

การเปรียบเทียบตัวเร่งปฏิกิริยาโลหะเดียวกับโลหะผสม โคบอลต์ นิกเกิล
บนตัวรองรับ $\text{Al}_2\text{O}_3/\text{ZSM-5}$ สำหรับปฏิกิริยาคาร์บอนไดออกไซด์รีฟอร์มมิงของมีเทน



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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

COMPARISON OF MONO METALLIC AND BIMETALLICS Co, Ni CATALYSTS SUPPORTED
ON Al₂O₃/ZSM-5 FOR CO₂ REFORMING OF METHANE

Miss Sutarat Thongratkeaw



A Thesis Submitted in Partial Fulfillment of the Requirements
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สุพาร์ตน์ ทองรัตแก้ว : การเปรียบเทียบตัวเร่งปฏิกิริยาโลหะเกี่ยวกับโลหะผสม โคบอลต์ นิกเกิลบนตัวรองรับ $\text{Al}_2\text{O}_3/\text{ZSM-5}$ สำหรับปฏิกิริยาคาร์บอนไดออกไซด์รีฟอร์มมิ่งของ มีเทน (COMPARISON OF MONO METALLIC AND BIMETALLICS Co, Ni CATALYSTS SUPPORTED ON $\text{Al}_2\text{O}_3/\text{ZSM-5}$ FOR CO_2 REFORMING OF METHANE) อ.ที่ปรึกษา วิทยานิพนธ์หลัก: ผศ. ดร. สุพจน์ พัฒนะศรี, 88 หน้า.

ปฏิกิริยารีฟอร์มมิ่งของมีเทนโดยใช้คาร์บอนไดออกไซด์ ผลิตก๊าซสังเคราะห์ที่มีไฮโดรเจน ต่อคาร์บอนมอนอกไซด์ในอัตราส่วนต่างๆซึ่งเป็นที่ต้องการสำหรับกระบวนการในอุตสาหกรรม ปฏิกิริยานี้ยังมีความสำคัญมากในด้านผลกระทบต่อสิ่งแวดล้อมเนื่องจากทั้งสองก๊าซ คาร์บอนไดออกไซด์และก๊าซมีเทนก่อให้เกิดภาวะเรือนกระจก จึงนำก๊าซเหล่านี้มาเป็นวัตถุดิบที่มีค่า ซึ่งอาจจะช่วยลดก๊าซคาร์บอนไดออกไซด์และก๊าซมีเทนในชั้นบรรยากาศ ในเบื้องต้นได้ทำการศึกษา เปรียบเทียบลำดับการโหลดโลหะนิกเกิลกับโลหะโคบอลต์บนตัวรองรับอะลูมินาผสมซีโอไลท์ชนิด $\text{ZSM-5}(\text{Al}_2\text{O}_3/\text{ZSM-5})$ ที่เปอร์เซ็นต์โหลดโลหะผสม 10เปอร์เซ็นต์จากนั้น นำวิธีการโหลดโลหะที่ เหมาะสมจากส่วนแรก มาเตรียมตัวเร่งปฏิกิริยาในส่วนที่สอง โดยใช้เปอร์เซ็นต์ของโลหะที่โหลดใน ปริมาณที่แตกต่างกันเป็น (10%Ni,7.5%Ni 2.5%Co,5%Ni 5%Co,2.5%Ni 7.5%Co,10%Co) บน ตัวรองรับ $\text{Al}_2\text{O}_3/\text{ZSM-5}$ และเปรียบเทียบ ตัวเร่งปฏิกิริยาโลหะผสมและโลหะเดี่ยว สำหรับปฏิกิริยา คาร์บอนไดออกไซด์รีฟอร์มมิ่งของมีเทน การวิเคราะห์ลักษณะและคุณสมบัติของตัวเร่งปฏิกิริยา กระทำโดย เทคนิคXRD,BET, SEM, NH_3 -TPD, H_2 -TPR, TGA และการดูดซับด้วยก๊าซคาร์บอนมอน ออกไซด์ ปฏิกิริยาคาร์บอนไดออกไซด์รีฟอร์มมิ่งของมีเทนได้ดำเนินการที่สภาวะ 700 องศาเซลเซียส อัตราส่วนคาร์บอนไดออกไซด์ต่อมีเทนเป็น 50:50 ตัวเร่งปฏิกิริยาโลหะผสม (5%Ni 5%Co/ $\text{Al}_2\text{O}_3/\text{ZSM-5}$) มีค่าการเลือกเกิดไฮโดรเจนสูงประมาณ 47เปอร์เซ็นต์ ค่าการเลือกเกิด คาร์บอนมอนอกไซด์ที่ต่ำประมาณ 53เปอร์เซ็นต์ อัตราผลตอบแทนไฮโดรเจนประมาณ 34 เปอร์เซ็นต์ อัตราผลตอบแทน คาร์บอนมอนอกไซด์ประมาณ 78เปอร์เซ็นต์ ค่าการดูดซับคาร์บอน มอนอกไซด์ ค่าการกระจายตัวของโลหะ ค่าตำแหน่งที่เกิดปฏิกิริยาและค่าเสถียรภาพมีค่าสูงแม้จะมี การสะสมตัวของไค้ก่อนข้างสูงกว่าตัวเร่งปฏิกิริยาอื่นๆ

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SUTARAT THONGRATKEAW: COMPARISON OF MONO METALLIC AND BIMETALLICS Co, Ni CATALYSTS SUPPORTED ON Al₂O₃/ZSM-5 FOR CO₂ REFORMING OF METHANE. ADVISOR: ASST. PROF. SUPHOT PHATANASRI, Ph.D., 88 pp.

Carbon dioxide dry reforming of methane produces synthesis gas with variable ratio of hydrogen to carbon monoxide, which is desirable for industrial synthesis processes. This reaction also has much importance in environmental implications since both carbon dioxide and methane contribute to the greenhouse effect. Converting these gases into valuable feedstocks may reduce the atmospheric emission of CO₂ and CH₄. Firstly, the different loading order between 10%Co and 10%Ni metals on Al₂O₃/ZSM-5 was studied. Then, the good catalyst from part one was selected to be investigated in part two. Secondly, the catalysts preparation with different molar ratios to obtain 10%Ni , 7.5%Ni 2.5%Co , 5%Ni 5%Co , 2.5%Ni 7.5%Co and 10%Co on Al₂O₃/ZSM-5 was investigated. Also, the monometallic and bimetallic were compared for CO₂ reforming of methane. The Characterization of chemical and physical properties of catalysts by techniques of X-Ray Diffraction pattern (XRD), Nitrogen physisorption, Scanning Electron Microscopy (SEM), NH₃ Temperature Programmed Desorption (NH₃-TPD), H₂ Temperature programmed reduction (H₂-TPR), Thermo gravimetric analyze (TGA), CO chemisorption was conducted. The CO₂ reforming of methane was carried out at 700 °C with CO₂:CH₄ ratio of 50:50. The bimetallic catalysts (5%Ni 5%Co/Al₂O₃/ZSM-5) had high H₂ selectivity of about 47% with low CO selectivity of about 53%, high H₂ yield of about 34 %, high CO yield 78 %, high volume of CO adsorption, high active site, high metal dispersion and high stability despite relatively higher coke formation than the other catalysts.

Department: Chemical Engineering Student's Signature

Field of Study: Chemical Engineering Advisor's Signature

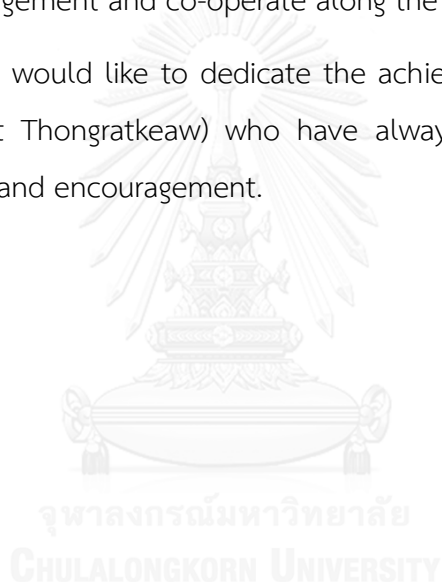
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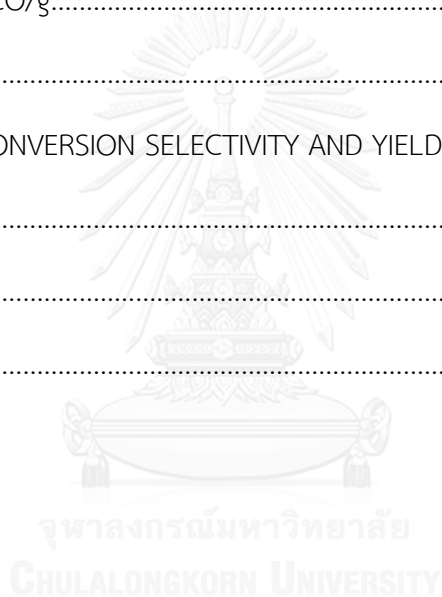
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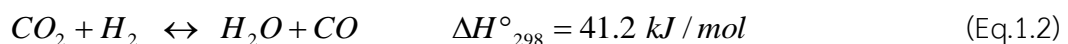
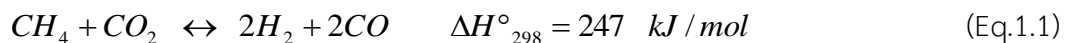
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CHAPTER I

INTRODUCTION

1.1 Background and rationale

In the last decade, carbon dioxide was released into the atmosphere. The production of carbon dioxide was generated by the oxidation of fossil fuels. The carbon dioxide molecules are stable. The emission of carbon dioxide was found in natural process, i.e. photosynthesis. In the future, it is expected that the amount of carbon dioxide in the atmosphere, due to fossil fuel burning and high pollution. The methane was produced by the biological processes to 98%; based on the behavior of bacteria and enzyme[1]. As carbon dioxide and methane are greenhouse gases, contributing to serious global warming. Dry reforming of methane (DRM) was interested for utilization these two greenhouses gases and producing valuable synthesis gases (H_2 and CO) as a feed-stock for synthetic fuel. The fuel is a clean fuel and can burn completely. The hydrogen and carbon monoxide are used as raw materials for the production process of methanol, ammonia and dimethyl ether, through the process of Fischer-Tropsch[2]. Dry reforming of methane is highly endothermic reaction (Eq.1.1). It's normally accompanied by secondary reaction of the reverse water gas shift (Eq.1.2).



In addition, this process is high energy consumption because it is highly endothermic reaction. Also, one serious problem is deactivation of catalyst by carbon formation and deposition (Eq.1.3, Eq.1.4)[3]. Many attentions have been paid to research aiming to improve and develop catalysts properties such as increased coke resistance.



The catalysts for this reaction are mainly divided into two groups: Transition metal such as Ruthenium, Platinum, Rhodium, and Palladium exhibit prominent activity and resistance to coke formation for dry reforming of methane. However, this noble metal is inappropriate to the adoption in industry due to it is valued more expensive and inadequate availability. The second group is Ni-based metal and Co-based metal such as Nickel and Cobalt, which are industrially more favorable due to their low cost and plentiful supply, although they are decrease activity and increase carbon deposition on catalysts[4]. The catalysts support is important involvement in optimizing the performance of catalyst. Alumina (Al_2O_3) and Zeolites are attractive support for dry reforming of methane because they possess high surface area, high thermal stability, well-defined structure and high affinity for carbon dioxide[5]. These properties are expected to enhance the catalyst selectivity and stability.

In this research demonstrates three main points; First, the loading order of cobalt and nickel metals, which are sequentially loaded on alumina mixed with zeolite ZSM-5 support are compared. Second, the selected sequence of metals loading from the first part were used to prepare the catalysts with metal molar ratio ($Ni + Co = 10$). The Comparison of catalytic activity between mono metallic and bimetallic catalyst

supported on γ -Al₂O₃/ZSM-5 zeolite and the last, the selected high catalytic performance and comparison of catalytic activity between differences supports (γ -Al₂O₃, ZSM-5, γ -Al₂O₃/ZSM-5) for carbon dioxide reforming of methane were investigated.

1.2 Research objectives

- 1.2.1 To compare the loading order of cobalt and nickel metals are loaded sequentially on alumina mixed with zeolite ZSM-5 support.
- 1.2.2 To compare the catalytic performance and stability for carbon dioxide reforming of methane between mono metallic and bimetallic catalyst supported on γ -Al₂O₃/ZSM-5 zeolite.

1.3 Research scopes

- 1.2.3 Preparation of the composite supports between alumina and zeolite ZSM-5 support by sol-gel method with alumina: zeolite ratio of 3: 1.
- 1.2.4 Preparation of the different loading order between cobalt and nickel metals which are loaded sequentially on alumina mixed with zeolite ZSM-5 support. The catalysts are prepared with 5wt%Ni and 5wt%Co by incipient wetness impregnation methods.
- 1.2.5 The selected metals loading order from the 1.3.2 are used to prepare the catalysts with different molar ratio to obtain 10wt%Ni, 7.5wt%Ni 2.5wt%Co, 5wt%Ni 5wt%Co, 2.5wt%Ni 7.5wt%Co and 10wt%Co respectively.
- 1.2.6 Characterization of chemical and physical properties of mono metallic and bimetallic catalyst supported on γ -Al₂O₃/ZSM-5 using various techniques:
 - X-Ray diffraction pattern (XRD) was used to determine crystallite size and phase.

- Nitrogen adsorption-desorption was used to determine BET specific surface area, pore size and pore volume.
- Scanning Electron Microscopy (SEM) was used to study morphology.
- Ammonia temperature program desorption (NH₃-TPD) was used to determine acidity of catalysts.
- Hydrogen temperature programmed reduction (H₂-TPR) was used to determine the metal oxide reduction.
- Carbon monoxide chemisorption (CO-CHEM) was used to determine quantities of active site of catalysts.
- Thermo gravimetric and differential thermal analysis (TG-DTA) was used to study carbon deposition.

1.2.7 Investigation of the catalytic performance of prepared catalysts via carbon dioxide reforming of methane reaction under the following condition:

- The catalysts were reduced *in situ* at 500 °C for 1 hr. in H₂ flow 50 ml/min.
- Reactant feed using the mixed gas between methane in carbon dioxide as ratio 1:1 was used with flow rate of 60 ml/min.
- The reaction was performed at the temperature of 700 °C at the atmospheric pressure.
- The gas compositions of the reactants and products were analyzed by thermal conductivity detector-type gas chromatography.

CHAPTER II

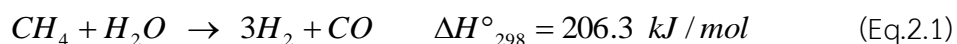
THEORY AND LITERATURE REVIEWS

In this research is based on data from other research that is associated with study. It is confirmed the results of experiment, this chapter two are offered theories; Synthesis gas and hydrogen production, Carbon dioxide reforming of methane, Supported catalyst, Metal catalyst and literature reviews;

2.1 Synthesis gas and hydrogen production

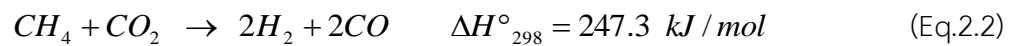
The production of hydrogen fuel can be produced many processes. However, the process is studied most commonly is reforming reaction because expected to developed into a commercial process. The reforming is divided to several categories depend on type of reactant used as follows:

- Steam reforming that produces hydrogen gas from water and a 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[6]. It is an effective process to produce hydrogen that low cost. Making it is used commercially. The principle of process is entering the steam in system to react with hydrocarbons compound at a gas phase.



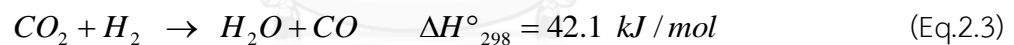
- Carbon dioxide reforming (also known as dry reforming) is a method of producing synthesis gas (mixtures of hydrogen and carbon monoxide) from the reaction of carbon dioxide with hydrocarbons such as methane. Synthesis gas is conventionally

produced via the steam reforming reaction. In recent years, increased concerns on the contribution of greenhouse gases to global warming have increased interest in the replacement of steam as reactant with carbon dioxide[7]. The dry reforming reaction may be represented by:

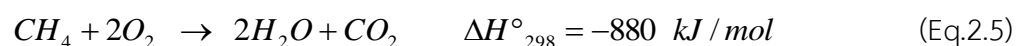
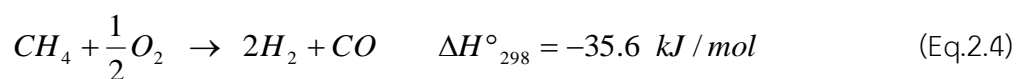


Thus, two greenhouse gases are consumed and useful chemical building blocks, hydrogen and carbon monoxide, are produced. A challenge to the commercialization of this process is that the hydrogen that is produced tends to react with the carbon dioxide. For example, the following reaction typically proceeds with lower activation energy than the dry reforming reaction itself:

The reverse water-gas shift reaction:



- The partial oxidation is a process between hydrocarbons and oxygen. This process have the advantage it does not require external energy input because the reaction is exothermic, resulting the generate energy in the system. But the limitations of this process, the amount of oxygen fed to the system must not too high because the rest of oxygen will react with hydrogen and convert to water. As a result a loss of hydrogen. In addition, another important limitation of this process is in commercial operation will higher cost than the other reforming. Due to the system must be separated oxygen from air before. If not separate the oxygen, the concentration of hydrogen decreased.



The synthesis gas produced is converted to organic hydrocarbons by Fischer-Tropsch synthesis. Instead of supplying heat to the steam reforming process, a partial oxidation reaction is also carried out to make it self-sustaining. Another possible method to produce carbon monoxide and hydrogen from methane is the dry reforming of CO_2 . The dry CO_2 reforming of methane is $\approx 20\%$ more endothermic than steam reforming of methane (see Reactions Eq.2.1, 2.2) and partial oxidation in shows that Eq.2.4, 2.5[8]. Synthesis gas was also using feed-stock for methanol synthesis. Another, hydrogen production was using feed-stock for ammonia synthesis, hydro treating, hydrogenation, and fuel cell power.

