

STUDY OF CO₂ AND BI-REFORMING OF METHANE ON MODIFIED
NICKEL-BASED CATALYSTS



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

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บนตัวเร่งปฏิกิริยาที่มีองค์ประกอบของนิกเกิลที่ปรับปรุง



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นิชากร บัวสุข : การศึกษารีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์และไบรีฟอร์มมิงบนตัวเร่งปฏิกิริยาที่มีองค์ประกอบของนิกเกิลที่ปรับปรุง. (STUDY OF CO₂ AND BI-REFORMING OF METHANE ON MODIFIED NICKEL-BASED CATALYSTS) อ.ที่ปรึกษาหลัก : ผศ. ดร.สุพจน์ พัฒนะศรี, อ.ที่ปรึกษาร่วม : อ. ดร.ศุภฤกษ์ ประเสริฐธรรม

ในปัจจุบันมีการปล่อยแก๊สคาร์บอนไดออกไซด์ มีเทน และไนตรัสออกไซด์ เพิ่มขึ้นอย่างต่อเนื่องในทุกๆปี ดังนั้นจึงต้องตระหนักถึงปัญหาดังกล่าว จึงมีแนวความคิดในการนำแก๊สคาร์บอนไดออกไซด์และแก๊สมีเทน มาเปลี่ยนเป็นแก๊สที่มีคุณค่าและมูลค่าสูง โดยใช้กระบวนการรีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์และไบรีฟอร์มมิง ดังนั้นงานวิจัยนี้เกี่ยวข้องกับการศึกษาความสามารถในการเร่งปฏิกิริยา และการต้านทานการเกิดโค้กในตัวเร่งปฏิกิริยา ที่มีนิกเกิลเป็นพื้นฐานบนตัวรองรับแกมมาอลูมินา ที่มีและไม่มีคาร์บอนเติมตัวส่งเสริม ตัวเร่งปฏิกิริยาที่เตรียมโดยวิธีการฝังตัวแบบแห้ง จะดีกว่าวิธีโซลเจลในแง่ของการเปลี่ยนสารตั้งต้นไปเป็นผลิตภัณฑ์ และการสะสมโค้ก การทดสอบกระบวนการรีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์ และและไบรีฟอร์มมิง ถูกดำเนินการในเครื่องปฏิกรณ์แบบเบดนิ่งภายใต้ความดันบรรยากาศ ที่อุณหภูมิ 700 องศาเซลเซียส ซึ่งเป็นอุณหภูมิที่ดีที่สุดสำหรับการทดสอบตัวเร่งปฏิกิริยา พบว่าการกระบวนการรีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์ มีค่าการเปลี่ยนแปลงของคาร์บอนไดออกไซด์และมีเทนที่มีความเสถียร และอัตราส่วนไฮโดรเจนและคาร์บอนมอนอกไซด์ใกล้เคียง 1 กระบวนการรีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์ มีค่าการเปลี่ยนของมีเทนสูงกว่าคาร์บอนไดออกไซด์ และอัตราส่วนไฮโดรเจนและคาร์บอนมอนอกไซด์ใกล้เคียง 2 ไบรีฟอร์มมิงมีปริมาณของไฮโดรเจนสูงกว่ากระบวนการรีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์ ทั้งสอง ปฏิกิริยาพบว่า เมื่อเพิ่มปริมาณนิกเกิล โค้กประเภทที่ 2 จะมีปริมาณเพิ่มขึ้น ในกรณีของกระบวนการรีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์ ตัวส่งเสริมกลุ่มแลนทาไนด์ทั้งหมดมีการค่าการเปลี่ยนของสารตั้งต้น ซึ่งน้อยกว่ากลุ่มของโลหะอัลคาไลน์เอิร์ท และยิ่งน้อยกว่าที่ไม่มีตัวส่งเสริม ในกรณีของไบรีฟอร์มมิง ตัวส่งเสริมทั้งสองกลุ่มมีค่าการเปลี่ยนของสารตั้งต้นลดลงน้อยกว่ากลุ่มที่ไม่มีตัวส่งเสริม

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KEYWORD: Dry reforming of methane (DRM) Bi-reforming of methane (BRM) alumina-supported nickel-based catalyst

Nichakorn Buasuk : STUDY OF CO₂ AND BI-REFORMING OF METHANE ON MODIFIED NICKEL-BASED CATALYSTS. Advisor: Asst. Prof. SUPHOT PHATANASRI, Ph.D. Co-advisor: SUPAREAK PRASERTHDAM, Ph.D.

Nowadays, several currently operated industrial factories significantly increase the rate of carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) far higher than those that should be normally. Therefore, various mitigation ways to reduce carbon dioxide and methane are increasingly important. The prevailing methods are dry reforming of methane and bi-reforming of methane. Therefore, this research involves the study of the catalytic activity and coke resistance on the Ni-based catalysts with and without a promoter. The activity tests on the dry reforming of methane reaction and bi-reforming of methane reaction were performed in a fixed-bed reactor under atmospheric pressure at 700°C, which is the best temperature for the activity of the catalysts. It has been found that dry reforming of methane had almost equal CO₂ and CH₄ conversions. The conversions were found to be extremely stable with H₂/CO ratio close to 1. The CH₄ conversion was higher than that of CO₂ conversion for bi-reforming with H₂/CO ratio close to 2. The bi-reforming had a higher H₂ yield than that of dry reforming. For both reactions it has been found that when increasing the nickel loading, coke type II (whiskers, C_v) and graphitic, C_g) increased. In case of dry reforming of methane, all lanthanide series had lower conversion than alkaline earth metal and also lower than those without promoters. As for bi-reforming of methane, both groups of promoters had CO₂ and CH₄ conversions lower than those of the group without promoters.

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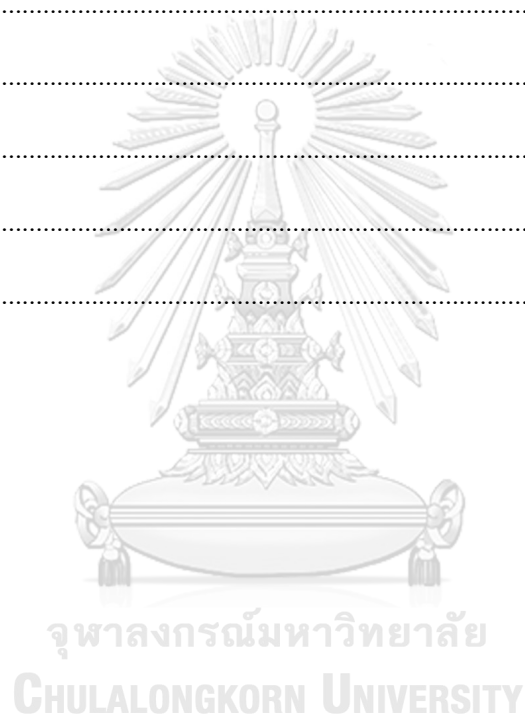
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CHAPTER I

INTRODUCTION

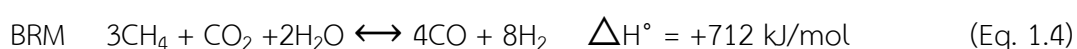
1.1 Motivation

Nowadays, global warming and the greenhouse effect are the ever-increasing serious problem all over the world. It can be witnessed from the global temperature that is continuously rising and polar ice continues to melt. This mainly due to human-made causes because greenhouse gases increase from human activities, such as burning coal and fuel as well as the various chemicals that human use which have a mixture of greenhouse gases as an element. A number of currently operated industrial factories also increase the rate of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) far higher than those should be normally.

Today the global population began to realize the serious threat of global warming and the greenhouse effect. This makes industrial plants to find ways to reduce carbon dioxide and methane. One of the prevailing methods is the reforming of methane, which also increases the production of hydrogen. Hydrogen is one of the important clean energy that causes neither pollution to the environment nor the public health problems.

There are several options to directly convert CO_2 and CH_4 to syngas. Dry reforming of methane (DRM, Eq.1),[1] is an endothermic reaction. It requires high temperature reaction at $700\text{-}1,000^\circ\text{C}$ [2, 3]. DRM produces the syngas with an H_2/CO ratio of 1. Oxy- CO_2 reforming of methane (ORM, Eq.2) suffers its own restrictions on the requirement of oxygen and safety issues is, therefore seriously concerned[1]. Steam reforming of methane (SRM, Eq.2) requires a large amount of steam and high temperature above $800\text{-}900^\circ\text{C}$ [4]. Combine steam, and dry reforming of methane (CSDRM, Eq.3) is a method used to adjust the ratio of syngas by H_2/CO ratio of 2,

which is suitable for ethanol synthesis [5]. In addition, addition of steam in the feed can also efficiently improve the coke-resistance of catalysts



Catalysts containing noble metals such as platinum (Pt), ruthenium (Ru), and rhodium (Rh) have high activity and good stability making it better resistant coke depositions. However, the noble metals are expensive which causes limitations in an application in the industry. Taken the economic aspects into account, nickel (Ni) is a popular choice due to its low price and high activity. Nonetheless, the main problem of nickel is the carbon decomposition on the surface of the catalyst, therefore some promoter is added to reduce the coke deposit the alumina-supported nickel catalyst is intended and increase the efficiency of the catalyst.

In this research, to be used as the main one. Then some promoters such as magnesium (Mg), calcium (Ca), cerium (Ce), lanthanum (La), and samarium (Sm) would be adopted for the improved catalytic performances on conversion, selectivity and stability of dry and bi-reforming of methane. The effects of promoters themselves as well as ways of introduction either as support promoters or nickel promoters are also investigated.

1.2 Objective of Research

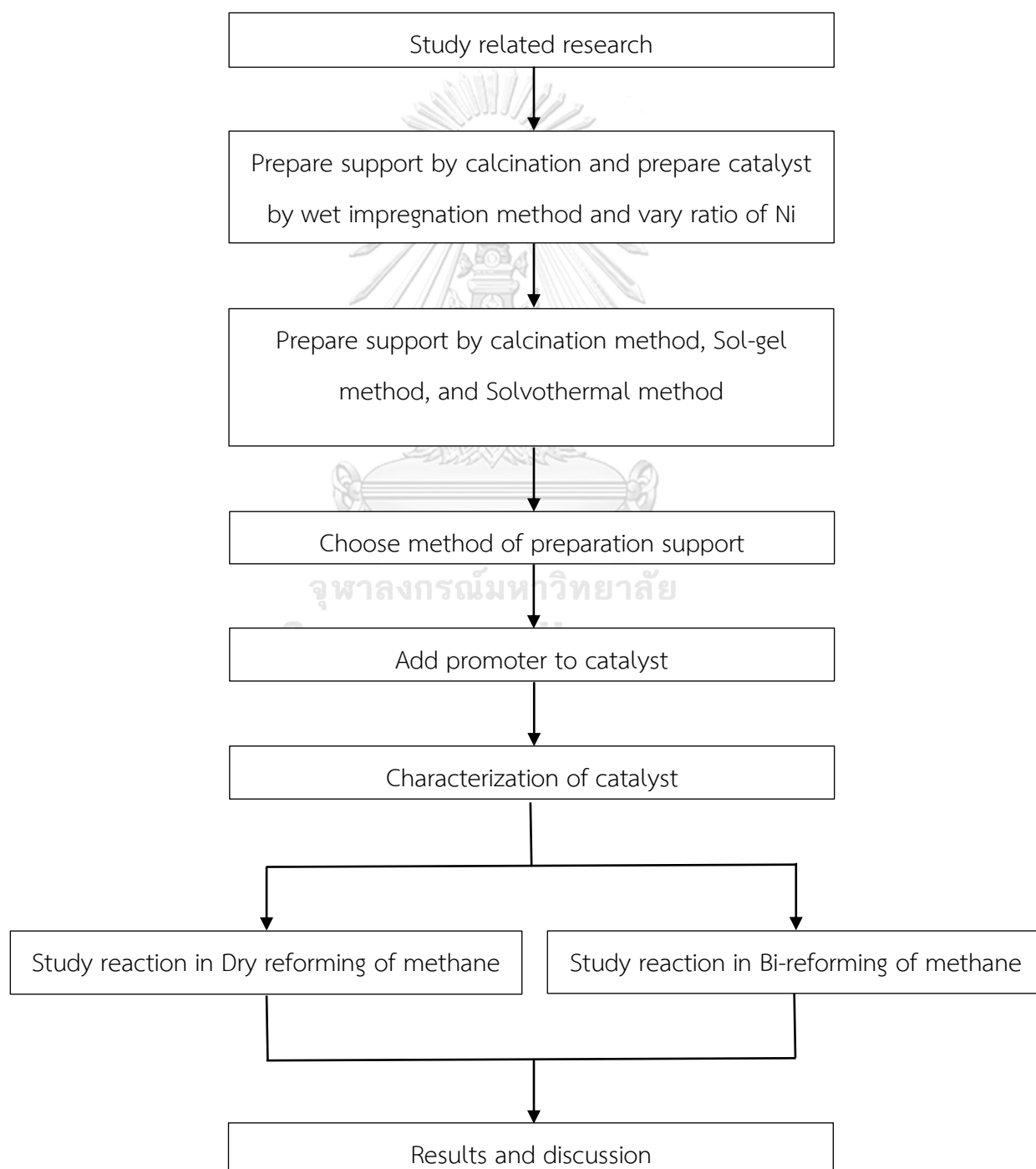
To improve the catalyst with improved nickel composition for the carbon dioxide reforming of methane and bi-reforming of methane.

1.3 Scope of Research

- 1.3.1 Prepare alumina-supported nickel catalyst with and without promoters by incipient wetness impregnation.
- 1.3.2 Investigate the performance of the prepared catalysts with carbon dioxide reforming of methane reaction and bi-reforming of methane under the following condition.
 - a. Before starting dry reforming of methane and bi-reforming of methane, the catalyst will be reduced by hydrogen at 500°C for 1 hour.
 - b. Methane with flow rate of 30 ml/min
 - c. Carbon dioxide flow rate with 30 ml/min
 - d. Steam flow rate with 30 ml/min (In case of bi-reforming of methane)
 - e. Fixed-bed continuous-flow quartz reactor was used with reaction temperature of 700°C.
 - f. Reactant and products were analyzed by thermal conductivity detector-type gas chromatography with Porapak Q and molecular sieve 5A columns.
- 1.3.3 Characterize physical and chemical properties of catalysts by using various techniques using Scanning Electron Microscopy (SEM) for morphology. Nitrogen adsorption-desorption was used to determine BET specific surface area, pore size, and pore volume. X-ray diffraction (XRD) for characterized the crystalline phase of catalysts. The surface basic determination of the catalyst was examined by Temperature Programmed Adsorption of Carbon dioxide (CO₂-TPD). Ammonia temperature program desorption (NH₃-TPD) was used to determine the acidity of catalysts. Hydrogen temperature-programmed reduction (H₂-TPR) was used to determine the metal oxide reduction. Hydrogen chemisorption (H₂-CHEM)

was used to determine quantities of the active site of catalysts. Thermogravimetric and differential thermal analysis (TG-DTA) was used to study carbon deposition.

