

CO₂ reforming of methane on Ni and Co containing γ -Al₂O₃/HY zeolite supported catalysts



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รีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์บนตัวเร่งปฏิกิริยาที่มีนิกเกิลและโคบอลต์ บนตัวรองรับ
แกมมาอะลูมินา และซีโอไลต์ HY



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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อัญชิษฐา หลิว : รีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์บนตัวเร่งปฏิกิริยาที่มี
 นิกเกิลและโคบอลต์ บนตัวรองรับแกมมาอะลูมินา และซีโอไลต์ HY . (CO₂ reforming
 of methane on Ni and Co containing γ -Al₂O₃/HY zeolite supported
 catalysts) อ.ที่ปรึกษาหลัก : ผศ. ดร.สุพจน์ พัฒนะศรี, อ.ที่ปรึกษาร่วม : อ. ดร.ศุภ
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ปฏิกิริยารีฟอร์มมิงของมีเทนด้วยคาร์บอนไดออกไซด์เป็นหนึ่งในกระบวนการที่มี
 ประสิทธิภาพสูงในการผลิตก๊าซสังเคราะห์ที่สามารถช่วยในการลดก๊าซเรือนกระจกได้ โดยในการ
 วิจัยนี้ได้ทำการศึกษาความสามารถในการเร่งปฏิกิริยาและการต้านทานการเกิดโค้กของตัวเร่ง
 ปฏิกิริยาที่มีนิกเกิลเป็นพื้นฐานร่วมกับโคบอลต์ (10%โดยน้ำหนัก) บนตัวรองรับแกมมาอะลูมิ
 นานา และซีโอไลต์ HY ซึ่งตัวเร่งปฏิกิริยาแต่ละตัวถูกเตรียมด้วยวิธีการโซลเจล ซึ่งปัจจัยที่ศึกษาคือ
 ปริมาณอัตราส่วนระหว่างโลหะโคบอลต์/นิกเกิลที่ไหลลงบนตัวรองรับ โดยความสามารถของ
 ตัวเร่งปฏิกิริยาถูกทดสอบในเครื่องปฏิกรณ์ชนิดเบดนิ่งโดยมีอัตราส่วนปริมาตรของสารตั้งต้นมีเทน:
 คาร์บอนไดออกไซด์เป็น 1:1 ภายใต้ความดันบรรยากาศที่อุณหภูมิ 700 องศาเซลเซียสซึ่งเป็น
 อุณหภูมิที่ดีที่สุดที่ทำให้ตัวเร่งปฏิกิริยามีความสามารถมากที่สุด จากการศึกษาด้วยการทดสอบ
 เวลาที่ใช้ในการไหลของสารพบว่า การเพิ่มโคบอลต์ในตัวเร่งปฏิกิริยาโลหะผสมทำให้ตัวเร่งปฏิกิริยา
 มีความสามารถและความต้านทานการเกิดโค้กสูงกว่าการใช้ตัวเร่งปฏิกิริยาโลหะเดี่ยว ดังนั้นตัวเร่ง
 ปฏิกิริยา 7%นิกเกิล-3%โคบอลต์/แกมมาอะลูมินา-ซีโอไลต์ HY จึงเป็นตัวเร่งที่มีการเปลี่ยนแปลง
 ของคาร์บอนไดออกไซด์และมีเทนพร้อมด้วยค่าการเลือกเกิดของไฮโดรเจนสูงที่สุด

จุฬาลงกรณ์มหาวิทยาลัย
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Anchittha Liu : CO₂ reforming of methane on Ni and Co containing γ -Al₂O₃/HY zeolite supported catalysts . Advisor: Asst. Prof. SUPHOT PHATANASRI, Ph.D. Co-advisor: Supareak Praserttham, Ph.D.

The carbon dioxide reforming of methane is one of the most effective processes to produce syngas while reducing greenhouse gases. In this study, the catalytic activity and coke resistance were studied on the Ni-based catalysts with or without Co (10%wt) over γ -Al₂O₃-HY zeolite support. Such catalysts were prepared by the sol-gel method with various different metal loadings and Co/Ni ratio. The activity tests on the carbon dioxide reforming reaction were performed in a fixed-bed reactor with the CH₄:CO₂ feed volume ratio of 1:1 under atmospheric pressure at 700°C which is the best temperature for the catalysts activity. It has been found that the addition of Co in the bi-metallic showed better catalytic activity and coking resistivity than the Ni monometallic system suggested by the time-on-stream results and the decrease in the amount of Ni oxide and Co oxide confirmed by the absence of their peaks. Therefore, the good catalyst was 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite that had the highest CO₂ and CH₄ conversion with highest H₂ selectivity.

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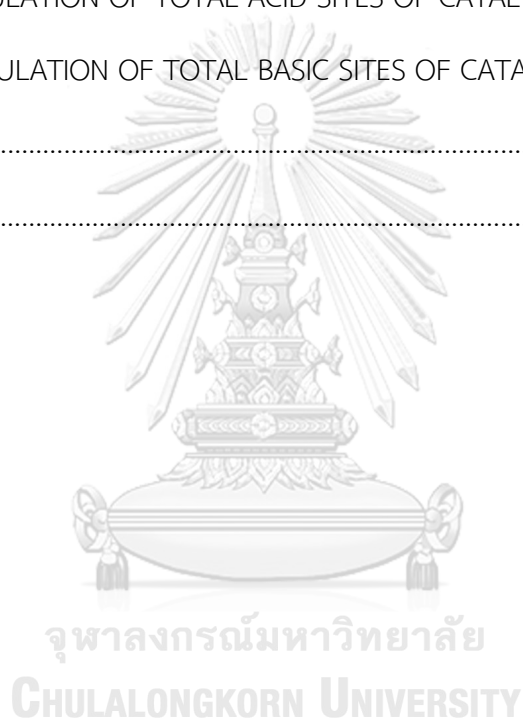
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CHAPTER I

INTRODUCTION

1.1 Background

In recent years, too much CO₂ in the atmosphere is a primary cause to the climate change problem. This greenhouse gas causes global warming because it is a heat-trapping gas emitted, that stays in the atmosphere longer than other major heat-trapping gases.[1] It enters the atmosphere from burning fossil fuels (coal, natural gas, and oil), trees and wood products, and also a result of chemical reactions. On the other hand, from the natural gas, the methane is also emitted, which was also one of the global warming's cause.[2] From the global warming problem, the surface temperature of the earth will become higher than usual.

Therefore, finding more clean and sustainable energy sources would be one way to reduce the global warming problems. The hydrogen can be selected as one of the most potential energy choices because it is efficient and environmentally-friendly.[3] So, many industrial processes are interesting in synthesis gas (CO and H₂) production, which is the main process to convert CO₂ and CH₄. The CO₂ reforming of methane (or dry reforming of methane (DRM)) (Eq.1) is one of the reactions used to convert two major greenhouse gases to syngas. [4]



This process is endothermic, thus, require high temperatures with low pressure. It is normally operated at a temperature varying from 600 to 900°C. It may be accompanied by a parallel reaction of the reverse water gas shift (Eq. 2), methanation (Eq. 3), carbon monoxide decomposition by the Boudouard reaction (Eq. 4), which is a big problem for the catalysts. In addition, the undesired methane decomposition reaction (Eq. 5), and CO reduction (Eq. 6) also occur.





However, the catalysts deactivation from coke formation is one of the main problems of the CO₂ reforming, which sets the motivation for this study. It requires adjustments of process parameters, for example, temperature, flow rate, support, and active phase in order to tackle the deactivation issue.

The nickel-based supported on alumina catalysts have been found as the most effective materials for CO₂ reforming of methane.[5] In many studies, the effects of active phase promoters were evaluated on Ni properties and it was revealed that Ni-Co bimetallic catalyst was the best option compared to other catalysts.[6]

Therefore, the aims of this study are to investigate the optimal composition of the bimetallic Ni-Co over γ -Al₂O₃-HY zeolite as support in the CO₂ reforming of methane reaction and study the effect of the mono and bimetallic system of the Ni-based catalysts over pure γ -Al₂O₃ and pure HY zeolite supports.

1.2 Objectives

To study the mono and bimetallic system of the Ni-based catalysts over γ -Al₂O₃ and HY zeolite support in terms of the catalytic properties in CO₂ reforming of methane reaction.

1.3 Scopes of the research

1.3.1 Synthesis of γ - Al_2O_3 and γ - Al_2O_3 -HY zeolite, that Si/Al molar ratio was 100, with a ratio of 1:3 by sol-gel method as support.

1.3.2 Preparation of monometallic (Ni, Co) and bimetallic catalysts with various Ni-Co loading amount (10%wt.Ni, 10%wt.Co, 3%wt.Ni-7%wt.Co, 5%wt.Ni-5%wt.Co, and 7%wt.Ni-3%wt.Co) over γ - Al_2O_3 -HY zeolite support by incipient wetness impregnation method.

1.3.3 Investigation of the catalytic performance of mono and bimetallic system of Ni-based catalysts over γ - Al_2O_3 -HY zeolite support in the CO_2 reforming of methane reaction under the following condition:

- The prepared catalysts were reduced at 500°C for 1 hour with 50ml/min of pure hydrogen.
- The feed volumetric flow rate of 1:1 ratio of CH_4 and CO_2 was 60 ml/min.
- The catalysts activity test on CO_2 reforming reaction was performed in a fixed-bed reactor under atmospheric pressure at 700°C .
- The composition of reactants and products was analyzed by Thermal Conductivity Detector-type gas chromatograph.

1.3.4 The selected metals loading amount from the 1.3.3 was used to investigate the activity of the catalyst at the various reaction temperature (600°C , 650°C , and 700°C).

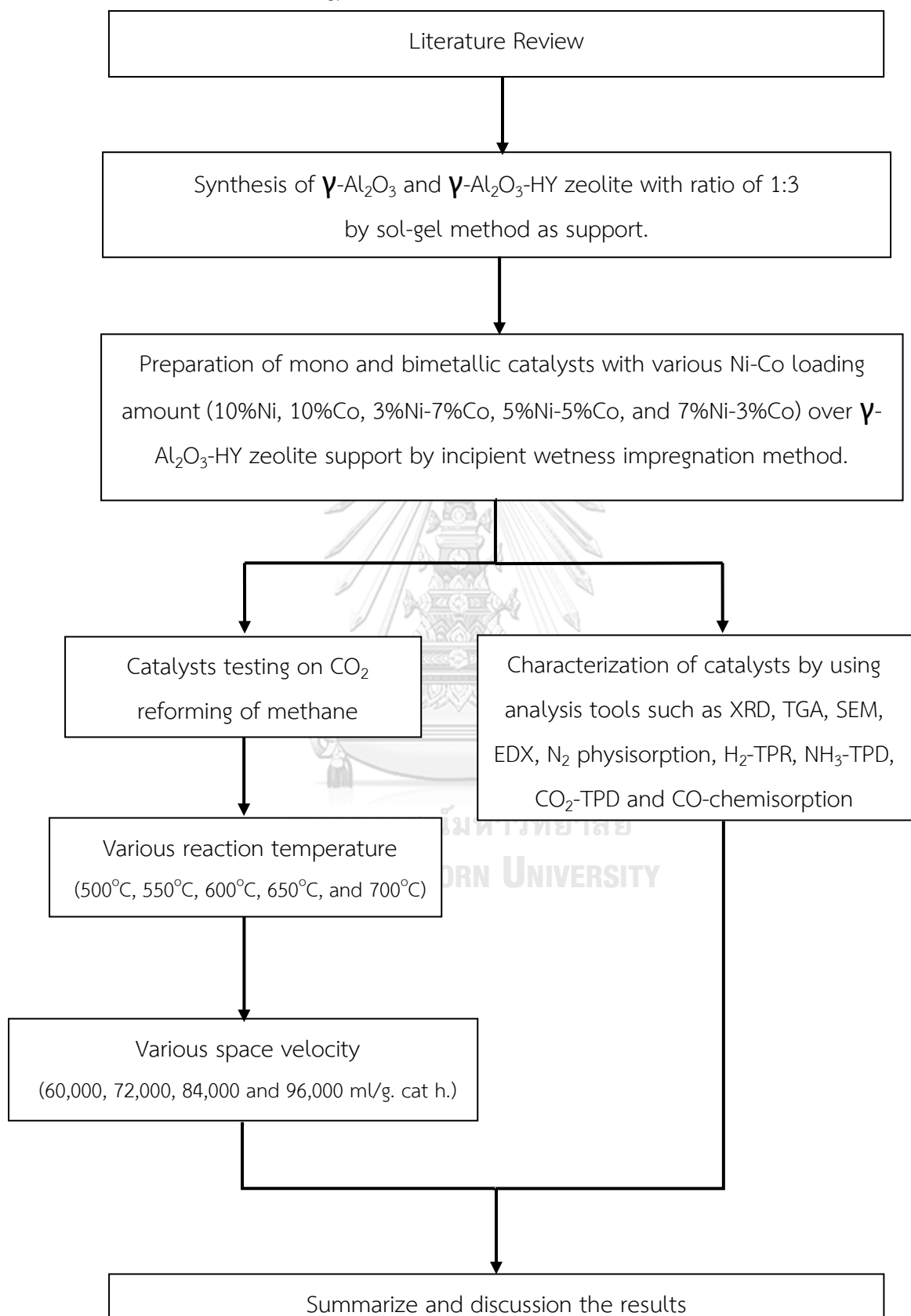
1.3.5 The selected reaction temperature from the 1.3.4 was used to investigate the activity of the catalyst with various feed volumetric flow rate (60 ml/min, and 70 ml/min).

1.3.6 Characterization of all catalysts by using various techniques:

- X-ray diffraction (XRD)
- Nitrogen adsorption.
- Thermogravimetric analysis (TGA).
- Scanning electron microscopy (SEM).
- Carbon monoxide chemisorption.
- Energy Dispersive X-ray Spectrometer (EDX).
- Ammonia temperature program desorption (NH₃-TPD).
- Carbon dioxide temperature program desorption (CO₂-TPD).
- Hydrogen temperature program reduction (H₂-TPR).



1.4 Research methodology



CHAPTER II

THEORY and LITERATURE REVIEW

2.1 Theory

2.1.1 CO₂ reforming of methane

The CO₂ reforming of methane is a method to produce synthesis gas, which is a fuel gas mixture of H₂ and CO, as known as dry reformation. Synthesis gas can convert by many exothermic reactions to other useful product, for example, methanol, ethanol, and acetone.

The reaction can be represented by Eq. 1. Therefore, CO₂ and CH₄ are useful to produce other useful chemical building blocks, hydrogen and carbon monoxide. [7]

2.1.2 Synthesis gas

The syngas is a mixture of hydrogen and carbon monoxide, used as a clean alternative to fossil fuels or for the liquid fuels production as synthetic diesel, dimethyl ether, and methanol.[8] It was produced from many sources, including natural gas, coal, biomass, or hydrocarbon feedstock. It was produced by the reaction with steam (steam reforming), carbon dioxide (dry reforming) or oxygen (partial oxidation). [9]

2.1.3 Alumina

Alumina or aluminum oxide, synthetically produced aluminum oxide, or Al₂O₃. It is a white or nearly colorless crystalline substance and commonly used as the raw material for many advanced ceramic products and a chemical processing active agent. [10] To produce the dense alumina products, from powder synthesis to sintering required to make a complete process control. During the heat treatment, aluminum oxides reform to transition alumina in the metastable structure form and ended up as α -Al₂O₃ thermodynamic stable phase (Fig. 2.1). Under a temperature

range of 500 to 550 °C with removing the water from the structural Boehmite transforms into γ -Al₂O₃ transition alumina.[11] In the automotive and petroleum industries, a most important catalyst and support is γ -alumina (γ -Al₂O₃) from the various transition of alumina. Because it requires textural properties, like surface area, pore volume, pore-size distribution, and characteristics of acid-base are depended on surface chemical composition, local microstructure, and phase composition. The γ -Al₂O₃ structure is normally considered as a cubic defect spinel type that the oxygen atoms are arranged in a cubic close packing and Al atoms occupy the octahedral and tetrahedral sites.[12]

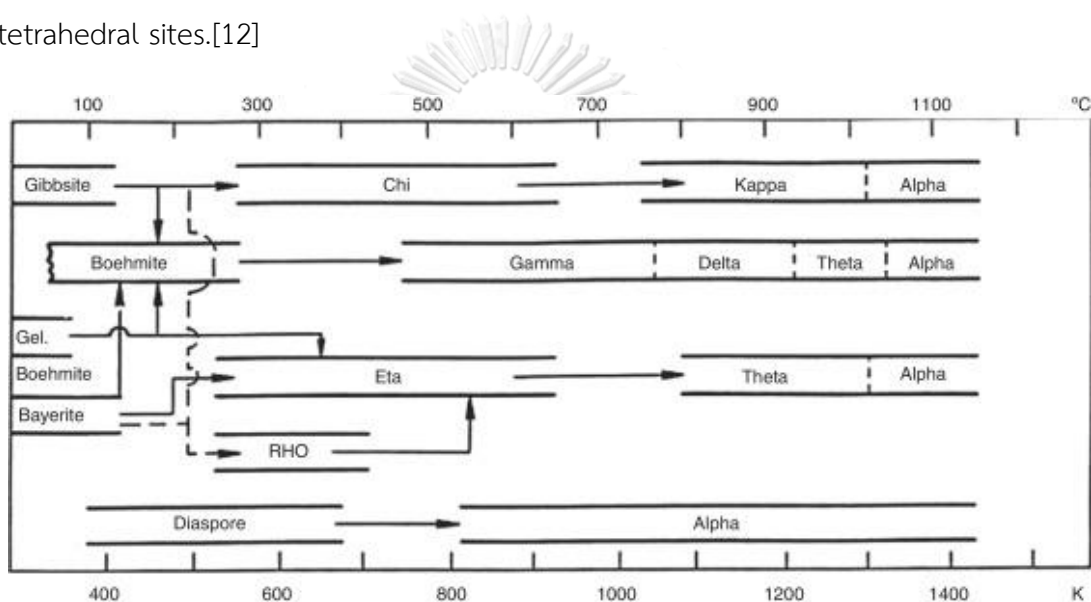


Figure 2.1 Transition alumina phase at a different temperature.