2.2 Carbon dioxide reforming of methane

The carbon dioxide reforming of methane is a very interesting reaction. There are studies both the academic and industrial utilization, as various advantages such as: (a) reducing of carbon dioxide and methane, which are both the greenhouse gases, (b) converting of methane and carbon dioxide to hydrogen and valuable synthesis gas, (c) producing synthesis gas with a hydrogen/carbon monoxide ratio is close to 1, which is more appropriate for use in the production of oxygenated compounds and the production of liquid hydrocarbons in the Fischer-Tropsch synthesis[9, 10]. The products of this reaction, hydrogen could be applied as fuel cells and more, as mentioned above. Another product is the synthesis gas, a mixture of carbon monoxide and hydrogen can be used a raw material in the production of methanol, dimethyl ether and Fischer-Tropsch synthesis.

Table 1 Overall reaction for carbon dioxide reforming of methane.

(1) $CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$	$\Delta H^\circ_{298} = 247.3 \text{ kJ/mol}$ $\Delta G^\circ = 61770 - 67.32T$	CO_2 reforming of CH_4
(2) $CH_4 \rightleftharpoons C + 2H_2$	$\Delta H^\circ_{298} = 75 \text{ kJ/mol}$ $\Delta G^\circ = 2190 - 26.45T$	CH_4 decomposition
(3) $2CO \rightleftharpoons CO_2 + C$	$\Delta H^\circ_{298} = -171 \text{ kJ/mol}$ $\Delta G^\circ = -39810 + 40.87T$	CO disproportionation or Boudouard
(4) $CO_2 + H_2 \rightleftharpoons CO + H_2O$	$\Delta H^\circ_{298} = 41 \text{ kJ/mol}$ $\Delta G^\circ = -8545 + 7.84T$	Reverse water-gas shift
(5) $CO + H_2 \rightleftharpoons C + H_2O$	$\Delta H^\circ_{298} = -131 \text{ kJ/mol}$	Reverse carbon gasification

The reaction equilibrium for carbon dioxide reforming of methane (1), usually occur simultaneously with reverse water-gas shift reaction (4), results a H_2/CO ratio of less than unity. In addition, the side reaction, CH_4 decomposition (2), and CO disproportionation or Boudouard reaction (3) were involved with carbon deposition on the surface catalyst[11].

The equilibrium constant of the carbon dioxide reforming of methane reaction (1), is a strongly endothermic reaction which the conversion are increases seriously with increasing reaction temperature[12]. However, methane decomposition (2), and reverse water-gas shift reaction (4), which are moderately endothermic reactions. Hence, the raising in temperature increases the rate of reactions. The Boudouard reaction (3) and the reverse carbon gasification reaction (5) are exothermic reaction. Therefore, the thermodynamic does not prefer at higher temperatures. In conclusion, high temperature is more favorable for the carbon dioxide reforming of methane (1) than those of the side reactions (2, 3, and 5).

Because the carbon dioxide reforming of methane reaction is strongly endothermic it required high temperature. Hence, the main drawback of this reaction is rapid deactivation by carbon deposition on surface catalyst or sintering of metallic particles or metal oxidation. Thus, the selection of appropriate catalysts and supports are needed to prevent the deactivation.

2.3 Supported catalyst and Metal catalyst

2.3.1 Supported catalyst

Alumina (Al_2O_3)

Aluminum oxide is a chemical compound of aluminum and oxygen with the chemical formula Al_2O_3 . It is the most commonly occurring of several aluminum oxides, and specifically identified as aluminum (III) oxide. It is commonly called alumina, and may also be called alloy oxide, or aluminum depending on particular forms or applications. It commonly occurs in its crystalline polymorphic phase α - Al_2O_3 , in which it composes the mineral corundum, varieties of which form the precious gemstones ruby and sapphire.

Physical Properties

Alumina is the most common commercial carriers because of their excellent thermal stability and wide range of chemical, physical, and catalytic properties. The alumina consists of more than a dozen well-characterized amorphous or crystalline structures. Which vary over wide range of surface area (0.5-600 m^2/g), pore size, pore distribution and acidity of surface.

The structure and properties of a given alumina depend on its preparation, purity, dehydration, and thermal treatment history. The more acidic, high-surface-area alumina hydrate produced at relatively low temperature and treatment at high temperature to 'transitional $\beta, \gamma, \eta, \chi, \delta$, and θ -alumina and ultimately α -alumina, all of lower surface area and acidity. Alumina phase present at different temperatures as a function of calcination in Figure 1, and the physical and structural characteristics of important alumina phase are listed in Table 2.

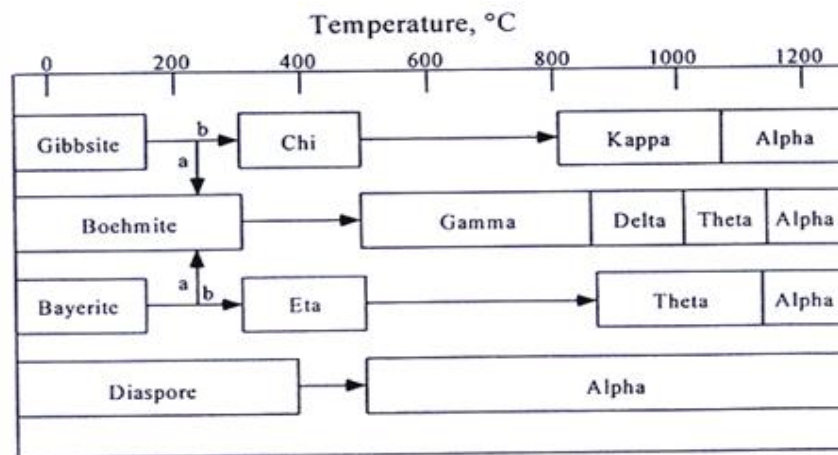


Figure 1 Alumina phase present at different temperatures: (a) corresponds to the path favored for fine crystals, (b) to the path for moist or particles.

Table 2 Physical and structural characteristic of common aluminum oxides.

$T_{\text{calc}}(^{\circ}\text{C})$	Alumina phase	SA, (m^2/g)	$V_{\text{pore}}, (\text{cm}^3/\text{g})$	$D_{\text{pore}}, (\text{nm})$
250	pseudoboehmite	390	0.50	5.2
450	γ -alumina	335	0.53	6.4
650		226	0.55	9.8
850		167	0.58	14
950	δ -alumina	120	0.50	16.6
1050	θ -alumina	50	0.50	28
1200	α -alumina	1-5		

Usability

Aluminum oxide is used in a variety of reactions including; benzene hydrogenation, catalytic reforming, hydrotreating, emission control, methanol synthesis, the water gas shift reaction, and oxchlorination. It is also useful for dehydration of alcohols to alkenes. Alumina serves as a catalyst support for many industrial catalysts, such as those used in hydrodesulfurization and some Ziegler-Natta polymerizations. Zeolites are produced from alumina.

Zeolite ZSM-5 (Faujasite)

Faujasite was discovered in 1842 by Damour and is named for Barthélemy Faujas de Saint-Fond, a French geologist and volcanologist.

Physical Properties

The faujasite framework consists of sodalite cages which are connected through hexagonal prisms. The pores are arranged perpendicular to each other. The pore, which is formed by a 12-membered ring, has a relatively large diameter of 7.4 Å. The inner cavity has a diameter of 12 Å and is surrounded by 10 sodalite cages. The unit cell is cubic with a length of 24.7 Å. Zeolite ZSM-5 has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 23. It thermally decomposes at 793 °C.

Usability

ZSM-5 has been used as a support material for catalysis. In one such example, copper is deposited on the zeolite and a stream of ethanol is passed through at temperatures of 240 to 320 °C as a vapor stream, which causes the ethanol to oxidize to acetaldehyde; two hydrogen atoms are lost by the ethanol as hydrogen gas. It appears that the specific pore size of ZSM-5 is of benefit to this process, which also functions for other alcohols and oxidations. The copper is

occasionally combined with other metals, such as chromium, to fine tune the diversity and specificity of the products, as there is likely to be more than one. Acetic acid is an example of one possible byproduct from hot copper oxidation.

2.3.2 Metal catalyst

Nickel

Nickel is silvery-white. Hard, malleable and ductile metal. It is of the iron group and it takes on a high polish. It is a fairly good conductor of heat and electricity. In its familiar compounds nickel is bivalent, although it assumes other valences. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen.

Physical Properties

From Table 3 shows the physical property of cobalt

Table 3 Physical properties of cobalt.(Othmer)

Parameters	Value
Name	Nickel
Symbol	Ni
Atomic number	28
Atomic mass	58.71 g.mol ⁻¹
Electronegativity according to Pauling	1.8
Density	8.9 g.cm ⁻³ at 20°C
Melting point	1453 °C
Boiling point	2913 °C
Vanderwaals radius	0.124 nm
Ionic radius	0.069 nm (+2) ; 0.06 nm (+3)
Isotopes	10

Cobalt

Cobalt-based catalysts began to be widely studied for the carbon dioxide reforming of methane because had good activity, availability and low cost. Moreover, cobalt also has good activity which may help to promote the carbon resistance of the catalyst. Many cobalt compounds are used in chemical reactions such as cobalt acetate is used for the convert of xylene to terephthalic acid, the precursor to the bulk polymer polyethylene terephthalate. Generally catalysts are the cobalt carboxylates. They are also used in paints, varnishes, and inks as "drying agents" through the oxidation of drying oils.

Cobalt-based catalysts are also important in reactions relate with carbon monoxide. The reforming reaction such as steam reforming and carbon dioxide reforming, useful in hydrogen production, uses cobalt oxide-base catalysts. Moreover, cobalt is also a catalyst in the Fischer–Tropsch reaction, used in the hydrogenation of carbon monoxide into liquid fuels.

Physical Properties

From Table 4 shows the physical property of cobalt

Table 4 Physical properties of cobalt

Parameters	Value
Name	Cobalt
Symbol	Co
Atomic number	27
Element category	transition metal
Atomic weight	58.93
Electronegativity	1.88 (Pauling scale)
Ionization energies, $\text{kJ}\cdot\text{mol}^{-1}$	
• 1 st	760.4
• 2 nd	1648
• 3 rd	3232
Latent heat of fusion	
Boiling point	395
Latent heat of vaporization at bp, $\Delta H_{\text{vap}}/\text{kJ}\cdot\text{g}^{\text{a}}$	3100
Specific heat, $\text{J}/(\text{g}\cdot^{\circ}\text{C})^{\text{a}}$	6276
• 15-100 $^{\circ}\text{C}$	
• Molten metal	0.442
Coefficient of thermalexperature, $^{\circ}\text{C}^{-1}$	0.560
• cph at room temperature	12.5
• fcc at 417 $^{\circ}\text{C}$	14.2

2.4 Literature Reviews

Table 5 Recently Reported Catalysts for Dry Reforming of Methane

Metal	Support	Preparation	Result	References
Ni	zeoliteA, zeoliteX, zeoliteY, ZSM-5	Incipient wetness impregnation	Ni/zeolite Y a weight of Ni loading at 7wt.% showed the best catalytic performance than the other types of zeolites.	[13]
Ni-Co	Al-Mg-O	Co- precipitation	The kinetic studies of Ni-Co/Al-Mg-O bimetallic catalyst in the temperature range 650-750 °C. The L-H kinetic model derived from the proposed mechanism was found to fit the kinetic measurement well. It was also found that the power-law model is able to satisfactorily fit the kinetic experimental results as well.	[14]
Ni-Co	γ -Al ₂ O ₃	Impregnation	Ni,Co and Ni-Co alumina supported catalysts highest cobalt content are the most active and stable, but they produce a large amount of carbon.	[15]

Metal	Support	Preparation	Result	References
Co-Mn	TiO ₂	Co-precipitated	The results presented in this work revealed that forming the catalyst under 75 bar compression pressure and 4 wt.% Syton binder led to the maximum selectivity.	[16]
Ni-Mg	Al ₂ O ₄	Incipient wetness impregnation	Ni/MgAl ₂ O ₄ and on gold modified Au-Ni/MgAl ₂ O ₄ samples in a plug flow reactor. The CO ₂ conversion of the reaction is complete at 800 °C for both catalysts although 0.5 wt% , whereas on long range the activity is improved in the presence of gold.	[17]
Ni, NiRh, NiCo	Ce-Zr-oxide	Wet impregnation	Alloyed NiRh, NiCo particles and sintered Ni were observed, with the simultaneous presence of carbidic carbon, carbon nanotubes and shell-type graphitic carbon deposition. Support degradation and segregation happened to some extent, but still there was a certain amount of Ni in strong interaction with the support. Broad metal particle size distribution seems to play a role in long term stability.	[18]

Metal	Support	Preparation	Result	References
Co ,Ni	CeO ₂	Co-precipitation	The Co-Ni/CeO ₂ catalyst is more active and more selective than the Co/CeO ₂ and Ni/CeO ₂ monometallic catalysts. Co-Ni/CeO ₂ and Co/CeO ₂ , show a substantially higher resistance to carbon deposition in comparison with Ni/CeO ₂ .	[19]
Ni	ZSM-5	Hydrothermal	Ni nanoparticle supported on mesoporous ZSM-5 was found highly active. The 5%Ni loaded Ni-ZSM-5 catalyst shows 96.2% methane conversion at 800 °C. It was also found that, acidic support decreases the activity of the catalyst mainly due to the weak ability of adsorption of CO ₂ on the acidic support. The deactivation of the catalyst is due to the coke deposition and also the formation of NiCO ₃ over the catalyst.	[20]
LaNiO ₃	SBA-15, MCM-41	Hydrothermal	LaNiO ₃ /MCM-41 exhibited the higher initial catalytic activity, owing to the higher Ni dispersion, while LaNiO ₃ /SBA-15 was superior to LaNiO ₃ /MCM-41 in the long-term stability, which could be due to the stable silica matrix restricted the agglomeration of nickel species.	[21]

Metal	Support	Preparation	Result	References
Ni	Al ₂ O ₃ -ZrO ₂	impregnation and so-gel	<ul style="list-style-type: none"> - The results of this study showed that the sole gel method had excellent effects on physicochemical properties of Ni/Al₂O₃-ZrO₂ nano catalyst in comparison to impregnation method. - Ni-Co/Al₂O₃-ZrO₂ had the excellent activity and selectivity. 	[22]
Ni , Pt	CeZrO ₂	Wet impregnation	The CeZrO ₂ supported catalyst in the presence of Pt shows high stability due to oxygen spillover. The addition of Pt to Ni reduces the induction period especially on the alumina supported catalyst.	[23]

CHAPTER III

EXPERIMENTAL

In this chapter consist of three sections involved in the preparation process of catalyst. First, prepare for alumina and alumina mixed with zeolite ZSM-5 support by sol-gel method, after that load cobalt and nickel metals on other types of support. The catalysts are prepared with molar ratio (Ni/Co = 1) by incipient wetness impregnation methods. Second, characterize physical properties of mono metallic and bimetallic catalysts supported on γ -Al₂O₃/ZSM-5 zeolite by using various techniques: X-Ray diffraction pattern (XRD), Nitrogen adsorption-desorption, Scanning Electron Microscopy (SEM-EDX), Ammonia temperature program desorption (NH₃-TPD), Carbon monoxide chemisorption and Thermo gravimetric and differential thermal analysis (TG-DTA). Last, investigate performance of catalysts for carbon dioxide reforming of methane reaction.

3.1 Catalyst Preparation

3.1.1 Alumina support by sol-gel method.

3.1.2 Alumina mixed with zeolite ZSM-5 support by sol-gel method.

Chemicals of alumina

- a) Alumina Isopropoxide: AIP, $[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$ from Aldrich.
- b) Ethanol, (C₂H₅OH) from Merck
- c) Hydrochloric acid, (HCl) from Merck

Chemicals of zeolite ZSM-5

Zeolite ZSM-5 (BET area 202 m²/g), was obtained from TOSOH Corporation (Japan) in proton form with SiO₂/AlO₃ mole ratio 23. Before used, zeolite ZSM-5 was powder.

Preparation of alumina support by sol-gel method.

The precursor, alumina isopropoxide dissolved in mixture of ethanol and deionized water with volume ratio 1:1 under mild stirring at 80°C for 1 hr. After that, hydrochloric acid is dropped into the solutions unit pH value is equaled to 2.5 and aged with stirring at 80°C about 5 hr. units eliminating the solvent and dried at 105°C overnight and calcination under air at 550°C for 2 hr.

Preparation of alumina mixed with zeolite ZSM-5 support by sol-gel method.

The precursor, alumina isopropoxide dissolved in mixture of ethanol and deionized water with volume ratio 1:1 under mild stirring at 80°C for 1 hr. Then temperature is increases to 90°C. After that, zeolite ZSM-5 is mixed into the solutions and hydrochloric acid are dropped into the solutions unit pH value is equal to 2.5 and aged with stirring at 90°C about 5 hr., unit eliminating the solvent. And then mixed with zeolite ZSM-5 support are dried at 105°C overnight and calcination under air at 550°C for 2 hr.

3.1.3 Nickel and Cobalt -base metal catalyst

Chemicals of nickel metal

- a) Nickel nitrate hexahydrate, $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Carlo Erba

Chemicals of cobalt metal

- b) Cobalt nitrate hexahydrate, $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Carlo Erba

Preparation of nickel and cobalt -base metal loading on alumina mixed with zeolite ZSM5 support by impregnation method.

The nickel and cobalt catalysts with various metal content (10wt.%Ni, 10wt.%Co) were prepared by the incipient wetness impregnation method using a alumina mixed with zeolite ZSM-5 (sol-gel) support and aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of the appropriate concentration to have the metal loading above. The impregnated support is kept at room temperature for 4 hr. to assure adequate distribution of metal complete. Then, the catalysts were dried at 105°C overnight and calcination under air at 500°C for 2 hr.

3.1.4 Bimetallic catalysts

Chemicals of bimetallic

- a) Nickel nitrate hexahydrate, $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Merck
- b) Cobalt nitrate hexahydrate, $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ from Carlo Erba

Preparation of Ni-Co bimetallic catalysts loading on alumina, ZSM-5 and alumina mixed with zeolite ZSM-5 support by impregnation method.

The bimetallic Ni-Co catalysts are loaded sequentially on alumina (5wt.%Ni 5wt.%Co), ZSM-5 (5wt.%Ni 5wt.%Co) and alumina mixed with zeolite ZSM-5 support with various compositions (5wt.%Ni 5wt.%Co, 5wt.%Ni-5wt.%Co, 5wt.%Co-5wt.%Ni, 7.5wt.%Ni-2.5wt.%Co and 2.5wt.%Ni-7.5wt.%Co) are prepared by the incipient wetness impregnation and method using a alumina mixed with zeolite ZSM-5 (sol-gel) support and aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of the appropriate concentration to have the metal loading above. The impregnated support was kept at room temperature for 4 hr. to assure adequate distribution of metal complete. Then, the catalysts were dried at 105°C overnight and calcination under air at 500°C for 2 hr.