1.4 Research Methodology



CHAPTER II

THEORY AND LITERATURE REVIEWS

In this research, based on data from other research related to the catalyst study and the reaction. In which this second chapter presents theories and literature reviews; metal catalysts, supporting catalysts, promoter catalysts, hydrogen production, carbon dioxide reforming of methane, bi-reforming of methane and literary reviews;

2.1 Theory

2.1.1 Metal catalyst

2.1.1.1 Nickel (Ni)

Nickel is a silvery-white metal. Nickel is commonly used for utilizing as a catalyst in various industries. Nickel is a fairly good conductor of heat and electricity and highly resistant to rusting and corrosion. Nickel is a metal that is among the 8B in the periodic Table. In nature, many oxidation numbers are found: 0, +1, +2, +3 and +4, but generally, they are most stable in the form of +2 charge [6].

Table 1 Properties of nickel

Properties	
Name	Nickel
Atomic Symbol	Ni
Atomic Number	28
Atomic weight	58.6934 g/mol
Element Category	Transition metal
Oxidation States	0, +1, +2, +3
Density	8.908 g/cm ³
Melting Point	1,455°C
Boiling Point	2,913°C

2.1.2 Support

2.1.2.1 Aluminum (Al)

Alumina or aluminium oxide is a chemical compound of aluminium and oxygen with the chemical formula Al_2O_3 . It has several names such as aloxide, alundum, or aloxite depend on applications, and several occurring form of aluminium oxide, which aluminium(III) oxide is the most common form.

Table 2 Properties of aluminum

Properties	
Name	Aluminum
Atomic Symbol	Al
Atomic Number	13
Atomic Weight	26.9815 g/mol
Oxidation State	+1, +2, +3
Density	2.6898 g/cm ³
Melting Point	660.2°C
Boiling Point	2480°C

Alumina preparation, purity, dehydration, and thermal treatment affect the crystal structures. There are many different types of crystal structure, such as α , γ , χ , κ , δ , θ , ρ , and η -alumina. The differences in crystal structure will cause different physical and chemical properties. The alumina phase, which is shown as a function of temperature, is shown in Fig 2.1, and the structure and properties of alumina at different sintering temperatures are shown in Table 2.3. The final crystal structure and properties are strongly affected by calcination temperature. γ -alumina is widely used as commercial support and catalyst for industry and laboratory because of its moderately high surface area and stable phase in a wide range of reaction temperatures [7, 8].

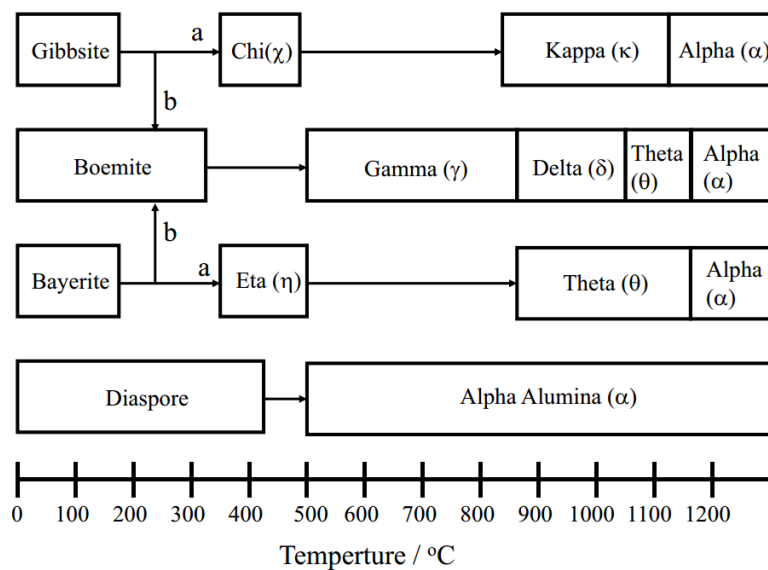


Fig 1 Alumina phase at different calcination temperature

Calcination temperature (°C)	Alumina phase	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
250	preudoboemite	390	0.50	5.2
450	γ -alumina	335	0.53	6.4
650	γ -alumina	226	0.55	9.8
850	γ -alumina	167	0.58	14
950	δ -alumina	120	0.50	16.6
1050	θ -alumina	50	0.50	28
1200	α -alumina	1-5	-	-

Fig 2 The structure and properties of alumina at different calcination temperature

2.1.3 Promoters

2.1.3.1 Magnesium (Mg)

Magnesium is silvery white and very light. Magnesium is known for a long time as the lighter structural metal in the industry, due to its low weight and to its capability of forming mechanically resistant alloys. Magnesium oxide nanoparticles are odourless and non-toxic. They possess high hardness, high purity, and a high melting point. Among these promoters, Magnesium oxide was reported to exhibit superior catalytic performance and coke suppression. Magnesium oxide promoter is also valid in promoting catalyst activity and stability through enhancing the sintering resistance and metal support interaction [9].

Table 3 Properties of magnesium [6]

Properties	
Name	Magnesium
Atomic Symbol	Mg
Atomic Number	12
Atomic Weight	24.305 g/mol
Oxidation State	+2
Density	1.74 g/cm ³
Melting Point	650°C
Boiling Point	1107°C

2.1.3.2 Calcium (Ca)

Calcium is Silvery-white metallic. It can be beaten into extremely thin sheets. It can be pressed, rolled, and cut. Highly reactivity with acids. When heated in air or oxygen, it ignites. Reacts with cold water rapidly at first, but the reaction is then slowed due to the formation of a film of Calcium hydroxide (Ca(OH)₂). Calcium oxide (CaO), also known as lime or, more specifically, quicklime. Calcium oxide will spontaneously absorb carbon dioxide from the atmosphere [7].

Table 4 Properties of calcium

Properties	
Name	Calcium
Atomic Symbol	Ca
Atomic Number	20
Atomic Weight	40.078 g/mol
Oxidation State	+2
Density	1.54 g/cm ³
Melting Point	842°C
Boiling Point	1484°C

2.1.3.3 Cerium (Ce)

Cerium is the most abundant of the rare-earth metals. Its iron-gray in colour. It oxidizes in the air at room temperature to form CeO₂. The metal slowly reacts with water, and it quickly dissolves in diluted acids, except hydrofluoric acid (HF). The redox properties of cerium oxide facilitate the oxidation of carbon deposits, expanding the lifetime of the catalysts. Cerium oxide modifies the metal-support interactions, increasing the active phase dispersion, and improving the stability of alumina at high temperatures [4].

Table 5 Properties of cerium

Properties	
Name	Cerium
Atomic Symbol	Ce
Atomic Number	58
Atomic Weight	140.116 g/mol
Oxidation State	+3, +4
Density	6.77 g/cm ³
Melting Point	799°C
Boiling Point	3443°C

2.1.3.4 Lanthanum (La)

Lanthanum is a ductile and malleable silvery white metal that is soft enough to be cut with a knife. It is the second most reactive of the rare-earth metals after europium. Lanthanum oxidizes in the air at room temperature to form La_2O_3 . It slowly reacts with water and quickly dissolves in diluted acids, except hydrofluoric acid (HF). The existence of moderate lanthanum could improve catalytic activity and significantly suppress coke deposition [10].

Table 6 Properties of lanthanum

Properties	
Name	Lanthanum
Atomic Symbol	La
Atomic Number	57
Atomic Weight	139.905 g/mol
Oxidation State	+3
Density	6.15 g/cm ³
Melting Point	920°C
Boiling Point	3464°C

2.1.3.5 Samarium (Sm)

Samarium is a silvery white in colour. It is relatively stable in air, slowly oxidizing to Sm_2O_3 . It rapidly dissolves in diluted acids except for hydrofluoric acid (HF). In addition to its more stable +3 oxidation state, samarium, unlike most of the rare earth, has a +2 oxidation state. The Sm^{2+} ion is a powerful reducing agent that rapidly reacts with oxygen, water, or hydrogen ions. Samarium plays an important role for a lower amount of coke depositions and enhancement of catalytic activity [11].

Table 7 Properties of samarium

Properties	
Name	Samarium
Atomic Symbol	Sm
Atomic Number	62
Atomic Weight	150.36 g/mol
Oxidation State	+2, +3
Density	7.52 g/cm ³
Melting Point	1072°C
Boiling Point	1794°C

2.1.4 Synthesis gas and hydrogen production

The production of hydrogen fuel can be produced in many processes. The most studied process is the reforming reaction because it is expected that it can be developed as a commercial process. Reforming is divided into many categories, depending on the type of substrate used. For example, steam reforming (Eq. 2.1) produces hydrogen gas from water and carbon containing feedstock, such as an alcohol or a hydrocarbon. The remaining oxygen from the water, hydrocarbons compound, and carbon residue combination as carbon monoxide. Carbon dioxide reforming (Eq. 2.2) is a method of producing mixtures of hydrogen and carbon monoxide from the reaction of carbon dioxide with hydrocarbons such as methane. Methane partial oxidation (Eq. 2.3) simultaneously to achieve a thermally neutral reaction [12].



2.1.5 Reforming of methane

In recent years, people are increasingly concerned about greenhouse gases that contribute to global warming. Researchers are interested in changing methane and carbon dioxide to be valuable gas. Therefore, two types of greenhouse gases are useful chemical blocks are hydrogen and carbon monoxide.

2.1.5.1 Dry reforming of methane

Dry reforming of methane (DRM, Eq. 2.2), a growing technology that utilizes these two greenhouse gases and transforms them into a value-added product (syngas composed of hydrogen and carbon monoxide), is proposed as a feasible way to obtain synthetic fuels from carbon dioxide and methane [13]. However, the dry reforming of methane can be accompanied by side reactions which involve reverse water gas shift (RWGS) Eq. 2.4, methane decomposition Eq. 2.5, CO disproportionation (Boudouard reaction) Eq. 2.6 [14], CO₂ Hydrogenation Eq. 2.7 and CO dehydrogenation Eq. 2.8 [6].



2.1.5.2 Bi-reforming of methane

Combined steam and carbon dioxide reforming or bi-reforming of methane (CSCRM, Eq. 2.9) have been regarded as a promising replacement to the general reforming process. It enables easier modification of the H₂/CO ratio through reactant feedstock regulation and, at the same time, converts anthropogenic CH₄ and CO₂ into other value-added products. Thus, the supplementary purification and separation steps are not required by tuning to the desired H₂/CO ratio [15]. Bi-reforming of

methane has also attracted researchers for the inherent advantage of less coke formation and production of syngas with H₂/CO ratio of 2 [16].



2.2 Literature reviews

2.2.1 Effect of support

In the first instance, the role of the support is literally to provide a high surface area (SiO₂ and Al₂O₃) for the dispersion of the active metals. Furthermore, the stability of the support is very important because it operates at high temperatures [17].

S. Ali et al. (2019) [18] was development of a highly efficient and coke-resistant. The catalysts with metal loading 5%Ni/Al₂O₃ prepared by two ways. The first approach was solution combustion synthesis (SCS) technique. The second way prepared by wetness impregnation method. The catalytic performances were tested for dry reforming of methane (DRM). The temperature between 500°C–900°C the catalyst was prepared by solution combustion synthesis exhibited significantly higher percentage conversions of CO₂ and CH₄ than that of the impregnation catalyst. For both catalysts, CH₄ conversion was slightly lower than CO₂. A catalytic stability test for dry reformation of methane over both catalysts was studied at CH₄/CO₂ ratio of one and at a reaction temperature of 800°C for a time-on-stream of 50 hours.

J. Janlamool et al. (2017) [19] studied effect of nanocrystalline alumina compared of γ - crystalline phases and χ -crystalline phases. The γ -crystalline phases and χ -crystalline phases prepared by the solvothermal method. The 25 grams of aluminium isopropoxide was dissolved in 100 ml with 100 ml butanol is name as γ -alumina. The 25 grams of aluminium isopropoxide was dissolved in 100 ml with 100 ml toluene is name as χ -alumina. χ -alumina structure better catalytic conversion and ethylene yield than γ -alumina.

H. Messaoudi et al. (2018) [20] studied effect of spinel and perovskite based catalysts in dry reforming of methane at difference temperature. The $MgAl_2O_4$ support has been prepared by sol-gel method as $MgAl_2O_4$ was impregnated with a solution of nickel and lanthanum nitrates. The results show that the perovskite is active at $650^\circ C$ with CH_4 and CO_2 conversions of 52% and 59% respectively, while the spinel catalyst is active from $700^\circ C$. For the supported samples the conversion of methane occurs since $750^\circ C$ and $800^\circ C$ for perovskite on support and spinel on support respectively.

2.2.2 Effect of metal

The development of highly active and stable catalysts with resistance against deactivation and economic feasibility is very important for successful industrialization of the reforming process. In general, active metals, supports, promoters, structure and methods for preparation and activation should be considered in designing an appropriate catalyst. DRM has been investigated over supported metal catalysts based on noble (Rh, Ru, Pd, Pt and Ir) and non-noble (Ni and Co) metals. Ni and Co-based catalysts were studied because of their cost effectiveness [17].

K. Jabbour et al. (2017) [21] studied thermodynamics aspects to determine the catalytic conditions and the catalyst was used for combined steam and dry reforming of methane (CSDRM). The effect of the Ni loading amount was studied with the addition of Mg and Ca as promoter. The thermodynamic study indicated that the reaction temperature above $600^\circ C$ was necessary. However, the temperature of $750^\circ C$ was needed in order to suppress the side reaction (particularly methane decomposition, WGS, and RWGS). The operating condition of $CH_4/CO_2/H_2O = 1/0.4/0.8$ at $800^\circ C$ for 40 hours on steam. The space velocity was kept at $138 L/g_{cat} \cdot h$. The catalyst of 5%Ni loading with 5%Mg addition showed the higher conversion of CH_4 and CO_2 compared with the same catalyst without Mg addition. However, when increasing Ni amount to 10% without any Mg loading, the higher conversion of CH_4 and CO_2 was achieved even without Mg addition. The catalyst with

Mg and Ca addition suppressed to a great extent the carbon deposition and hence the high coke resistance.

Y. Khani et al. (2016) [22] studied the suitability of different catalysts, i.e. 10%Ni, 3%Pt, 3%Ru, for each reaction of dry reforming (DRM), Steam reforming (SRM), and combined dry-steam reforming of methane (CRM). The reaction temperature was varied during 600-800°C with varying GHSV of 3,500, 7,000, and 10,500 h⁻¹. The conversion and yield decreased with the increasing GHSV. The coke formation on the catalyst was faster at the higher GHSV. The CH₄ conversions of DRM, SRM, and CRM were 100%, 85%, and 90%, respectively. It has been found that CH₄ conversion in case of SRM was higher than that of DRM with lower coke formation. In addition, H₂/CO ratio decrease with the increasing temperature for both SRM and CRM. The authors proposed 3%Ru/ZnLaAlO₄ as the catalyst exhibiting the best catalytic performance of all the reactions.