2.1.4 Metal catalyst

2.1.4.1 Nickel (Ni)

Nickel is a silvery-white lustrous metal with a slight golden tinge. It is a transition metal, which is hard and ductile. It is one of four ferromagnetic elements (Iron, Cobalt, and Gadolinium) at or near room temperature. Its Curie temperature (T_c) is 355°C (671°C). It is useful for its properties of being ductile and corrosion resistant.

The metallurgy of nickel is complicated according to the particular ore being processed. Normally, the ore is transformed to dinickel trisulfide (Ni_2S_3), which is nickel in the +3-oxidation state, it is roasted in air to give nickel oxide, NiO (+2 state), then obtaining the metal by reduced with carbon. For some high-purity used the carbonyl process to make a nickel.[13]

Table 2.1 Physical properties of Nickel.

Element Properties	
Name	Nickel
Symbol	Ni
Atomic number	28
Atomic weight	58.69 g/mol
Melting point	$1,453^\circ\text{C}$ ($2,647^\circ\text{F}$)
Boiling point	$2,732^\circ\text{C}$ ($4,950^\circ\text{F}$)
Density	8.902 g/cm^3 at 25°C
Oxidation states	0, +1, +2, +3

2.1.4.2 Cobalt (Co)

Cobalt is found only in the chemically combined form in the Earth's crust. Reductive smelting produces the free element of cobalt, that is a hard, lustrous, silver-gray metal. Its properties are similar to nickel and iron. It is stable in air and unaffected by water; however, it is slowly attacked by dilute acids.

Cobalt has been used for a long time for jewelry and paints. Now a day, cobalt is mostly used in the producing of magnetic, wear-resistant and high-strength alloys. It occurs naturally as only one stable isotope (cobalt-59) and cobalt-60 is an important radioisotope, which used as a radioactive tracer and for produce the high energy of gamma rays. It is commonly used in industries because of its low cost and relative abundance world over.[14, 15]

Table 2.2 Physical properties of Cobalt.

Element Properties	
Name	Cobalt
Symbol	Co
Atomic number	27
Atomic weight	58.9332 g/mol
Melting point	1,495 °C (2,723°F)
Boiling point	2,927 °C (5,301°F)
Density	8.86 g/cm ³ at 25 °C

2.2 Literature Review

Factors affect the performance of catalysts used in CO₂ reforming of methane reaction are discussed in this chapter. These are the effect of support, and the effect of metal.

2.2.1 Effect of support

T. Stroud et al. (2018) [16] studied the effect of two different Sn loadings on Ni-base catalyst have been tested 20 hours for the dry and bi-reforming of methane reactions (DRM and BRM, respectively), after that selecting the most appropriate Sn/Ni ratio and promoting the 20 wt.% of CeO₂ with alumina. The result that reaching an equilibrium H₂/CO product ratio in the process showed the good conversions for DRM, but BRM was more stable conversions. In fact, this work showed how multicomponent Ni catalysts can be effective to produce syngas streams from CO₂/CH₄ mixtures as an efficient route for CO₂ utilization.

S. Khajeh Talkhonchek et al. (2016) [17] studied the effect of Al₂O₃-Clinoptilolite-CeO₂ support with different Al₂O₃ and clinoptilolite contents used in Ni-based Nanocatalysts for increasing the catalyst production costs by using clinoptilolite instead of Al₂O₃. In addition, CeO₂ has a positive effect on surface morphology and enhance NiO particles size and activity. The best activity is the Ni/Al₂O₃-CeO₂ nanocatalyst, which the highest specific surface area, appropriate NiO species dispersion and flat surface morphology.

S. Mahdi et al. (2015) [6] studied the optimized composition of Ni-Co bimetallic catalyst over zeolite Y. The Ni₇Co₃/Y catalyst had small particles size and more distribution than a Ni₃Co₇/Y catalyst, which from the FESEM images showed. Moreover, from BET analysis results, the Ni and Co composition had an effect to the catalyst specific surface area. Finally, the activity tests at GHSV = 24 l/g h, P = 1 atm, CH₄/CO₂ = 1, and the temperature range of 550 – 850°C. The results showed that Ni₇Co₃/Y had the highest activity at all temperature and stable for 10 hours.

A. H. Fakeeha et al. (2013) [18] studied the stabilities and catalytic activities of three 5 wt% of Ni catalysts, supported on alumina, Y-zeolite, and H-ZSM-5 zeolite. The catalysts were prepared by the incipient wetness impregnation method. The most stable catalyst is H-ZSM-5-supported Ni catalyst, and it had the lowest carbon deposition.

A. Luengnaruemitchai and A. Kaengsilalai (2008) [19] studied the catalytic performance of Ni-based on zeolite A, zeolite X, zeolite Y, and ZSM-5. The catalysts were prepared by incipient wetness impregnation has been tested for the catalytic carbon dioxide reforming of methane into synthesis gas at 700 °C, at atmospheric pressure, and at a CH₄/CO₂ ratio of 1. The results showed that Ni/zeolite Y has the best catalytic performance and the most stability from the other types of studied zeolites. Moreover, the 7wt% of Ni loading showed the best catalytic activity on each zeolite support, but the 7wt% Ni catalysts had a higher amount of coke than the 3 and 5% Ni loadings.

2.2.2 Effect of metal

J. Horlyck et al. (2018) [20] studied the significant impact of Ni and Co on the performance of catalysts for the dry reforming of methane. The side reactions showed that Co deposits have high performance to remove the carbon species via oxidation whereas Ni is more active towards CH₄ decomposition. Therefore, the best catalytic performance is a combination of the high activity of Ni with the stabilizing effect and carbon-resistance of Co.

T. Ji Siang et al. (2018) [21] studied the bimetallic 5%Ni–10%Co/Al₂O₃ catalyst for methane dry reforming reaction at different reaction temperatures, that was synthesized by impregnation method. On γ -Al₂O₃ support surface had formed NiO, Co₃O₄ and spinel metal aluminates, namely, CoAl₂O₄ and NiAl₂O₄ phases during the calcination process. CH₄ and CO₂ conversions were stable on-stream for 4 hours and had the optimum at 67% and 71%, respectively at 973 K while H₂ selectivity and

yield were higher than 49%, but the ratio of H₂/CO was less than unity for all runs because of the presence of reverse water–gas shift reaction.

T. SonPhan et al. (2018) [22] studied the high thermal stability of Hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂) as a catalyst support Co-Ni bimetallic for the dry reforming of methane (DRM) process. On the surface of HAP, Nanoparticles containing both nickel and cobalt were well formed by impregnation methods. DRM reaction was tested at 700–750 °C and around 1.6 bar in a fixed-bed reactor the was fed a mixture of 20%vol CH₄, 20%vol CO₂, and 60%vol N₂. The result showed CH₄ and CO₂ conversion nearly to 60 and 68% at 700 °C, respectively, and 73 and 79% at 750 °C, respectively during 50–160 hours of reaction times.

A. S.A.AL-Fatesh et al. (2011) [23] studied the Ca, Ce, and Zr promoters on catalyst stability, coke deposition, and the H₂/CO ratio of Ni catalysts performance supported over γ -Al₂O₃, that were synthesized by an impregnation method in methane dry reforming. The reactions proceeded in a microreactor with a 1:1 of CO₂:CH₄ feed ratio, the F/W = 2640 ml/(h·g), reaction temperatures between 500-850°C, and at atmospheric pressure. The result showed that the best performance with less coke formation is 3%Ni/ γ -Al₂O₃ promoted with 0.15% Ce and 0.05% Ca. The highest CH₄ and CO₂ conversion activities that were found to be 94.1% and 98.3% at 850°C, respectively. Furthermore, the amount of carbon, that was formed, was negligible and no more than 1.5 wt%.

Z. Jianqiang et al. (2011) [24] studied the Ni/SiO₂ catalysts promoted by La, Mg, Co, and Zn for CO₂ reforming of methane into synthesis gas. Finding the addition of a suitable amount of La promoter exhibited high activity and excellent stability, which more dispersion of NiO and interaction between NiO and SiO₂. For the Ni–Mg/SiO₂ catalyst might be deactivation by inert carbon deposited on the catalyst, whereas the main reason for the deactivation of Ni-Co/SiO₂ catalyst might be the sintering of metallic Ni. Finally, the addition of La and Mg decreased the contribution of reverse water-gas shift reaction, leading to higher H₂ yield.

CHAPTER III

EXPERIMENT

In this chapter consists of four sections that description about the chemicals for the preparation of supports and catalysts, the supports and catalyst preparation, characterization and performance of catalysts for CO₂ reforming of methane.

3.1 The chemicals for the preparation of supports and catalysts

The chemicals used for the preparation of supports and catalysts are included in Table 3.1

Table 3.1 The chemicals that were used for preparing supports and catalysts.

Chemical	Formula	Purity	Supplier
Aluminum isopropoxide	C ₉ H ₂₁ O ₃ Al	>98%	Aldrich
HY-zeolite (Si/Al molar ratio= 100)	C ₂ H ₅ OH	99%	TOSHO
Ethanol		37.7%	Merck
Hydrochloric acid	HCl	98%	Merck
Nickel (II) nitrate hexahydrate	Ni(NO ₃) ₂ .6H ₂ O	98%	Aldrich
Cobalt (II) nitrate hexahydrate	Co (NO ₃) ₂ .6H ₂ O		Aldrich

3.2 The preparation of supports and catalyst

3.2.1 Preparing γ -Al₂O₃-HY zeolite supports by sol-gel method

The γ -Al₂O₃-HY zeolite was prepared by Sol-gel method to use as the supports. Al₂O₃ precursor and organic solvent used aluminum isopropoxide and ethanol. First, aluminum isopropoxide dissolved in a mixture volume ratio 1:1 of ethanol and deionized water under mild stirring at 80°C for 1 hour. Then, increased the temperature of the solution to 90°C and added HY-zeolite into the solution, that was 1:3 weight ratio of Al₂O₃/HY zeolite. The next step was dropping hydrochloric acid to adjust the pH value of the solution equal to 2.5. After that continuous stirring at 90°C until it becomes viscous. Finally, Drying the supports overnight at 110°C and calcination under an air flow at 550°C for 2 hours.

3.2.2 Preparing catalysts by incipient wetness impregnation method

The mono and bimetallic Ni-Co catalysts were prepared by the incipient wetness impregnation method, used Ni (NO₃)₂·6H₂O and Co (NO₃)₂·6H₂O as metal precursors. Start with dissolved Ni (NO₃)₂·6H₂O and Co (NO₃)₂·6H₂O, which 10wt% Ni, 3wt%Ni-7wt%Co, 5wt%Ni-5wt%Co, 7wt%Ni-3wt%Co, and 10wt%Co, in the same volume of deionized water with a pore volume of the support. After that, the solution drops to above the support. Next, keeping the impregnated catalysts at room temperature for 4 hours to assure adequate distribution of metal complete. Lastly, the catalysts were dried overnight at 110°C and calcined under an air flow at 550°C for 2 hours.

3.3 The characterization of catalysts

3.3.1 X-ray diffraction (XRD)

The crystalline phase of the supports and catalysts were characterized by X-ray diffraction (XRD) analysis, that used an X-ray diffractometer SIEMENS D 5000 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 speed was 0.5°.

3.3.2 Thermogravimetric analysis (TGA)

The as-spun alumina fibers are subjected to the thermogravimetric and differential thermal analysis (Diamond Thermogravimetric and Differential Analyzer, TA Instruments SDT Q600) to determine the carbon content in the sample, 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 of air flow.

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

A scanning electron microscope (SEM) and energy x-ray spectroscopy (EDX) used to determine the morphology structure of sample and 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.

3.3.4 Nitrogen physisorption

The widest method used to determine the surface area of solid materials is Brunauer- Emmett-Teller Method (BET) method and involve the use of the BET equation. BET is used to find specific surface area, pore volume and pore diameter of prepared catalysts. 0.1 grams of each sample, that was dried (to remove the moisture in the sample), there were analyzed by N₂ adsorption-desorption isotherm

used Micromeritics ASAP 2020 at liquid nitrogen temperature of -196°C . Moreover, the Barret-Joyner-Halenda (BJH) method is used to determine the pore diameter and pore volume of the catalysts.

3.3.5 Hydrogen Temperature Programmed Reduction (H_2 -TPR)

The reducing temperatures of prepared catalysts were determined by Temperature Programmed Reduction of Hydrogen (H_2 -TPR) equipment by using Micromeritics chemisorb 2750 Pulse Chemisorption System. Using 0.1g of the samples placed in a quartz tube and pretreated it in 25ml/min of nitrogen flow at 500°C for 1 hour. After that, using 10% H_2 in Ar gas mixture flow rate of 25 ml/min from 30°C to 800°C to determine the H_2 -TPR profiles. Finally, the TCD measured the Hydrogen consumption during the TPR experiments as a function of temperature.

3.3.6 Ammonia temperature program desorption (NH_3 -TPD)

The acid properties of catalysts were observed by Temperature Programmed Adsorption of Ammonia (NH_3 -TPD) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. 0.1 g of the sample put in a quartz tube and pretreated at 500°C in a helium flow for 1 hour after that applied ammonia 30 min. Next, the sample was heated from 30 to 800°C with a heating rate of $10^{\circ}\text{C}/\text{min}$. The amount of ammonia, that was desorbed, was measured by TCD signal as a function of temperature.

3.3.7 Carbon dioxide temperature program desorption (CO_2 -TPD)

Temperature Programmed Adsorption of Carbon dioxide (CO_2 -TPD) equipment, which using Micromeritics chemisorp 2750 Pulse Chemisorption System, was used to observe the basic properties of catalysts. A quartz tube, which had 0.1 g of the sample inside, was pretreated at 500°C in a helium flow for 1 hour before applied carbon dioxide for 30 min. Afterthat, the sample was heated from 30 to 800°C with a heating rate of $10^{\circ}\text{C}/\text{min}$. The amount of carbon dioxide, that was desorbed, was measured by TCD signal as a function of temperature.

3.3.8 CO chemisorption

CO chemisorption technique was used to study the number of active metal sites and metal dispersion. In this method, it used Micromeritics Chemisorb 2750 and ASAP 2101CV.3.00 software unit fitted with a Thermal Conductivity Detector (TCD). The sample about 0.05 g was put in a glass U-tube and reduced at 500°C for 1 hour with 25 mL/min of hydrogen flow, then cooled down to the room temperature that was adsorbed temperature. Lastly, 20 μL of CO was injected into the catalyst until the desorption peaks were constant. The amount of CO adsorption on the catalyst was assumed that on one metal site can adsorb only one CO molecule.