3.2 Catalyst characterization

3.2.1 X-ray diffraction (XRD)

The analysis of crystalline phases is performed by X-ray diffraction (XRD) patterns of the samples are carried on an X-ray diffraction SIEMENS D 5000 connected to a personal computer with Diffract AT version 3.3 program for fully control of XRD analyzer. The XRD analysis is conducted to Cu-K α radiation between 20° - 80° with a generator voltage and current of 30 kV and 30 mA, respectively.

3.2.2 Nitrogen adsorption-desorption

The catalyst 0.1 gram are study BET surface area, pore volume and pore diameter are measured by N₂ adsorption–desorption isotherm at liquid nitrogen temperature (-196 °C) using a Micromeritics ASAP 2020. The surface area and pore distribution are calculated according to Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods.

3.2.3 Scanning Electron Microscopy (SEM-EDX)

Scanning Electron Microscopy is employed for including morphology metal dispersion of catalysts. The JEOL JSM-35 CF model at the Scientific and Technology Research Equipment Centre, Chulalongkorn University (STREC) was used for this purpose.

3.2.4 Ammonia temperature program desorption (NH₃-TPD)

The acid properties of prepared catalysts are observed by Temperature Programmed Adsorption of Ammonia (NH₃-TPD) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. In an experiment, 0.10 g of the catalyst sample is placed in a quartz tube and pretreated at 200°C in a flow of helium. The sample was saturated with 15%NH₃/He. After saturation, the physisorbed ammonia was desorbed in a helium gas flow about 30 min. Then the sample was heated from 40 to 500°C at a heating rate 10°C/min. The amount of ammonia in effluent was measured via TCD signal as a function of temperature.

3.2.5 Hydrogen temperature programmed reduction (H₂-TPR)

The reducing temperatures of prepared catalysts are observed by Temperature Programmed Reduction of Hydrogen (H₂-TPR) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. In an experiment, about 0.10 g of the catalyst sample is placed in a quartz tube and pretreated at 200 °C in a flow of nitrogen. The sample is reduced with 10%H₂/Ar. Then the sample is heated from 30 to 800 °C at a heating rate 10 °C /min. The amount of hydrogen consumption in effluent is measured via TCD signal as a function of temperature.

3.2.6 Carbon monoxide chemisorption

Static CO chemisorption at room temperature on the reduce catalysts will be used to determine the number of reduce surface nickel and cobalt metal atoms. The total CO chemisorption will be calculated from the number of injection of a known volume. CO chemisorption will be carried out following the procedure using a Micromeritics chemisorb 2750 Pulse Chemisorption System. In an experiment, about 0.10 g of the catalyst sample is placed in a quartz tube. Prior to chemisorption, the catalysts will be reduced at 500°C for 1 hour after ramping up at a rate of 10°C/min. After that, carbon monoxide 20 microliter was inject to catalyst and repeat until desorption peak constant. Amount of carbon monoxide adsorption on catalyst was relative amount of active site.

3.2.7 Thermal gravimetric and differential thermal analysis (TG-DTA)

The as-spun alumina fibers is subjected to the thermo gravimetric and differential thermal analysis (Diamond Thermo gravimetric and Differential Analyzer, TA Instruments SDT Q600) to determine the carbon content in the sample, as well as their thermal behaviors in the range of 30 - 1000°C. The analysis was performed at a heating rate of 10°C /min in 100 ml/min flow of air.

3.3 Catalytic performance test

3.3.1 Chemicals for reaction

- a) Feed gas: consisted of 50% methane balance carbon dioxide (molar ratio 1:1)
- b) UHP Nitrogen gas, 99.999%
- c) UHP Hydrogen gas, 99.999%

3.3.2 Instrument and Apparatus

- a) Reactor: The reactor is a fixed bed flow reactor made from a quartz tube length of 47 mm. and inner diameter of 12 mm.
- b) Automatic Temperature and controller: There is a magnetic switch connected to a variable voltage transformer and a temperature controller connected to a thermocouple attached to the catalyst bed in reactor. A dial setting established a set point at any temperature within the range between 0°C to 1000°C.
- c) Electric Furnace: This supply the required heated to the reactor for reaction. The reactor could be operating at 700°C.
- d) Gas Controlling System: Gas was equipped with pressure regulator (0-120 psig), an on-off valve and needle valve are used adjust flow of gas.

e) Gas Chromatographs: Operating conditions are shown in Table 6.

Table 6 Operating condition of gas chromatograph for CO₂ reforming of CH₄

Gas Chromatograph	Shimazu, GC 8A	Shimazu, GC 8A
Detector	TCD	TCD
Column	Polapack-Q	Molecular sieve 5A
Carrier gas	Argon	Argon
Carrier gas flow	30 ml/min	30 ml/min
Column Temperature		
- Initial	70 °C	70 °C
- Final	70 °C	70 °C
Detector temperature		
Injector Temperature	100 °C	100 °C
Analyzed gas	CO ₂	CH ₄ , CO, H ₂

3.3.3 Reaction Method

The carbon dioxide reforming of methane is carried out at atmospheric pressure in fixed-bed flow reactor (quartz tube, length 47 mm and inner diameter 12 mm) packed with 0.05 g catalyst. The reactor temperature is measured and controlled by K-type thermocouple positioned at the middle of catalyst bed. The catalysts are reduced in pure hydrogen (50 ml/min) at 600°C for 1 h. Then, the hydrogen is replaced by pure nitrogen (50 ml/min) and the system is heated (10°C/min) to the reaction temperature for 40 min before. The catalytic performance test is carried out at 700°C. The feed gas consisted of methane and carbon dioxide (molar ratio 1:1), and feed flow rate 60 ml/min. Figure 2 shown the scheme diagram of CO₂ reforming of CH₄ reaction.

The gas compositions of reactants and products is analyzed by thermal conductivity detector-type gas chromatograph (Shimudzu, GC-8A) equipped with a Porapak-Q and Molecular sieve 5A packed column. Argon is used as carrier gas (30 ml/min).

The conversions of CO₂ and CH₄ are defined in Equation (3.1) and (3.2) and the selectivity of H₂ and CO are defined in Equation (3.3) and (3.4), respectively

$$X_{CH_4} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100 \quad (\text{Eq.3.1})$$

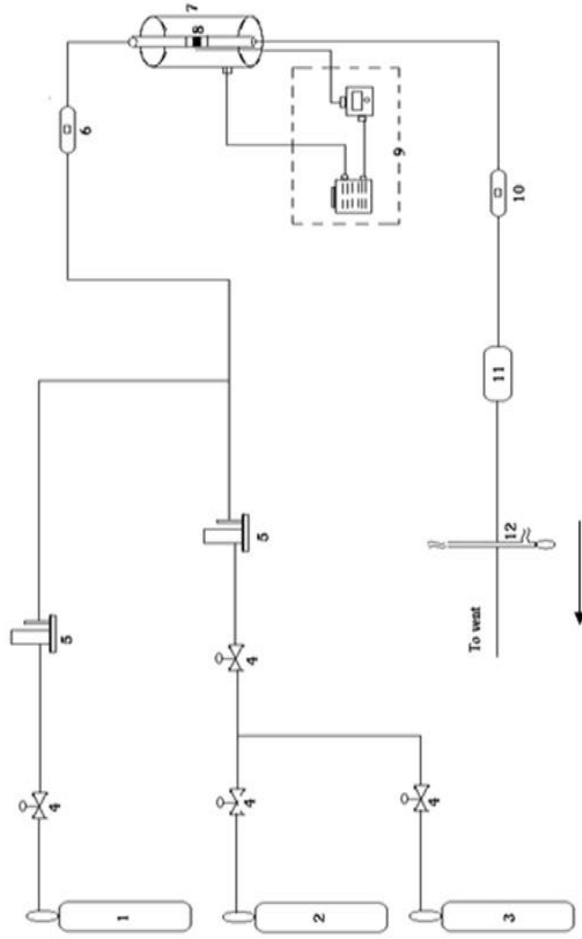
$$X_{CO_2} = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100 \quad (\text{Eq.3.2})$$

$$S_{H_2} = \frac{[H_2]_{out}}{[H_2]_{out} + [CO]_{out}} \times 100 \quad (\text{Eq.3.3})$$

$$S_{CO} = \frac{[CO]_{out}}{[H_2]_{out} + [CO]_{out}} \times 100 \quad (\text{Eq.3.4})$$

Where $[CH_4]_{in}$ and $[CO_2]_{in}$ are the flow rates of the reactants feed and $[CH_4]_{out}$, $[CO_2]_{out}$, $[H_2]_{out}$ and $[4]_{out}$ are the flow rates of the corresponding gas compositions in the carbon dioxide reforming of methane reaction.





1. 50% CH₄/CO₂ cylinder
2. N₂ cylinder
3. H₂ cylinder
4. Ball valve
5. Mass flow controllers
6. Sampling injection port
7. Furnace
8. Quartz tube fixed bed reactor
9. Temperature controller and variable voltage transformer
10. Gas sample
11. Gas liquid separation
12. Bubble flow meter

Figure 2 Scheme diagram reaction of CO₂ reforming of methane.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter compose of two sections. Firstly, 4.1 study of the different loading order between cobalt and nickel metals. Secondly, 4.2 study the catalysts with different molar ratio to obtain 10%Ni , 7.5%Ni-2.5%Co , 5%Ni-5%Co , 2.5%Ni-7.5%Co and 10%Co on mix supported. Each section presents catalyst characterization by several techniques such as X-Ray diffraction pattern (XRD), Nitrogen adsorption-desorption, Scanning Electron Microscopy (SEM-EDX), Ammonia temperature program desorption (NH₃-TPD), Hydrogen temperature programmed reduction (H₂-TPR), Carbon monoxide chemisorption, Thermo gravimetric and differential thermal analysis (TG-DTA) and catalytic activities and selectivity in carbon dioxide reforming of methane reaction.

4.1 Study of the different loading order between cobalt and nickel metals.

4.1.1 Characterization of catalyst

4.1.1.1 X-Ray Diffraction

The X-Ray Diffraction patterns of the γ -Al₂O₃ prepared by sol gel methods, ZSM-5 commercial and mix supported γ -Al₂O₃/ZSM-5 prepared by sol gel methods shown in Figure 3. The XRD patterns of the γ -Al₂O₃ were shown at 36.6°, 45.5°, 67[24], ZSM-5 commercial were shown at 20.8°, 23°-24.4°, 29.2°-30.1°, 45.5°, 66.8 and mix phased γ -Al₂O₃/ZSM-5 were shown similar ZSM-5 pattern[25].

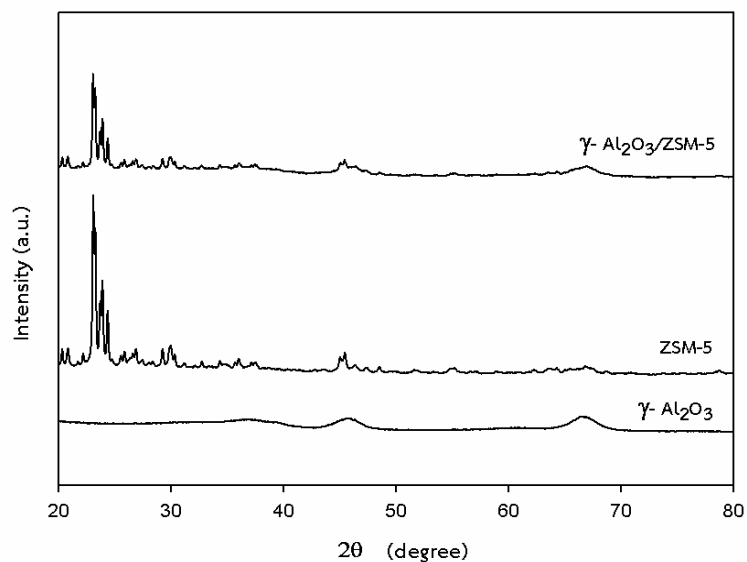


Figure 3 The XRD patterns of γ -Al₂O₃, ZSM-5 and γ -Al₂O₃/ZSM-5 support.

After loading order between cobalt and nickel metals on Al₂O₃/ZSM-5 supports shown in Figure 4. The XRD patterns fresh catalyst were shown peak NiO, CoO, Co₃O₄ and NiAl₂O₃ at 37°, 45°, 59°, 65° and 67° respectively [25, 26]. There has small peak because percentage of loaded metal has less.

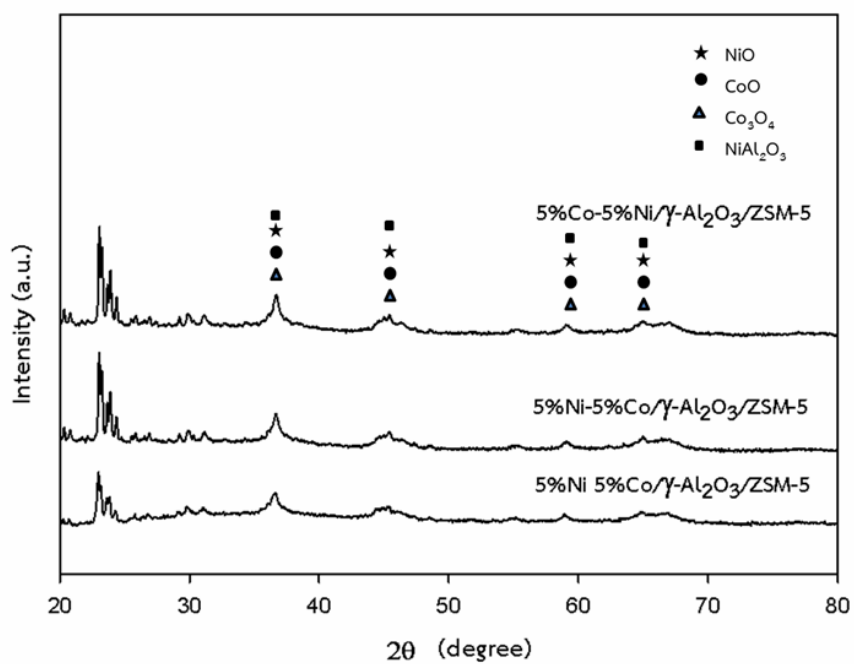


Figure 4 The XRD patterns of fresh catalyst 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5, 5%Ni- 5%Co/ γ -Al₂O₃/ZSM-5 and 5%Co-5%Ni/ γ -Al₂O₃/ZSM-5.

4.1.1.2 Nitrogen adsorption-desorption

The specific surface area, pore volume and pore size of the catalyst of γ -Al₂O₃ prepared by sol gel methods, ZSM-5 commercial and mix supported γ -Al₂O₃/ZSM-5 and catalysts were determined by technical analysis with Brunauer-Emmitt-Teller Method (BET). The results demonstrate in table 7 for the γ -Al₂O₃ and ZSM-5 supports have specific surface area 200 m²/g. In addition, specific surface area of mix supported γ -Al₂O₃/ZSM-5 increased 259m²/g. The specific surface area and the pore volumes of a bimetal was decreased suggests that the metals are deposited inside the pores of supports. However, [27].

Table 7 Physical properties of support and bimetallic catalysts.

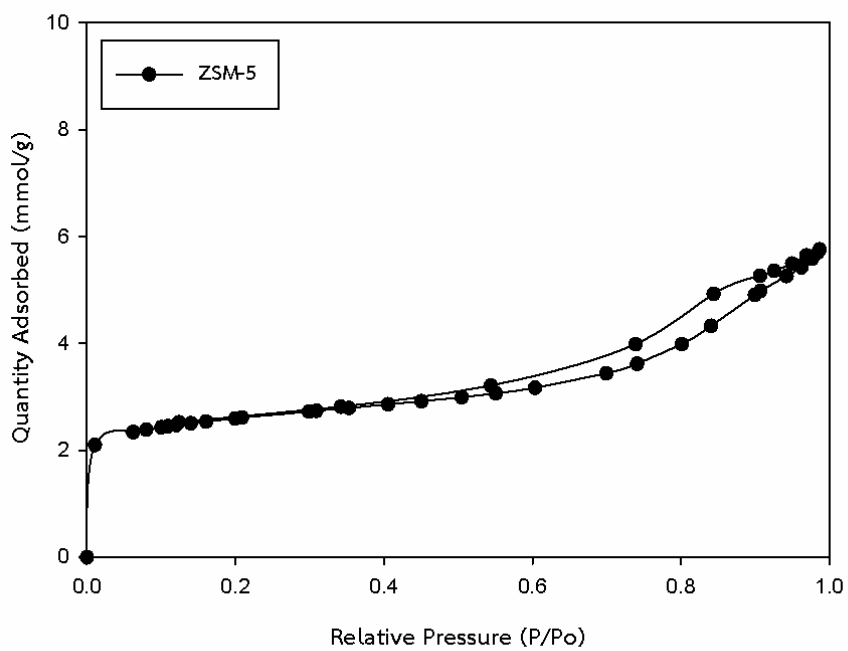
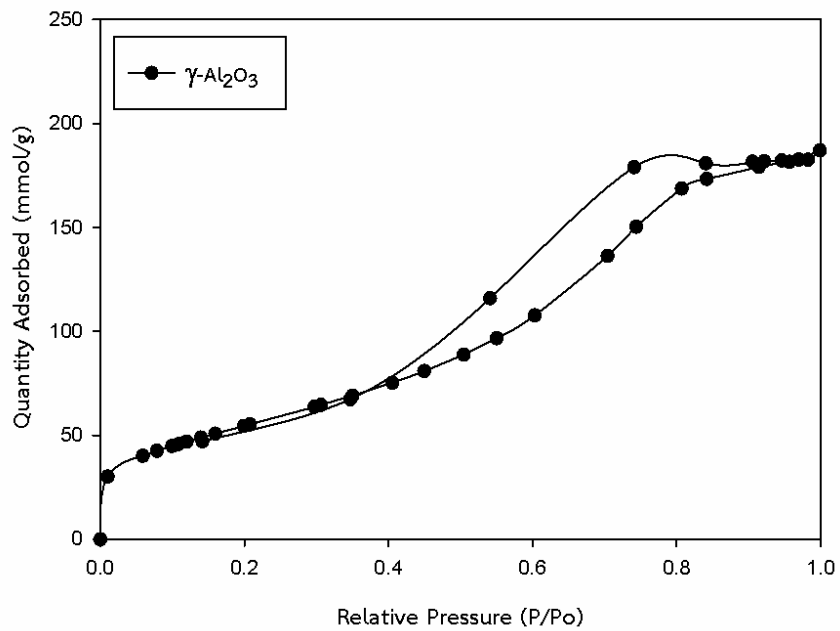
Catalysts	S _{BET} ^a (m ² /g)	P _v ^b (cm ³ /g)	P _s ^c (nm)
γ -Al ₂ O ₃	200	0.30	3.8
ZSM-5	200	0.16	6.3
γ -Al ₂ O ₃ /ZSM-5	259	0.30	4.7
5%Ni 5%Co/ γ - Al ₂ O ₃ /ZSM-5	204	0.23	4.7
5%Ni-5%Co/ γ - Al ₂ O ₃ /ZSM-5	201	0.21	4.7
5%Co-5%Ni/ γ -Al ₂ O ₃ /ZSM-5	161	0.22	5.2

S_{BET}^a : Specific surface area ; calculated by the BET equation.

