.cat)	
Ni/La ₂ O ₃ /Al ₂ O ₃	-The species and amount deposited on the catalysts depended on size of Ni particles and texture of supported. -Metallic Ni particles <15 nm can effectively suppress the formation of carbon filaments and thus decrease the amount of carbon deposition.	(Junke et al., 2009)
Ni-Pd bimetallic catalyst on various support	-The catalytic activity decreases in the following ranking ZrO ₂ -La ₂ O ₃ , La ₂ O ₃ >ZrO ₂ >SiO ₂ >Al ₂ O ₃ >TiO ₂ -Bimetallic is more active than Ni and Pd alone. -A Ni to Pd ratio=4 at metal loading of 7.5wt% showed the best result.	(Bernd et al., 2009)

2.6 Catalyst preparation

There are few steps to prepare the catalyst. First, the metal precursor is introduced on the support by impregnation method, co precipitation method or deposition precipitation method. Impregnation method is usually used since it appears to be more simple and economic. In its essential features, this procedure requires that the support is contacted with a certain amount of solution of the metal precursor, usually a salt; it is then aged for a certain time under stirring, dried and calcined. Drying process is carried out in order to eliminate the solvent used in the previous impregnation step. The drying treatment is generally performed at temperature ranged between 353K and 473K. On the other hand, the purpose of calcinations is to decompose the metal precursor with formation of an oxide and removal of gaseous products such as water and carbon dioxide (Francesco, 1998).

Previous studies show how rare earth promoted alumina supported cobalt catalysts was prepared by using incipient wetness impregnation method. First, cobalt (20% wt) was loaded onto γ -alumina using cobalt nitrate. Lanthanum nitrate solution was then added into it. Catalyst impregnation was performed at a constant pH of 2 through the addition of 3M nitric acid under constant stirring. It was then dried for 12 hours in an oven at temperature of 393K. The resulting solid was then calcined at 673K for 8 hours (Kok et al., 2011).

Another study shows the $\text{LaNi}_x\text{Al}_{1-x}\text{O}_3$ catalyst prepared by sol-gel method. Lanthanum nitrate, nickel nitrate and aluminium nitrate were separately dissolved in hot propionic acid and stirred in a reflux process. The respective amounts of salt used with x value was varying from 0 to 1. Nickel and aluminium propionic solutions were mixed and added to the lanthanum solution rapidly. The resulting solution was evaporated under reflux condition till the resin was formed. The resins were calcined at 1023K with a temperature increase of 3K min^{-1} from 298K and kept at maximum temperature for 4 hours (Parvary, 2001).

2.7 Catalyst deactivation

Catalyst is used in many industries in order to reduce the activation energy of a chemical reaction and thus increases the production rate. However, catalyst deactivation remains an unsolved issue to the industrial. It results in the loss of a catalyst's activity and selectivity over the operation time. Consequently, the performance of catalyst deteriorates and production rate gradually decreases. Coke deposition that leads to catalyst deactivation is currently the major issue in the dry reforming reaction. Deactivation of catalyst due to the carbon deposition can be represented by two reactions which are carbon monoxide disproportionation (2.4) or methane decomposition (2.5).



All reactions involve in carbon formation can be relatively affected by operational parameters due to their low equilibrium constants. Carbon deposition and formation of