3.4 Performance of catalysts for CO₂ reforming of methane

3.4.1 Gas materials for reaction

The gas material that was used in CO₂ reforming of methane were listed in Table 3.2

Table 3.2 Gas materials for CO₂ reforming of methane

Gas material or reagent	Purity	Supplier
Methane in Carbon dioxide	50%	The Linde group
Ultra-high purity grade argon	99.999%	Thai industrial Gases Limited
Ultra-high purity grade nitrogen	99.999%	Thai industrial Gases Limited
Ultra-high purity grade hydrogen	99.999%	Thai industrial Gases Limited

3.4.2 Instruments and apparatus

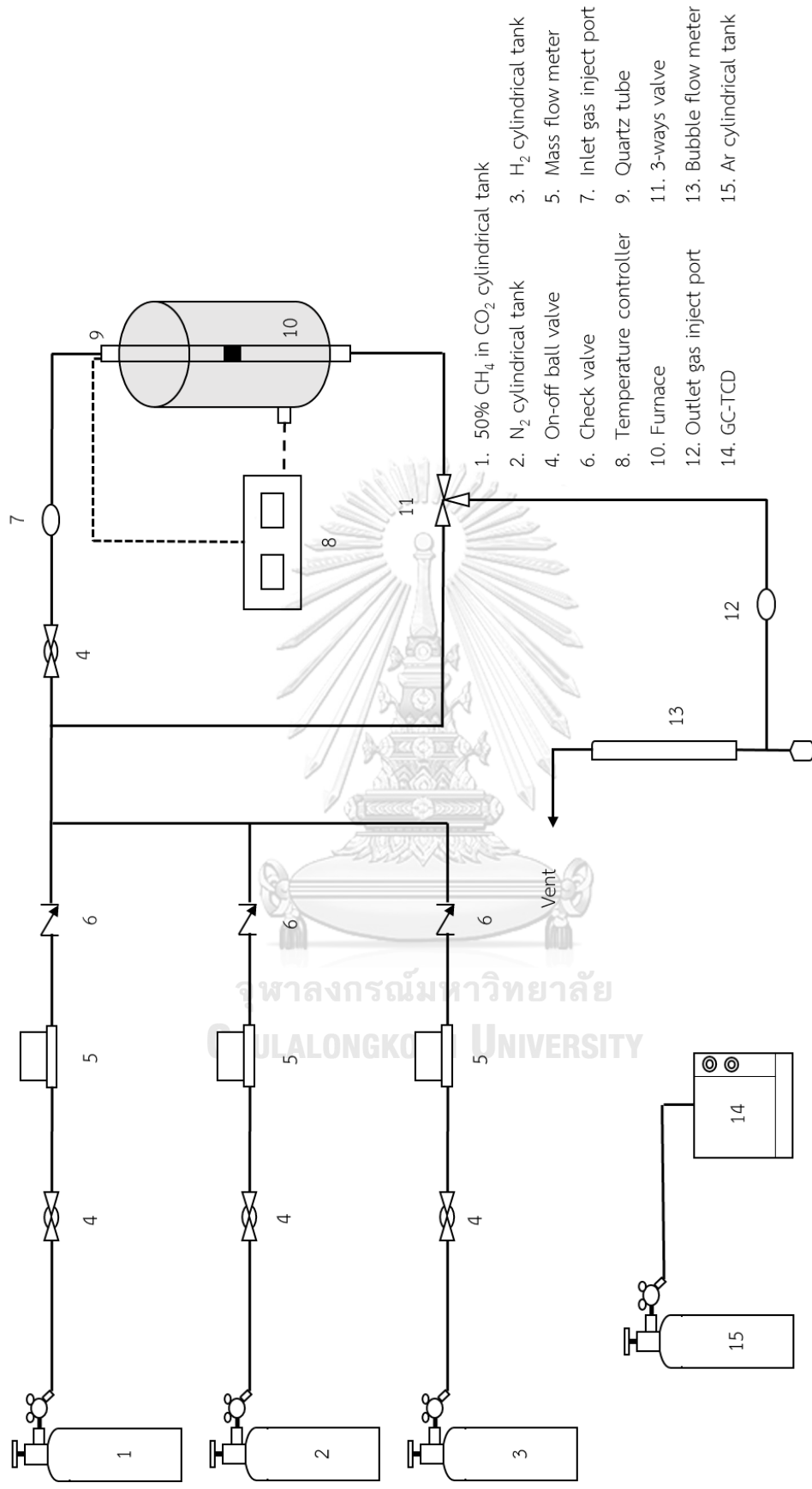


Figure 3.1 CO₂ reforming of methane's scheme diagram

From Fig. 3.1, the experimental setup that tested the performance of the catalyst consist of;

Reactor: The reactor is fixed-bed continuous-flow reactor made from quartz tube, which 49.3 cm of length and 0.9 cm of inner diameter.

Temperature controller: The temperature controller connected to a thermocouple in the fixed-bed reactor to control the furnace temperature.

Furnace: The catalysts in the fixed-bed reactor was heated by the furnace, which was controlled by the temperature controller.

Gas chromatography (GC): A gas chromatography was used to analyze the gas inlet and outlet compounds. It was operated at the conditions in Table 3.3.

Table 3.3 Gas chromatography operating conditions.

Gas Chromatograph	Shimudzu, GC-8A	
Detector	TCD	TCD
Column	Porapack-Q	Molecular sieve 5A
Carrier gas	Argon	Argon
Carrier gas flow	50 mL/min	50 mL/min
Carrier gas flow: Initial	70°C	70°C
Carrier gas flow: Final	70°C	70°C
Detector temperature	100°C	100°C
Inject temperature	100°C	100°C
Current	80 mA	80 mA
Analyzed gas	CO ₂	H ₂ , CH ₄ , CO

3.4.3 Reaction method

CO₂ reforming of methane was carried out in a fix-bed reactor continuous-flow quartz reactor. The reactor had a K-type thermocouple at the middle of the catalyst bed to control the reactor temperature. Next, the 0.05g of catalysts was put on quartz wool at the middle of the quartz reactor. Reducing the catalyst by flowing 50ml/min of hydrogen at 500°C for 1 hour before operating the reaction. After that purged 50ml/min of nitrogen to replace hydrogen and heated the catalyst to the reaction temperature (700°C) with a heating rate of 10°C/min. The 1:1 feed volumetric flow rate ratio of CH₄: CO₂ with a total flow rate of 60 ml/min was fed into the reactor to test the catalyst performance for 3 hours. Finally, the feed and final product gas were analyzed the composition by Thermal Conductivity Detector type gas chromatograph (Shimudzu, GC-8A) equipped with Porapak-Q and Molecular sieve 5A packed column, which using Argon as a carrier gas.

CHAPTER IV

RESULT AND DISCUSSION

In this chapter consists of two parts. The first part studies 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 temperature programmed reduction (H₂-TPR), Carbon monoxide chemisorption, Thermo gravimetric analysis (TGA). The second study the catalysts performance that can classify to four parts: (1) Effect of bimetallic catalysts with different loading ratio of nickel metal and cobalt metal on γ -Al₂O₃-HY zeolite support, (2) Effect of monometallic (10%Ni, 10%Co) and bimetallic (7%Ni-3%wt.Co) on γ -Al₂O₃-HY zeolite support, (3) Effect of temperature, and (4) Effect of space velocity.

4.1. Catalysts characterization

4.1.1 N₂-physisorption

A key function in catalyst activity is a surface area.[6] Consequently, the monometallic catalysts (10%Ni, 10%Co), bimetallic catalysts (3%Ni-7%Co, 5%Ni-5% and 7%Ni-3%Co) and γ -Al₂O₃-HY support surface area were measured by the BET method and the result was showed in Table 4.1. The surface areas of monometallic and bimetallic catalysts were ranged between 513-543 m²/g, compared to no loaded metal on supports the monometallic and bimetallic have lower specific surface area. It was found that specific surface area of 7%Ni-3%Co/ γ -Al₂O₃-HY was less than 3%Ni-7%Co/ γ -Al₂O₃-HY and 5%Ni-5%Co/ γ -Al₂O₃-HY because Co addition increase BET surface area. It probably the support pores was led to blocking by Ni and Co. And, from the previous study found that using high average pore diameter of the catalyst can improve active metals dispersion pore structures and provide larger active surface area per unit weight of the active metal. [25, 26] Pore volume of monometallic catalysts (10%Ni, 10%Co), bimetallic catalysts (3%Ni-7%Co, 5%Ni-5%,

and 7%Ni-3%Co) and γ -Al₂O₃-HY support were range between 0.23-0.31 cm³/g. The pore volume of the monometallic and bimetallic catalysts were lower than γ -Al₂O₃-HY support due to blocking of some nickel and cobalt metal loading of support[27]. Then, the average pore size of monometallic catalysts, bimetallic catalysts and γ -Al₂O₃-HY were range between 5.9-6.4 nm that is characteristic of mesoporous solids. The average pore size of the monometallic and bimetallic catalysts has no significant change.

Table 4.1 Physical properties and chemical composition of catalysts.

Catalysts	N ₂ physisorption results		
	BET surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Average pore diameter ^a (nm)
γ -Al ₂ O ₃ -HY	635.47	0.31	5.9
10%Ni/ γ -Al ₂ O ₃ -HY	524.68	0.26	6.1
10%Co/ γ -Al ₂ O ₃ -HY	543.84	0.25	6.4
3%Ni-7%Co/ γ -Al ₂ O ₃ -HY	520.01	0.23	6.3
5%Ni-5%Co/ γ -Al ₂ O ₃ -HY	539.53	0.25	6.2
7%Ni-3%Co/ γ -Al ₂ O ₃ -HY	513.58	0.23	6.3

^aBJH desorption pore volume.

BJH desorption average pore diameter.

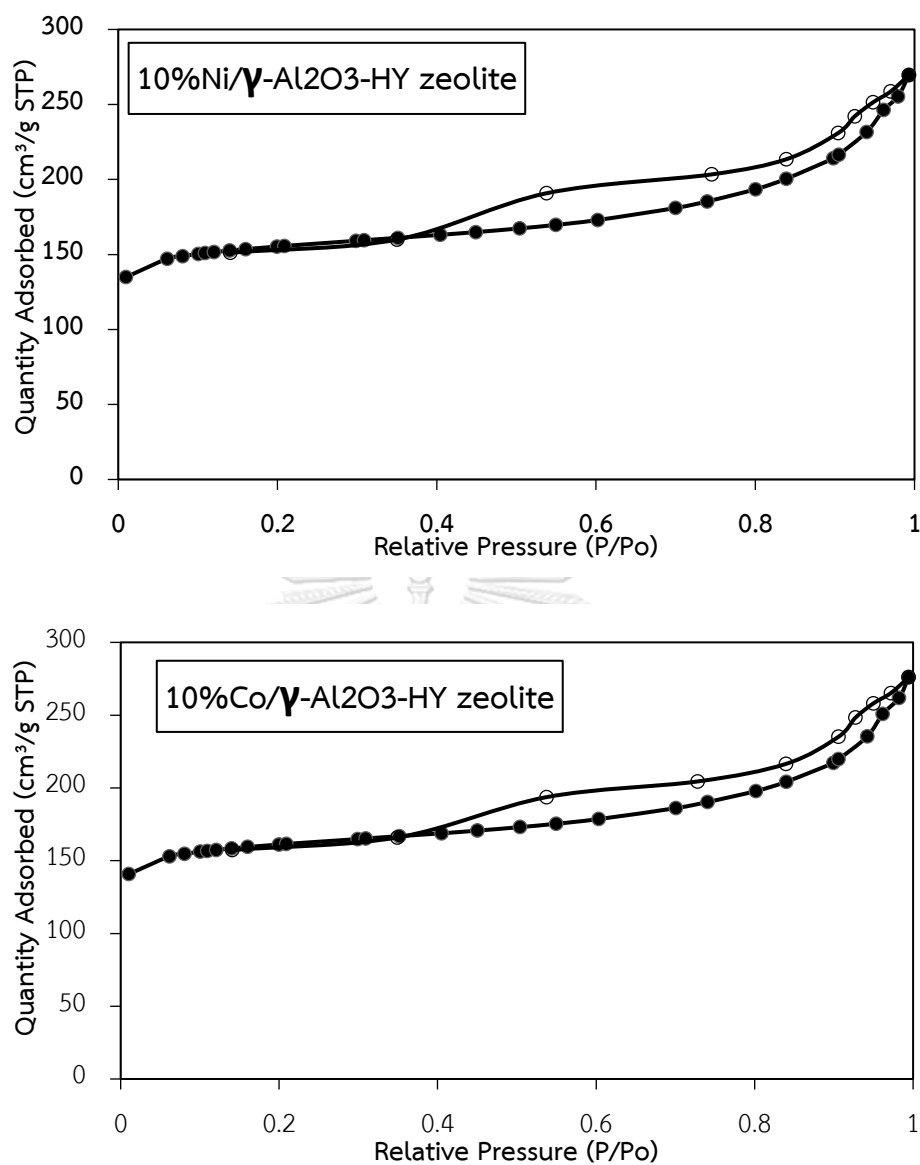


Figure 4.1 N₂ adsorption-desorption isotherm of Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite. (Continue)

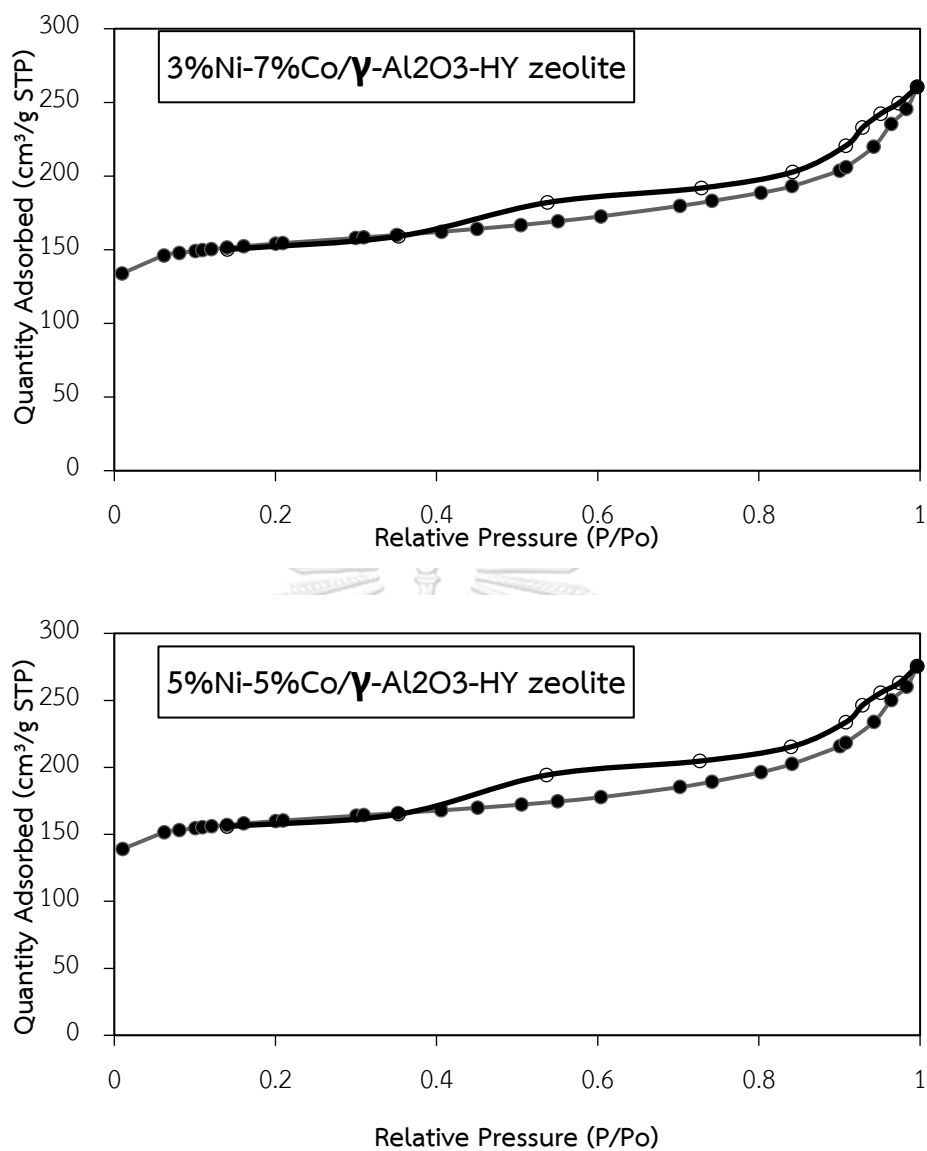


Figure 4.1 N₂ adsorption-desorption isotherm of Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite. (Continue)

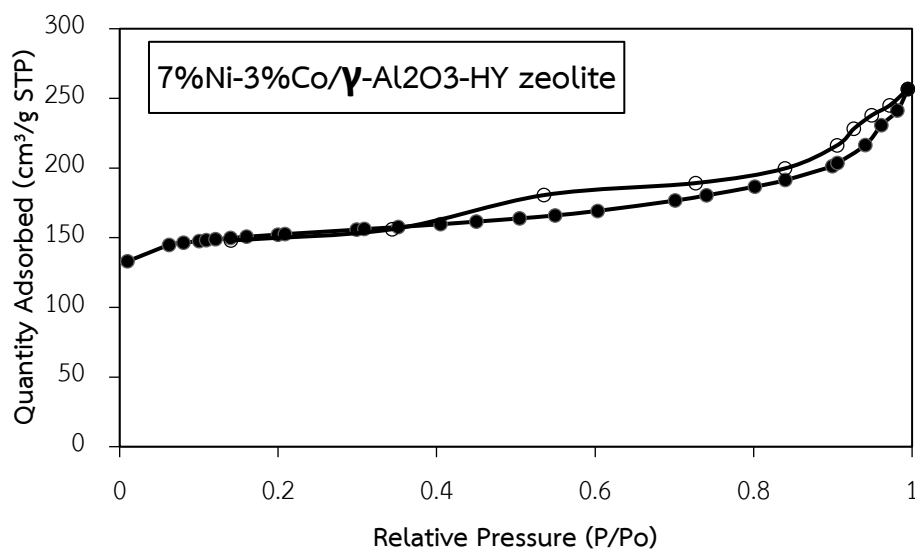


Figure 4.1 N₂ adsorption-desorption isotherm of Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite.