P_v^b : BJH desorption pore volume.

P_s^c : BJH desorption average pore diameter.

The N₂ adsorption/desorption isotherms for the prepared support and catalysts display in Figure 5 and Figure 6, respectively. The isotherm of ZSM-5 has type I, characteristic of the microporous structure. While, the isotherms of γ -Al₂O₃, ZSM-5 and γ -Al₂O₃/ZSM-5 supports and different loading order bimetallic catalyst can be classified as a type IV , characteristic for micro-mesoporous materials.[28, 29]



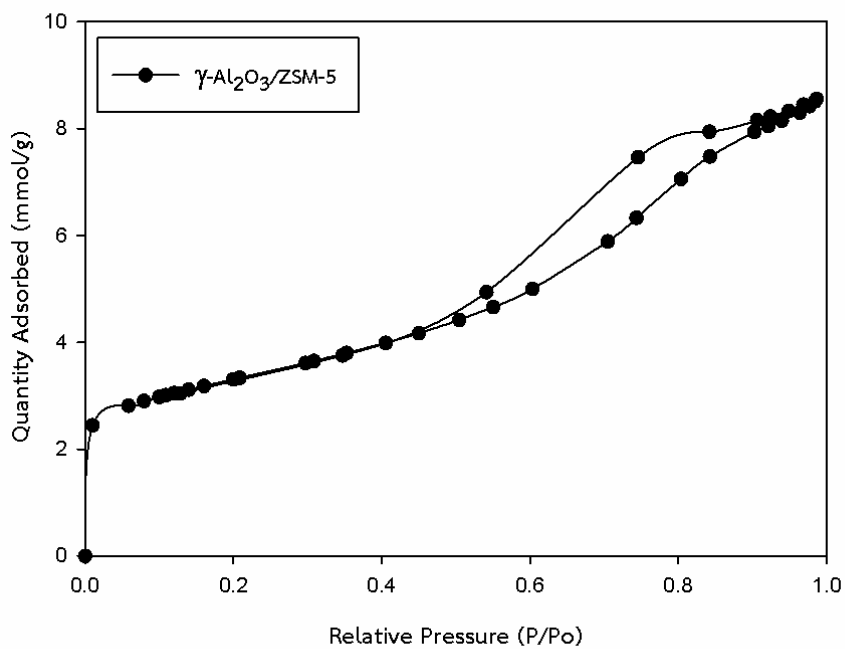


Figure 5 The nitrogen adsorption/desorption isotherms of support.

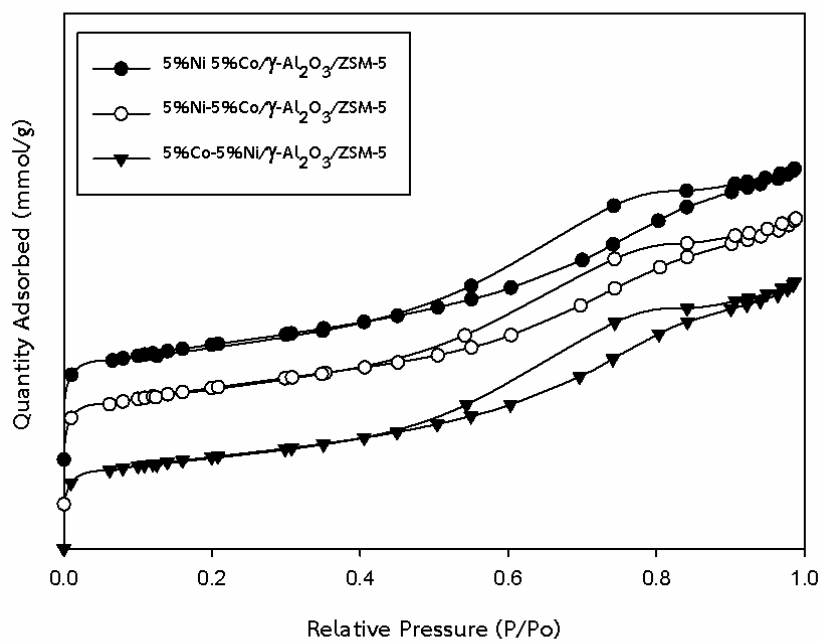


Figure 6 The nitrogen adsorption/desorption isotherms of different loading order bimetallic catalyst.

4.1.1.3 Scanning Electron Microscopy (SEM-EDX)

The morphology of the γ -Al₂O₃, ZSM-5 and γ -Al₂O₃/ZSM-5 supports were shown in Figure 7. The morphology of the different loading order between cobalt and nickel metals catalysts are appeared in Figure 8. The image of loaded sample shows that the original crystallinity of the supports is not affected by NiO and CoO loading hence the morphology of catalysts is significant similarity of supports in Figure 7[30]. Moreover, used catalysts were indicated in Figure 9. The surface of the 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5, 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5 and 5%Co-5%Ni/ γ -Al₂O₃/ZSM-5 catalysts were covered by filamentous carbon[31].

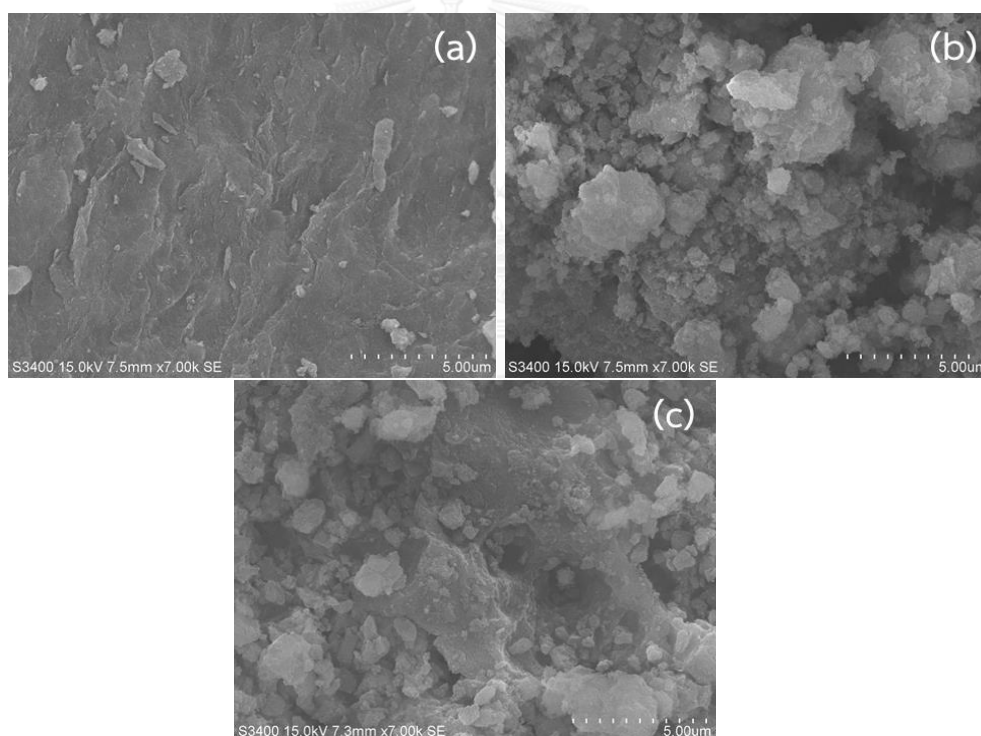


Figure 7 The SEM images of the (a) γ -Al₂O₃, (b) ZSM-5 and (c) γ -Al₂O₃/ZSM-5 supports.

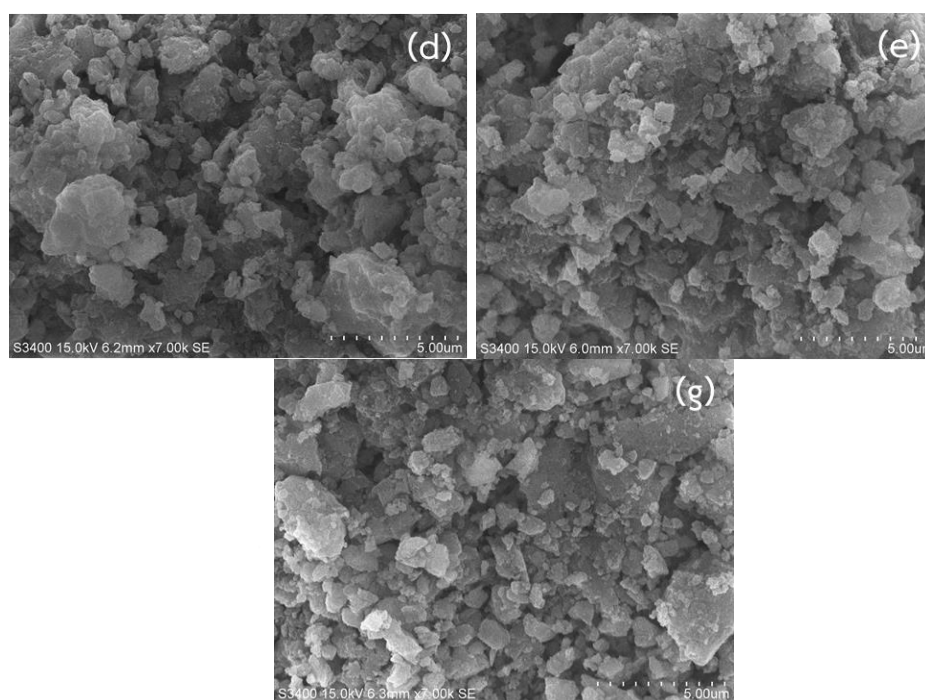


Figure 8 The SEM images of (d) 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5, (e) 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5 and (g) 5%Co-5%Ni / γ -Al₂O₃/ZSM-5 fresh catalysts.

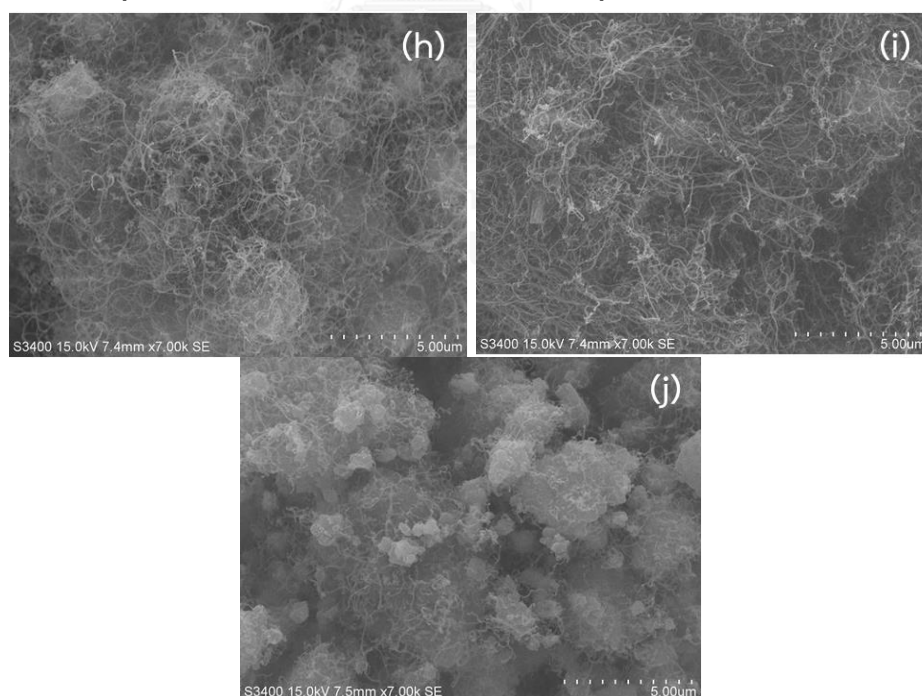


Figure 9 The SEM images of (h) 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5, (i) 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5 and (j) 5%Co-5%Ni/ γ -Al₂O₃/ZSM-5 used catalysts time on the stream 5hr.

4.1.1.4 Ammonia temperature program desorption (NH_3 -TPD)

The corresponding desorption curves NH_3 -TPD profiles of the γ - Al_2O_3 , ZSM-5 and γ - Al_2O_3 /ZSM-5 supports are showed in Figure 10. The NH_3 -TPD found weak acid sites at low temperature in range 70-350°C. Besides, ZSM-5 supports have strong acid sites at high temperature of in range 470°C. Furthermore, The different loading order between cobalt and nickel metals: 5%Ni 5%Co/ γ - Al_2O_3 /ZSM-5, 5%Ni-5%Co/ γ - Al_2O_3 /ZSM-5 and 5%Co-5%Ni/ γ - Al_2O_3 /ZSM-5 catalysts were represent in Figure 11. The catalysts have weak acid sites at low temperature in range 80-350°C. In addition, the amounts of acid sites on the surface of supports and catalysts were calculated as showed in Table 8. The acidity of bimetallic catalysts 5%Ni 5%Co/ γ - Al_2O_3 /ZSM-5 have high acidity than 5%Ni-5%Co/ γ - Al_2O_3 /ZSM-5 and 5%Co-5%Ni/ γ - Al_2O_3 /ZSM-5 catalysts.

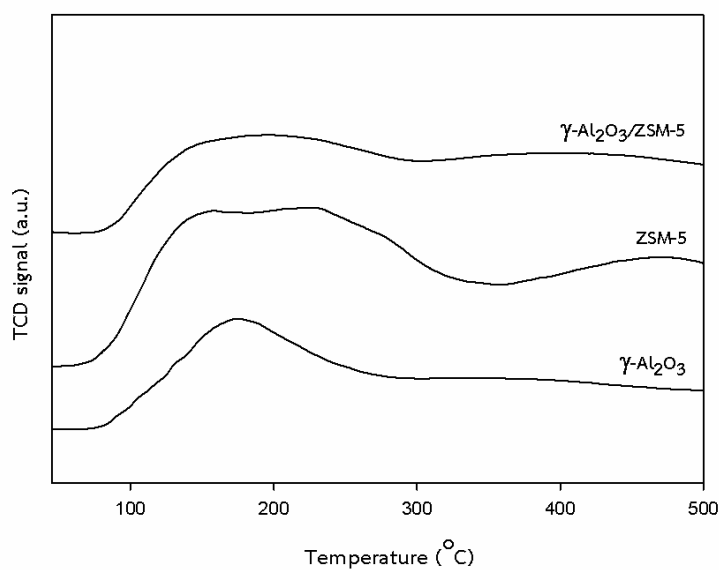


Figure 10 The NH_3 -TPD profiles of the supports.

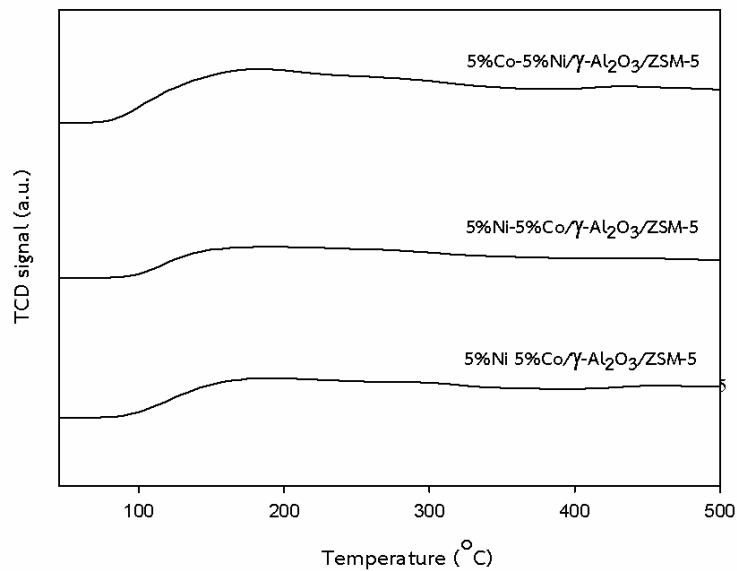


Figure 11 The NH_3 -TPD profiles of the different loading order between cobalt and nickel metals on $\gamma\text{-Al}_2\text{O}_3/\text{ZSM-5}$ support.

Table 8 The acidity of supported and the different loading order between cobalt and nickel metals catalysts.

Catalysts	Total acid site, (mmol H ⁺ /g)
$\gamma\text{-Al}_2\text{O}_3$	6.46
ZSM-5	2.91
$\gamma\text{-Al}_2\text{O}_3/\text{ZSM-5}$	1.73
5%Ni 5%Co/ $\gamma\text{-Al}_2\text{O}_3/\text{ZSM-5}$	1.17
5%Ni-5%Co/ $\gamma\text{-Al}_2\text{O}_3/\text{ZSM-5}$	1.12
5%Co-5%Ni/ $\gamma\text{-Al}_2\text{O}_3/\text{ZSM-5}$	1.25

4.1.1.5 Hydrogen temperature programmed reduction (H_2 -TPR)

Hydrogen temperature - programmed reduction (H_2 -TPR) were conducted to examine the reducibility of the catalysts. The TPR profiles are shown in Figure 12. The reduction peaks in Ni-Co bimetallic catalyst are included totally two peaks. First, weak peak were reduced NiO and CoO range at 300-450 °C as a result of very low metal-support interactions. Second, strong peak indicates that a broad peak at higher temperature range at 450-600 °C so assigned to reduction of NiO and CoO particles with high interaction with the supports [5, 32].