A. Nakhaei Pour et al. (2015) [23] studied the effect of the Ni-Mg particle size of Ni/Mg/ α -Al₂O₃ catalyst. The specific surface area and total pore volume of catalysts decreased with the increasing Ni loading amount. Though the feed conversion increased with higher Ni loading, the structure-related reaction sensitivity may not be concluded as the metal-catalyzed reaction was conducted on the catalyst surface. The turn-over frequency (TOF) increased as the size of Ni-Mg decreased. The coke formation was increased with the increasing Ni loading. The smaller particle size was found to affect the increased coke deposition rate.

2.2.3 Effect of promoter

Promoters are classified as two types: textural (structural) and chemical (electronic). Textural promoters are typically utilized to avoid and delay the sintering of active species by enhancing the textural properties of the catalysts. Chemical promoters function to provide additional new active sites or to enhance the chemical property relating to the reactivity of the catalysts such as basicity or redox

property. In particular, these chemical promoters help to moderate the formation of carbon and to oxidize carbonaceous species [17].

J. Shen et al. (2019) [12] was studied Oxidative dry reforming was catalyzed by Ni catalysts supported on an MgAl_2O_4 spinel at different loadings at 500-700°C, CO_2/CH_4 molar ratio of 0.76, and variable O_2/CH_4 molar ratio (0.12-0.47). That ways synthesis found that wet impregnation technique provides excellent interaction between metal precursor and support, leading to homogeneous Ni distribution on an MgAl_2O_4 spinel. The 3.4wt% Ni/ MgAl_2O_4 catalyst with a mean Ni nanoparticle diameter of 9.8 nm showed stable performance during oxidative dry reforming for 100 hours on stream without deactivation by sintering or coke deposition.

M. Boudjeloud et al. (2019) [3] studied ratio of Ni/La of 7/3, 8/2 and 9/1, respectively. The material with total loading of 10 wt%. The catalyst performance during steam reforming of methane at difference temperature. Substituting Ni by La leads to strong metal support interaction (SMSI) with a sensitive decrease of average Ni particles size existing in highly dispersion state. The La may cause strong change at the NiO surface with significant modifications in the reducibility. Moreover, incorporation of La increases the spacing between active nickel particles and prevents their agglomeration and sintering. The highest H_2 yield is obtained with 7Ni-3La/Al catalyst at 800°C.

J. Jeon et al. (2018) [24] studied effect of promoter for coke resistance for dry reforming of methane. The precious metals promoter such as Ru, Rh, Pt, Pd and alkaline earth promoter such as Mg, Ca, Sr, Ba. The nickel-based base catalysts were prepared by incipient. The precious metals add small amount of 0.5wt%. and the alkaline earth metal added at 1–15 wt.%. That were impregnated into 10 wt.% Ni/alumina. The catalysts loaded with both the alkaline earth metal (5 wt.%) and Ru (0.5 wt.%) were prepared by sequentially impregnating. The optimized catalyst composition is 0.5 wt.% Ru/5 wt.% Mg/10 wt.% Ni/alumina, which displayed coke resistance in the long-term stability test of steam methane reforming and 40 hours.

A. R. Kim et al. (2017) [11] studied effects of structural promoters such as Sm, Ce, Mg metal oxides on the Ni/Al₂O₃ catalysts. The catalyst was synthesized by a conventional impregnation method at a fixed amount of 5 wt% of each metal promoter. The catalyst stability test of combined steam and carbon dioxide reforming of methane from coke oven gas. The Ce, Sm and Mg were important roles for a less amount coke depositions and enhancement of catalytic activity. The Ni/Sm-Al₂O₃ was responsible for a less coke deposition and best catalytic performances.

E.-h. Yang et al. (2015) [25] compared the catalytic performance of perovskite with and without Ce as promoter. The reaction temperatures were varied between 900°C and 600°C for each 3 hours of experiment. CH₄ and CO₂ conversions were found to decrease with the decreasing temperature. The stability test was also observed at 650°C, GHSV of 3,000 h⁻¹ for 45 hours on steam. Ce was found to enhance the slightly higher conversion; however, the optimum amount of Ce was important. The addition of Ce as promoter clearly indicated its advantage on promoting the stable catalyst performance over 45 hours, compared with one without Ce.

K. Y. Koo et al. (2014) [26] studied the effect of the Ce addition as promoter on NiO crystallite size, metal dispersion, and degree of reduction. The catalysts with different Ce/Ni ratio were tested for combined steam and CO₂ reforming of methane at GHSV of 530,000 ml/g_{cat}·h, 700°C for 5 hours. The catalyst with Ce/Ni ratio of 0.25 exhibited the highest metal dispersion and activity as the smallest NiO crystallite size (8.3 nm) was also observed. The CH₄ and CO₂ conversions of 81.3%, 65.9%, respectively were obtained. The coke formation was investigated at 600°C for 16 hours. It has been found that the catalyst of 10Ni-2.5Ce/MgAl₂O₄ had the least carbon deposited. The author also found that the least coke formation was observed at 700°C.

K. Y. Koo et al. (2012) [27] studied Ce-promoted catalysts prepared by three different ways. The first approach was the co-impregnation of Ce and Ni solution on Al_2O_3 (Ni-Ce/ Al_2O_3). As for the second approach, Ni was loaded on pre-calcined Ce/ Al_2O_3 support (Ni/Ce/ Al_2O_3). The consecutive addition of Ce and Ni (Ce/Ni/ Al_2O_3) was conducted as the third approach. The prepared catalysts were used for combined steam and CO_2 reforming of methane with feed ratio of $\text{CH}_4/\text{H}_2\text{O}/\text{CO}_2/\text{N}_2$ as 1.0/0.8/0.4/1.0, GHSV of $530,000 \text{ mL/g}_{\text{cat}} \cdot \text{h}$, and reaction temperature of 750°C . Of all the catalysts, the co-impregnated one exhibited the higher Ni dispersion, degree of reduction as well as the higher activity which was close to thermodynamic equilibrium value. The low coke formation was also observed on the co-impregnate Ni-Ce/ Al_2O_3 catalyst.

2.2.4 Effect of condition to operate reaction

T. Stroud et al. (2018) [4] studied dry and bi reforming of methane and selected the most appropriate Sn/Ni ratio while promoting the alumina base with 20 wt.% of CeO_2 . All catalysts were prepared by sequential impregnation. The reforming of methane reaction was carried out at 700°C for over 20 hours with the $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O}$ ratio of 1/1/1 and WHSV of $60,000 \text{ mL/g}_{\text{cat}} \cdot \text{h}$. The catalyst was reduced with hydrogen at a flow rate of 60 mL/min for 1 hour. Products were analyzed by GC with Porapak Q and MS-5A column. Bi-reforming of methane exhibited higher CH_4 and CO_2 conversions and H_2/CO than those of dry reforming of methane. Certainly, a high-quality syngas was obtained in the bi-reforming experiments accordingly.

M. A. Soria et al. (2011) [28] studied the thermodynamical and experimental aspects when adding steam into dry reforming of methane at low temperatures during $400\text{-}500^\circ\text{C}$. As per thermodynamical aspect, CH_4 conversion increased and CO_2 conversion decreased with the steam addition. Although the experiment was done under non-equilibrium, the results obtained were in line with those should be as per thermodynamic equilibrium. The considerable increase of CH_4 conversion was not distinct during the steam addition of 1-4%vol. However, with the steam amount of

5%vol, CH₄ conversion was found to increase remarkably. CO₂ gradually decreased with the increasing steam amount from 1%vol to 5%vol. The steam addition had pronounced effect on catalyst stability, which was significantly enhanced by increasing the amount of steam added. At the presence of 1, 2, and 5% vol of H₂O, the deactivation was 11, 8 and 5%, respectively.

I. H. Son et al. (2013) [29] studied the effect of catalyst pretreatment with steam at high temperature of 850°C. The catalyst test was prolonged as 200 hours for combined steam and carbon dioxide reforming of methane. The size of Ni nanoparticles increased higher than that without steam pretreatment. The CH₄ conversion (98.3%) and CO₂ conversion (82.4%) of the pretreated catalysts were close to the equilibrium corresponding values, i.e. CH₄ and CO₂ conversions of 99.0% and 81.2%, respectively. The higher activity was achieved on the steam-pretreatment. However, the higher H₂/CO ratio was obtained in case of non-pretreated catalyst. The author believed that the steam pretreatment contributed to the carbon deposition at early stage significantly, and hence the CH₄ and CO₂ conversions were enhanced with long-term stability.

CHAPTER III

EXPERIMENT

This chapter describes the details of materials and chemicals, preparation and characterization of catalyst, and reforming of methane.

3.1 Materials and chemicals

Materials and chemicals that were used for the catalyst are listed in Table 3.1

Table 8 Lists of chemicals for Dry and Bi-reforming of methane

Chemicals	Formula	Purity	Suppliers
Aluminum isopropoxide	$C_9H_{21}O_3Al$	>98%	Sigma-Aldrich
Alumina oxide anhydrous (γ -alumina)	Al_2O_3	Lab grade	Kemaus
Calcium nitrate tetrahydrate	$Ca(NO_3)_2 \cdot 4H_2O$	>99%	Sigma-Aldrich
Cerium(III) nitrate hexahydrate	$Ce(NO_3)_3 \cdot 6H_2O$	Extra pure	Merck
Ethanol	C_2H_5OH		Merck
Hydrochloric acid	HCl		Merck
Lanthanum(III) nitrate hexahydrate	$La(NO_3)_3 \cdot 6H_2O$	99.99%	Sigma-Aldrich
Magnesium nitrate hexahydrate	$Mg(NO_3)_2 \cdot 6H_2O$	Grade AR	Qrec
Nickel(II) nitrate hexahydrate	$Ni(NO_3)_2 \cdot 6H_2O$	99%	LOBA CHEMIE
Samarium(III) nitrate hexahydrate	$Sm(NO_3)_3 \cdot 6H_2O$	99.9%	Sigma-Aldrich
Toluene	C_7H_8		Merck

3.2 The preparation of support

3.2.1 The pretreatment of γ - Al_2O_3 supports by calcination method

The commercial γ - Al_2O_3 as support was pretreated by calcination method. Calcination is used as the thermal pretreatment for alumina phase change. The alumina was put into boat and inserted to tube furnace. Operation was made under air flow of 95 ml/min, ramp rate 10°C/min, temperature set point 800°C and hold for 4 hours.

3.2.2 The preparation of Al_2O_3 supports by sol-gel method

The Al_2O_3 as support was prepared by Sol-gel. First, the aluminum isopropoxide as precursor was dissolved in a mixture of ethanol and deionized water with a volume ratio of 1:1 under stirring at 80°C for 1 hour. After that, the temperature of the solution was increased to 90°C and dropped hydrochloric acid until pH value is equal to 2.5 and continuous stirring at 90°C. After that, the solution has become viscous. The formed gel was dried overnight at 110°C and calcined under air flow at 550°C for 2 hours.

3.3 The preparation of catalysts

The first series of catalysts were prepared to study the effect of Nickel loading. The Ni-based catalysts with Ni loadings of 10 wt%, 7.5 wt%, 5 wt%, and 2.5 wt% were impregnated on Al_2O_3 supported. The second series of the catalysts were prepared to study the effect of promoters such as Calcium (Ca), Cerium (Ce), Lanthanum (La), Magnesium (Mg) and Sumarium (Sm).

3.3.1 The preparation of catalyst by the incipient wetness impregnation method

The Ni catalysts were prepared by the incipient wetness impregnation method using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Start with dissolving $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized water. After that, the solution was dropped to cover the support (Al_2O_3). Next, the catalysts were dried overnight at 110°C . Finally, they were calcined under an air flow at 550°C for 2 hours.

As for the catalyst with the promoter, metal nitrate precursor was dissolved in deionized water at room temperature at a fixed amount of 0.5 wt% of each metal promoter. The solution was mixed with the $\gamma\text{-Al}_2\text{O}_3$, the slurry was dried overnight at 110°C , then it was calcined under an air flow at 550°C for 2 hours. After calcination of the promoter- $\gamma\text{-Al}_2\text{O}_3$ support, nickel precursor was dissolved in deionized water at room temperature at a fixed amount of 5 wt% followed by incipient wetness impregnation. Finally, the slurry was dried overnight at 110°C , then it was calcined under an air flow at 550°C for 2 hours again.

3.4 The characterization of catalysts

3.4.1 Nitrogen physisorption

Nitrogen physisorption require 0.05 to 0.1 grams of catalyst for each sample. The sample that was dried to remove the moisture. N_2 adsorption-desorption isotherm using Micromeritics ASAP 2020 at liquid nitrogen temperature of -196°C . The Brunauer–Emmett–Teller (BET) method is used for the determination of surface area. The Barret-Joyner-Halenda (BJH) method is used to determine the pore diameter and pore volume of the catalysts.

3.4.2 Scanning Electron Microscope (SEM) and energy x-ray spectroscopy (EDX)

A scanning electron microscope (SEM) used to determine the morphology structure of sample and energy x-ray spectroscopy (EDX) determine metal dispersion over the catalysts surface. The sample was studied by JEOL JSM-35. The SEM model was JEOL mode JSM-5800LV and Link Isis Series 300 program was performed for EDX.

3.4.3 X-ray diffraction (XRD)

The crystalline phase of catalysts was characterized by X-ray diffraction (XRD) analysis, that used an X-ray diffractometer SIEMENS D5000 connected to a personal computer with Diffract AT version 3.3 program for full control of XRD analyzer. The XRD analysis was conducted to Cu-K α radiation between 20° and 80° with a generator voltage and current of 30 kV and 30 mA, respectively. The scan step was 0.06°. The scan speed was 0.5°.

3.4.4 Thermogravimetric analysis (TGA)

The sample was subjected to thermogravimetric analysis (Diamond Thermogravimetric and Differential Analyzer, TA Instruments SDT Q600) to determine carbon deposition, while their thermal behaviors in the range of room temperature to 1000°C. The analysis was operated at a heating rate of 10°C/min in 100 mL/min in synthetic air flow.

3.4.5 Hydrogen Temperature Programmed Reduction (H₂-TPR)

Temperature Programmed Reduction of Hydrogen (H₂-TPR) using Micromeritics chemisorp 2750 Pulse Chemisorption System. The reducing temperatures use to prepared catalysts. In an experiment, about 0.05 grams of the catalyst is placed in a quartz tube and pretreated at 250°C in a flow of nitrogen. The sample is reduced

with 10% H_2 /Ar. Then the sample was heated from 30 to 800°C at a heating rate of 10°C /min. The amount of hydrogen consumed is measured via the TCD signal, which is a function of temperature.