The N₂ adsorption-desorption isotherm of monometallic and bimetallic on γ -Al₂O₃-HY zeolite support are provided in Fig. 4.1. The isotherms of all sample can be classified as a type IV isotherm with H4-shaped hysteresis loops that are implied mesoporous structure associated with the narrow slit-like pore.[28]

4.1.2 X-Ray diffraction pattern (XRD)

The XRD patterns of fresh catalysts are shown in Fig. 4.2. The XRD peaks of NiO at $2\Theta = 37.2^\circ$, 43.3° and 62.8° indicate the (111), (200), and (220) diffractions planes of NiO (JCPDS 01-073-1519), respectively. The XRD peaks of Co_3O_4 cubic phase at 36.9° , 44.9° , and 65.3° indicate (311), (400), and (440) planes of Co_3O_4 (JCPDS 01-076-1802), respectively. It has been demonstrated that Ni and Co species were well dispersed on catalysts surface due to the existing overlaps peaks of NiO and Co_3O_4 of bi-metallic catalysts XRD pattern are difficult to differentiate [29]. The decreasing intensity of NiO and Co_3O_4 over bi-metallic catalysts, when Co was increased, suggested that the incorporation of Co addition species increased the dispersion of NiO, which is in the same way with the other researchers reported results. [18, 24]

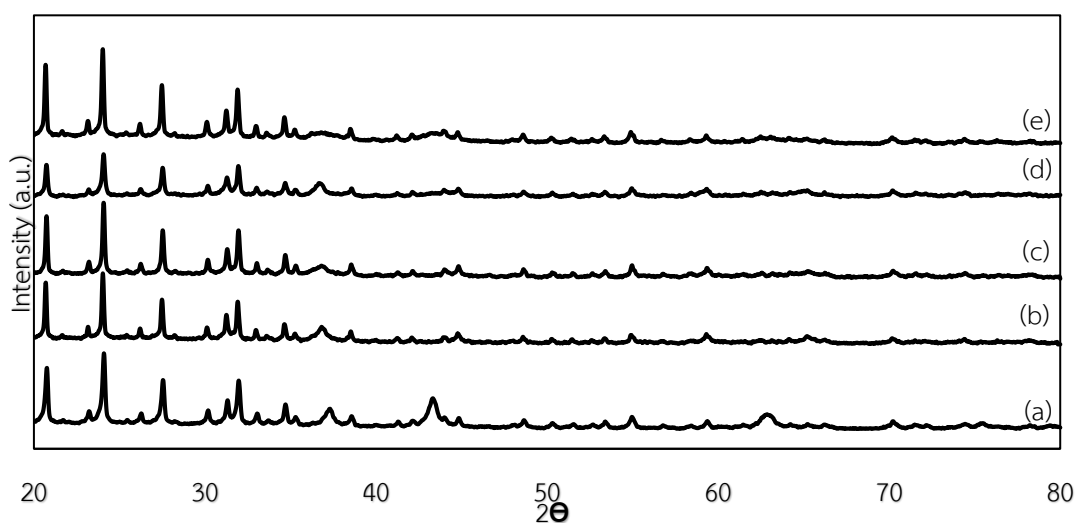


Figure 4.2 The x-ray diffraction pattern of Ni-Co catalysts supported on $\gamma\text{-Al}_2\text{O}_3\text{-HY}$ zeolite. (a:10%Ni/ $\gamma\text{-Al}_2\text{O}_3\text{-HY}$ zeolite, b: 10%Co/ $\gamma\text{-Al}_2\text{O}_3\text{-HY}$ zeolite, c: 3%Ni-7%Co/ $\gamma\text{-Al}_2\text{O}_3\text{-HY}$ zeolite, d: 5%Ni-5%Co/ $\gamma\text{-Al}_2\text{O}_3\text{-HY}$ zeolite, and e: 7%Ni-3%Co/ $\gamma\text{-Al}_2\text{O}_3\text{-HY}$ zeolite)

4.1.3 Scanning Electron Microscopy (SEM)

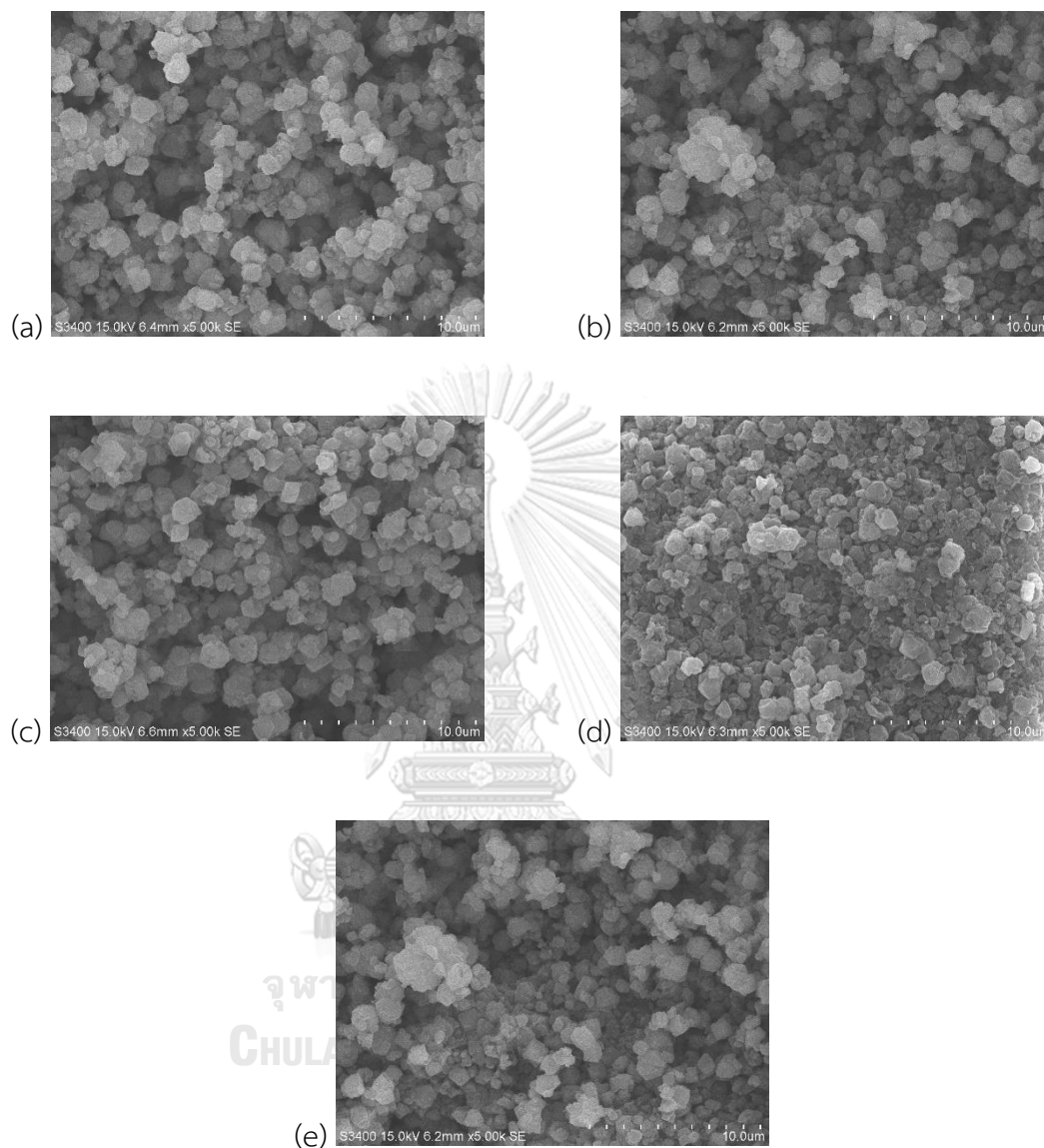


Figure 4.3 SEM images of fresh catalysts. (a: 10%Ni/ γ -Al₂O₃-HY zeolite, b:10%Co/ γ -Al₂O₃-HY zeolite, c: 3%Ni-7%Co/ γ -Al₂O₃-HY zeolite, d: 5%Ni-5%Co/ γ -Al₂O₃-HY zeolite, e: 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite)

Fig. 4.3 shows the morphology of fresh Ni-Co over Al₂O₃-HY zeolite catalysts which was studied by Scanning Electron Microscopy (SEM). Most catalysts had similar surface morphology and particle size, which is similar to the BET pore volume and average pore diameter results.

4.1.4 CO chemisorption

Table 4.2 CO chemisorption results of Ni, Co, and Ni-Co over γ -Al₂O₃-HY zeolite catalysts.

Catalysts	Active sites (x10 ¹⁸)	%Dispersion
10%Ni/ γ -Al ₂ O ₃ -HY	1.16	0.11
10%Co/ γ -Al ₂ O ₃ -HY	4.64	0.45
3%Ni-7%Co/ γ -Al ₂ O ₃ -HY	0.51	0.05
5%Ni-5%Co/ γ -Al ₂ O ₃ -HY	1.05	0.11
7%Ni-3%Co/ γ -Al ₂ O ₃ -HY	13.81	1.35

Table 4.2 shows the amount of CO chemisorption for Ni-Co over γ -Al₂O₃-HY zeolite at room temperature. The amount of CO adsorption on the catalysts was used to calculate the active site of the catalyst. 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite had the highest active site and the metal dispersion. In accordance with another research reporting that using high average pore diameter of the catalyst can improve active metals dispersion pore structures and provide larger active surface area per unit weight of the active metal.[25, 26] In addition, from XRD result the bi-metallic catalyst has lower intensity peak of NiO and Co₃O₄ than the monometallic catalyst. In the same ways, the bi-metallic catalyst had decreased the oxide form but increased the amount of metal due to the amount of CO adsorbed to the metal on the surface. While the dispersion of metal atoms on the catalyst surface can be illustrated by the ratio between the total number of metal atoms that is accessible to the adsorbate divided by the total metal atoms in sample[30][30].

4.1.5 EDX analysis

Moreover, the EDX analysis was used to confirm the metal dispersion. The results showed the uniform in the dispersion of Ni, Co, Si, and Al. The density of Ni and Co were shown as a dot in Fig. 4.4 of the 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite was highest compared to the others, that equal to the results calculated from the amount of adsorbed carbon monoxide from CO chemisorption.

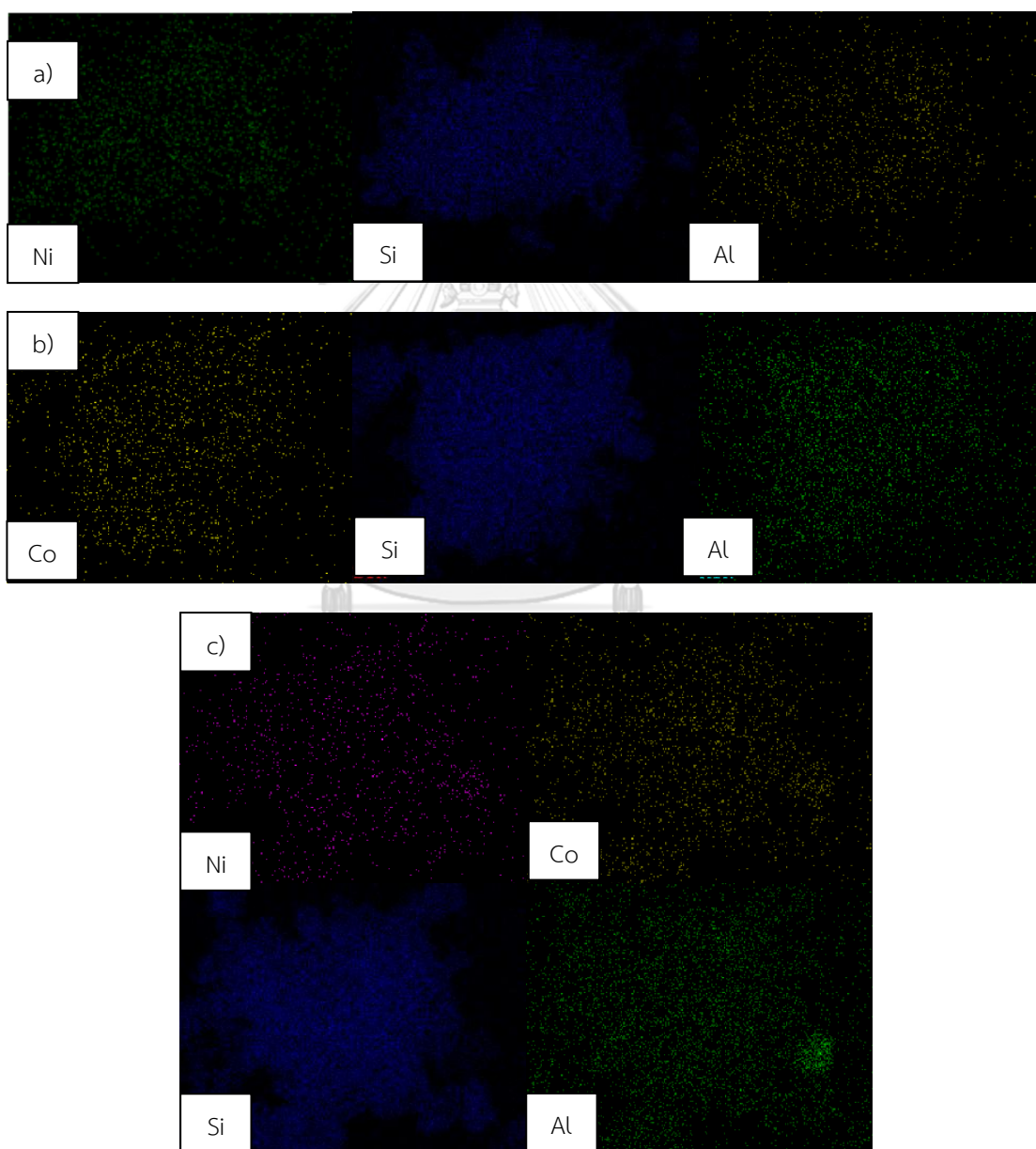


Figure 4.4 EDX analysis of the Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite.

(Continue)

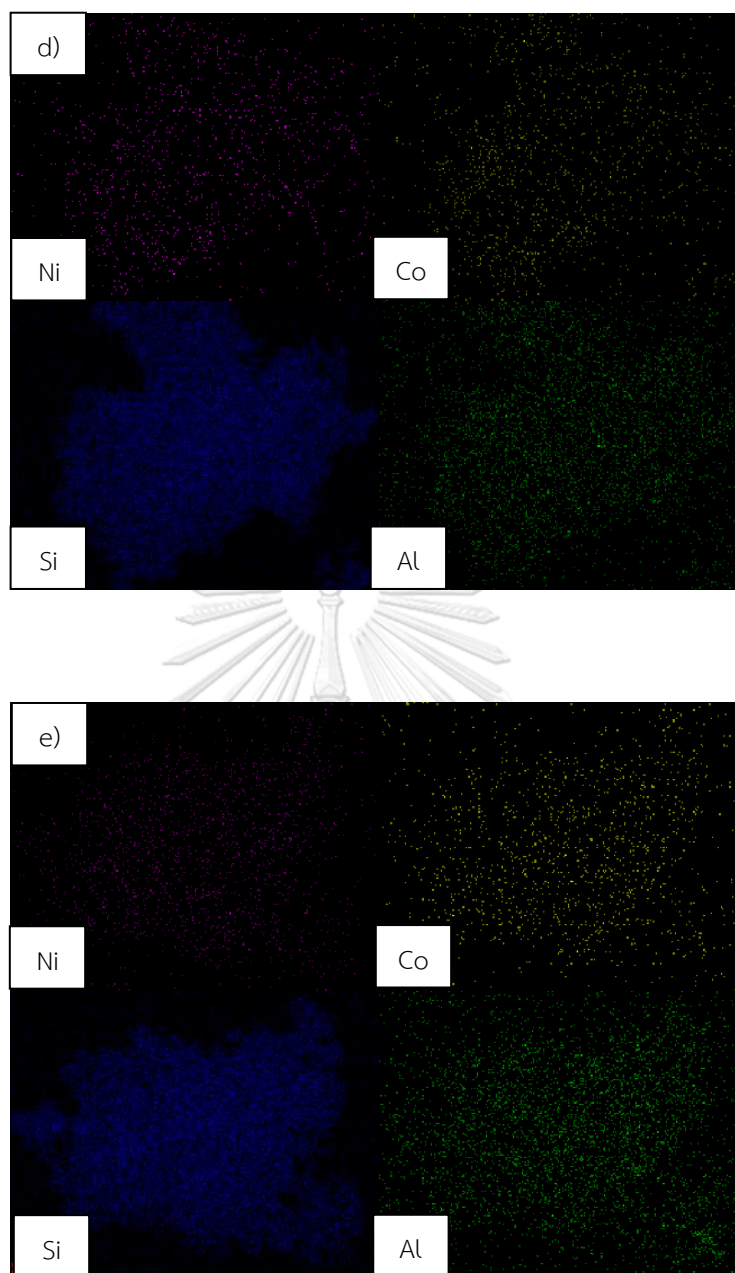


Figure 4.4 EDX analysis of the Ni-Co catalysts supported on γ - Al_2O_3 -HY zeolite. (a:10%Ni/ γ - Al_2O_3 -HY zeolite, b:10%Co/ γ - Al_2O_3 -HY zeolite, c: 3%Ni-7%Co/ γ - Al_2O_3 -HY zeolite, d: 5%Ni-5%Co/ γ - Al_2O_3 -HY zeolite, and e: 7%Ni-3%Co/ γ - Al_2O_3 -HY zeolite)