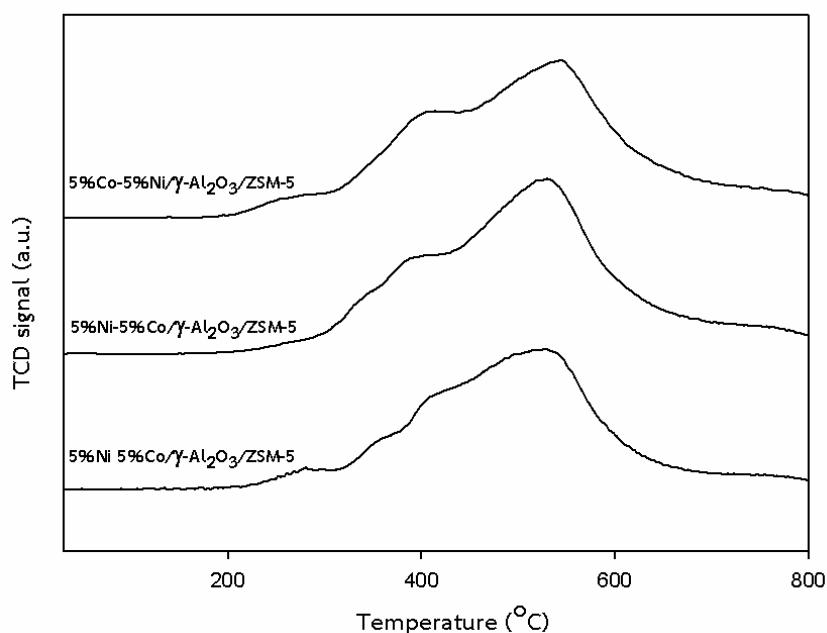


Figure 12 The TPR profiles of the different loading order between cobalt and nickel bimetallic catalysts calcined at 500 °C.

4.1.1.6 Carbon monoxide chemisorption

The active site of the catalyst was investigated amount of carbon monoxide adsorption. The carbon monoxide adsorption directly is proportional the active site. The result amount of carbon monoxide adsorption and dispersion of the catalyst as shown in Table 9. The 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5 catalyst has good dispersion because carbon monoxide were high adsorbed and high active site.

Table 9 The amount of carbon monoxide adsorbed and dispersion on a catalyst.

Catalysts	volume of	%	Active site (*10 ¹⁹ molecu CO/g)
	CO adsorption (cm ³ /g)		
5%Ni 5%Co/ γ -Al ₂ O ₃ /ZSM-5	0.42	1.1	1.12
5%Ni-5%Co/ γ -Al ₂ O ₃ /ZSM-5	0.27	0.7	0.73
5%Co-5%Ni/ γ -Al ₂ O ₃ /ZSM-5	0.27	0.7	0.73

4.1.1.7 Thermo gravimetric and differential thermal analysis (TG-DTA)

A quantitative analysis of coke formation over the used catalyst after the reaction was investigated by TGA-DTG in air. The results are shown in Figure 13. The rate of coke formation decreases in the following order: 5%Co-5%Ni/ γ -Al₂O₃/ZSM-5 > 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5 > 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5. Therefore, catalysts were deactivated and break down.

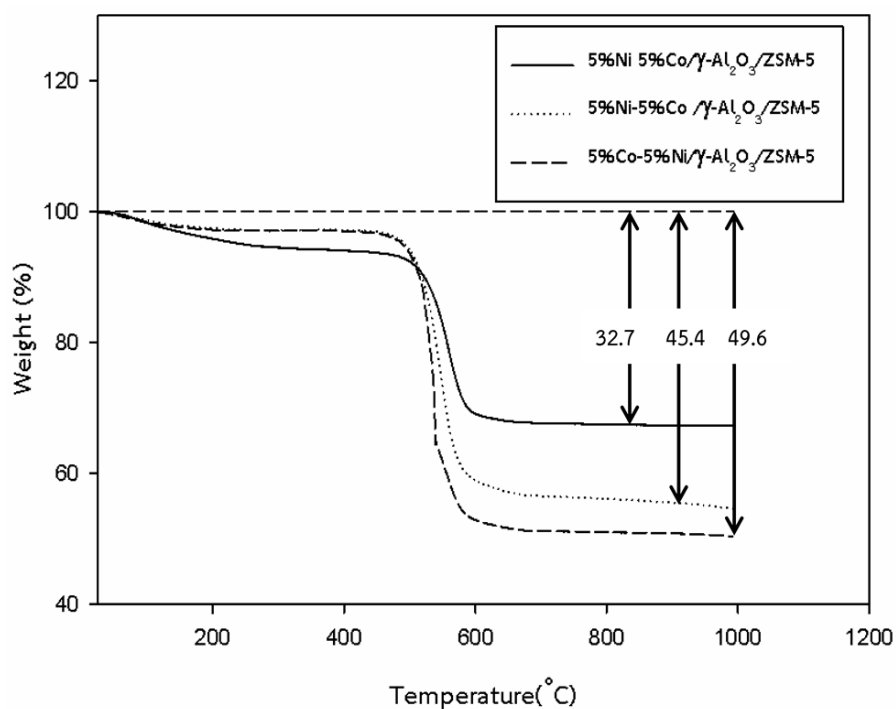


Figure 13 Thermo gravimetric profiles of catalysts after 5 hr. of reaction

4.1.2 Catalytic activity and selectivity

There are studied catalysts performances for carbon dioxide reforming of methane reaction. The catalysts were reduced in H₂ at 500 °C for 1 hr. in fixed bed reactor. Then, the reaction was operated to feed CH₄ mixed with CO₂ flow rate 60 ml/min at 700 °C for 1 atm.

The CH₄ and CO₂ conversion of catalysts for carbon dioxide reforming of methane reaction were indicated in Figure 14. The catalysts 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5, 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5 and 5%Co-5%Ni/ γ -Al₂O₃/ZSM-5 have conversion of methane 74% ,49% and 82%. Additionally, the catalysts have conversion of carbon dioxide 87%, 70% and 83%. Moreover, The H₂ and CO selectivity were demonstrated in Figure 15. The catalysts 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5 had high H₂ selectivity 47% in contrast the catalysts has low CO selectivity 53%.

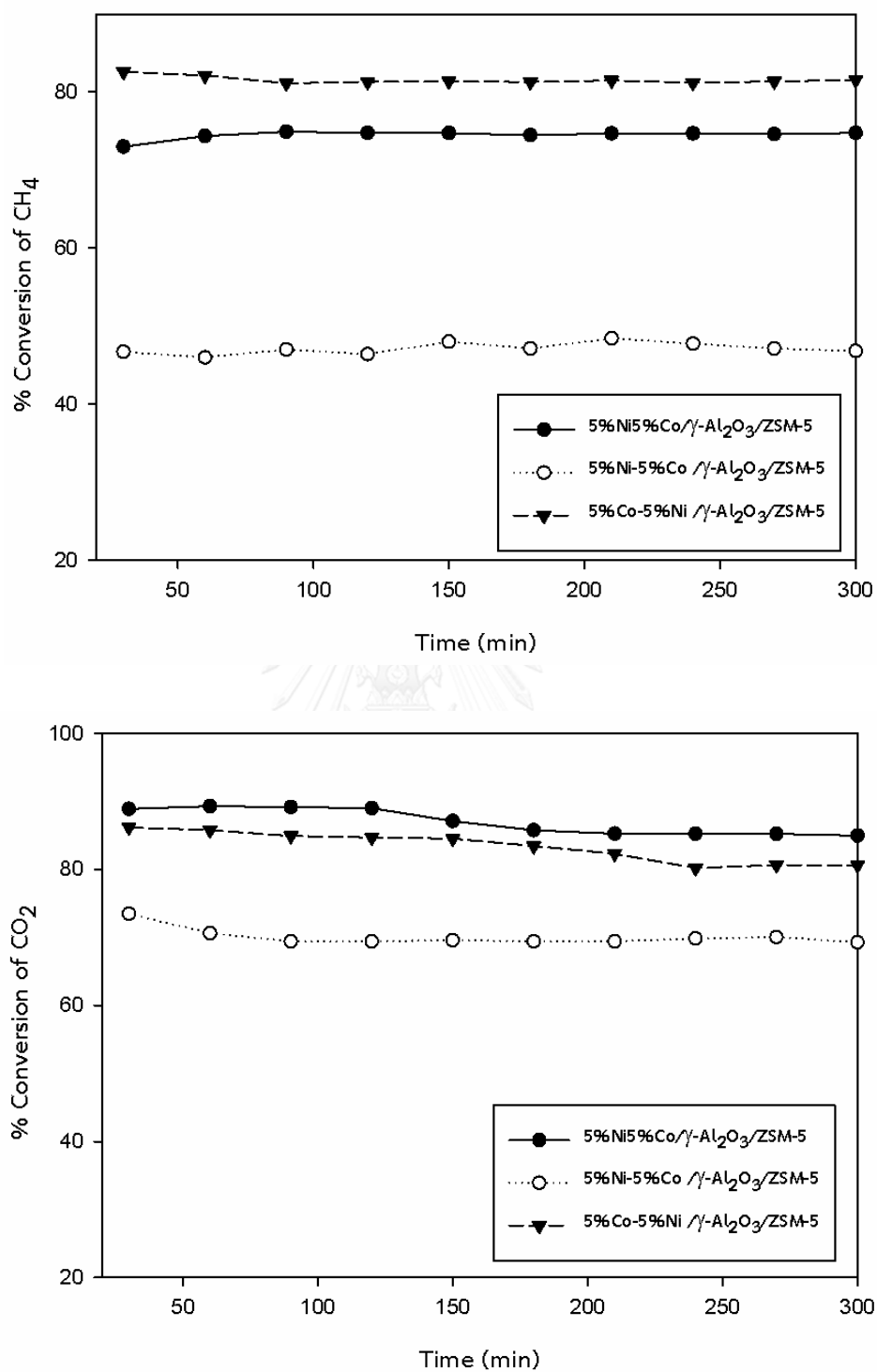


Figure 14 The CH₄ and CO₂ conversion of catalysts; 5%Co/ γ -Al₂O₃/ZSM-5, 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5 and 5%Co-5%Ni/ γ -Al₂O₃/ZSM-5

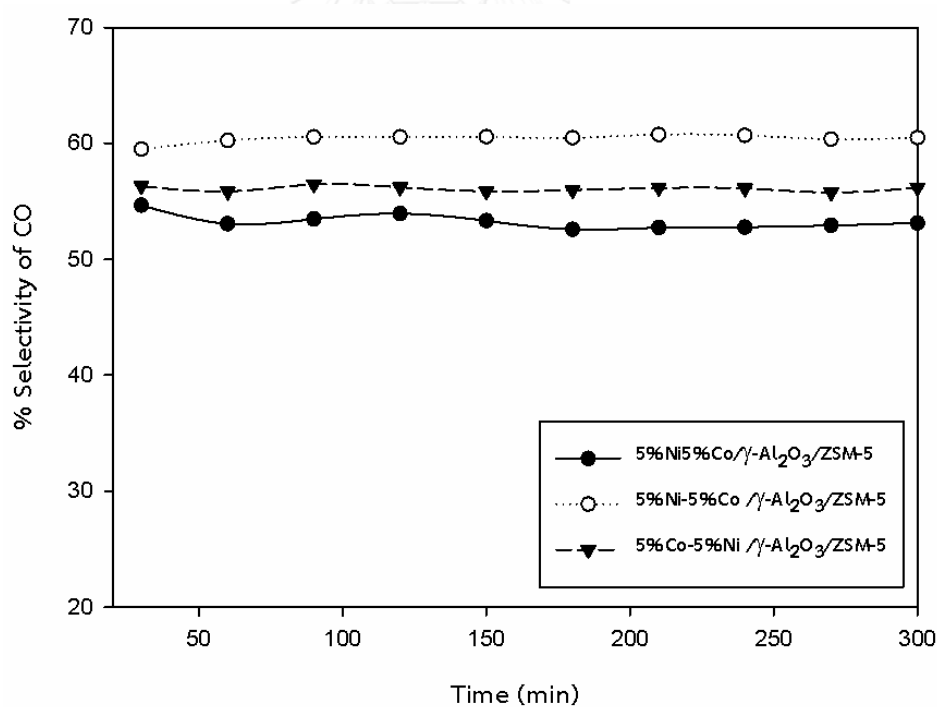
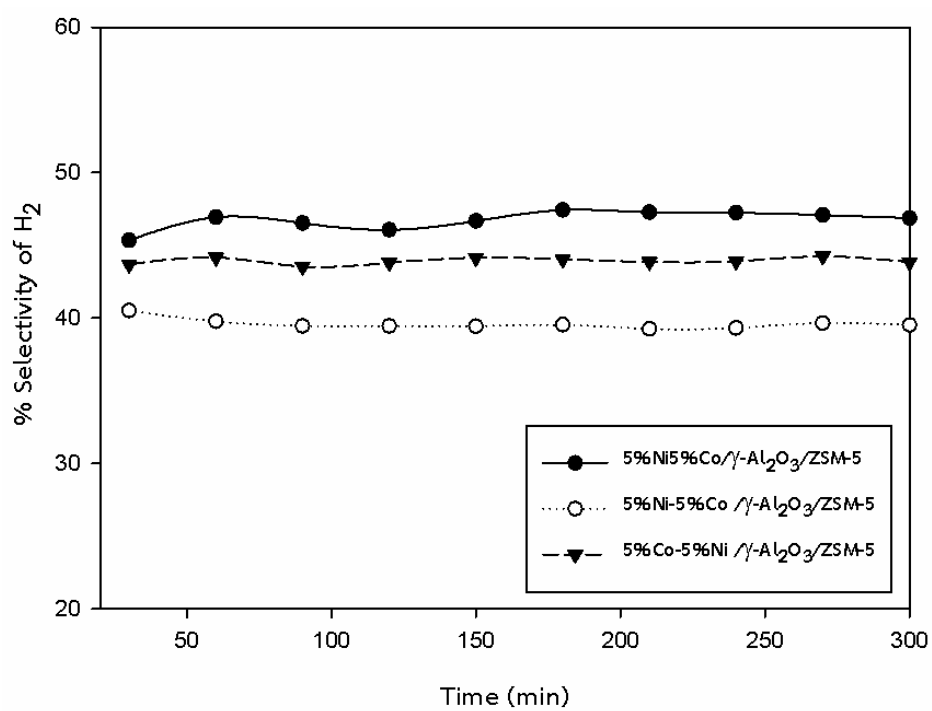


Figure 15 The H₂ and CO selectivity of catalysts; 5%Co/ γ -Al₂O₃/ZSM-5, 5%Ni-5%Co/ γ -Al₂O₃/ZSM-5 and 5%Co-5%Ni/ γ -Al₂O₃/ZSM-5

4.2 Study the catalysts with different molar ratio on mix supported.

4.2.1 Characterization of catalyst

4.2.1.1 X-Ray Diffraction

There are XRD patterns of mono metallic and bimetallic catalysts supported on γ -Al₂O₃/ZSM-5 zeolite indicated in Figure 16. The catalysts were prepared by incipient wetness impregnation. Then, there were calcinated under air at 500°C. The XRD patterns fresh mono metallic 10%Ni/Al₂O₃/ZSM-5 display pecks of NiO and NiAl₂O₃. Also, 10%Co/Al₂O₃/ZSM-5 shown pecks of CoO and Co₃O₄. As well as, the XRD patterns fresh bimetallic demonstrate pecks NiO , CoO ,Co₃O₄ and NiAl₂O₃ at 37°, 45°, 59°, 65° and 67°. The mono metallic and bimetallic catalysts have XRD patterns like Figure 4.2[33, 34].

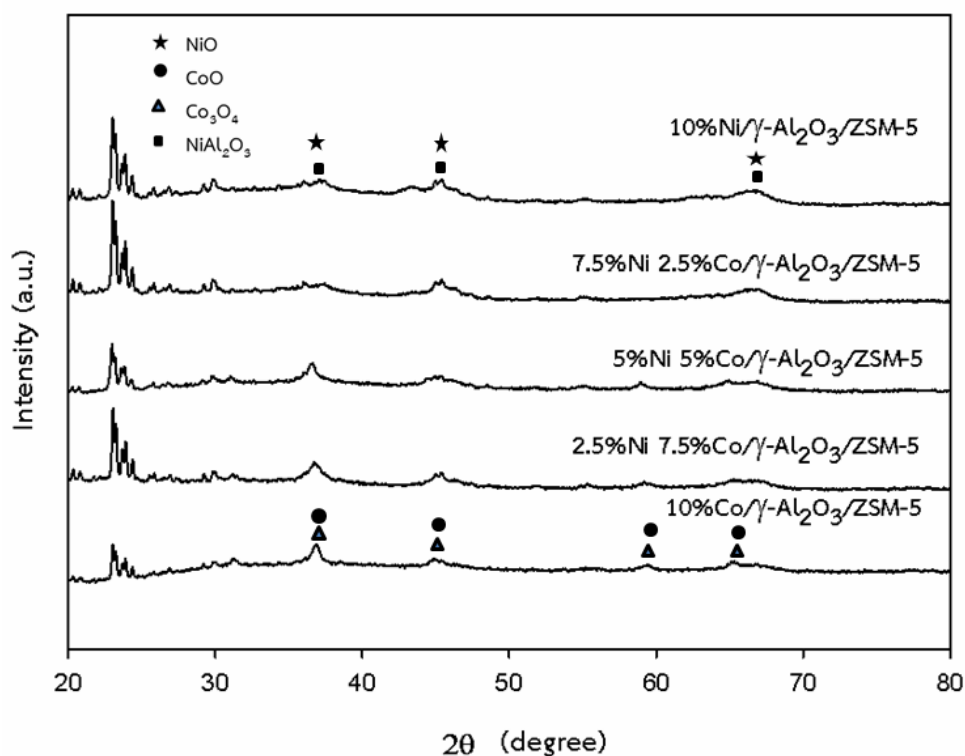


Figure 16 The XRD patterns of monometallic and bimetallic catalysts supported on γ -Al₂O₃/ZSM-5

4.2.1.2 Nitrogen adsorption-desorption

There are characteristic investigations of mono metallic and bimetallic catalysts by BET (Brunauer-Emmett-Teller). The specific surface area, pore volume and pore size of the mono metallic (10%Ni, 10%Co) and bimetallic (7.5%Ni 2.5%Co, 5%Ni 5%Co and 2.5%Ni 7.5%Co) on γ -Al₂O₃/ZSM-5 support represent at Table 10. For mono metallic and bimetallic have specific surface area 171-204 m²/g. The bimetallic catalysts 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5 has higher specific surface area than other catalysts. Moreover, both the average pore diameter and pore size were no significant difference whole catalysts.

Table 10 Physical properties of bimetallic and monometallic catalysts.