3.4.6 Ammonia temperature program desorption (NH_3 -TPD)

The surface acidity determination of the catalyst was examined by Temperature Programmed Adsorption of Ammonia (NH_3 -TPD) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. In an experiment, 0.05 grams of the catalyst sample is placed in a quartz tube and pretreated at 250°C in a flow of helium at 1 hour. The sample was adsorbed with 15% NH_3 /He. After that the sample was heated from 30 to 800°C at a heating rate 10°C/min so that ammonia was desorbed in a helium gas flow. The strong acid site will release the basic at high temperatures. The amount of ammonia consumed measured via TCD signal, which is a function of temperature.

3.4.7 Carbon dioxide temperature program desorption (CO_2 -TPD)

The surface basic determination of the catalyst was examined by Temperature Programmed Adsorption of Carbon dioxide (CO_2 -TPD) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. In an experiment, 0.05 grams of the catalyst sample is placed in a quartz tube and pretreated at 250°C in a flow of helium at 1 hour. The sample was adsorbed with carbon dioxide 1 hour. After that the sample was heated from 30 to 800°C at a heating rate 10°C/min. So that carbon dioxide was desorbed in a helium gas flow. The strong basic site will release the acid at high temperatures. The amount of carbon dioxide consumed measured via TCD signal, which is a function of temperature.

3.4.8 Hydrogen chemisorption (H₂-CHEM)

Hydrogen chemisorption technique was used to study the number of active metal sites and metal dispersion. In this method, it used Micrometric's Chemisorb 2750 and ASAP 2101CV.3.00 software unit fitted with a Thermal Conductivity Detector (TCD). In an experiment, 0.05 grams of the catalyst sample is placed in a quartz tube and reduced at 500°C for 1 hour with 25 ml/min of hydrogen flow. After that cooled down to 100°C that was adsorbed temperature. Last, 10 μ l of hydrogen was injected into the catalyst and repeat until desorption peak constant. Amount of hydrogen adsorption on catalyst was relative amount of active site.

3.5 Performance of catalysts for dry or bi reforming of methane

3.5.1 Gas materials for reaction

Gas materials that were used for the catalytic testing are listed in Table 3.2

Table 9 Gas materials for reaction

Gas material or reagent	Purity	Supplier
Ultra-high purity methane	99.99%	The Linde group
High purity carbon dioxide	99.99%	Bangkok industrial gas
Ultra-high purity grade argon	99.999%	The Linde group
Ultra-high purity grade nitrogen	99.999%	The Linde group
Ultra-high purity grade hydrogen	99.999%	The Linde group

3.5.2 Instrument and apparatus

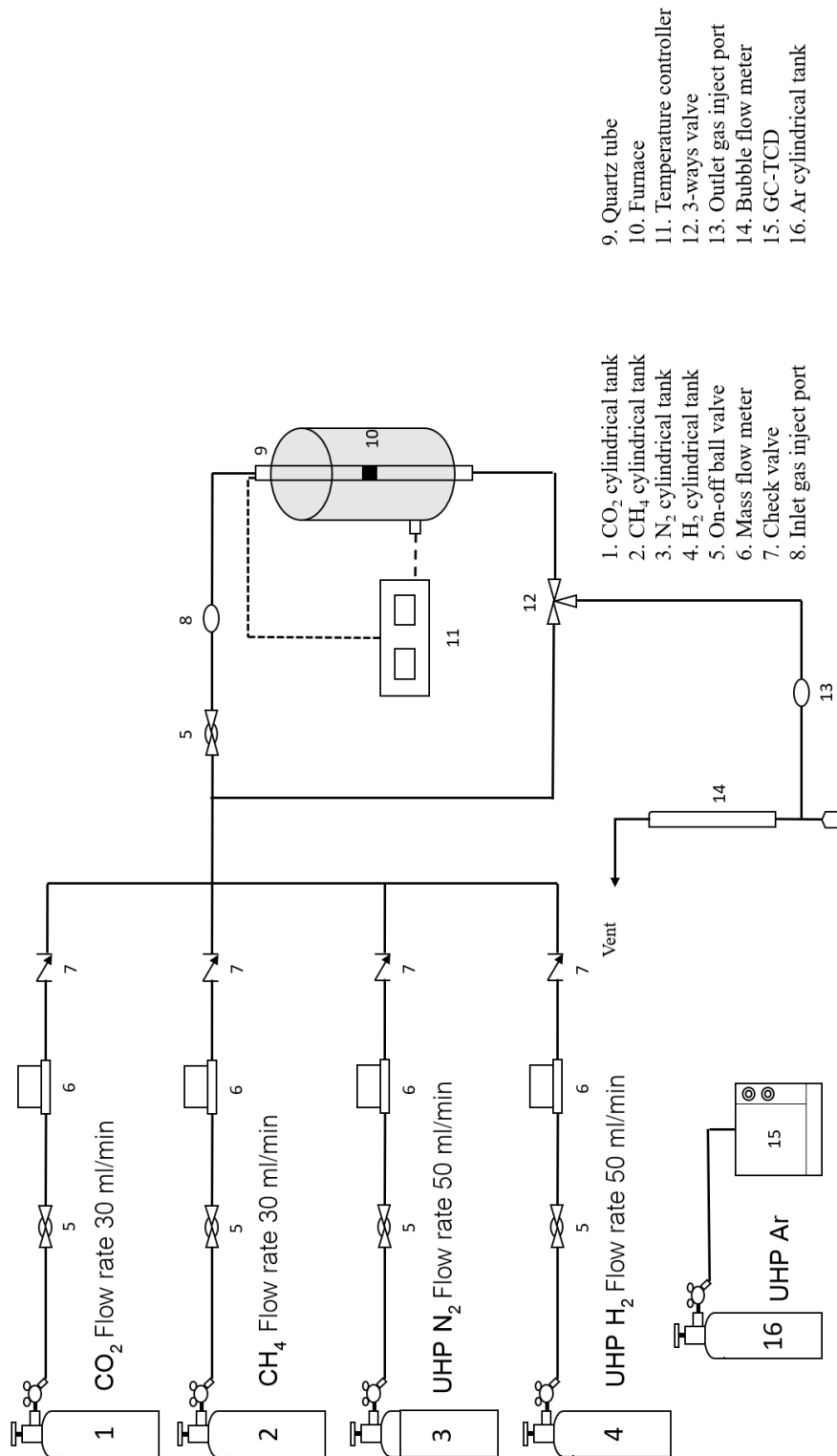


Fig 3 Dry reforming of methane's scheme diagram

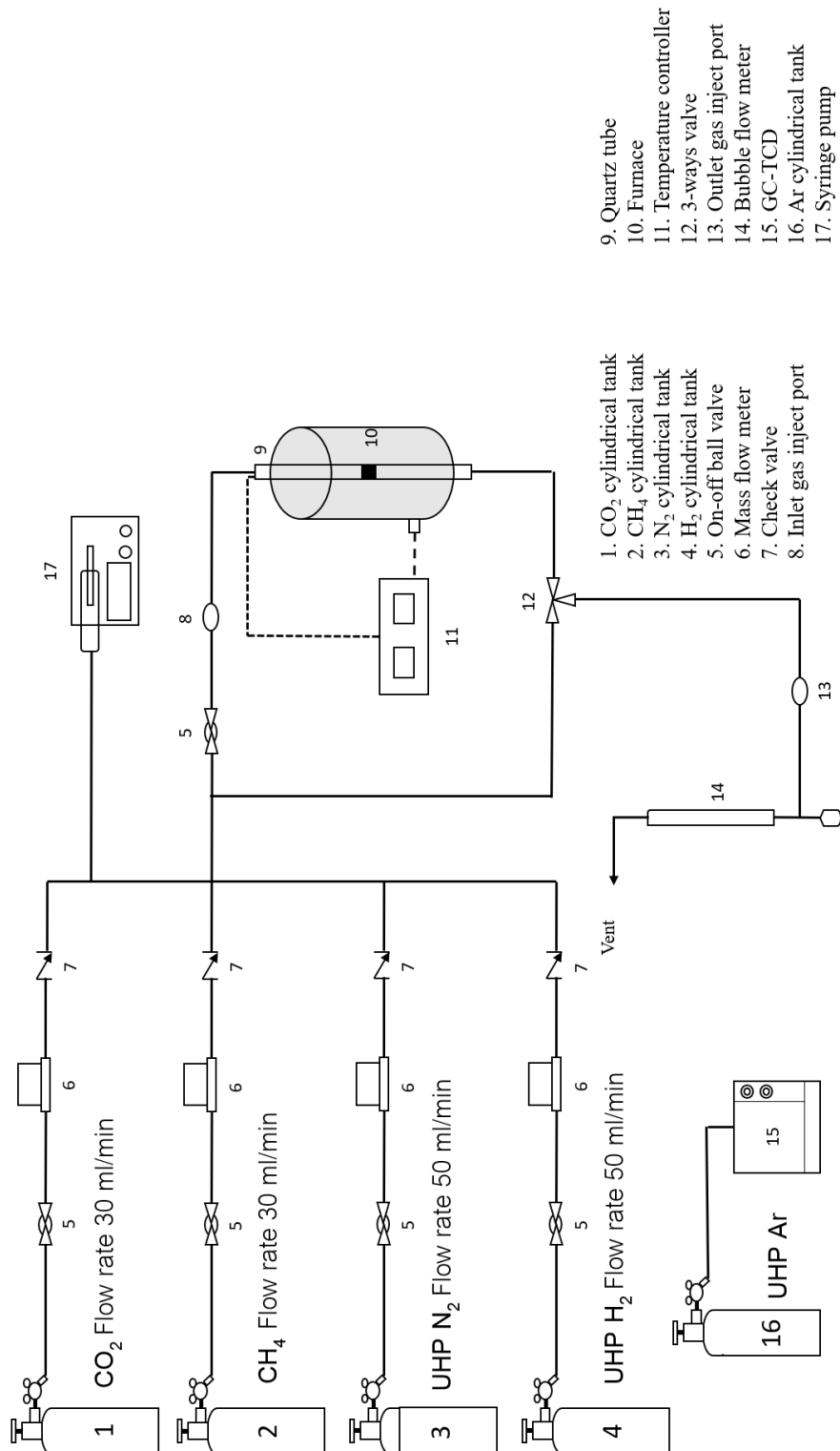


Fig 4 Bi-reforming of methane's scheme diagram

From Fig 3.1-3.2 the experimental setup that tested the performance of the catalyst consist of;

Reactor: The reactor is a fixed-bed continuous-flow quartz reactor. The quartz tube length 47 mm, inner diameter 9 mm, and outside diameter 12 mm.

Temperature controller: The temperature controller connected to a thermocouple in the fixed-bed continuous-flow quartz reactor to control the furnace temperature. The temperature within the range between 30°C to 1000°C

Furnace: The catalysts was heated by the furnace, that was controlled by the temperature controller.

Gas chromatography (GC): The gas chromatography was used to analyze the gas inlet and gas outlet compounds. That was operating under conditions in Table 3.3

Syringe pump: The syringe pump was used to feed steam into reaction that require very small fluid.

Table 10 Gas chromatography operating conditions.

Gas chromatography	Shimudzu, GC-8A	
Detector	TCD	TCD
Column	Porapack-Q	Molecular sieve 5A
Carrier gas	Argon	Argon
Column temperature; initial	70°C	70°C
Column temperature; Final	70°C	70°C
Detector temperature	150°C	150°C
Injector temperature	150°C	150°C
Current	70 mA	70 mA
Analyzed gas	CO ₂	H ₂ , CH ₄ , CO

3.5.3 Reaction method

Dry reforming of methane and bi-reforming of methane were carried out in a fixed-bed continuous-flow quartz reactor. (quartz tube, length 47 mm, inner diameter 9 mm, and outside diameter 12 mm). The reactor had a K-type thermocouple at the middle of the catalyst bed to control the reactor temperature. The portion of 0.1 grams of catalysts was put between quartz wool at the middle of the quartz reactor. Before starting reaction, the catalyst was reduced by hydrogen at 500°C for 1 hour. After that, flow 50ml/min of nitrogen to replace hydrogen and heated reaction temperature to 700°C with a heating rate of 10°C/min. The feed volumetric flow rate for CH₄ of 30 ml/min and CO₂ of 30 ml/min and N₂ of 50 ml/min were adopted to test the catalyst performance for 3 hours. In case of Bi-reforming of methane, water was added into the system. The product samples were injected into Thermal Conductivity Detector type gas chromatograph (Shimudzu, GC-8A) every 15 minutes. Porapak-Q packed column was used to analyze CO₂ and Molecular sieve 5A for H₂, CH₄, and CO. Finally, the used catalysts were analyzed for coke formation.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter consists of two parts. The first part deals with the catalysts characterization by x-Ray diffraction pattern (XRD), nitrogen adsorption-desorption, scanning electron microscopy (SEM), ammonia temperature program desorption (NH₃-TPD), carbon dioxide temperature program desorption (CO₂-TPD), hydrogen chemisorption and thermogravimetric analysis (TGA). The second study the performance of the catalyst that can be classified into three section: (1) effect of nickel loading, (2) effect of temperature, and (3) effect of promoter.

4.1. Catalysts characterization

4.1.1 N₂-physisorption

The main parameters that affect the catalyst are surface area and pore volume and the pore diameter (Table 11). The surface area and pore volume decreased when increasing the amount of nickel [30]. The type of porosity can be described in isotherms (Fig 5). All isotherms of the sample can be classified as isotherm type IV by IUPAC. The mesoporous structure has a pore size between 2-50 nm, causing multi-layer adsorption and the condensation of gas in the pores.

Table 12 is shows BET surface area, pore volume, and pore size of the promoters containing catalysts. It had been found that adding promoter as small as 0.5wt% did not significant affect the BET surface area.

Table 11 BET surface area, pore volume, and pore size of support and catalysts.

Catalysts	BET surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Average pore diameter ^b (nm)
Al ₂ O ₃	112.45	0.249	5.43
2.5%Ni/Al ₂ O ₃	102.31	0.224	5.39
5%Ni/Al ₂ O ₃	100.43	0.218	5.26
7.5%Ni/Al ₂ O ₃	93.59	0.202	5.28
10%Ni/Al ₂ O ₃	85.47	0.184	5.14

^a BJH desorption pore volume^b BJH desorption average pore diameter**Table 12** BET surface area, pore volume, and pore size of support and promoter-containing catalysts.