4.1.6 Hydrogen Temperature Programmed Reduction (H₂-TPR)

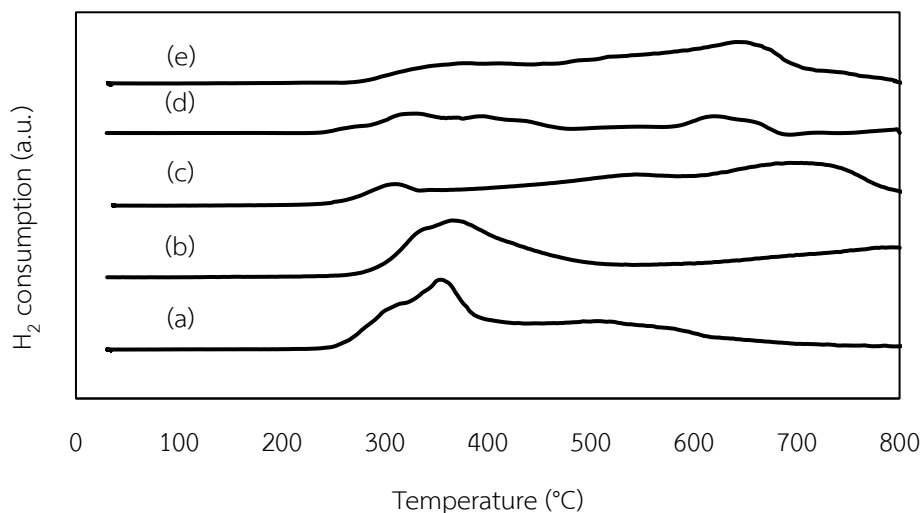


Figure 4.5 The H₂-TPR profiles of the Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite. (a:10%Ni/ γ -Al₂O₃-HY zeolite, b:10%Co/ γ -Al₂O₃-HY zeolite, c: 3%Ni-7%Co/ γ -Al₂O₃-HY zeolite, d: 5%Ni-5%Co/ γ -Al₂O₃-HY zeolite, and e: 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite)

The reduction behavior of samples can be observed in the several peaks in H₂-TPR profiles of the catalysts as shown in Fig. 4.5. Metal, support, and metal-support interaction affect the H₂-TPR profiles, resulting in difference of reducibility and reduction temperature of catalysts. According to Afzal et al.[31], the reduction of the Ni²⁺ localized in the supercage and/or sodalite cavities are the reduction peaks at low temperature, while at the high temperature are the reduction of the Ni²⁺ localized in hexagonal cavities. According to Fig. 4.5, it was obvious that bi-metallic Ni-Co catalysts exhibited two reduction peaks. From the previous research study, the first peak is related to the reduction from Co₃O₄ to CoO species which were observed at 274°C, 392°C and 367°C for 3%Ni-7%Co/ γ -Al₂O₃-HY zeolite, 5%Ni-5%Co/ γ -Al₂O₃-HY zeolite and 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite respectively. The second peak is related to a reduction from NiO to Ni and CoO to Co metallic that was located at 702 °C, 611 °C and 622 °C for 3%Ni-7%Co/ γ -Al₂O₃-HY zeolite, 5%Ni-5%Co/ γ -Al₂O₃-HY zeolite and 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite in catalysts, respectively. It was consistent with

the previous research that at low temperature a reduction of peak area would be consistent with the Ni content on the catalyst surface. [19] In the same way, the monometallic Co catalysts also exhibited two closely reduction peaks. The peaks of 10%Co/ γ -Al₂O₃-HY zeolite was observed at 337°C and 376°C. However, the monometallic Ni catalysts exhibited only one peak at 378°C with is related to a reduction from NiO to Ni [32].

4.1.7 Ammonia temperature program desorption (NH₃-TPD)

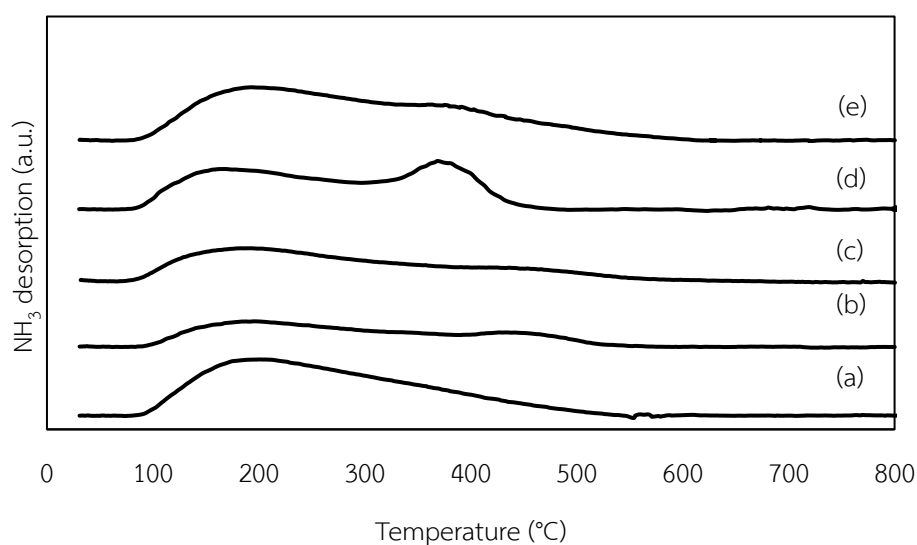


Figure 4.6 The NH₃-TPD profiles of the Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite. (a:10%Ni/ γ -Al₂O₃-HY zeolite, b:10%Co/ γ -Al₂O₃-HY zeolite, c: 3%Ni-7%Co/ γ -Al₂O₃-HY zeolite, d: 5%Ni-5%Co/ γ -Al₂O₃-HY zeolite, and e: 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite)

The ammonia temperature program desorption was a technique used to measure the acidity of the catalysts. According to S. R. Kirumakki et.al., the acid site could be separated into three types: weak acid (150–250°C), medium acid (250–350 °C), and strong acid (350-450°C) strength[33]. The NH₃-TPD profiles of the Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite are shown in Fig. 4.6. The NH₃-TPD profile of 10%Ni/ γ -Al₂O₃-HY zeolite referred to weak acid sites that composed of one broad

peak at low-temperature range of 100 to 500°C. While the Ni-Co/ γ -Al₂O₃-HY zeolite and the 10%Co/ γ -Al₂O₃-HY zeolite indicated two types of acidic sites. Moreover, the acid properties of catalysts were also reported in Table 4.3. The amount of total acid site of bi-metallic catalysts increased with increasing Ni and the 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite had the highest amount of acid sites.

Table 4.3 The acidity of the Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite.

Catalysts	Total acid site, (mmol NH ₃ /g cat)
10%Ni/ γ -Al ₂ O ₃ -HY	43.6273
10%Co/ γ -Al ₂ O ₃ -HY	22.4211
3%Ni-7%Co/ γ -Al ₂ O ₃ -HY	29.6212
5%Ni-5%Co/ γ -Al ₂ O ₃ -HY	37.7807
7%Ni-3%Co/ γ -Al ₂ O ₃ -HY	47.2313

4.1.8 Carbon dioxide temperature program desorption (CO₂-TPD)

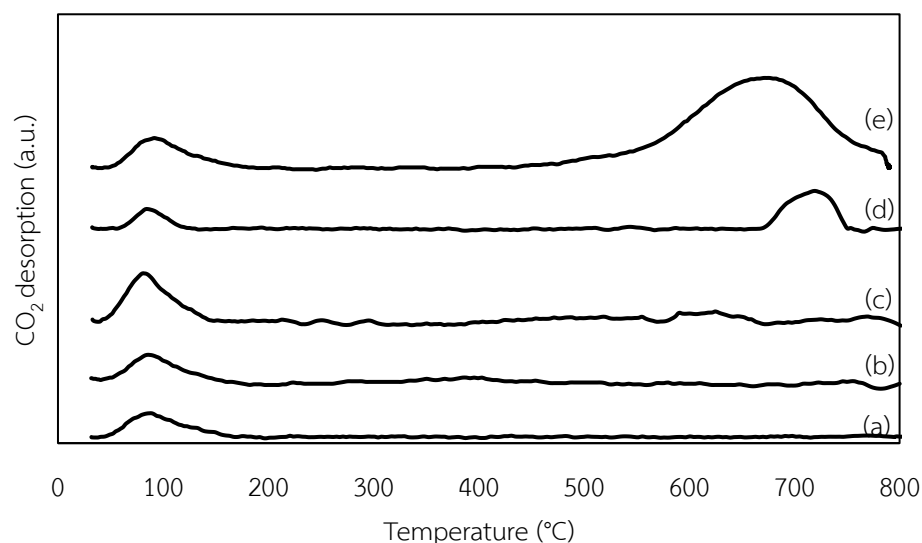


Figure 4.7 The CO₂-TPD profiles of the Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite. (a:10%Ni/ γ -Al₂O₃-HY zeolite, b:10%Co/ γ -Al₂O₃-HY zeolite, c: 3%Ni-7%Co/ γ -Al₂O₃-HY zeolite, d: 5%Ni-5%Co/ γ -Al₂O₃-HY zeolite, and e: 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite)

The basicity of the catalyst is a key property for determining the resistance against carbon formation in CO₂ reforming of methane. The CO₂-TPD profiles of the fresh catalysts were used to determine the catalysts basicity, were illustrated in Fig. 4.7. The CO₂ desorption patterns of bi-metallic catalysts exhibit the highest peak compare to the monometallic catalysts, in which the first peak around 90°C and the second around 655°C attributed to the weak and strong basic sites, respectively. The quantity of basic site of the catalysts is shown in Table 4.4. The 7%Ni-3%Co/ γ -Al₂O₃-HY showed the highest amount of basic sites. According to W. J. Jang et.al., the mildly acidic CO₂ activation that oxidizes the surface carbon can be accelerated by increasing the basicity of the catalysts. Therefore, the bi-metallic catalysts might activate CO₂ on the catalyst surface, which would be provided from basicity higher than other catalysts[34, 35].

Table 4.44 The basicity of the Ni-Co catalysts supported on γ -Al₂O₃-HY zeolite.

Catalysts	Total basic site, ($\mu\text{mol CO}_2/\text{g cat}$)
10%Ni/ γ -Al ₂ O ₃ -HY	5.0099
10%Co/ γ -Al ₂ O ₃ -HY	5.6194
3%Ni-7%Co/ γ -Al ₂ O ₃ -HY	9.2512
5%Ni-5%Co/ γ -Al ₂ O ₃ -HY	10.6920
7%Ni-3%Co/ γ -Al ₂ O ₃ -HY	15.3839



4.2 Catalysts performance

4.2.1 Effect of bimetallic catalysts with different loading ratio of nickel metal and cobalt metal on γ - Al_2O_3 -HY zeolite support.

4.2.1.1 Catalysts activity and stability.

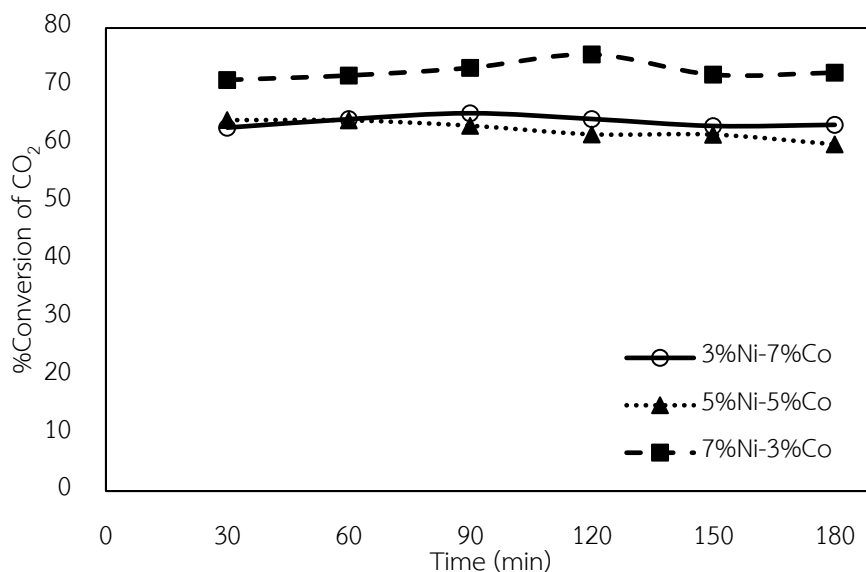


Figure 4.8 CO₂ conversion of Ni-Co over γ - Al_2O_3 -HY zeolite with difference loading ratio of nickel metal and cobalt metal.

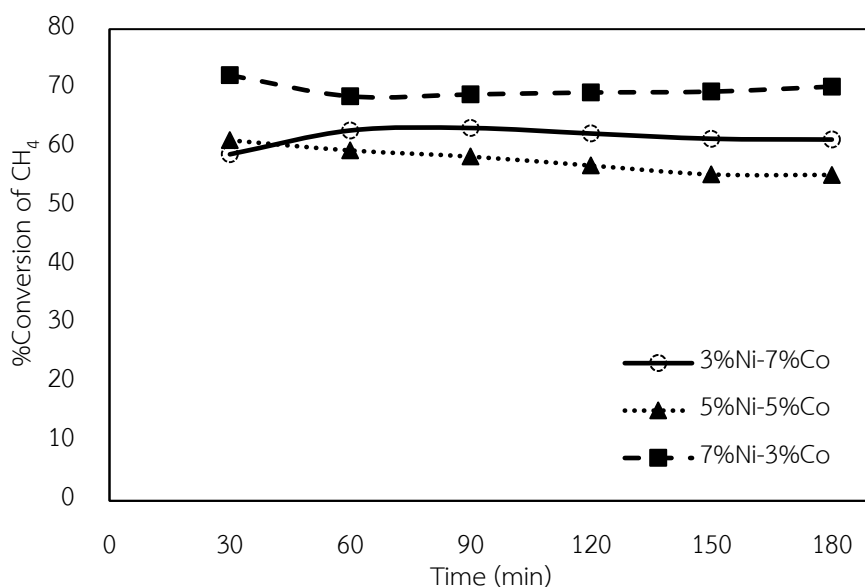


Figure 4.9 CH₄ conversion of Ni-Co over γ - Al_2O_3 -HY zeolite with difference loading ratio of nickel metal and cobalt metal.

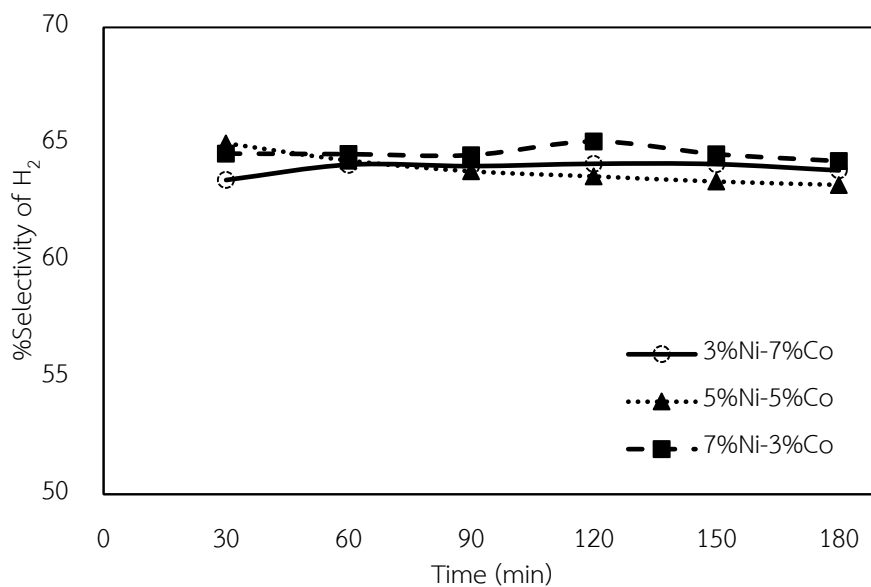


Figure 4.10 H₂ selectivity of Ni-Co over γ -Al₂O₃-HY zeolite with difference loading ratio of nickel metal and cobalt metal.

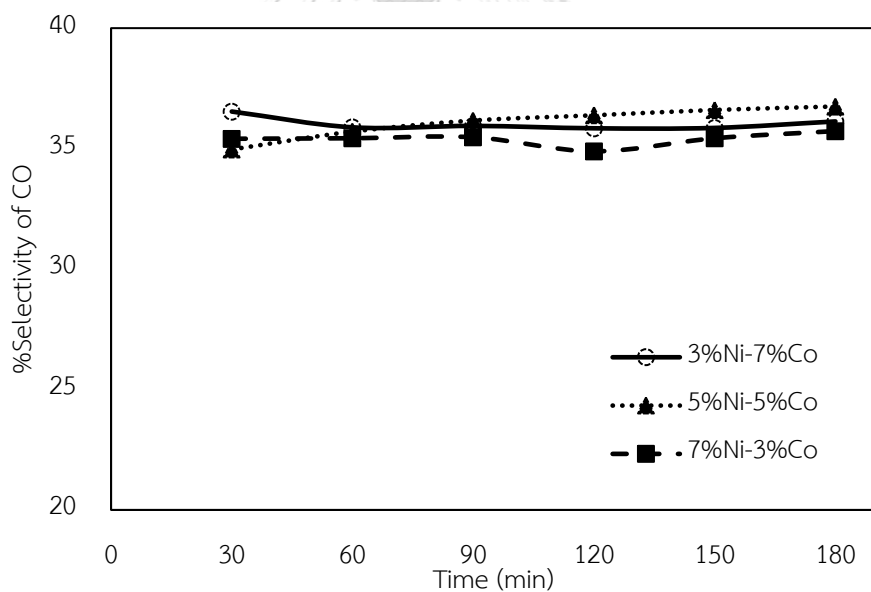


Figure 4.11 CO selectivity of Ni-Co over γ -Al₂O₃-HY zeolite with difference loading ratio of nickel metal and cobalt metal.