Catalysts	S _{BET} ^a (m ² /g)	P _v ^b (cm ³ /g)	P _s ^c (nm)
10%Ni/ γ - Al ₂ O ₃ /ZSM-5	200	0.24	4.8
7.5%Ni 2.5%Co/ γ -Al ₂ O ₃ /ZSM-5	197	0.22	4.9
5%Ni 5%Co/ γ - Al ₂ O ₃ /ZSM-5	204	0.23	4.7
2.5%Ni 7.5%Co/ γ - Al ₂ O ₃ /ZSM-5	171	0.20	5.0
10%Co/ γ - Al ₂ O ₃ /ZSM-5	188	0.24	4.8

S_{BET}^a : Specific surface area ; calculated by the BET equation.

P_v^b : BJH desorption pore volume.

P_s^c : BJH desorption average pore diameter.

Furthermore, the nitrogen adsorption/desorption isotherms of bimetallic (7.5%Ni 2.5%Co, 5%Ni 5%Co and 2.5%Ni 7.5%Co) and monometallic (10%Ni, 10%Co) on γ -Al₂O₃/ZSM-5 were revealed in Figure 17. Both, bimetallic and mono metallic have characteristic isotherm type IV for micro-mesoporous materials[35].

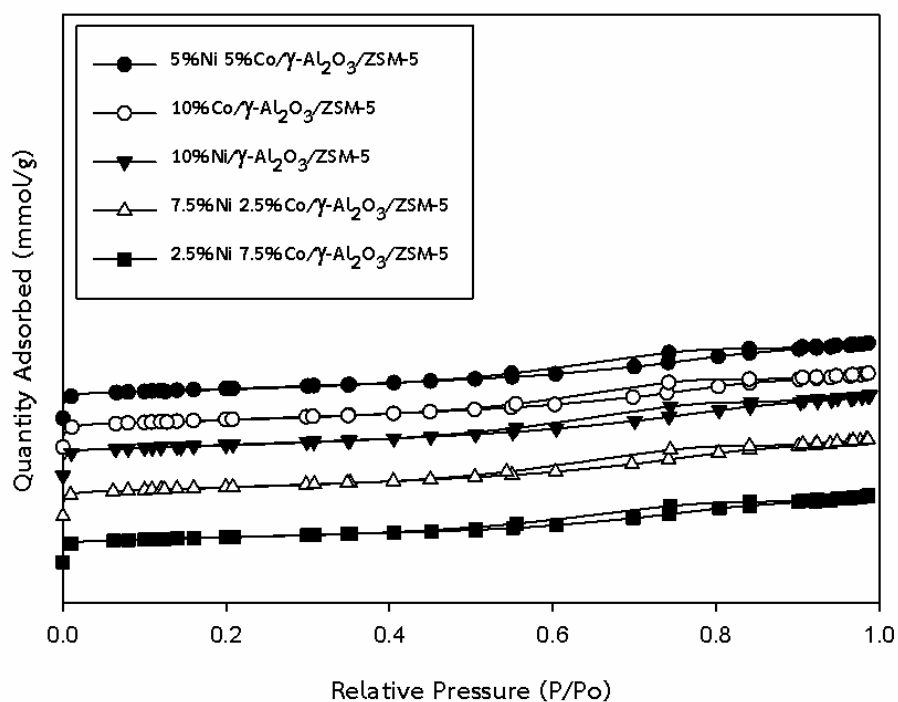
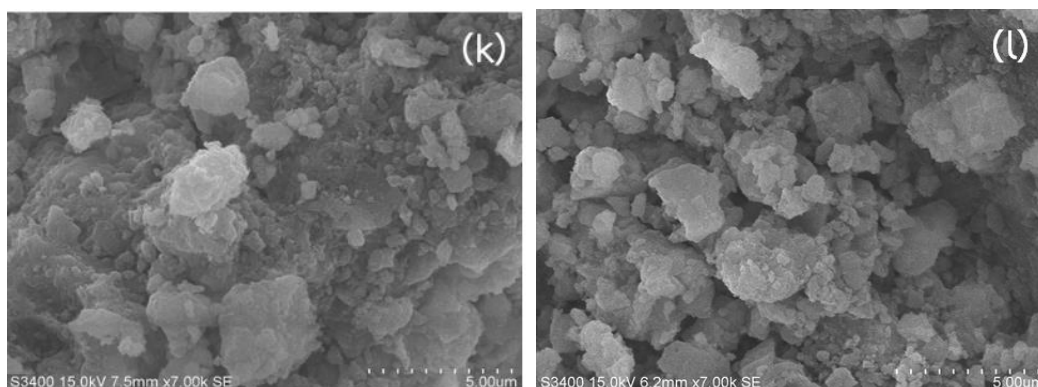


Figure 17 The nitrogen adsorption/desorption isotherms of bimetallic and monometallic catalysts.

4.2.1.3 Scanning Electron Microscopy (SEM)

Characterizations of bimetallic and mono metallic fresh catalysts were further carried out with SEM. The SEM micrographs shown in Figure 18 the Figure morphology of samples have significant similarity of supports in Figure 7. Additionally, The SEM images of bimetallic and mono metallic catalysts were used time on the stream 5 hr. demonstrate in Figure 19 the surface catalysts were deposited by higher amount of filamentous carbon[36].



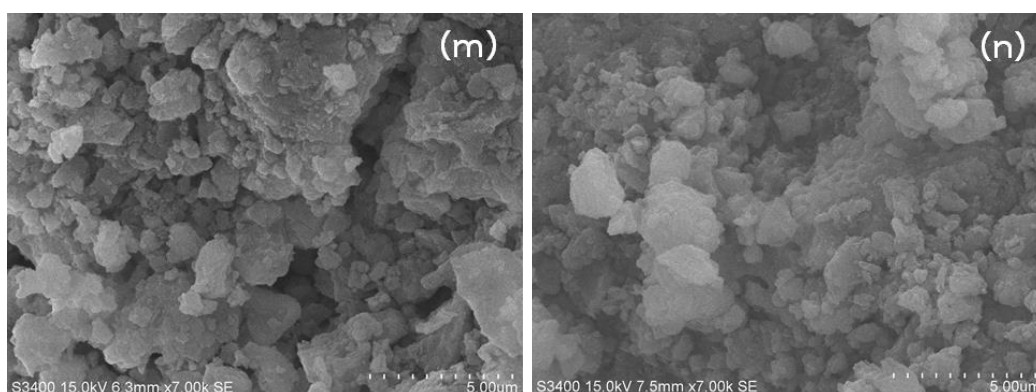


Figure 18 The SEM images of (k) 10%Ni/ γ -Al₂O₃/ZSM-5, (l) 7.5%Ni 2.5%Co/ γ -Al₂O₃/ZSM-5, (m) 2.5%Co 7.5%Ni / γ -Al₂O₃/ZSM-5 and (n) 10%Co/ γ -Al₂O₃/ZSM-5 fresh catalysts.

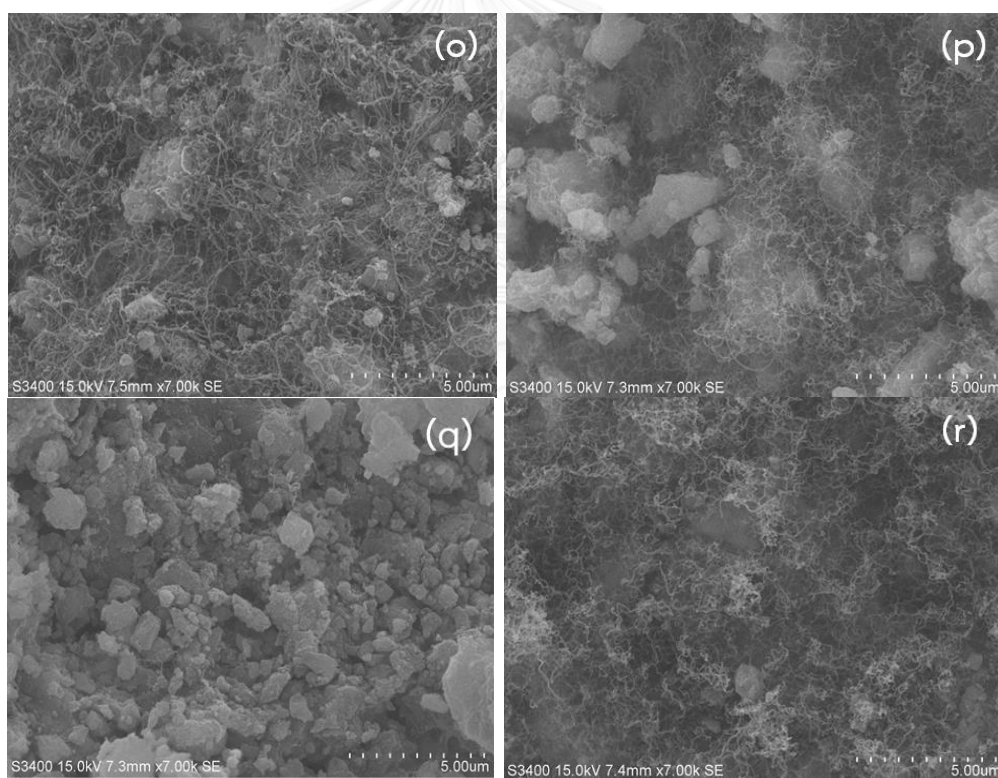


Figure 19 The SEM images of (o) 10%Ni/ γ -Al₂O₃/ZSM-5, (p) 7.5%Ni 2.5%Co/ γ -Al₂O₃/ZSM-5, (q) 2.5%Co 7.5%Ni / γ -Al₂O₃/ZSM-5 and (r) 10%Co/ γ -Al₂O₃/ZSM-5 used catalysts time on the stream 5 hr.

4.2.1.4 Ammonia temperature program desorption (NH₃-TPD)

The NH₃-TPD profiles for different molar ratio loading of bimetallic and mono metallic are shown in Figure 20. The profiles are composed of one broad peak at low temperature range of 30 to 500°C refer to weak acid sites. The acid properties of catalysts with different molar ratio on mix supported are also reported in Table 11. The bimetallic 5%Ni 5%Co/Al₂O₃/ZSM-5 has acidity more than other catalysts.

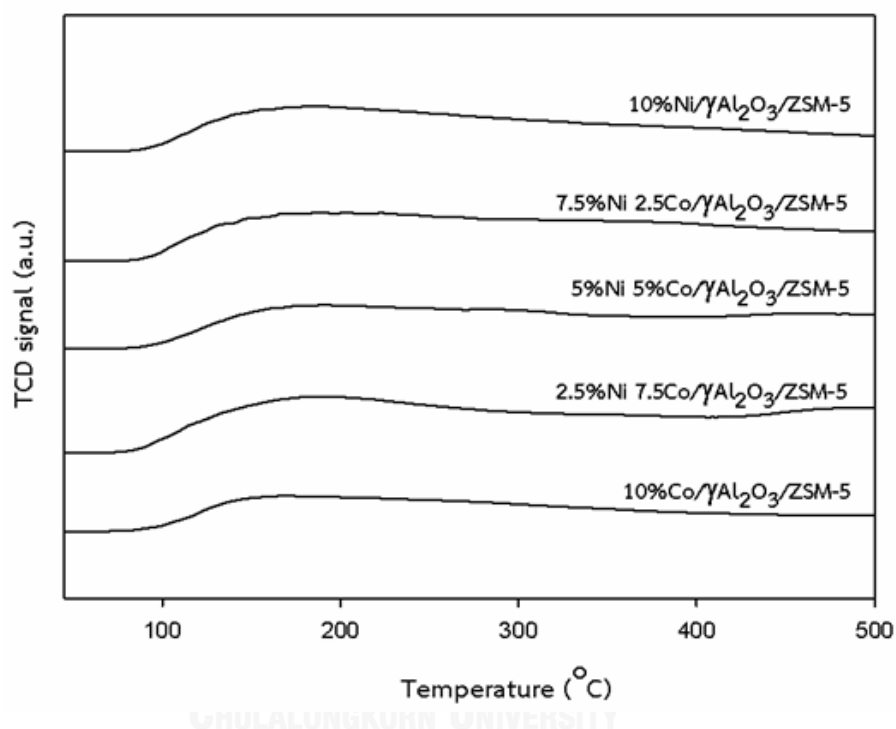


Figure 20 The NH₃-TPD profiles for different molar ratio loading of bimetallic and monometallic.

Table 11 The acidity of catalysts with different molar ratio on mix supported.

Catalysts	Total acid site, (mmol H ⁺ /g)
10%Ni/γ- Al ₂ O ₃ /ZSM-5	0.96
7.5%Ni 2.5%Co/γ-Al ₂ O ₃ /ZSM-5	0.87
5%Ni 5%Co/γ- Al ₂ O ₃ /ZSM-5	1.17
2.5%Ni 7.5%Co/γ- Al ₂ O ₃ /ZSM-5	0.85
10%Co/γ- Al ₂ O ₃ /ZSM-5	0.87

4.2.1.5 Hydrogen temperature programmed reduction (H_2 -TPR)

The H_2 -TPR patterns of bimetallic and mono metallic shown in Figure 21. Both bimetallic and mono metallic have reduction peak rang at 300-600 °C. The peaks are free NiO and CoO species, which have weak interaction with support.

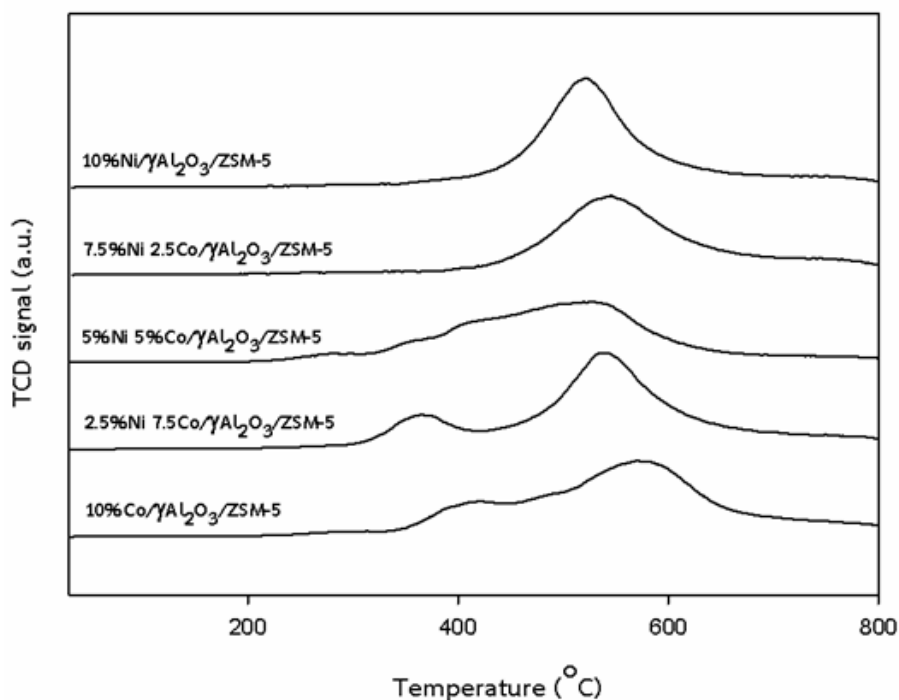


Figure 21 The H_2 -TPR patterns of bimetallic and mono metallic

4.2.1.6 Carbon monoxide chemisorption

The amount CO chemisorption of bimetallic and mono metallic at room temperature is display in Table 12. The reduced catalysts are used to calculate amount of active surface Ni and Co metal. Active sites of catalysts were calculated from amount of carbon monoxide adsorption on catalysts. The bimetallic 5%Ni 5%Co/ γ - Al_2O_3 /ZSM-5 has high volume of CO adsorption 0.4 cm^3/g hence the bimetallic (5%Ni 5%Co) has high active site and high metal dispersion.

Table 12 The amount of carbon monoxide adsorbed and dispersion on a catalyst.

Catalysts	volume of CO adsorption (cm ³ /g)	% Dispersion	Active site (*10 ¹⁹ molecuul CO/g)
10%Ni/ γ -Al ₂ O ₃ /ZSM-5	0.40	1.1	1.10
7.5%Ni 2.5%Co/ γ -Al ₂ O ₃ /ZSM-5	0.31	0.8	0.84
5%Ni 5%Co/ γ -Al ₂ O ₃ /ZSM-5	0.42	1.1	1.12
2.5%Ni 7.5%Co/ γ -Al ₂ O ₃ /ZSM-5	0.35	0.9	0.93
10%Co/ γ -Al ₂ O ₃ /ZSM-5	0.37	1.0	0.99

4.2.1.7 Thermo gravimetric and differential thermal analysis (TG-DTA)

Thermo gravimetric analysis was characterized amount of coke. Figure 22 showed the percent weight loss of spent different molar ratio loading of bimetallic and mono metallic. The results showed the coke decomposition over 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5 > 10%Ni/ γ -Al₂O₃/ZSM-5 > 7.5%Ni 2.5%Co/ γ -Al₂O₃/ZSM-5 > 10%Co/ γ -Al₂O₃/ZSM-5 > 2.5%Ni 7.5%Co/ γ -Al₂O₃/ZSM-5.

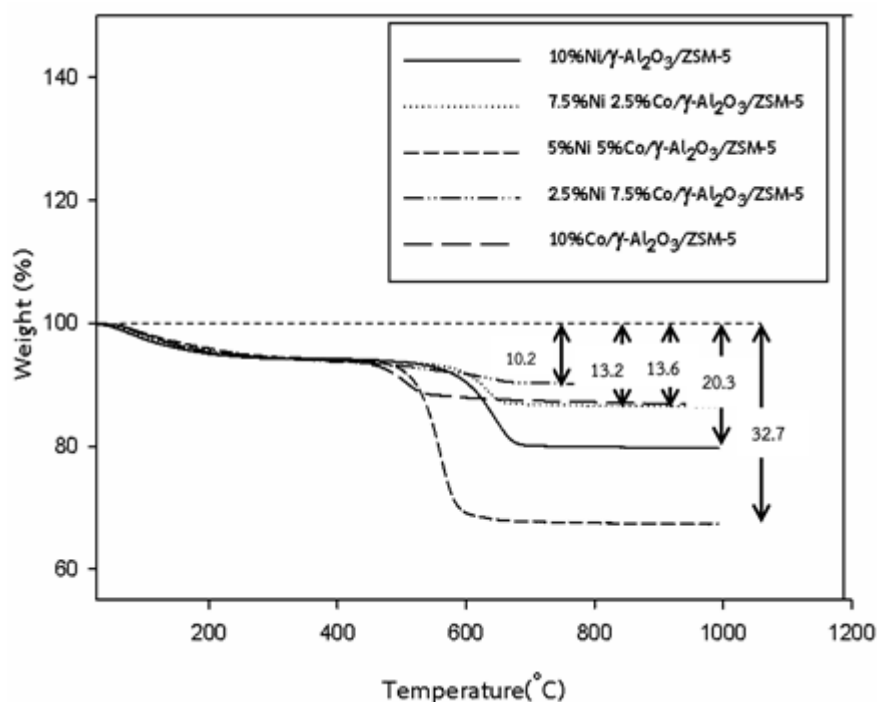


Figure 22 Thermo gravimetric profiles of different molar ratio loading of bimetallic and monometallic after 5 hr. of reaction.