Catalysts	BET surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Average pore diameter ^b (nm)
Al ₂ O ₃	112.45	0.249	5.43
5%Ni/Al	100.43	0.218	5.26
5%Ni(0.5%Ca/Al)	93.69	0.199	5.33
5%Ni(0.5%Mg/Al)	100.75	0.212	5.27
5%Ni(0.5%La/Al)	105.39	0.216	5.06
5%Ni(0.5%Sm/Al)	102.09	0.213	5.00
5%Ni(0.5%Ce/Al)	106.17	0.216	5.06

^a BJH desorption pore volume^b BJH desorption average pore diameter

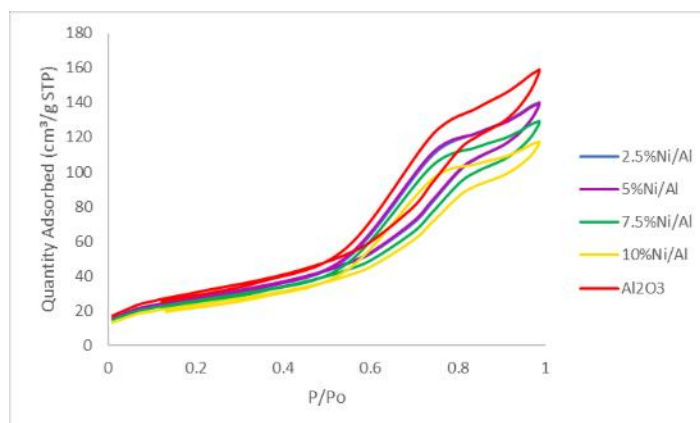


Fig 5 N₂ adsorption-desorption isotherm of γ -Al₂O₃, 10%Ni/Al₂O₃, 7.5%Ni/Al₂O₃, 5%Ni/Al₂O₃, 2.5%Ni/Al₂O₃)

4.1.2 X-Ray diffraction pattern

The study of crystal structure and phase using X-ray (XRD) is shown in Fig 6. It has been found that the XRD patterns of gamma-alumina showed the specific sharp peaks at $2\theta=36.9^\circ$, 39.5° , 45.9° , and 67.0° [18]. When adding nickel, it showed the of NiO at $2\theta = 37.2^\circ$, 43.3° and 62.8° indicating that the (111), (200), and (220) diffractions planes of NiO[31] are present.

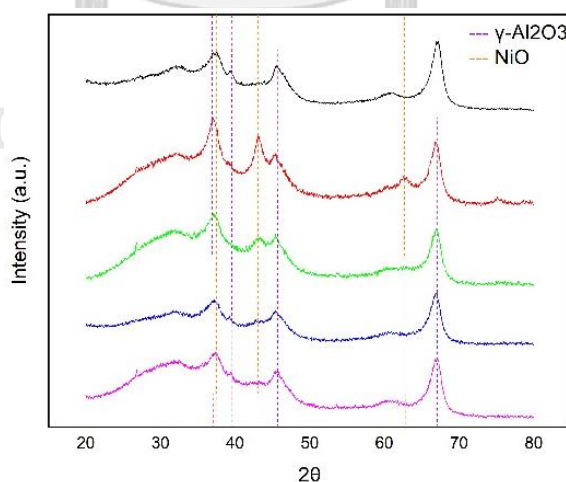


Fig 6 X-ray diffraction pattern of N catalyst supported on γ -Al₂O₃ (a: γ -Al₂O₃, b: 10%Ni/Al₂O₃, c: 7.5%Ni/Al₂O₃, d: 5%Ni/Al₂O₃, e: 2.5%Ni/Al₂O₃)

4.1.3 EDX analysis

From Fig 7, SEM-EDS shows high Ni dispersion with no large Ni metallic particle. Similarly, Fig 8 shows high Ni dispersion and the appearance of the promoters added on the catalyst. The peaks of the promoters were not noticed in their XRD patterns, probably due to too little quantity. However, the metal dispersion cannot be concluded unless the amount of adsorbed hydrogen from H₂ chemisorption is taken into account.

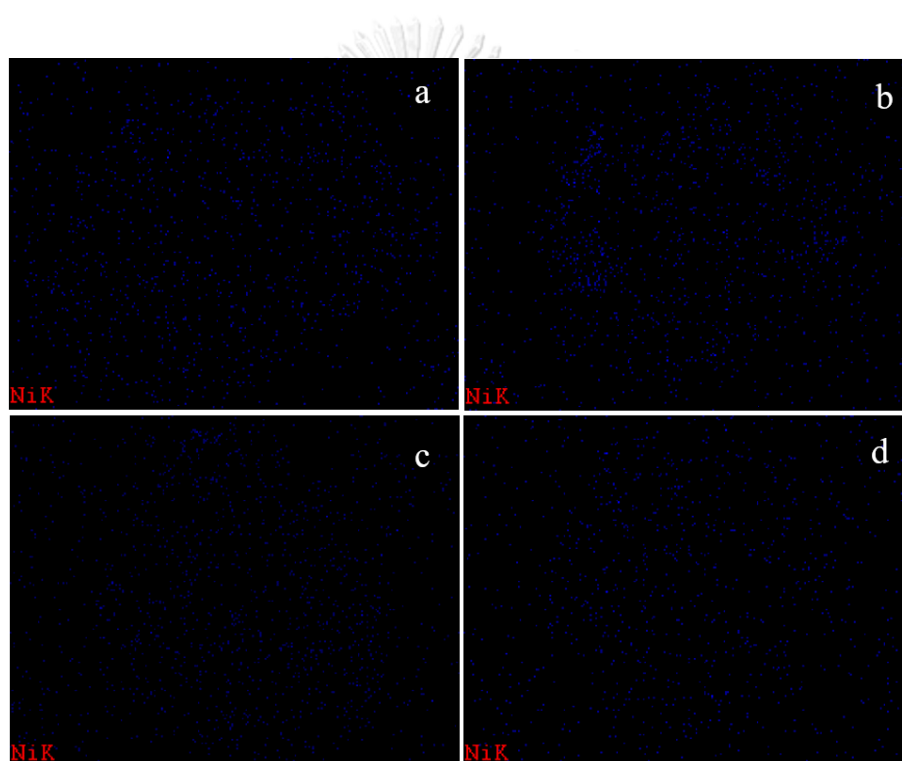


Fig 7 SEM-EDS images of fresh catalysts (a: 10%Ni/Al₂O₃, b: 7.5%Ni/Al₂O₃, c: 5%Ni/Al₂O₃, d: 2.5%Ni/Al₂O₃)

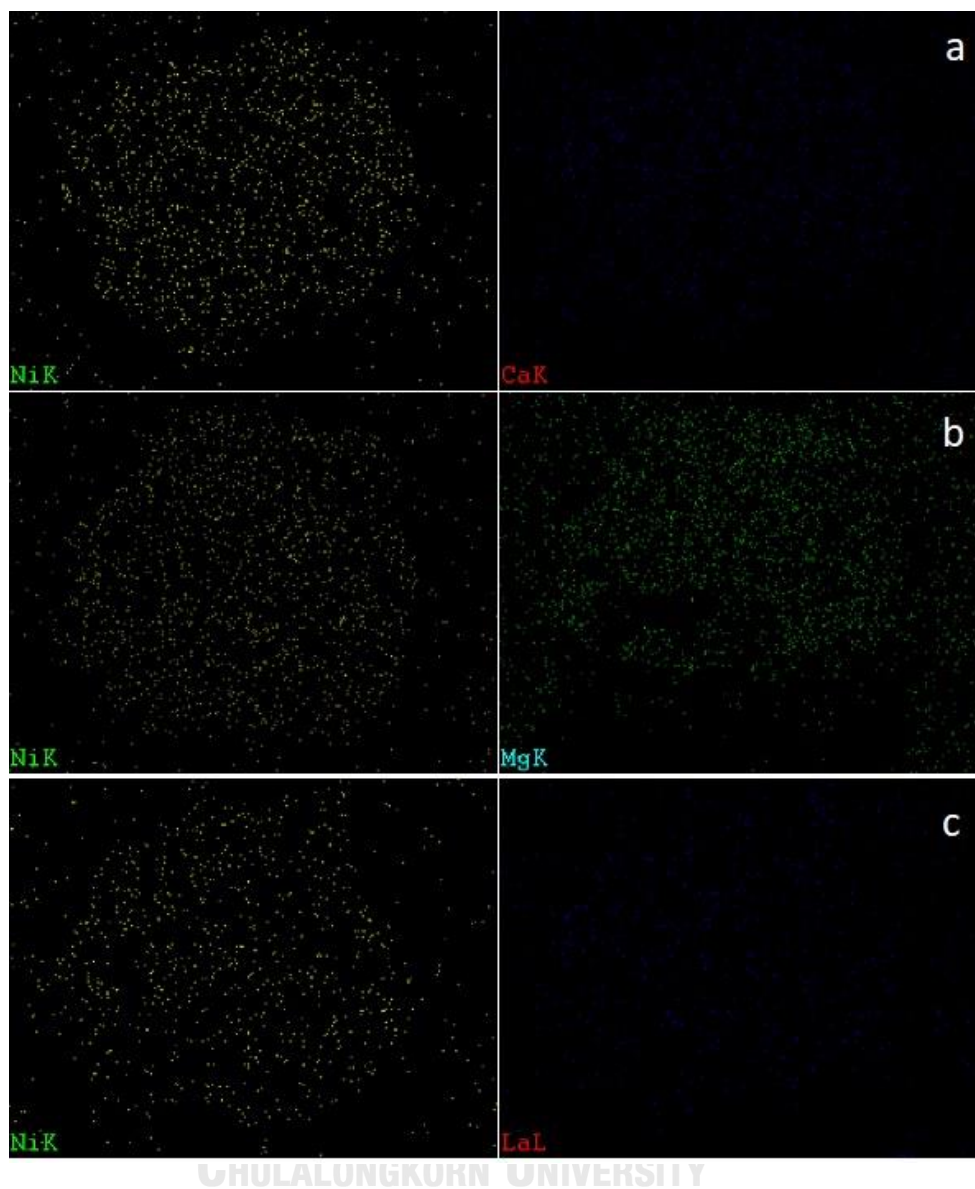


Fig 8 SEM-EDS images of fresh catalysts (a: 5%Ni(0.5%Ca/Al₂O₃),
b: 5%Ni(0.5%Mg/Al₂O₃), c: 5%Ni(0.5%La/Al₂O₃), d: 5%Ni(0.5%Sm/Al₂O₃),
e: 5%Ni(0.5%La/Al₂O₃))

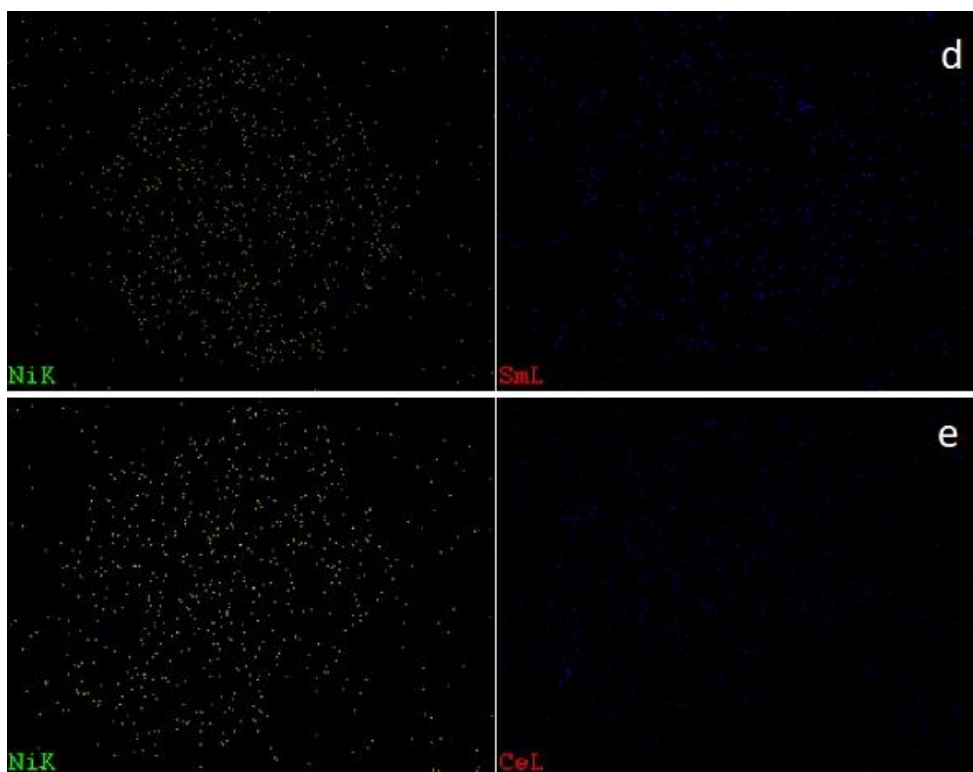


Fig 8. SEM-EDS images of fresh catalysts (a: 5%Ni(0.5%Ca/Al₂O₃),
 b: 5%Ni(0.5%Mg/Al₂O₃), c: 5%Ni(0.5%La/Al₂O₃), d: 5%Ni(0.5%Sm/Al₂O₃),
 e: 5%Ni(0.5%La/Al₂O₃)) (Continue)

4.1.4 Temperature program desorption

As shown in Table 13, the acidity of the catalysts follows the order 10%Ni/Al₂O₃ > 2.5%Ni/Al₂O₃ > 5%Ni/Al₂O₃ > 7.5%Ni/Al₂O₃. The basicity of the catalysts follows the order 2.5%Ni/Al₂O₃ > 10%Ni/Al₂O₃ > 5%Ni/Al₂O₃ > 7.5%Ni/Al₂O₃. The catalyst containing the lowest acidity may contribute to good stability [32]. The decreasing acidity improved the performance of the catalyst since acid surfaces are responsible for carbon deposition via hydrocarbon cracking [33]. The high basicity promotes dissociative adsorption of CO₂, resulting in the suppression of carbon formation by producing a higher number of oxygen atoms near the catalytic active metal surface [6]. Table 14 and 15 show the amount of acidity and basicity of all the promoter-containing catalysts, which will be discussed in the part of the catalyst test.

Table 13 The amount of acidity and basicity of all catalysts

Catalysts	Total acid site	Total basic site
	(micromole NH ₃ /g _{catalyst})	(micromole CO ₂ /g _{catalyst})
2.5%Ni/Al ₂ O ₃	1116.11	46.88
5%Ni/Al ₂ O ₃	1066.50	42.03
7.5%Ni/Al ₂ O ₃	1052.47	39.28
10%Ni/Al ₂ O ₃	1150.40	45.69

Table 14 The amount of acidity of all promoter-containing catalysts

Catalyst	Acid site (micromole NH ₃ /g _{catalyst})			
	week	medium	strong	total
5%Ni/Al	295.20	287.71	483.59	1066.50
5%Ni(0.5%Ca/Al)	240.47	218.26	496.35	955.08
5%Ni(0.5%Mg/Al)	135.71	282.78	517.56	936.05
5%Ni(0.5%La/Al)	208.78	243.93	600.45	1053.16
5%Ni(0.5%Sm/Al)	224.86	235.50	690.87	1151.23
5%Ni(0.5%Ce/Al)	280.22	210.16	656.75	1147.13

Table 15 The amount of basicity of all promoter-containing catalysts

Catalyst	Basic site (micromole CO ₂ /g _{catalyst})			
	Weak	medium	strong	total
5%Ni/Al	3.37	10.20	28.46	42.03
5%Ni(0.5%Ca/Al)	6.01	13.43	25.88	45.32
5%Ni(0.5%Mg/Al)	5.25	20.86	17.30	43.41
5%Ni(0.5%La/Al)	6.31	12.21	21.01	39.53
5%Ni(0.5%Sm/Al)	5.28	14.03	27.10	46.41
5%Ni(0.5%Ce/Al)	5.19	18.91	26.81	50.91

4.2 Catalyst test

The catalysts performance test that can be classified into three parts: (1) effect of preparation method, (2) effect of temperature (3) effect of nickel loading, and (4) effect of promoters. The carbon dioxide and methane conversions and H₂/CO ratio are shown as a function of time on stream. The catalytic stability test for dry reforming of methane over all the catalysts was studied at CO₂/CH₄ ratio of 1, and bi-reforming of methane was studied at CO₂/CH₄/H₂O ratio of 1 for 3 hours on stream.