The catalysts have been tested the stability at 700°C for 180 min. Before the reaction, the prepared catalysts were reduced in flowing H₂ for 1 hr. The feed conversion and product selectivity, that was calculated based on the amount of H₂ and CO product of Ni-Co/ γ -Al₂O₃-HY zeolite for dry reforming of methane are shown in Fig. 4.8 - 4.11. Since the occurrence of reverse water-gas shift reaction that occurs all the time, the CO₂ conversion of all catalysts is higher than the CH₄ conversion[36]. After 180 min, the results showed that there was no significant deactivation for all catalysts. It means that during the activity test, the activity of the catalysts was stable with increasing time on steam. However, the 7%Ni-3%Co/Al₂O₃-HY zeolite had the highest CO₂ conversion, CH₄ conversion, and H₂ selectivity but had the lowest CO selectivity, that was in accordance with the CO chemisorption result expressing the high active site and high metal dispersion of the catalysts[25, 26].

4.2.1.2 Catalysts characterization after the performance test

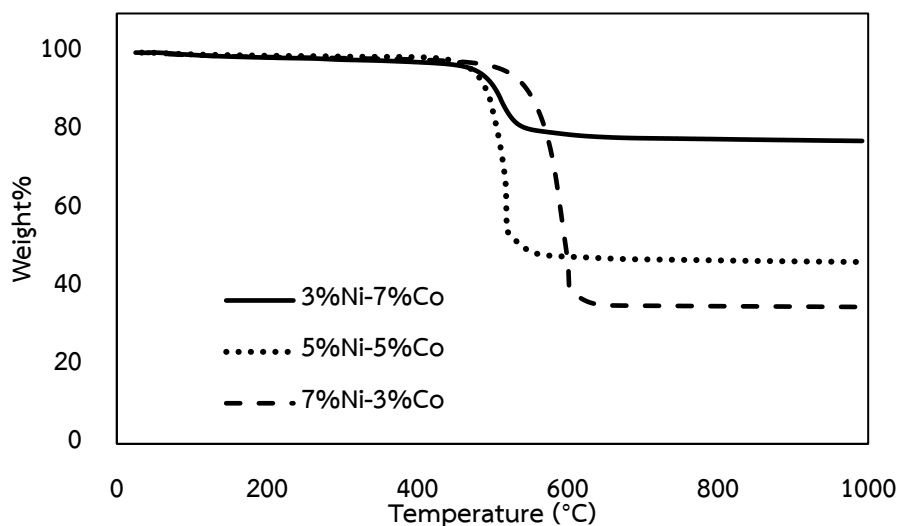


Figure 4.12 Thermogravimetric analysis of the spent catalysts after 180 min of reaction.

Thermogravimetric analysis with heating temperature ranging from room temperature to 1000°C was used to investigate the possible coke deposition of the used catalysts as shown in Fig. 4.12. The moisture and other volatile contents may

correspond to the weight loss at the temperature range up to 500-600°C[37]. According to the result, the weight loss of 7%Ni-3%Co/Al₂O₃-HY zeolite represented the higher weight loss (65%) than 5%Ni-5%Co/Al₂O₃-HY zeolite (53.5%) and 3%Ni-7%Co/Al₂O₃-HY zeolite represented the lowest weight loss (26.6%) due to the Ni had a major role in coke accumulation[38] while Co decreased the amount of deposited carbon[39]. According to the catalysts activity and stability although the 7%Ni-3%Co/Al₂O₃-HY zeolite had the highest weight loss from TGA results but the catalytic performance on 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite catalyst had the promising activity compared with the other catalysts.



4.2.2 Effect of monometallic (10%Ni, 10%Co) and bimetallic (7%Ni-3%wt.Co) on γ -Al₂O₃-HY zeolite support.

4.2.2.1 Catalysts activity and stability.

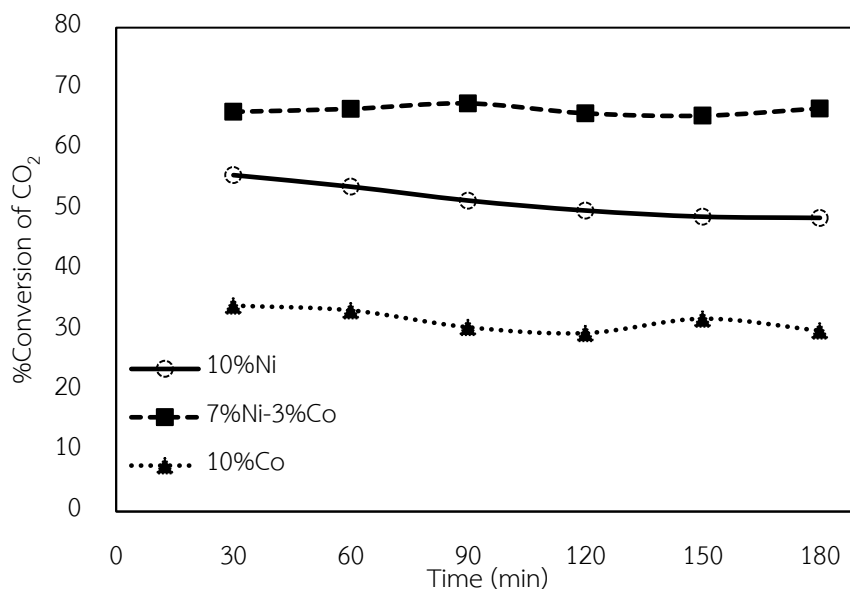


Figure 4.13 CO₂ conversion of monometallic and bimetallic on γ -Al₂O₃-HY zeolite support.

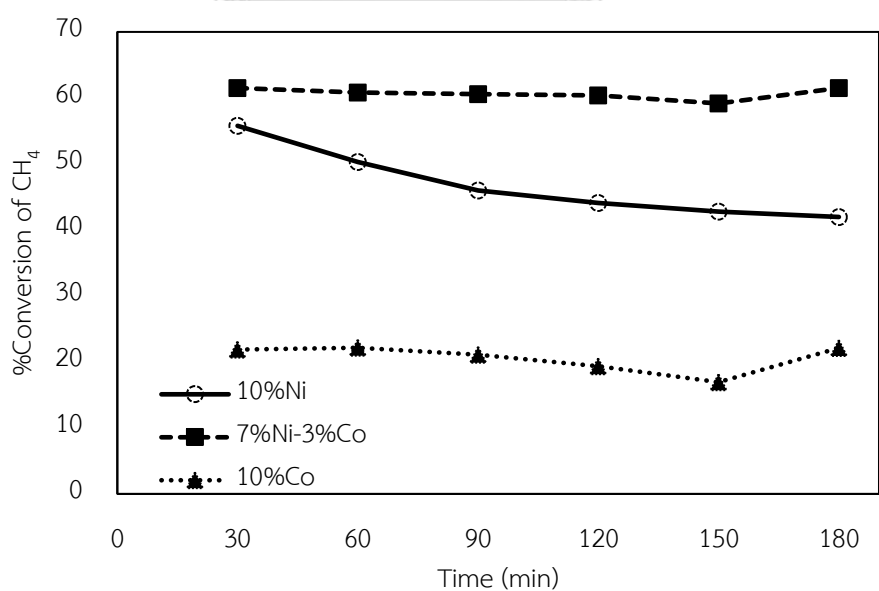


Figure 4.14 CH₄ conversion of monometallic and bimetallic on γ -Al₂O₃-HY zeolite support.

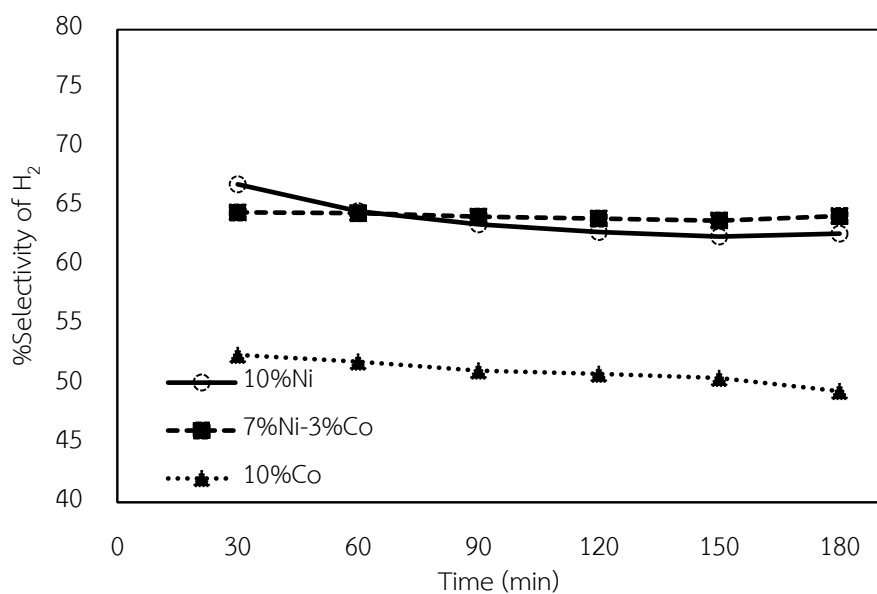


Figure 4.15 H₂ selectivity of monometallic and bimetallic on γ -Al₂O₃-HY zeolite support.

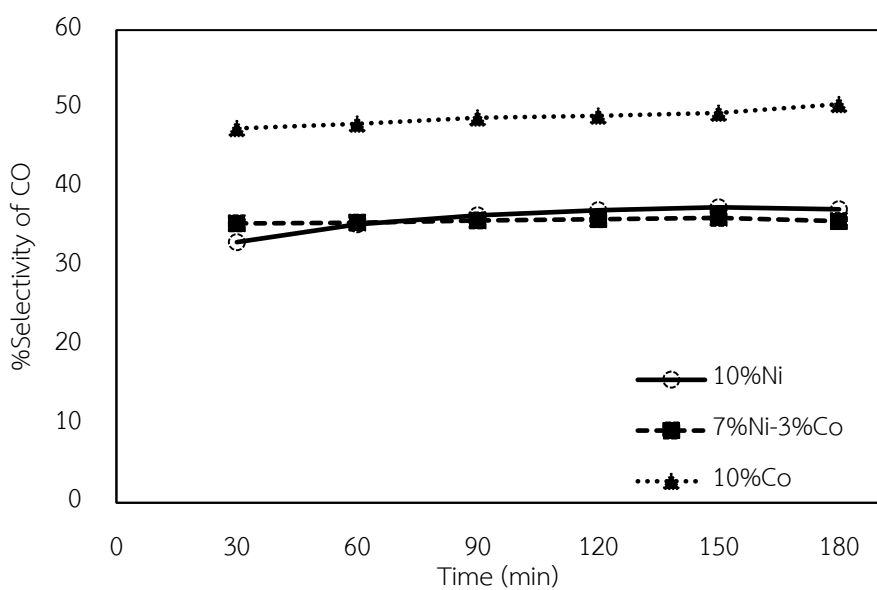


Figure 4.16 CO selectivity of monometallic and bimetallic on γ -Al₂O₃-HY zeolite support.

The monometallic and bimetallic, that was the best activity from part 4.2.1, were tested the stability at 700°C for 180 min. According to Fig. 4.13 – 4.16 which provided the catalysts activity and stability results. The results showed that there was no significant deactivation for 7%Ni-3%Co/ γ -Al₂O₃-HY and 10%Co/ γ -Al₂O₃-HY catalyst after 180 min meaning that during the activity testing the activity of 7%Ni-3%Co/ γ -Al₂O₃-HY and 10%Co/ γ -Al₂O₃-HY catalyst is stable while the 10%Ni/ γ -Al₂O₃-HY catalysts were decreased verified by time-on-steam. This is due to the amount of coke deposition during DRM over all of the catalysts [40]. According to the CO chemisorption results, high amount of active sites and high metal dispersion of catalysts are important for a stable and active DRM catalyst[25, 26]. Moreover, the 10%Co/ γ -Al₂O₃-HY catalyst had lower activity than the other two catalysts due to lower activity of Co metal compared to Ni[41]. According to Tanios C. et. al., the amount of deposited carbon can be reduced by the addition of Co. Nevertheless, the Co decreases the activity[39]. Therefore, the catalytic performance on bi-metallic catalyst had a better activity trend than monometallic catalysts.

4.2.2.2 Catalyst characterization after the performance test

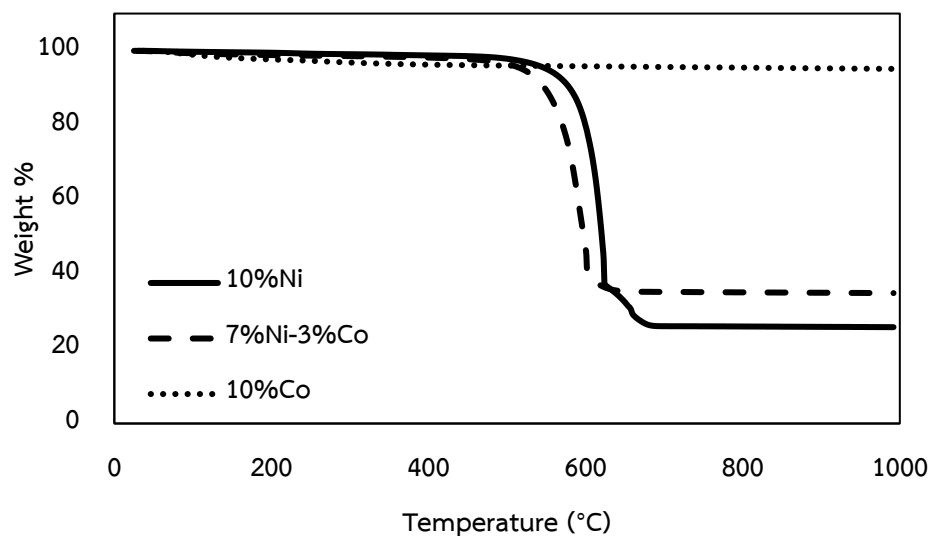


Figure 4.17 Thermogravimetric analysis of the spent catalysts after 180 min of reaction.

According to the result in Fig. 4.17, the weight loss of 10%Ni/ γ -Al₂O₃-HY zeolite represented the higher weight loss (75%) than that of 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite (65%) and 10%Co/ γ -Al₂O₃-HY zeolite represented the lowest weight loss. The results confirmed that Ni had a major role in coke accumulation[42] while Co decreased the amount of deposited carbon[39].

4.2.3 Effect of temperature

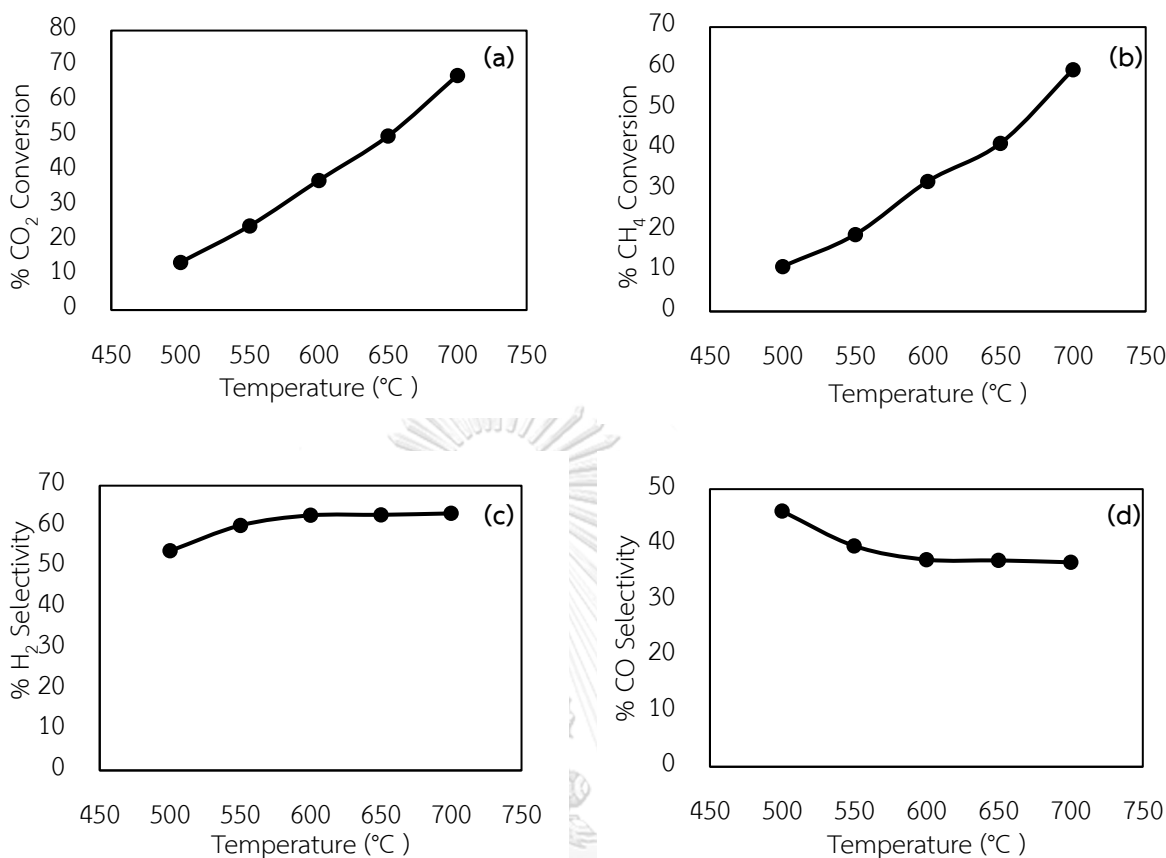


Figure. 4.18 CO₂ reforming of methane over a range of temperature. (a: CO₂ conversions, b: CH₄ conversions, c: H₂ selectivity, and d:CO selectivity)

From the 4.2.2 part, the 7%Ni-3%Co/ γ -Al₂O₃ catalyst was used to test the CO₂ reforming of methane over a range of temperature from 500°C to 700°C. CO₂ conversions are improved with increasing temperature as shown in Fig. 4.18, and also CH₄ conversions are similarly improved from 13% at 500°C to 67% at 700°C. The feed conversions are increased due to the fact that the CO₂ reforming of methane is the endothermic reaction that will be more efficient at high temperature. A reasonably higher conversion of CO₂ than the conversion of CH₄ is exhibited at every temperature due to the reverse water gas shift reaction[16].