4.2.2 Catalytic activity and selectivity

There are presented catalysts performances for carbon dioxide reforming of methane over different molar ratio loading of bimetallic and monometallic in Figure 23. The bimetallic 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5 has conversion of CH₄ 81%. Moreover, it has conversion of CO₂ 96%. Also, the mono metallic 10%Ni/ γ -Al₂O₃/ZSM-5 has conversion of CH₄ 68% and CO₂ 94%. Furthermore, the bimetallic 7.5%Ni 2.5%Co/ γ -Al₂O₃/ZSM-5 has conversion of CH₄ 66% and CO₂ 85%. As well as, both the bimetallic 2.5%Ni 7.5%Co/ γ -Al₂O₃/ZSM-5 and mono metallic 10%Co/ γ -Al₂O₃/ZSM-5 have similarly conversion of CH₄ 58% but conversion of CO₂ 76% and 91%, respectively. Additionally, the selectivity of H₂ and CO all catalysts shown in Figure 24 at the bimetallic 5%Ni 5%Co/ γ -Al₂O₃/ZSM-5 has selectivity H₂ 47% and CO 56% more than other catalysts.

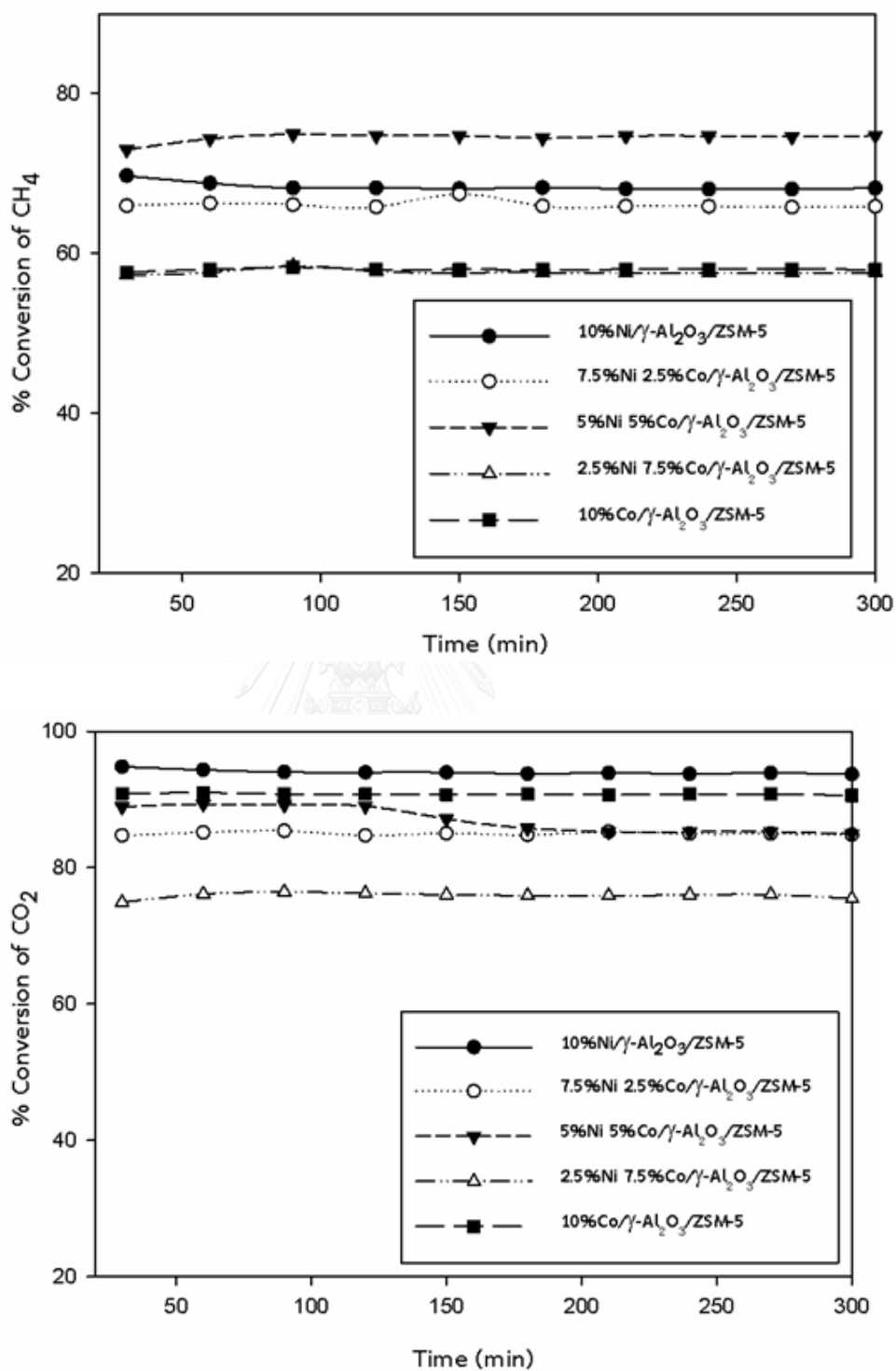


Figure 23 The CH₄ and CO₂ conversion of catalysts; 10%Ni/γ-Al₂O₃/ZSM-5, 7.5%Ni 2.5%Co/γ-Al₂O₃/ZSM-5, 5%Ni 5%Co/γ-Al₂O₃/ZSM-5, 2.5%Ni 7.5%Co/γ-Al₂O₃/ZSM-5 and 10%Co/γ-Al₂O₃/ZSM-5.

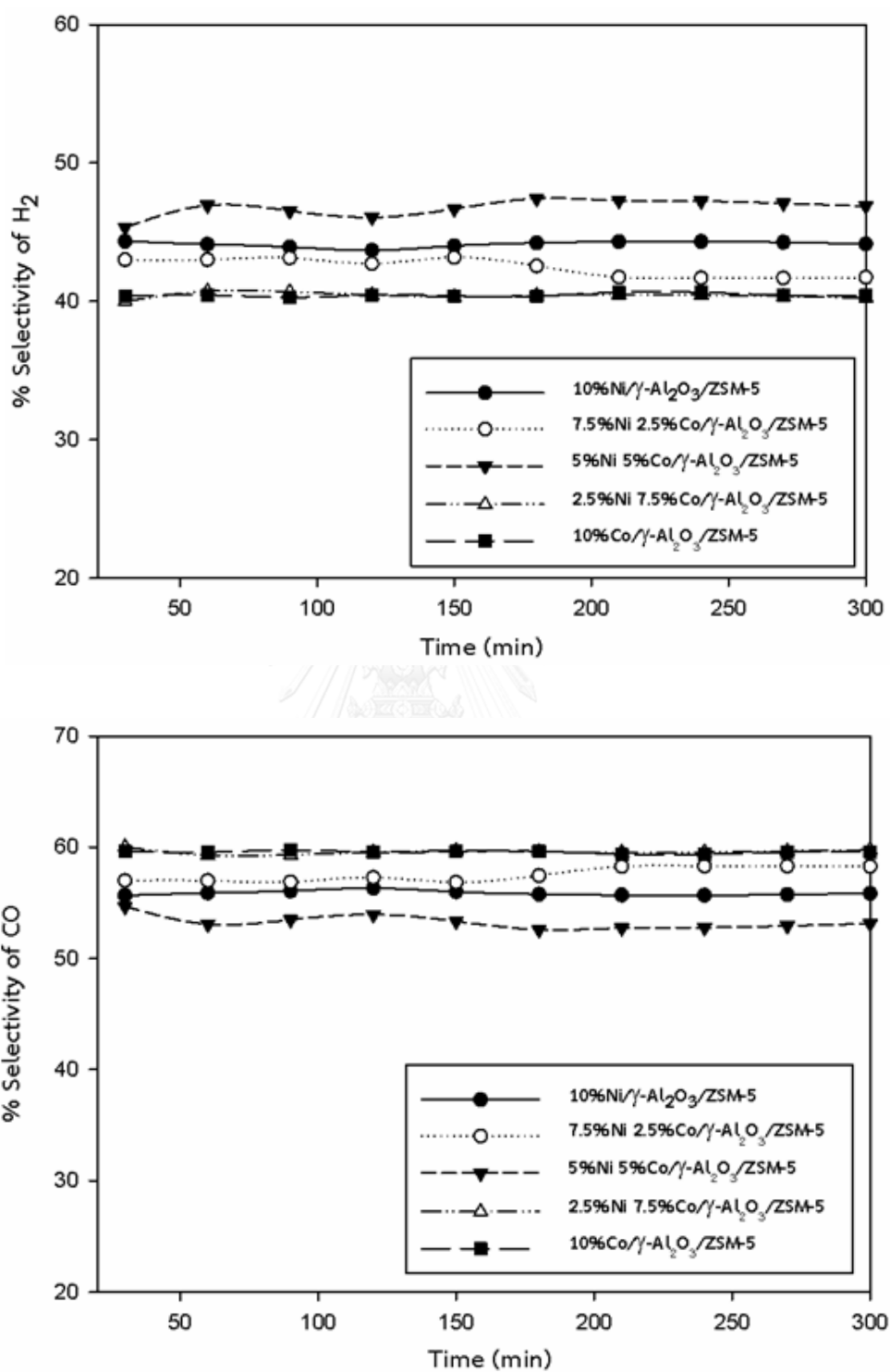


Figure 24 The H₂ and CO selectivity of catalysts; 10%Ni/γ-Al₂O₃/ZSM-5, 7.5%Ni 2.5%Co/γ-Al₂O₃/ZSM-5, 5%Ni 5%Co/γ-Al₂O₃/ZSM-5, 2.5%Ni 7.5%Co/γ-Al₂O₃/ZSM-5 and 10%Co/γ-Al₂O₃/ZSM-5

The H₂ and CO product yields (%) obtained after 5 h for CO₂ reforming of methane are reported in Table 13 the bimetallic catalysts (5%Ni 5%Co/ Al₂O₃/ZSM-5) had high H₂ yield of about 34 % and high CO yield 78 % than the other catalysts.

Table 13 H₂ and CO yield (%) obtained during CO₂ reforming of methane.

Catalysts	H ₂ Yield (%)	CO Yield (%)
5%Ni 5%Co/ γ - Al ₂ O ₃ /ZSM-5	34	78
5%Ni - 5%Co/ γ - Al ₂ O ₃ /ZSM-5	21	23
5%Co - 5%Ni/ γ - Al ₂ O ₃ /ZSM-5	31	28
7.5%Ni 2.5%Co/ γ -Al ₂ O ₃ /ZSM-5	28	28
2.5%Ni 7.5%Co/ γ - Al ₂ O ₃ /ZSM-5	24	25
10%Ni/ γ - Al ₂ O ₃ /ZSM-5	31	28
10%Co/ γ - Al ₂ O ₃ /ZSM-5	25	26

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

The CO₂ reforming of methane was carried out at 700 °C with CO₂:CH₄ ratio of 50:50. The bimetallic catalysts (5%Ni 5%Co/ Al₂O₃/ZSM-5) had high H₂ selectivity of about 47% with low CO selectivity of about 53%, high H₂ yield of about 34 % , high CO yield 78 % ,high volume of CO adsorption, high active site , high metal dispersion and high stability despite relatively higher coke formation than the other catalysts.

5.2 Recommendations

From this experiment, we have expected to improve acidity, quantity of metal loading catalyst for syngas production. Recommendations for the future work are the following:

To determine type of acidity (Bronsted and Lewis) with pyridine desorption and Fourier Transform Infrared Spectrophotometer (FTIR) for synthetic catalyst.

To the elements metal with inductively coupled plasma (ICP).

To study interaction of Al₂O₃ cover on ZSM-5 by X-Ray photoelectron spectroscopy.

To provide elemental identification and quantitative compositional information by Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX).



REFERENCES

จุฬาลงกรณ์มหาวิทยาลัย
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- [1] Fan, M.-S., Abdullah, A.Z., and Bhatia, S. Catalytic Technology for Carbon Dioxide Reforming of Methane to Synthesis Gas. *ChemCatChem* 1(2) (2009): 192-208.
- [2] Taufiq-Yap, Y.H., Sudarno, Rashid, U., and Zainal, Z. CeO₂-SiO₂ supported nickel catalysts for dry reforming of methane toward syngas production. *Applied Catalysis A: General* 468(0) (2013): 359-369.
- [3] Tang, M., Xu, L., and Fan, M. Effect of Ce on 5 wt% Ni/ZSM-5 catalysts in the CO₂ reforming of CH₄ reaction. *International Journal of Hydrogen Energy* 39(28) (2014): 15482-15496.
- [4] Albarazi, A., Beaunier, P., and Da Costa, P. Hydrogen and syngas production by methane dry reforming on SBA-15 supported nickel catalysts: On the effect of promotion by Ce_{0.75}Zr_{0.25}O₂ mixed oxide. *International Journal of Hydrogen Energy* 38(1) (2013): 127-139.
- [5] Fakeeha, A.H., Khan, W.U., Al-Fatesh, A.S., and Abasaeed, A.E. Stabilities of zeolite-supported Ni catalysts for dry reforming of methane. *Chinese Journal of Catalysis* 34(4) (2013): 764-768.
- [6] Edlund, D., LaVen, A., Mace, T., Pledger, W., Studebaker, R., and Wambaugh, D. Steam reforming fuel processor. 2003, Google Patents.
- [7] Halmann, M.M. "Carbon Dioxide Reforming". *Chemical fixation of carbon dioxide: methods for recycling CO₂ into useful products.* (1993).
- [8] Charienseri, S. Combined carbon dioxide reforming and partial oxidation of methane under periodic operation. Chulalongkorn university. Master's Thesis, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn university. (2007).
- [9] Ozkara-Aydinoglu, S.O., E.; and Aksoylu, A.E. . The effect of impregnation strategy on methane dry reforming activity of Ce promoted Pt/ZrO₂. . *International Journal of Hydrogen Energy* 34 ((2009):): 9711-9722.
- [10] Bradford, M.C.J.a.V., M. A. . Filamentous carbon formation caused by catalytic metal particles from iron oxide. *Journal of Catalysis* (173 (1998):): 157-171.
- [11] Zhang, J., Wang, H., and Dalai, A.K. Development of stable bimetallic catalysts for carbon dioxide reforming of methane. *Journal of Catalysis* 249(2) (2007): 300-310.

- [12] Topalidis, A.P., D.E.; Ladavos, A.; Loukatzikou, L.; and Pomonis, P.J. *Catalyst Today* 127 (2007): 238–245.
- [13] Luengnaruemitchai, A. and Kaengsilalai, A. Activity of different zeolite-supported Ni catalysts for methane reforming with carbon dioxide. *Chemical Engineering Journal* 144(1) (2008): 96-102.
- [14] Jianguo Zhang, H.W., * and Ajay K. Dalai. <Kinetic Studies of Carbon Dioxide Reforming of Methane.pdf>. *Ind. Eng. Chem.* 48 (2009): 677–684.
- [15] San-José-Alonso, D., Juan-Juan, J., Illán-Gómez, M.J., and Román-Martínez, M.C. Ni, Co and bimetallic Ni–Co catalysts for the dry reforming of methane. *Applied Catalysis A: General* 371(1-2) (2009): 54-59.
- [16] Zakeri, M., Samimi, A., Khorram, M., Atashi, H., and Mirzaei, A. Effect of forming on selectivity and attrition of co-precipitated Co–Mn Fischer–Tropsch catalysts. *Powder Technology* 200(3) (2010): 164-170.
- [17] Guzzi, L., et al. Methane dry reforming with CO₂: A study on surface carbon species. *Applied Catalysis A: General* 375(2) (2010): 236-246.
- [18] Horváth, A., Stefler, G., Geszti, O., Kienneman, A., Pietraszek, A., and Guzzi, L. Methane dry reforming with CO₂ on CeZr-oxide supported Ni, NiRh and NiCo catalysts prepared by sol–gel technique: Relationship between activity and coke formation. *Catalysis Today* 169(1) (2011): 102-111.
- [19] Luisetto, I., Tuti, S., and Di Bartolomeo, E. Co and Ni supported on CeO₂ as selective bimetallic catalyst for dry reforming of methane. *International Journal of Hydrogen Energy* 37(21) (2012): 15992-15999.
- [20] Sarkar, B., et al. Reforming of methane with CO₂ over Ni nanoparticle supported on mesoporous ZSM-5. *Catalysis Today* 198(1) (2012): 209-214.
- [21] Wongkaew, K., Pancharoen, U., Phatanasri, S., Leepipatpiboon, N., and Lothongkum, A.W. Effect of diluent polarity on membrane stability in the separation of trace Pd(II) from wastewater by HFSLM using LIX84-I. *Journal of Industrial and Engineering Chemistry* 21 (2015): 212-220.
- [22] Sharifi, M., Haghighi, M., Rahmani, F., and Karimipour, S. Syngas production via dry reforming of CH₄ over Co- and Cu-promoted Ni/Al₂O₃–ZrO₂ nanocatalysts

- synthesized via sequential impregnation and sol–gel methods. *Journal of Natural Gas Science and Engineering* 21 (2014): 993-1004.
- [23] Mahoney, E.G., Puseh, J.M., Stagg-Williams, S.M., and Faraji, S. The effects of Pt addition to supported Ni catalysts on dry (CO₂) reforming of methane to syngas. *Journal of CO₂ Utilization* 6 (2014): 40-44.
- [24] Alipour, Z., Rezaei, M., and Meshkani, F. Effect of Ni loadings on the activity and coke formation of MgO-modified Ni/Al₂O₃ nanocatalyst in dry reforming of methane. *Journal of Energy Chemistry* 23(5) (2014): 633-638.
- [25] E. L. Wu, S.L.L., D. H. Olson, A. C. Rohrman, Jr., and G. T. Kokotailo. ZSM-5-Type Materials. Factors Affecting Crystal Symmetry. *Physicdl Cbemisfry* 83(21) (1979): 2083-2777.
- [26] Hasin1, P., , N.K., and , A.L., *. <Nickelaluminium complex.pdf>. *Science and Technology* (2008): 140-149.
- [27] Ruckenstein, E. and Hang Hu, Y. Role of Support in CO₂Reforming of CH₄to Syngas over Ni Catalysts. *Journal of Catalysis* 162(2) (1996): 230-238.
- [28] Yousheng Tao, † Hirofumi Kanoh,† Lloyd Abrams,‡ and Katsumi Kaneko*,†. Mesopore-Modified Zeolites: Preparation, Characterization, and Applications. *Chem. Rev.* (106) (2006): 896-910.
- [29] Rutkowska, M., Macina, D., Mirocha-Kubieñ, N., Piwowarska, Z., and Chmielarz, L. Hierarchically structured ZSM-5 obtained by desilication as new catalyst for DME synthesis from methanol. *Applied Catalysis B: Environmental* 174 (2015): 336-343.
- [30] Shams-Ghahfarokhi, Z. and Nezamzadeh-Ejhieh, A. As-synthesized ZSM-5 zeolite as a suitable support for increasing the photoactivity of semiconductors in a typical photodegradation process. *Materials Science in Semiconductor Processing* 39 (2015): 265-275.
- [31] F. Bonnet, F.R., Y. Berthier and P. Marcus. Filamentous carbon formation caused by catalytic metal particles from iron oxide. *Materials and Corrosion* 11(54) (2003): 870-880.