4.2.1 Effect of preparation method

The catalyst test for dry reforming of methane was performed at 700°C. The 5% nickel supported over the γ -Al₂O₃ catalyst was prepared by sol-gel and incipient wetness impregnation methods. According to Fig 9., the catalyst prepared by the incipient wetness impregnation method had higher conversions of CO₂ and CH₄ than those of the catalyst prepared by the sol-gel method. It has also been found the catalyst prepared by the incipient wetness impregnation method had lower coke deposition (ca. 3.06%) than that in case of the sol-gel method (ca. 7.8%).

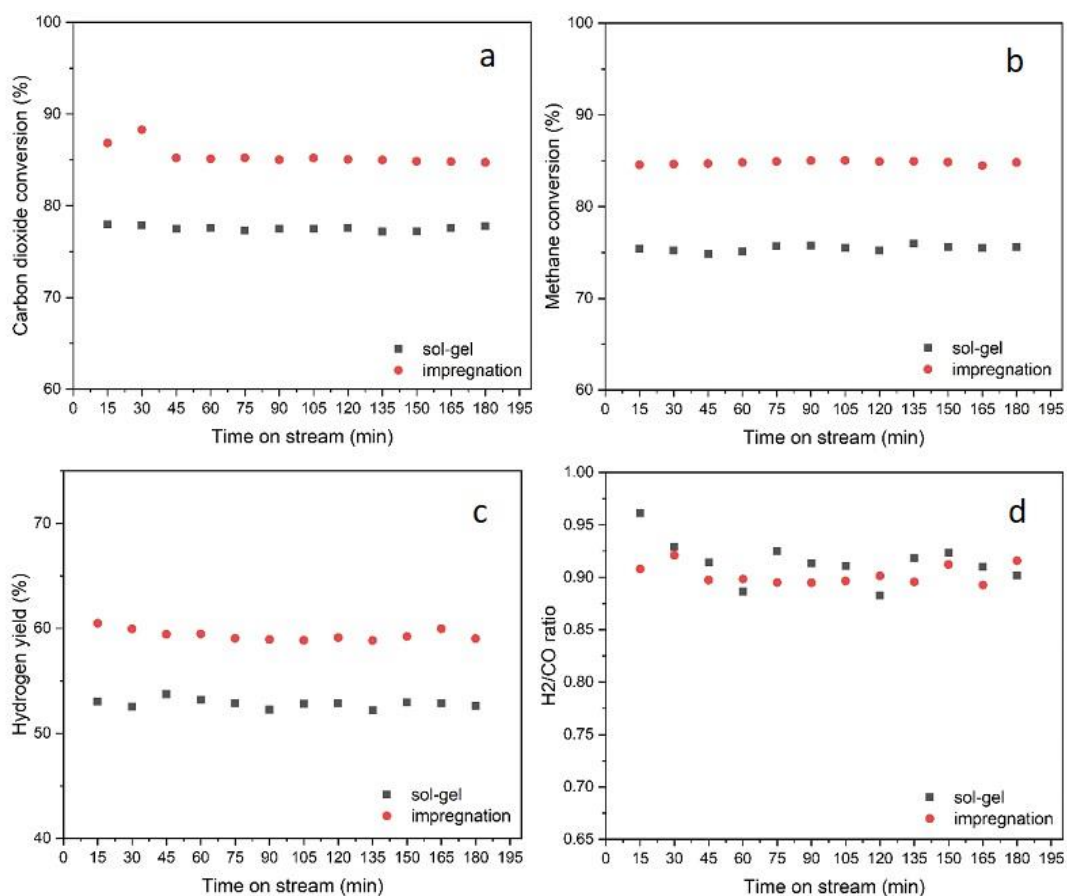


Fig 9 Catalyst performance of (a) CO₂ conversion, (b) CH₄ conversion, (c) H₂ yield, and (d) H₂/CO ratio for the effect of method of dry reforming of methane

4.2.2 Effect of temperature

The effect of reaction temperature on the activity of 5% nickel loading catalyst was studied. The CO₂ and CH₄ conversions, H₂ yield, and H₂/CO ratio during the temperature range of 500-800°C, respectively as shown in Fig 10. Both CO₂ and CH₄ conversions increased with the increasing temperature. The CO₂ and CH₄ conversions at 15 min-on-stream were increased from 20.48% and 9.33% at 500°C to 85.05% and 82.91%, respectively, at 800°C. This may be attributed to the naturally endothermic reaction of dry reforming of methane that will be more efficient at high temperatures [34, 35]. After 3 hours of reaction, it was found that both CO₂ and CH₄

conversions remained almost stable ($\sim 80\%$) at 700°C . Therefore, the reaction temperature of 700°C was found to be the optimum temperature for the catalyst test. The CH_4 conversion was slightly lower than CO_2 conversion at any temperature, probably due to the reverse water gas shift reaction [4, 6, 21].

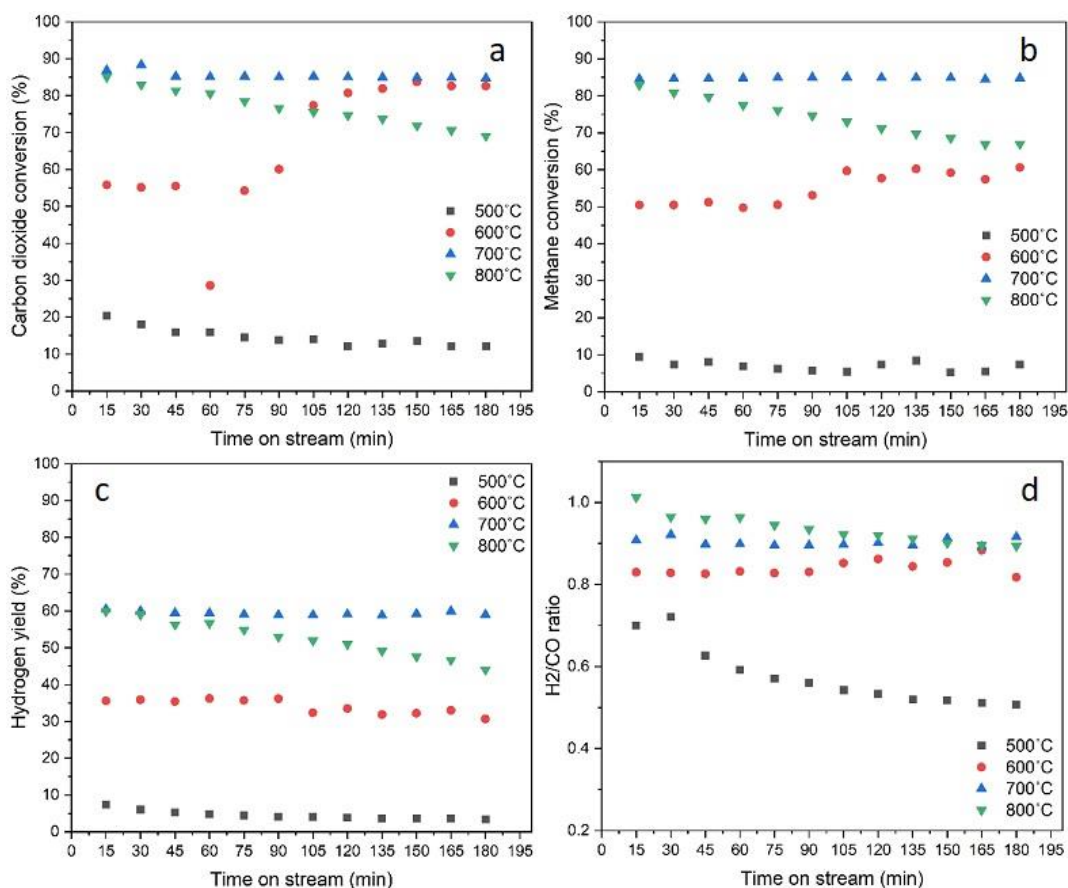


Fig 10 Catalyst performance of (a) CO_2 conversion, (b) CH_4 conversion, (c) H_2 yield, and (d) H_2/CO ratio for the effect of reaction temperature of dry reforming of methane

4.2.3 Effect of nickel loading

The catalyst was prepared by incipient wetness impregnation and studied at 700°C, as shown in Fig 11. Dry reforming of methane had significantly stable CO₂ and CH₄ conversions as noticed from time on stream test. The 5%Ni/Al₂O₃ and 7.5%Ni/Al₂O₃ catalysts exhibited similar CO₂ conversions of 87.82% and 86.84%, respectively. As for CH₄ conversion, it was found that 5%Ni/Al₂O₃ had a higher conversion (84.56%) than that of 7.5%Ni/Al₂O₃ (71.40%).

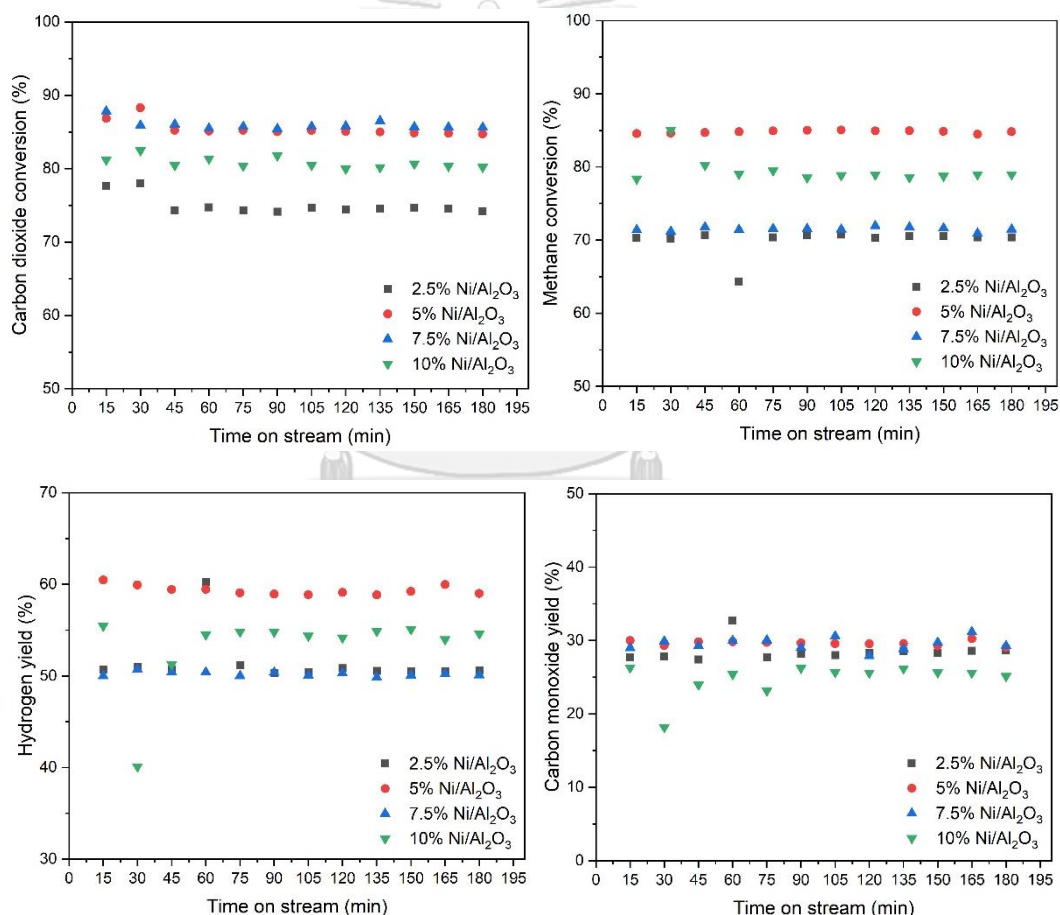


Fig 11 Catalyst performance of (a) CO₂ conversion, (b) CH₄ conversion, (c) H₂ yield, and (d) CO yield for dry reforming of methane

Dry reforming has the limitations in terms of the H_2/CO ratio; thus, the bi-reforming was studied. In the bi-reforming, reaction conditions were controlled to be comparable to that of the dry reforming. The catalytic stability test for bi-reforming of methane over catalysts was studied at the $CO_2/CH_4/H_2O$ ratio of 1. For bi-reforming of methane (Fig 12), the CH_4 conversion was higher than that of the CO_2 conversion. The bi-reforming had a higher H_2 yield than that of dry reforming. The improvement of methane conversion can be attributed to the presence of steam reforming as a parallel reaction, which also helps to enhance the hydrogen yield [4, 21]. Fig 13 indicates that bi-reforming has H_2/CO ratio close to 2.