4.2.4 Effect of space velocity

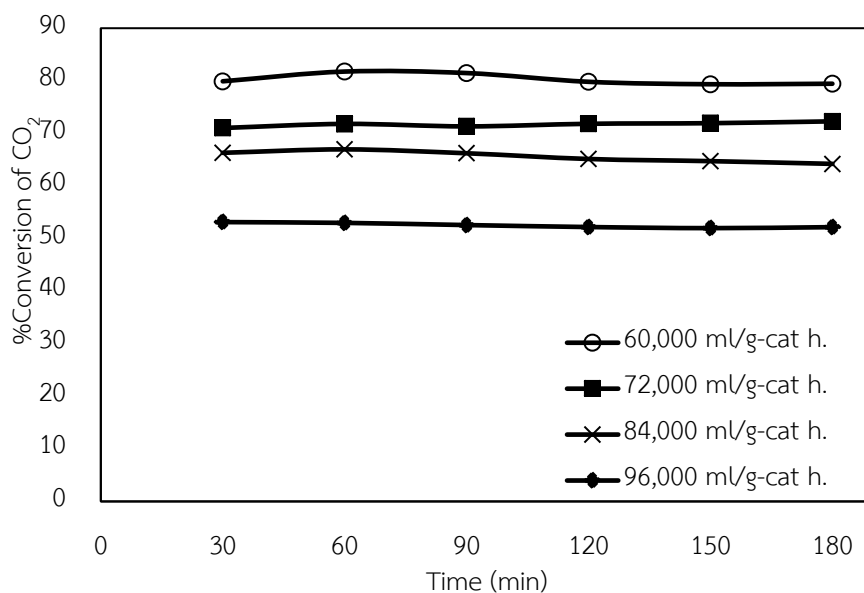


Figure 4.19 CO₂ conversion of 7%Ni-3%Co over γ -Al₂O₃-HY zeolite with difference space velocity at 700°C.

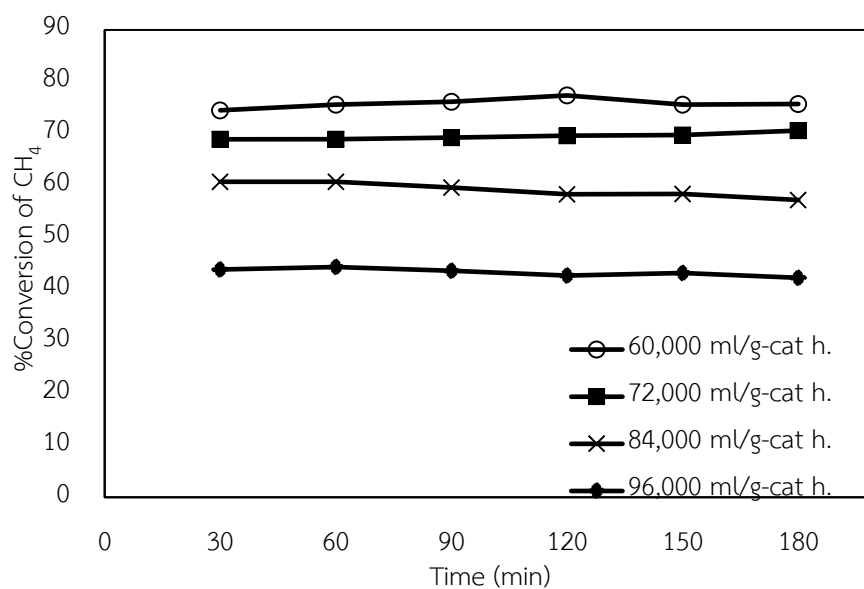


Figure 4.20 CH₄ conversion of 7%Ni-3%Co over γ -Al₂O₃-HY zeolite with difference space velocity at 700°C.

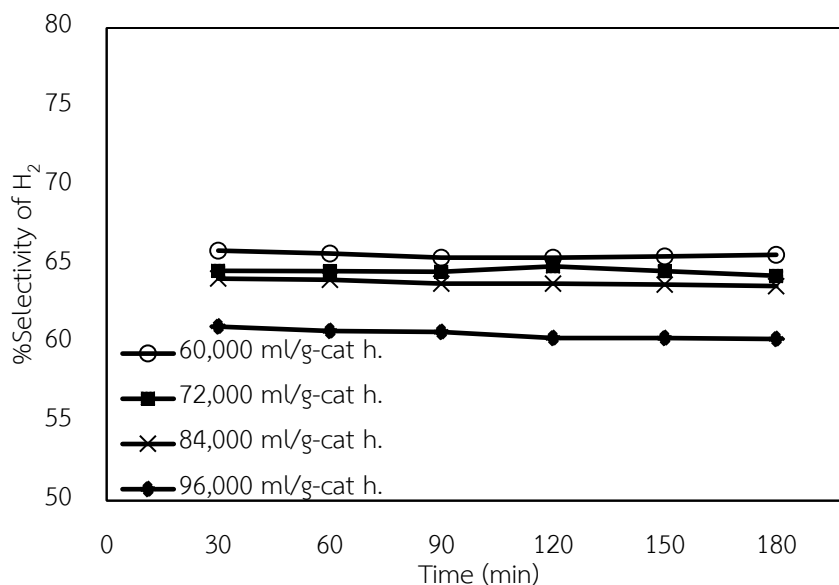


Figure 4.21 H₂ selectivity of 7%Ni-3%Co over γ -Al₂O₃-HY zeolite with difference space velocity at 700°C.

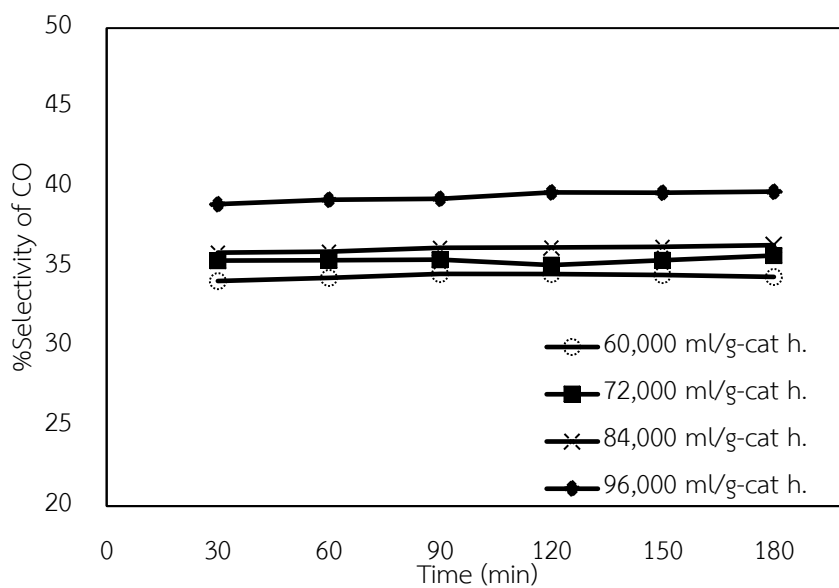


Figure 4.22 CO selectivity of 7%Ni-3%Co over γ -Al₂O₃-HY zeolite with difference space velocity at 700°C.

Space velocity is a key parameter which relates the rate of feed of reactants to the weight of the catalyst. From the 4.2.2 and 4.2.3 parts, the 700°C was chosen for the temperature reaction tests with difference GHSV values. The conversion of CH₄ and CO₂ and the selectivity of H₂ and CO were illustrated in Fig. 4.19 - 4.22,

respectively. At GSHV= 60,000 ml/g-cat h. had the highest percentage of CO₂ conversion (average of 79%), CH₄ conversion (average of 76%), and H₂ selectivity (average of 65%) whereas had the lowest percentage of CO selectivity (average of 34%). They decreased with increasing the GHSV except for the selectivity of CO that was increased when increasing the WHSV. The increasing WHSV values caused the decreasing of the residence time, which may not enough time for carbon gasification to occur that reduce carbon poisoning[5, 16]. Therefore, better conversions were related to higher residence time.

4.3 Mechanistic of CO₂ reforming of methane

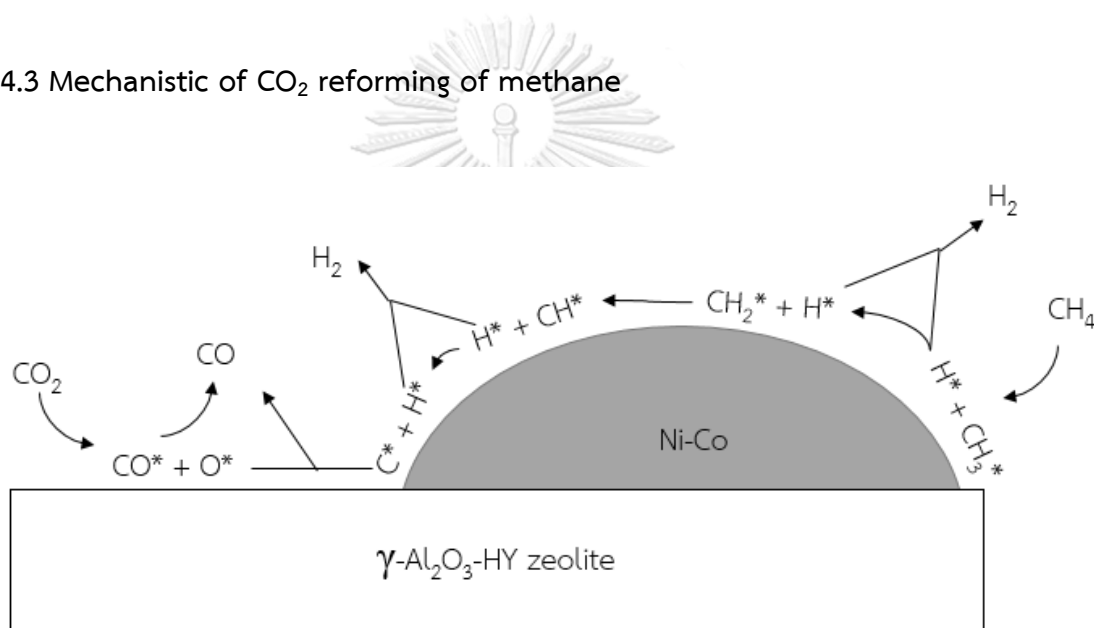


Figure 4.23 Proposed mechanism of the Ni-Co catalysts over $\gamma\text{-Al}_2\text{O}_3\text{-HY}$ zeolite for CO₂ reforming of methane.

The mechanistic concept of CO₂ reforming of methane is shown in Fig. 4.23. As shown, CH₄ may be adsorbed on metal surface via dissociative adsorption to yield CH_x (x=0-3) and H₂. On the other hand, CO₂ was proposed to be adsorbed on support surface, dissociating to CO and O species. In addition, some C* radical and O* radical species may also react to form CO as well[43-45].

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this research studied the CO₂ reforming of methane was studied the effect of bi-metallic catalysts with different loading ratio of nickel metal and cobalt metal on γ -Al₂O₃-HY zeolite support, the effect of monometallic and bimetallic on γ -Al₂O₃-HY zeolite support, the effect of temperature reaction, and the effect of space velocity. The results can conclude as follows:

1) The bi-metallic catalysts over γ -Al₂O₃-HY zeolite had been tested the stability at 700°C for 180 min. It has been found that the CO₂ conversion of all catalysts is more than the CH₄ conversion due to the occurrence of reverse water-gas shift reaction and 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite was the best option among the other catalysts. The optimum catalyst had higher metal dispersion and high metal active sites. Moreover, the high CO₂ adsorption induced by which may be responsible for the improved catalytic activity and selectivity for dry reforming of CH₄.

2) In the second part, the bi-metallic catalysts support over γ -Al₂O₃-HY zeolite had higher activity and stability than the monometallic catalysts because it had high metal dispersion, many active sites, and strong metal support interaction between the Ni-Co bimetallic and γ -Al₂O₃-HY zeolite.

3) In the third part, studying the effect of reaction temperature can found that CO₂ and CH₄ conversions were improved with increasing temperature. Therefore, 700°C was the temperature given the highest CO₂ and CH₄ conversions with high H₂ selectivity.

4) In the last part studied the effect of space velocity which is a key parameter that relates to the rate of feed of reactants to the weight of the catalyst at 700°C with using 7%Ni-3%Co/ γ -Al₂O₃-HY zeolite as the catalyst for CO₂ reforming

of methane. It was found that CO_2 conversion, CH_4 conversion, and H_2 selectivity decreased with increasing the GHSV due to the decreasing of the residence time so the better conversions were related to the higher residence time.

5.2 Recommendations

From this research study, the author recommended to improve catalytic performance for the future study as follows:

1. Study the catalytic performance in different synthesis calcination temperature.
2. The catalytic performance of bimetallic Ni-Co/ γ - Al_2O_3 -HY zeolite should be investigated the type of acidity (Bronsted and Lewis) with pyridine desorption and Fourier Transform Infrared Spectrophotometer (FTIR) for the synthetic catalyst.
3. Study the catalytic performance in different feed reactant ratio.
4. Study the catalytic performance in different reduce temperature.

Appendix A

CALCULATION FOR CATALYSTS PREPARATION

A.1. Preparation of γ -Al₂O₃-HY zeolite Supports by Sol-gel method

The preparation of γ -Al₂O₃-HY zeolite used as the support by the sol-gel method was prepared by the following calculation:

Reagent:	Aluminum isopropoxide (98%)	Molecular weight = 204.24 g/mol
	HY-zeolite	Si/Al molar ratio = 100
	Ethanol	
	Deionized water	Molecular weight = 18 g/mol
		Density = 1 g/cm ³
	Hydrochloric acid (37.7%)	

Calculation: Weight ration of γ -Al₂O₃ : HY zeolite = 1:3

Based on 5 g of Aluminum isopropoxide.

$$\begin{aligned} \text{HY} &= 5 \text{ g} \times \frac{3}{1} \\ &= 15 \text{ g} \end{aligned}$$

Therefore used 15 g of HY zeolite.

For molar ratio of Al₂O₃/H₂O = 0.1/15

$$\begin{aligned} \text{Aluminum isopropoxide} &= 0.1 \text{ mol} \\ &= 0.1 \text{ mol} \times 204.24 \text{ g/mol} \\ &= 20.42 \text{ g} \\ \text{H}_2\text{O} &= 15 \text{ mol} \\ &= 15 \text{ mol} \times 18 \text{ g/mol} \\ &= 270 \text{ g} \\ \text{Used aluminum isopropoxide} &= 5 \text{ g} \\ \text{Therefore, required H}_2\text{O} &= \frac{5 \text{ g} \times 270 \text{ g}}{20.42 \text{ g}} \\ &= 66.10 \text{ g} \end{aligned}$$

For volume ratio of H₂O/Ethanol = 1/1

$$\begin{aligned} \text{H}_2\text{O} &= 66.10 \text{ g} \times \frac{1 \text{ cm}^3}{1 \text{ g}} \\ &= 66.10 \text{ cm}^3 \\ \text{Therefore, required Ethanol} &= 66.10 \text{ cm}^3 \end{aligned}$$

A.2 Preparation of Ni-Co over γ -Al₂O₃-HY zeolite by incipient wetness impregnation method

The preparation of Ni-Co over γ -Al₂O₃-HY zeolite by incipient wetness impregnation method with different loading ratio of nickel metal and cobalt metal were prepared by the following calculation:

Example: The preparation of 5%Ni-5%Co/ γ -Al₂O₃-HY zeolite.