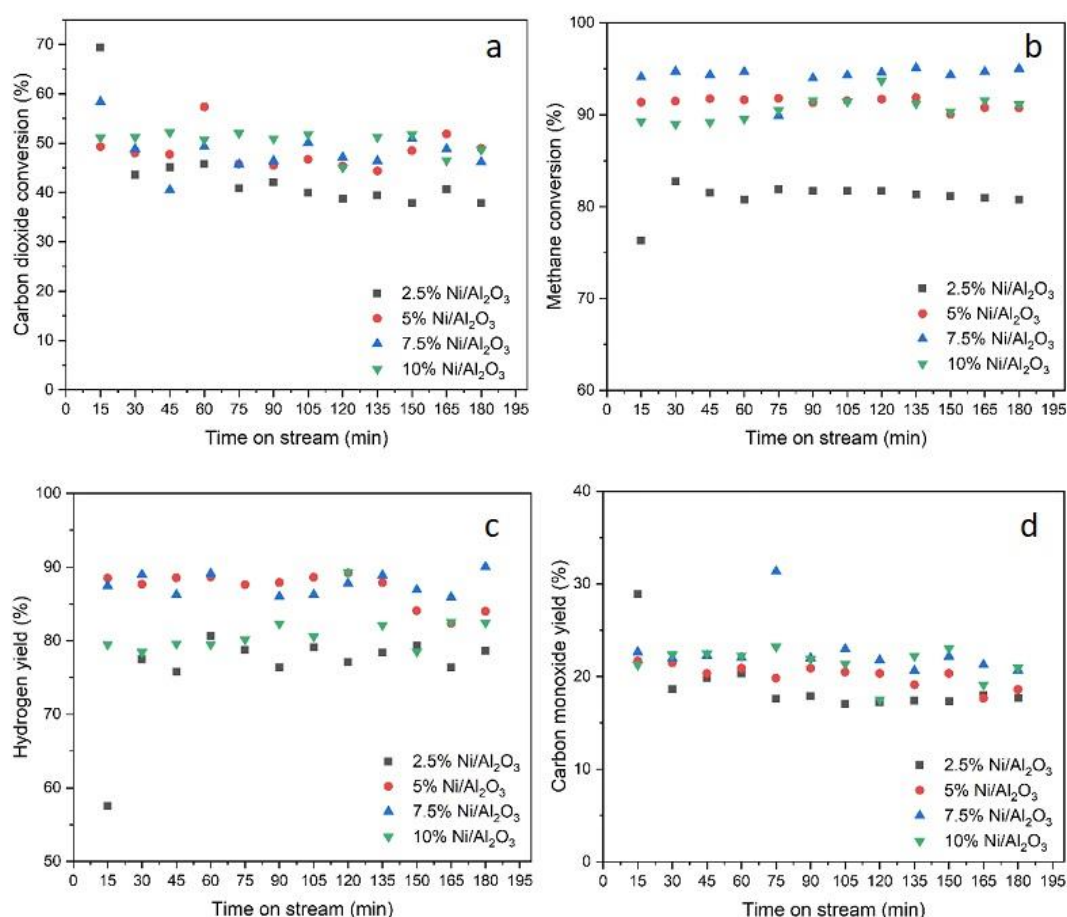


Fig 12 Catalyst performance of (a) CO_2 conversion, (b) CH_4 conversion, (c) H_2 yield, and (d) CO yield for bi-reforming of methane

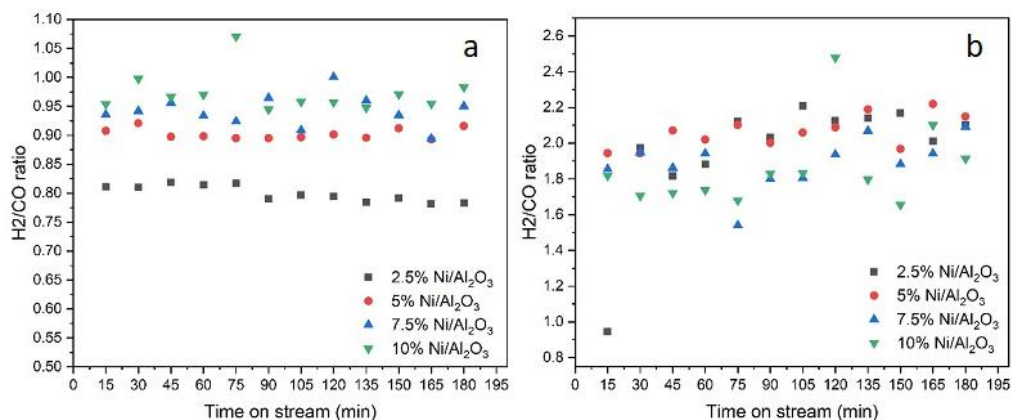


Fig 13 Catalyst performance of (a) H₂/CO ratio of dry reforming of methane, and (b) H₂/CO ratio of bi-reforming of methane

The thermogravimetric analysis with heating temperature ranging from room temperature to 1000°C was used to investigate the total coke deposition of the used catalysts, and the coke characteristic was classified into two types according to the temperature used to eliminate carbon. Coke type I consists of adsorbed atomic carbon (C_α), polymeric carbon film (C_β), and nickel carbide (bulk, C_γ) of carbon formed at low temperatures. Coke type II consists of whiskers (C_ν) and graphitic (C_ε) of carbon form at high temperatures, as shown in Table 16-17. It has been found that when increasing the nickel loading, coke type II increased. In case of bi-reforming of methane, coke type II was found starting from 2.5%Ni, but 7.5%Ni and 10%Ni have type II less than in the case of dry reforming of methane. In case of dry reforming of methane, coke type II was not found at 2.5%Ni and 5%Ni loading. As for bi-reforming of methane, coke type II was found starting from 2.5%Ni with less amount than that in case of dry reforming of methane for 7.5%Ni and 10%Ni loading. Bi-reforming of methane seemed to reduce the generation of coke type I. Deactivation of catalysts at high reaction temperatures may be caused by carbon block on the active sites at the Ni surface layers. This may obstruct the contact between H₂O and hydrocarbon, causing no decrease of coke formation[36]. When the amount of coke type I was

low, both CO₂ and CH₄ conversions were for both dry and bi-reforming of methane high. Therefore, coke type I should be controlled to maintain the stability of the catalyst.

Table 16 Coke deposition of the spent catalyst after 3 hours of dry reforming of methane reaction

Catalysts	Coke deposition	Form of carbon species	
	(%)	Group of C _α , C _β , C _γ	Group of C _c , C _v
2.5%Ni/Al ₂ O ₃	2.98	100%	-
5%Ni/Al ₂ O ₃	3.06	100%	-
7.5%Ni/Al ₂ O ₃	4.17	63.04%	36.96%
10%Ni/Al ₂ O ₃	2.35	57.01%	42.99%

Table 17 Coke deposition of the spent catalyst after 3 hours of bi-reforming of methane reaction

Catalysts	Coke deposition	Form of carbon species form	
	(%)	Group of C _α , C _β , C _γ	Group of C _c , C _v
2.5%Ni/Al ₂ O ₃	3.25	93.08%	6.92%
5%Ni/Al ₂ O ₃	3.06	86.95%	13.05%
7.5%Ni/Al ₂ O ₃	2.30	75.47%	24.53%
10%Ni/Al ₂ O ₃	2.16	59.10%	40.90%

4.2.4 Effect of promoters

The catalysts were doped with promoters on the support using incipient wetness impregnation method. Promoters are divided into two groups, which are alkaline earth metals (Ca and Mg) and lanthanide series (La, Sm, and Ce). From Table 18, in case of dry reforming of methane, both CO₂ and CH₄ conversions of calcium-containing catalyst were higher than those of the catalyst without the promoter. All Lanthanide series had lower conversion than those without promoters and lower than alkaline earth metal. In case of bi-reforming of methane, both groups of promoters had lower CO₂ and CH₄ conversions than those without the promoters except the samarium (Sm) that had slightly increase of CH₄ conversion.

Table 18 CO₂ and CH₄ conversion after 3 hours of operation

Catalyst	DRM		BRM	
	CO ₂ conversion	CH ₄ conversion	CO ₂ conversion	CH ₄ conversion
5%Ni/Al	84.7%	84.8%	48.9%	90.7%
5%Ni(0.5%Ca/Al)	94.5%	85.7%	44.4%	87.0%
5%Ni(0.5%Mg/Al)	79.8%	73.6%	46.9%	90.6%
5%Ni(0.5%La/Al)	74.3%	72.2%	44.3%	89.4%
5%Ni(0.5%Sm/Al)	76.2%	75.5%	43.0%	91.4%
5%Ni(0.5%Ce/Al)	75.4%	73.0%	40.6%	86.8%

Table 19 Coke deposition of the spent catalyst after 3 hours of dry reforming of methane reaction

Catalysts	Coke deposition (%)	Form of carbon species	
		Group of C α , C β , C γ	Group of C c , C v
5%Ni/Al ₂ O ₃	3.06	100%	-
5%Ni(0.5%Ca/Al)	4.05	60.25%	39.75%
5%Ni(0.5%Mg/Al)	2.17	58.06%	41.94%
5%Ni(0.5%La/Al)	2.66	70.80%	29.18%
5%Ni(0.5%Sm/Al)	2.86	87.17%	12.83%
5%Ni(0.5%Ce/Al)	3.67	84.52%	15.48%

Table 20 Coke deposition of the spent catalyst after 3 hours of bi-reforming of methane reaction

Catalysts	Coke deposition (%)	Form of carbon species	
		Group of C α , C β , C γ	Group of C c , C v
5%Ni/Al ₂ O ₃	3.06	86.95%	13.05%
5%Ni(0.5%Ca/Al)	3.94	85.79%	14.21%
5%Ni(0.5%Mg/Al)	3.53	80.20%	19.80%
5%Ni(0.5%La/Al)	3.97	90.01%	9.99%
5%Ni(0.5%Sm/Al)	3.40	87.38%	12.62%
5%Ni(0.5%Ce/Al)	4.10	90.14%	9.86%

Both CO₂ and CH₄ conversions were affected by acid site (Table 14), basic site (Table 15), amount of coke, and amount of carbon species form (Table 19 and 20). Dry reforming of methane on alkaline earth-containing catalysts was found to have weak acid site decrease and weak basic site increase, with the increase of coke type II. As for lanthanide series-containing catalysts, the increase of weak basic site and

decrease strong basic site were found, with the increase the coke type II. Both CO_2 and CH_4 conversions were greatly affected by the presence of coke type II.

Bi-reforming of methane on alkaline-earth-containing catalyst was found to have strong basic site decrease, with the increase of coke type II increases. It has been found that alkaline earth metal affected that the decrease coke type I, while the lanthanide series affected the decrease of coke type II.



CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

In this research the dry reforming and bi-reforming were studied concerning the effect of preparation method, the effect of temperature, the effect of nickel loading, and the effect of promoters. The results can be concluded as follows:

5.1 Conclusions

1. The effects of synthesis method were observed on dry reforming of methane at 700 °C. It was found that incipient wetness impregnation method had higher conversions of CO₂ and CH₄ with less coke deposition than the case sol-gel method.

2. The effect of reaction temperature was studied on dry reforming of methane over 5% nickel loading catalyst during the temperature range of 500-800 °C. Both CO₂ and CH₄ conversions increased with the increasing reaction temperature. It was found that both conversions remained almost stable at 80% at 700 °C.

3. Dry reforming of methane had significantly equal CO₂ and CH₄ conversions irrespective of nickel loading H₂/CO ratio close to 1. Bi-reforming of methane over catalysts studied at the CO₂/CH₄/H₂O ratio of 1 was found to have higher CH₄ conversion than CO₂ conversion with H₂/CO ratio close to 2. The bi-reforming had a higher H₂ yield than dry reforming. Coke type II was found to increase with the increasing nickel loading for both dry and bi-reforming of methane. On the other hand, coke type I was found to decrease with the increasing nickel loading for both reaction

4. In case of dry reforming of methane, both CO₂ and CH₄ conversions of calcium-containing catalyst were higher than those of the catalyst without the promoter. All Lanthanide series had lower conversion than those without promoters

and lower than alkaline earth metal. In case of bi-reforming of methane, both groups of promoters had lower CO_2 and CH_4 conversions than those without the promoters except the samarium (Sm) that had slightly increase of CH_4 conversion

5.2 Concluding remarks

Having been widely known as active catalyst for steam reforming of methane (SRM), Ni-based catalysts have also been found to be the active catalysts for both dry reforming of methane (DRM) and bi-reforming of methane (BRM) in this study. The effects of promoters for both alkaline earth and lanthanide groups on the activity improvement of Ni-based catalysts were not clearly observed. However, the effect promoters may be better noticed on the prolonged reaction at higher time on stream than 3 hours.

It is worth to note that the coke type II defined as higher temperature coke than 300°C significantly affected the catalyst activity of Ni-based catalysts, particularly on dry reforming of methane. It has been discussed that dissolved carbon of coke type II can diffuse through the Ni clusters and nucleate at the Ni-support interface, where they form carbon filaments (whiskers) that grow, lifting the Ni cluster from the support. Finally, this process results in fragmentation of the catalyst [37, 38]. The buildup of these whiskers plug the channel, and the resulting pressure drop due to the catalyst fragmentation leads to the need to replace the catalyst [38, 39]. Generally, these whiskers are mechanically very strong and accelerate the mechanical deformation of the catalyst. It would be interesting to investigate whether or not the regenerated catalysts exhibit the comparable activity with fresh ones. In other words, the further study on catalyst regeneration should be conducted. Also, the different $\text{CO}_2/\text{H}_2\text{O}$ ratios should be examined to observe their effect on H_2/CO ratio.

5.3 Recommendations

1. The type of acidity (Bronsted and Lewis) with pyridine desorption should be taken into consideration for the investigation of catalyst performance.
2. Study the catalytic performance of different feed reactant ratios.
3. Study the catalytic performance at different H₂ reduction temperatures.
4. Study the effect of promoters loading amount.



APPENDIX



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX A

CALCULATION FOR CATALYSTS PREPARATION

A.1. Preparation of γ - Al_2O_3 supports by sol-gel method

The following calculation prepared the preparation of γ - Al_2O_3 used as the support by the sol-gel method:

Reagent: Aluminum isopropoxide (98%) Molecular weight = 204.24 g/mol

Ethanol

Deionized water

Molecular weight = 18 g/mol

Density = 1 g/cm³

Hydrochloric acid (37.7%)

Calculation:

Based on 5 g of aluminum isopropoxide.

$$\begin{aligned}
 \text{Aluminum isopropoxide} &= 0.1 \text{ mol} \\
 &= 0.1 \text{ mol} \times 204.24 \text{ g/mol} \\
 &= 20.42 \text{ g} \\
 \text{Deionized water} &= 15 \text{ mol} \\
 &= 15 \text{ mol} \times 18 \text{ g/mol} \\
 &= 270 \text{ g}
 \end{aligned}$$

Used aluminum isopropoxide 5 g

$$\text{Therefore, required Deionized water} = \frac{2 \text{ g} \times 270 \text{ g}}{20.42 \text{ g}}$$

$$= 66.10 \text{ g}$$

For volume ratio of Deionized water/Ethanol = 1/1

$$\begin{aligned} \text{Deionized water} &= 66.10 \text{ g} \times \frac{1 \text{ cm}^3}{1 \text{ g}} \\ &= 66.10 \text{ cm}^3 \end{aligned}$$

Therefore, required Ethanol = 66.10 cm³

A.2 Preparation of Ni over Y-Al₂O₃ by incipient wetness impregnation method

The preparation of Ni over Y-Al₂O₃ by incipient wetness impregnation method with different loading ratio of nickel metal were prepared by the following calculation:

Example: The preparation of 5%Ni/Y-Al₂O₃

Reagent:

Nickel (II) nitrate hexahydrate (98%) Molecular weight = 290.8 g/mol

Nickel Molecular weight = 58.693 g/mol

Calculation: Based on 2 g catalyst contains 5%wt metal over Y-Al₂O₃.

Therefore, Ni = 0.05 × 2 g

$$= 0.1 \text{ g}$$

Required Y-Al₂O₃ = 2 g - 0.1 g

$$= 1.9 \text{ g}$$

5%Ni/Y-Al₂O₃ was prepared by used Ni(NO₃)₂·6H₂O as metal precursors.

$$\begin{aligned} \text{Required Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O} &= \frac{\text{Ni required} \times \text{MW of Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{MW of Ni} \times 0.98} \\ &= \frac{0.1 \text{ g} \times 290.8 \frac{\text{g}}{\text{mol}}}{58.693 \frac{\text{g}}{\text{mol}} \times 0.98} \\ &= 0.5056 \text{ g} \end{aligned}$$

A.3 Preparation of Ni and promoter over $\text{Y-Al}_2\text{O}_3$ by incipient wetness impregnation method

Reagent:

Calcium nitrate tetrahydrate	Molecular weight = 236.15 g/mol
Magnesium nitrate hexahydrate	Molecular weight = 256.41 g/mol
Lanthanum(III) nitrate hexahydrate	Molecular weight = 433.01 g/mol
Samarium(III) nitrate hexahydrate	Molecular weight = 444.47 g/mol
Cerium(III) nitrate hexahydrate	Molecular weight = 434.23 g/mol

Example: The preparation of 5%Ni(0.5%Ca/ $\text{Y-Al}_2\text{O}_3$)

Calculation: Based on 2 g catalyst contains 5%wt metal over $\text{Y-Al}_2\text{O}_3$.

$$\text{Therefore, Ni} = 0.05 \times 2 \text{ g}$$

$$= 0.1 \text{ g}$$

$$\text{Ca} = 0.005 \times 2 \text{ g}$$

$$= 0.01 \text{ g}$$

$$\text{Required } \text{Y-Al}_2\text{O}_3 = 2 \text{ g} - 0.1 \text{ g} - 0.01 \text{ g}$$

$$= 1.89 \text{ g}$$

5%Ni(0.5%Ca/ $\text{Y-Al}_2\text{O}_3$) was prepared by used $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ as metal precursors.

$$\text{Required } \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = \frac{\text{Ni required} \times \text{MW of } \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{MW of Ni} \times 0.98}$$

$$= \frac{0.1 \text{ g} \times 290.8 \frac{\text{g}}{\text{mol}}}{58.693 \frac{\text{g}}{\text{mol}} \times 0.98}$$

$$= 0.5056 \text{ g}$$

$$\text{Required } \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} = \frac{\text{Ca required} \times \text{MW of } \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}}{\text{MW of Ca} \times 0.99}$$

$$= \frac{0.01 \text{ g} \times 236.15 \frac{\text{g}}{\text{mol}}}{40.078 \frac{\text{g}}{\text{mol}} \times 0.99}$$

$$= 0.1060 \text{ g}$$

APPENDIX B

CALIBRATION CURVES

This appendix showed the calibration curves which used to calculate the mole composition of reactants and products in dry reforming of methane reaction and bi-reforming of methane reaction.

The feed and product gas were analyzed the composition by Thermal Conductivity Detector type gas chromatograph (Shimadzu, GC-8A) equipped with Porapak-Q packed column was used to analyze carbon dioxide and Molecular sieve 5A for methane, hydrogen, and carbon monoxide.

Y-axis and X-axis display mole of gas and area reported by gas chromatography, respectively. Fig. B.1 – B.4 illustrated the calibration curves.

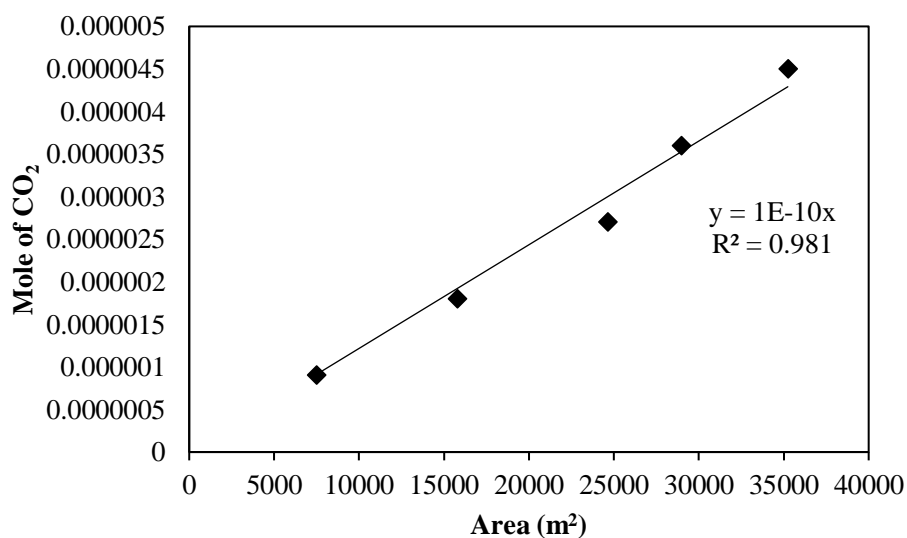


Fig B.1 The calibration curve of carbon dioxide.

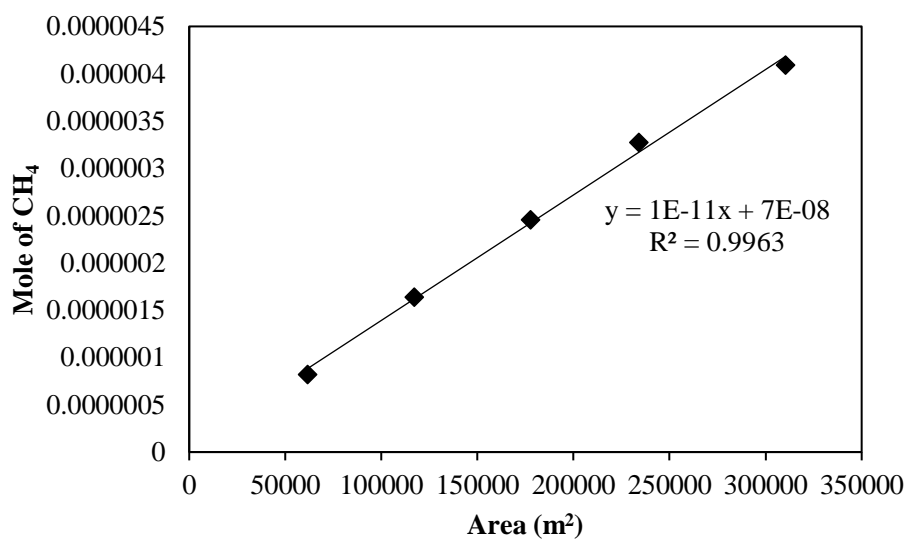


Fig B.2 The calibration curve of methane

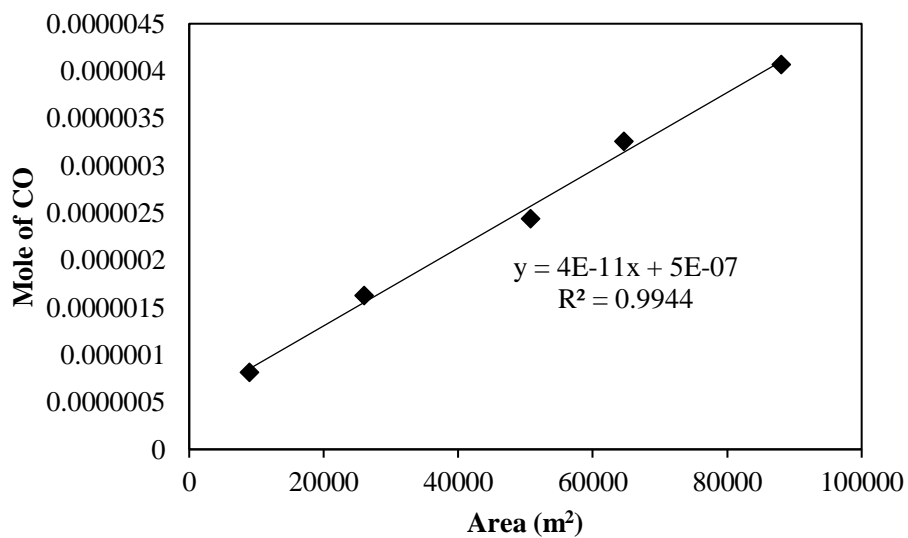


Fig B.3 The calibration curve of carbon monoxide

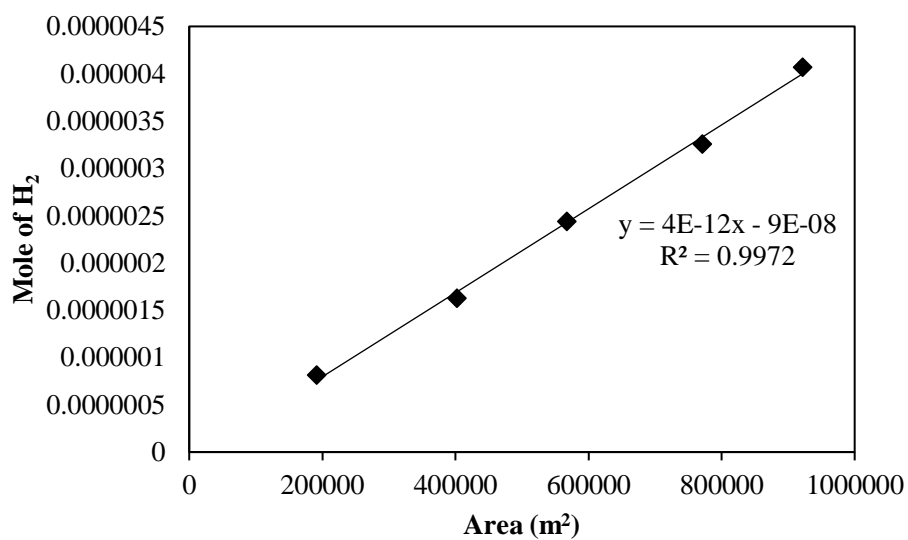


Fig B.4 The calibration curve of hydrogen



APPENDIX C

CALCULATION FOR CONVERSION AND SELECTIVITY

The reactants conversion, product yield and production selectivity based on hydrogen and carbon monoxide, were calculated as the following equations:

Carbon dioxide conversion

$$CO_2 \text{ conversion (\%)} = \frac{(Mole CO_2)_{in} - (Mole CO_2)_{out}}{(Mole CO_2)_{in}} \times 100 \quad \text{Eq. C1}$$

Methane conversion

$$CH_4 \text{ conversion (\%)} = \frac{(Mole CH_4)_{in} - (Mole CH_4)_{out}}{(Mole CH_4)_{in}} \times 100 \quad \text{Eq. C2}$$

Carbon monoxide yield

$$CO \text{ yield (\%)} = \frac{Mole CO}{(Mole CO_2)_{in} + (Mole CH_4)_{in}} \times 100 \quad \text{Eq. C3}$$

Hydrogen yield

$$H_2 \text{ yield (\%)} = \frac{Mole H_2}{2(Mole CH_4)_{in}} \times 100 \quad \text{Eq. C4}$$

Carbon monoxide selectivity

$$CO \text{ selectivity} = \frac{(mole CO)_{out}}{(mole H_2)_{out} + (mole CO)_{out}} \times 100 \quad \text{Eq. C5}$$

Hydrogen selectivity

$$H_2 \text{ selectivity} = \frac{(mole H_2)_{out}}{(mole H_2)_{out} + (mole CO)_{out}} \times 100 \quad \text{Eq. C6}$$

APPENDIX D

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

The number of active metal sites and metal dispersion, which were study by hydrogen chemisorption technique (a stoichiometry of $H_2/Ni = 2$), were calculated by the following calculation procedure:

Example: 5%Ni/Y-Al₂O₃

Let,

S_f	= Stoichiometry factor ($H_2:Ni$)	= 2
m	= Weight of sample	= 0.1 g
V_{inj}	= Volume of injected H_2	= 0.02 cm ³ /g
V_{abs}	= Volume adsorbed	= 0.4188 cm ³ /g
V_g	= Molar volume of gas at STP	= 22414 cm ³ /mol
m.w.	= Molecular weight of metal (Ni)	= 58.6934 g/mol
N_A	= Avogadro's number	= 6.03×10^{23} molecules/mol
%M	= % Metal loading	= 5% Ni

$$\begin{aligned}
 \text{Metal dispersion (\%D)} &= S_f \times \frac{V_{abs}}{V_g} \times \frac{m.w.}{\%M} \times 100\% \times 100\% \\
 &= 2 \times \frac{0.4188 \text{ cm}^3/\text{g}}{22414 \text{ cm}^3/\text{mol}} \times \frac{58.6934 \text{ g/mol}}{5\%} \times 100\% \times 100\% \\
 &= 4.386\%
 \end{aligned}$$

$$\begin{aligned}
 \text{Metal dispersion (\%D)} &= S_f \times \frac{V_{abs}}{V_g} \times N_A \\
 &= 2 \times \frac{0.4188 \text{ cm}^3/\text{g}}{22414 \text{ cm}^3/\text{mol}} \times 6.02 \times 10^{23} \text{ molecules/mol} \\
 &= 2.249 \times 10^{19} \text{ molecules of } H_2/\text{g}
 \end{aligned}$$

APPENDIX E

CALCULATION OF TOTAL ACID SITES OF CATALYST

The calculation of total acid sites of catalysts, it can be calculated from ammonia temperature programmed, were profile as follows:

To calculate mole of NH_3 desorption from the calibration curve of NH_3 as follow:

$$\text{NH}_3 \text{ desorption (mole)} = 0.0003 \times A$$

Where, A is area under peak of the NH_3 -TPD profile.

Example: 5%Ni/ γ - Al_2O_3

$$\text{Peak area of the } \text{NH}_3\text{-TPD profiles (A)} = 3.8962$$

$$\text{Sample weight} = 0.1096 \text{ g}$$

$$\text{Acidity of catalysts} = \frac{\text{mole of } \text{NH}_3 \text{ desorption}}{\text{amount of dry catalyst}}$$

$$= \frac{0.0003 \times 3.8962}{0.1096 \times 10}$$

$$= 1066.478 \times 10^{-6} \text{ mole } \text{NH}_3/\text{g}_{\text{catalyst}}$$

$$= 1066.478 \text{ micromole } \text{NH}_3/\text{g}_{\text{catalyst}}$$

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APPENDIX F

CALCULATION OF TOTAL BASIC SITES OF CATALYST

The calculation of total basic sites of catalysts, it can be calculated from carbon dioxide temperature programmed, were profile as follows:

To calculate mole of CO₂ desorption from the calibration curve of CO₂ as follow:

$$\text{CO}_2 \text{ desorption (micromole)} = 17.7 \times A$$

Where, A is area under peak of the CO₂-TPD profile.

Example: 5%Ni/Y-Al₂O₃

$$\text{Peak area of the CO}_2\text{-TPD profiles (A)} = 2.3939$$

$$\text{Sample weight} = 0.1008 \text{ g}$$

$$\text{Basicity of catalysts} = \frac{\text{mole of CO}_2 \text{ desorption}}{\text{amount of dry catalyst}}$$

$$= \frac{17.7 \times 2.3939}{0.1006 \times 10}$$

$$= 42.119 \text{ micromole CO}_2/\text{g}_{\text{catalyst}}$$

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