Reagent: Nickel (II) nitrate hexahydrate (98%)	Molecular weight = 290.79 g/mol
Nickel	Molecular weight = 58.693 g/mol
Cobalt (II) nitrate hexahydrate (98%)	Molecular weight = 291.03 g/mol
Cobalt	Molecular weight = 58.933 g/mol

Calculation: Based on 1.5 g catalyst contains 10%wt metal over γ -Al₂O₃-HY zeolite.

$$\begin{aligned} \text{Therefore, Ni} &= 0.05 \times 1.5 \text{ g} \\ &= 0.075 \text{ g} \\ \text{Co} &= 0.05 \times 1.5 \text{ g} \\ &= 0.075 \text{ g} \\ \text{Required } \gamma\text{-Al}_2\text{O}_3\text{-HY zeolite} &= 1.5 \text{ g} - 0.075 \text{ g} - 0.075 \text{ g} \\ &= 1.35 \text{ g} \end{aligned}$$

5%Ni-5%Co/ γ -Al₂O₃-HY zeolite was prepared by used Ni(NO₃)₂.6H₂O and Co(NO₃)₂.6H₂O as metal precursors.

$$\begin{aligned} \text{Required Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O} &= \frac{\text{Ni required} \times \text{MW of Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{MW of Ni} \times 0.98} \\ &= \frac{0.075 \text{ g} \times 290.79 \text{ g/mol}}{58.693 \text{ g/mol} \times 0.98} \\ &= 0.3792 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Required Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} &= \frac{\text{Co required} \times \text{MW of Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{MW of Co} \times 0.98} \\ &= \frac{0.075 \text{ g} \times 291.03 \text{ g/mol}}{58.933 \text{ g/mol} \times 0.98} \\ &= 0.3779 \text{ g} \end{aligned}$$



APPENDIX B

CALIBRATION CURVES

This appendix showed the calibration curves which used to calculate the mole composition of reactants and products in CO₂ reforming of methane reaction.

The feed and final product gas were analyzed the composition by Thermal Conductivity Detector type gas chromatograph (Shimadzu, GC-8A) equipped with Poropak-Q and Molecular sieve 5A packed column.

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 of carbon dioxide, methane, hydrogen, and carbon monoxide.

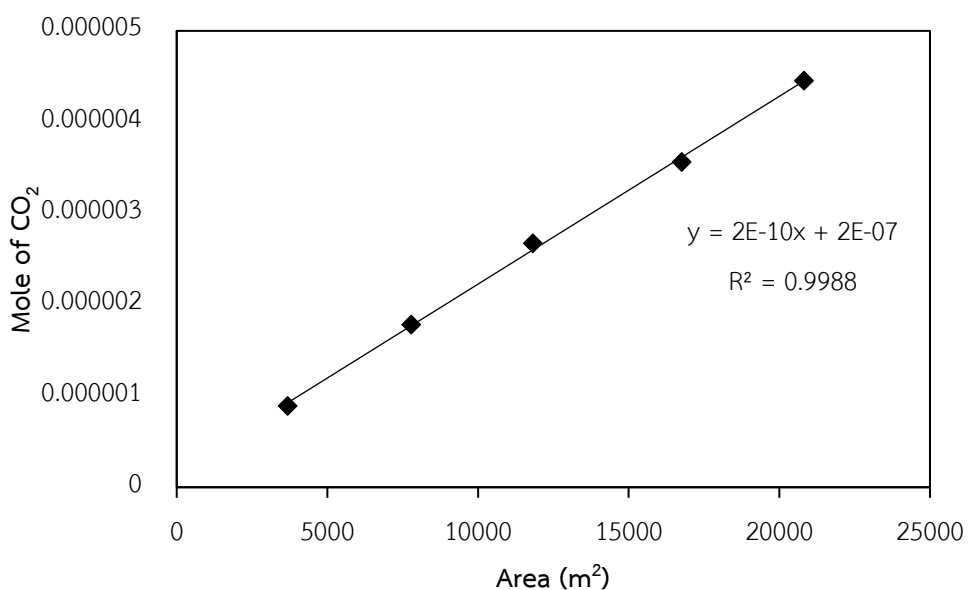


Figure B.1 The calibration curve of carbon dioxide.

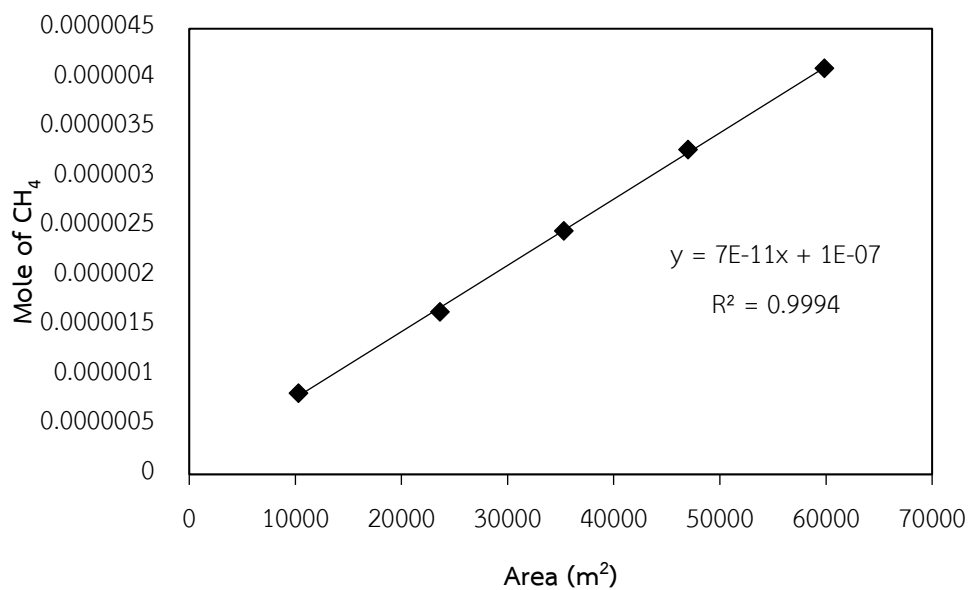


Figure B.2 The calibration curve of methane.

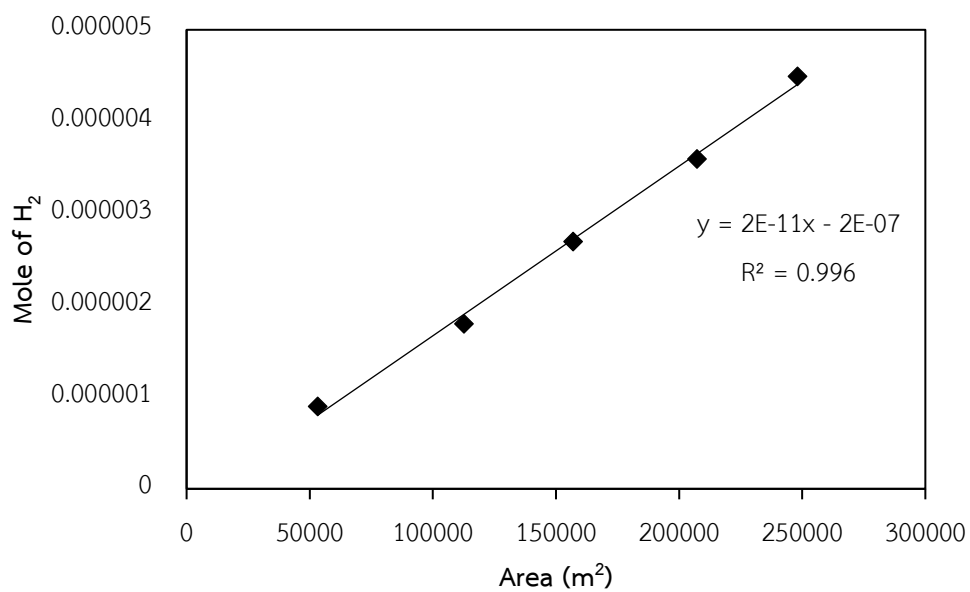


Figure B.3 The calibration curve of hydrogen.

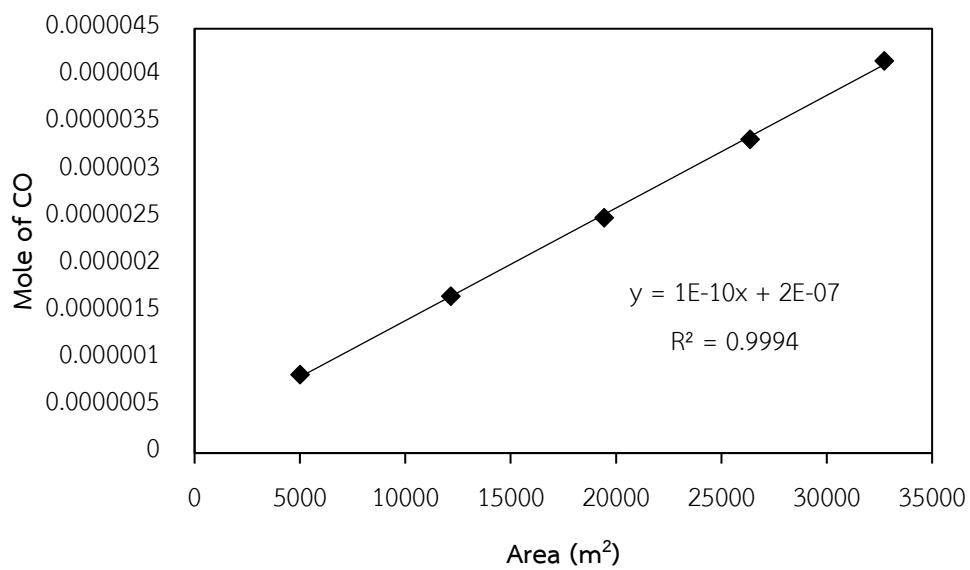


Figure B.4 The calibration curve of carbon monoxide.



APPENDIX C

CALCULATION FOR CONVERSION AND SELECTIVITY

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

Carbon dioxide conversion

$$X_{\text{CO}_2}(\%) = \frac{\text{Mole of CO}_2 \text{ in} - \text{Mole of CO}_2 \text{ out}}{\text{Mole of CO}_2 \text{ in}} \times 100\% \quad \text{Eq. C.1}$$

Methane conversion

$$X_{\text{CH}_4}(\%) = \frac{\text{Mole of CH}_4 \text{ in} - \text{Mole of CH}_4 \text{ out}}{\text{Mole of CH}_4 \text{ in}} \times 100\% \quad \text{Eq. C.2}$$

Hydrogen selectivity

$$S_{\text{H}_2}(\%) = \frac{\text{Mole of H}_2 \text{ out}}{\text{Mole of H}_2 \text{ out} + \text{Mole of CO out}} \times 100\% \quad \text{Eq. C.3}$$

Carbon monoxide selectivity

$$S_{\text{CO}}(\%) = \frac{\text{Mole of CO out}}{\text{Mole of H}_2 \text{ out} + \text{Mole of CO out}} \times 100\% \quad \text{Eq. C.4}$$

Appendix D

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

The number of active metal sites and metal dispersion, which were study by CO chemisorption technique (a stoichiometry of CO/Ni = 1 and CO/Co = 1), were calculated by the following calculation procedure:

Example: 10%Ni/ γ -Al₂O₃-HY zeolite

Let,	S_f	= Stoichiometry factor (CO:Ni)	= 1
	m	= Weight of sample	= 0.05 g
	V_{inj}	= Volume of injected CO	= 0.02 cm ³ /g
	V_{abs}	= Volume adsorbed	= 0.0433 cm ³ /mol
	V_g	= Molar volume of gas at STP	= 22414 cm ³ /mol
	m.w.	= Molecular weight of metal (Ni)	= 59 g/mol
	N_A	= Avogadro's number	= 6.03 × 10 ²³ molecules/mol
	%M	= % Metal loading	= 10% Ni

$$\begin{aligned} \text{Metal dispersion (\%D)} &= S_f \times \frac{V_{abs}}{V_g} \times \frac{m.w.}{\%M} \times 100\% \times 100\% \\ &= 1 \times \frac{0.0433 \text{ cm}^3/\text{g}}{22414 \text{ cm}^3/\text{mol}} \times \frac{59 \text{ g/mol}}{10\%} \times 100\% \times 100\% \\ &= 0.11\% \end{aligned}$$

$$\begin{aligned} \text{Metal active site} &= S_f \times \frac{V_{abs}}{V_g} \times N_A \\ &= 1 \times \frac{0.0433 \text{ cm}^3/\text{g}}{22414 \text{ cm}^3/\text{mol}} \times 6.02 \times 10^{23} \text{ molecules/mol} \\ &= 1.16 \times 10^{18} \text{ molecule of CO/g} \end{aligned}$$

APPENDIX E

CALCULATION OF TOTAL ACID SITES OF CATALYST

The calculation of total acid sites of catalysts, which were study by Ammonia Temperature Programmed, were displayed as follows:

Example: 10%Ni/ γ -Al₂O₃-HY zeolite

Peak area of the NH ₃ -TPD profiles (A)	=	9.60098
Sample weight	=	0.0647 g

The mole of NH₃ was calculated from the calibration curve of NH₃ as formula:

The mole of NH ₃ of the sample	=	0.294 x A mmole
---	---	-----------------

The total acidity of sample	=	<u>The mmole of NH₃ of sample</u> Sample weight
-----------------------------	---	---

	=	<u>0.294 x 9.60098</u> 0.0647
--	---	--

	=	43.6273 mmol NH ₃ /g catalyst
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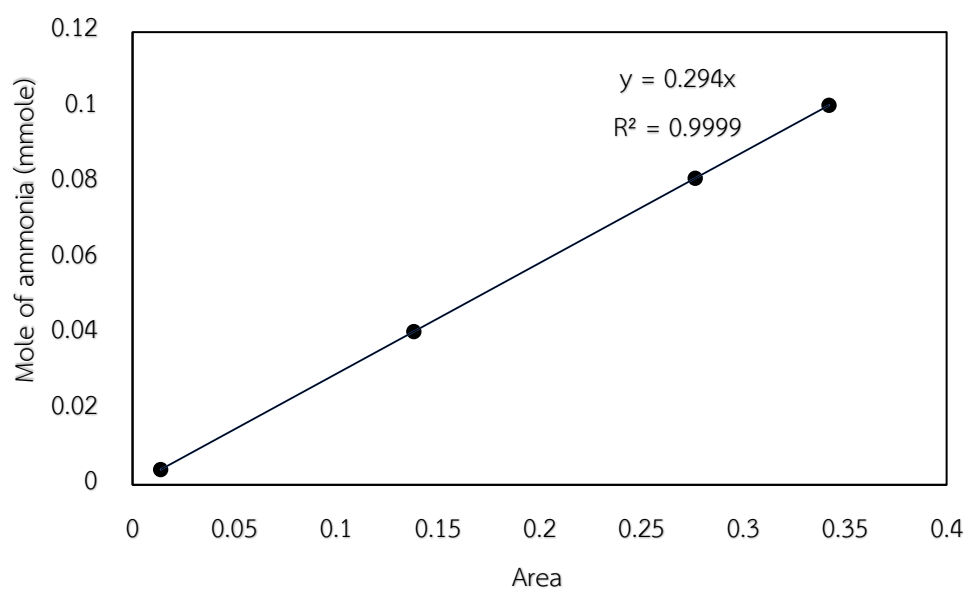


Figure E.1 The calibration curve of ammonia from Micromeritics Chemisorp 2750



APPENDIX F

CALCULATION OF TOTAL BASIC SITES OF CATALYST

The calculation of total basic sites of catalysts, which were study by Carbon dioxide Temperature Programmed, were displayed as follows:

Example: 10%Ni/ γ -Al₂O₃-HY zeolite

Peak area of the CO ₂ -TPD profiles (A)	=	0.021
Sample weight	=	0.0685 g

The mole of CO₂ was calculated from the calibration curve of CO₂ as formula:

The mole of CO ₂ of the sample	=	16.342 x A mmole
---	---	------------------

The total basicity of sample	=	<u>The mmole of CO₂ of sample</u> Sample weight
------------------------------	---	---

	=	<u>16.342 x 0.021</u> 0.0685
--	---	---

	=	5.0099 μ mol CO ₂ /g catalyst
--	---	--

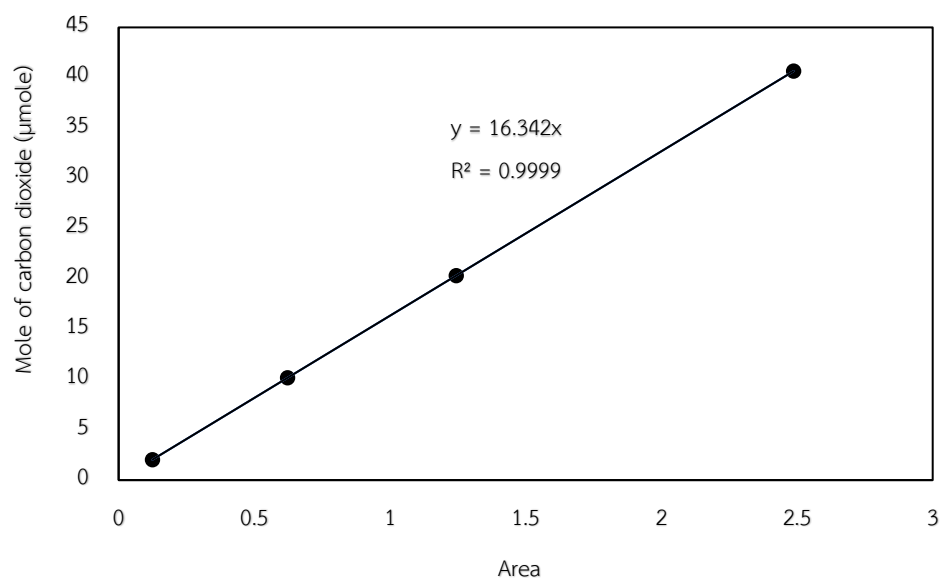


Figure F.1 The calibration curve of carbon dioxide from Micromeritics Chemisorp 2750



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