- [32] Ruckenstein, E. and Wang, H.Y. Carbon dioxide reforming of methane to synthesis gas over supported cobalt catalysts. *Applied Catalysis A: General* 204(2) (2000): 257-263.
- [33] Sajjadi, S.M., Haghghi, M., and Rahmani, F. Sol-gel synthesis of Ni-Co/Al₂O₃-MgO-ZrO₂ nanocatalyst used in hydrogen production via reforming of CH₄/CO₂ greenhouse gases. *Journal of Natural Gas Science and Engineering* 22 (2015): 9-21.
- [34] Chang, L.M., An, M.Z., Guo, H.F., and Shi, S.Y. Microstructure and properties of Ni-Co/nano-Al₂O₃ composite coatings by pulse reversal current electrodeposition. *Applied Surface Science* 253(4) (2006): 2132-2137.
- [35] Rostamizadeh, M. and Taeb, A. Highly selective Me-ZSM-5 catalyst for methanol to propylene (MTP). *Journal of Industrial and Engineering Chemistry* (2015).
- [36] Pinheiro, A.N., Valentini, A., Sasaki, J.M., and Oliveira, A.C. Highly stable dealuminated zeolite support for the production of hydrogen by dry reforming of methane. *Applied Catalysis A: General* 355(1) (2009): 156-168.



APPENDIX A

CALCULATION FOR CATALYST PREPARATION

1. Preparation of 10%Ni/Al₂O₃/ZSM-5 monometallic catalyst by impregnation.

Example: Preparation of the 10%Ni/Al₂O₃/ZSM-5 catalyst

Reagent: Ni(NO₃)₂·6H₂O, Molecular weight = 292 g/mol

Ni, Molecular weight = 59 g/mol

At 1 gram catalyst, consisted of: Alumina = 0.9 g

Cobalt = 0.1 g

Calculation:

$$\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O} = (0.1 \times 292) / 59 = 0.4949 \text{ g}$$

The 10%Ni/Al₂O₃/ZSM-5 catalyst was prepared from the 0.4949 g of Ni(NO₃)₂·6H₂O impregnated on 0.9 g of Al₂O₃/ZSM-5 supported.

2. Preparation of Ni-Co/ Al₂O₃/ZSM-5 bimetallic catalyst by co-impregnation

Preparation of Ni-Co/Al₂O₃/ZSM-5 bimetallic catalysts by co-impregnation method with various nickel-cobalt contents were 5% 5% that showed as follows:

Example: Preparation of the 5%Ni 5%Co/Al₂O₃/ZSM-5 catalyst.

<u>Reagent:</u>	Ni(NO ₃) ₂ ·6H ₂ O, Molecular weight	= 292 g/mol
	Ni, Molecular weight	= 59 g/mol
	Co(NO ₃) ₂ ·6H ₂ O, Molecular weight	= 292 g/mol
	Co, Molecular weight	= 59 g/mol

At 1 gram catalyst, consisted of: Alumina = 0.9 g

Nickel = 0.05 g

Cobalt = 0.05 g

Calculation:

$$\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O} = (0.05 \times 292) / 59 = 0.2475 \text{ g}$$

$$\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} = (0.05 \times 292) / 59 = 0.2475 \text{ g}$$

The 5%Ni 5%Co/ Al₂O₃/ZSM-5 catalyst bimetallic catalyst was prepared from the 0.2475 g of Ni(NO₃)₂·6H₂O and 0.2475 g of Co(NO₃)₂·6H₂O impregnated on 0.9 g of Al₂O₃/ZSM-5 supported.

APPENDIX B

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of composition of products and reactants in carbon dioxide reforming of methane over $\text{Al}_2\text{O}_3/\text{ZSM-5}$ supported. The main products of this reaction are carbon monoxide and hydrogen.

The Thermal Conductivity Detector (TCD), gas chromatography Shimadzu model 8A was used to analyze the concentration of products and reactants by using molecular sieve 5A and porapack-Q column.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of methane, carbon dioxide, hydrogen and carbon monoxide are illustrated in Figure C1-C4, respectively.

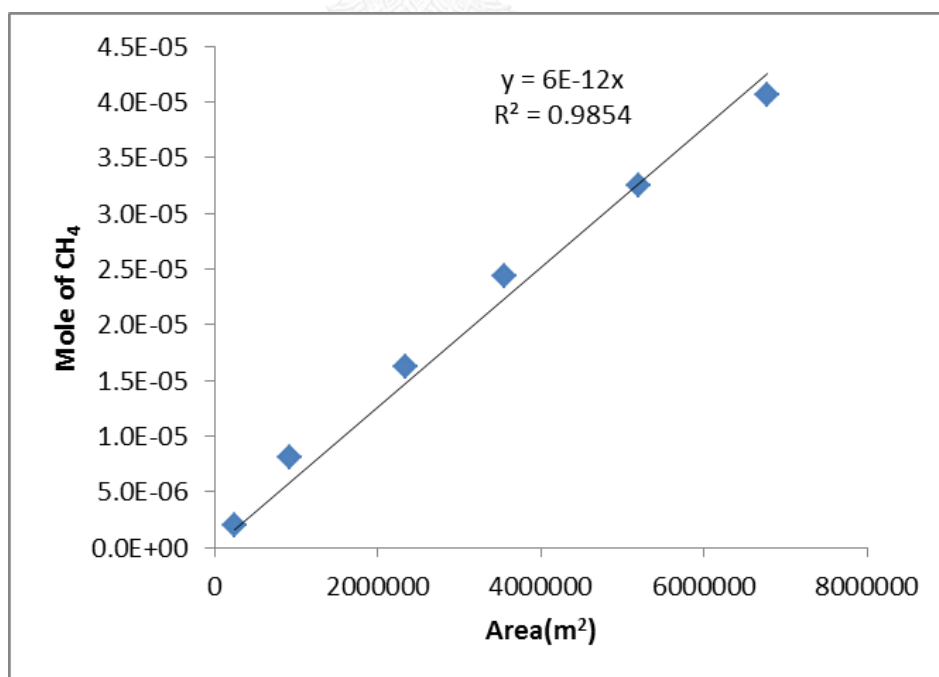


Figure B1 The calibration curve of methane.

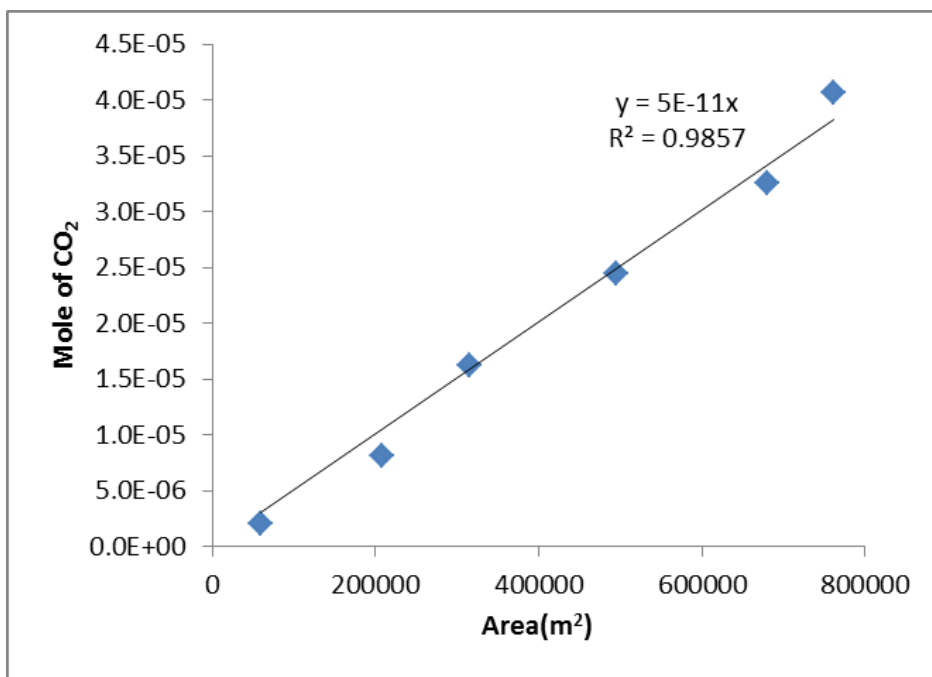


Figure B2 The calibration curve of carbon dioxide.

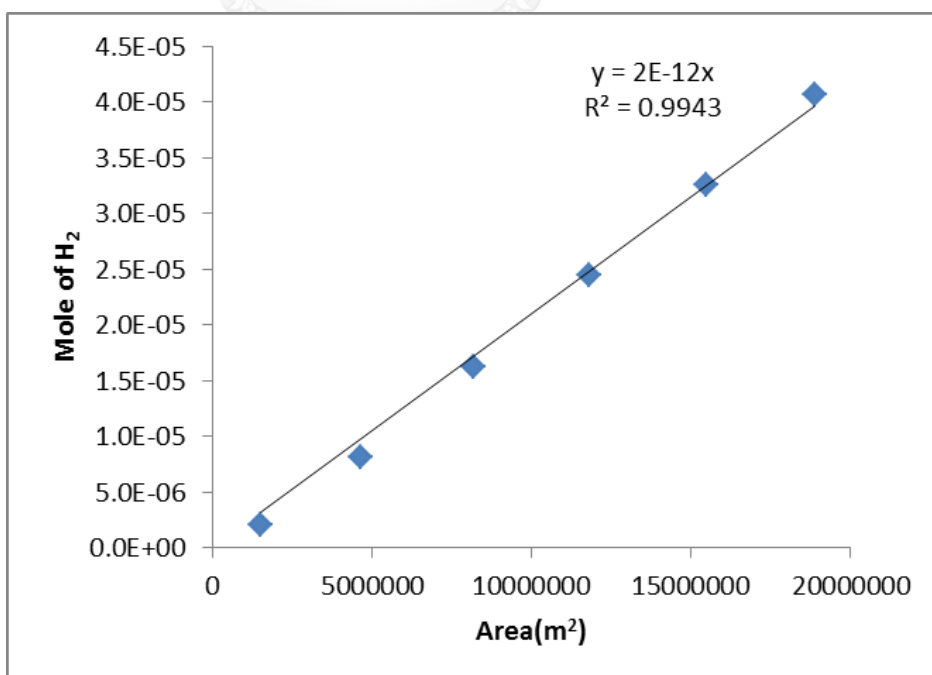


Figure B3 The calibration curve of hydrogen.

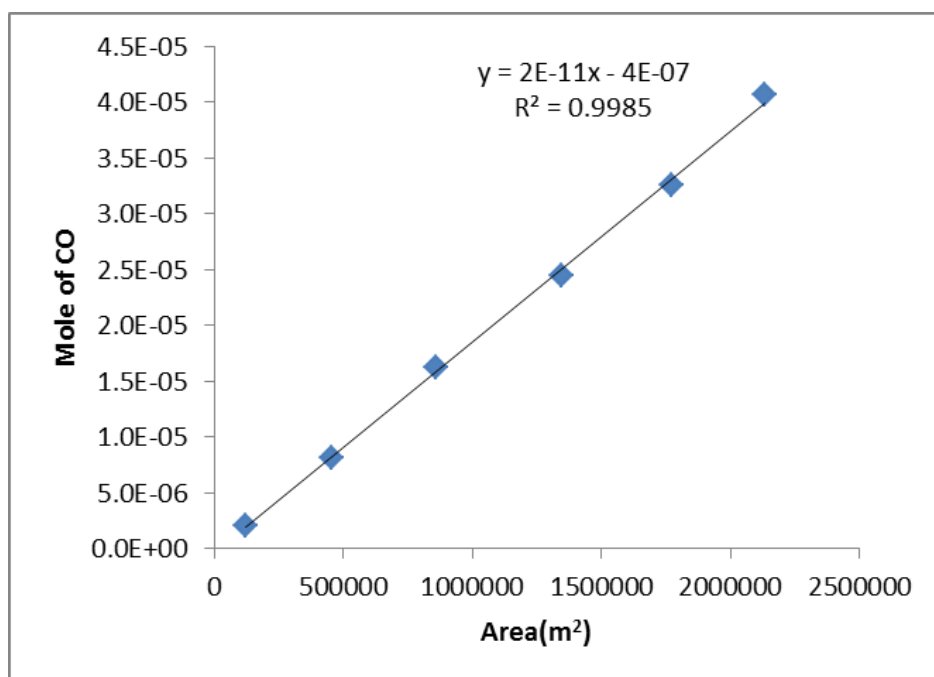


Figure B4 The calibration curve of carbon monoxide.

APPENDIX C

DATA FOR CALCULATION OF ACID SITE

The total acid site of prepared catalyst is calculated as follows.

Calculation

Total acidity is calculated from the NH₃-TPD profiles as the following step.

The NH₃-TPD profiles:

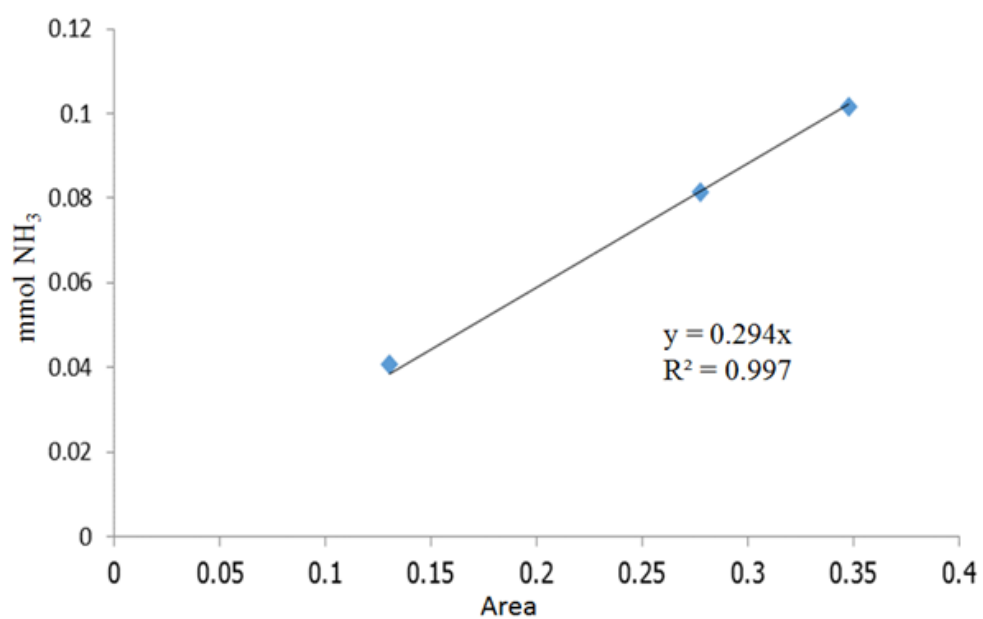
- Under area of the NH₃-TPD profiles of the sample = A
- The mole of NH₃ was calculated from the calibration curve of NH₃ as formula:

The mole of NH₃ of the sample = 0.294×A mmole.

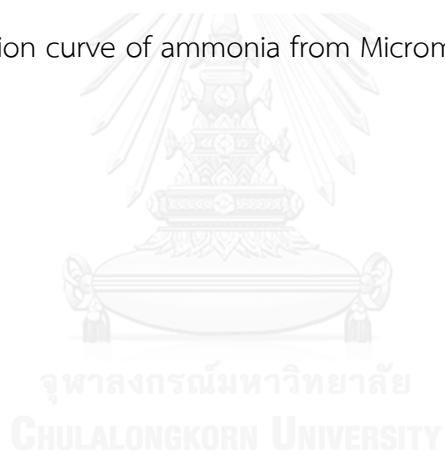
- Amount of sample = B g.

The total acidity of sample = $\frac{\text{The mmole of NH}_3 \text{ of the sample}}{\text{Amount of dry catalyst}}$

= (0.294×A)/B mmol NH₃/g catalyst



C1 The calibration curve of ammonia from Micromeritics Chemisorp 2750



APPENDIX D

CALCULATION FOR METAL ACTIVE SITES AND DISPERSION

Calculation of the total CO chemisorption and metal dispersion of the catalyst, a stoichiometry of CO/Ni = 1 and CO/Co = 1. The calculation procedure is as follows:

Example: Calculation of the total CO chemisorption of 10%Ni/Al₂O₃/ZSM-5

S_f	=stoichiometry factor CO:Ni	= 1
V_{ads}	=volume adsorbed	= 0.62 cm ³ /g
V_g	= molar volume of gas at STP	= 22414 cm ³ /mol
m.w.	=molecular weight of metal = Ni	= 59 g/mol
%M	=%metal	= 10%Ni
V_{injet}	=volume injected	= 0.02 cm ³
M	=mass of sample	= 0.1 g

$$\begin{aligned} \% \text{ Metal Dispersion (\%D)} &= S_f \cdot (V_{ads}/V_g) \cdot (m.w./\%M) \cdot 100\% \cdot 100\% \\ &= 1 \cdot (0.62 / 22414) \cdot (58.6934/10) \cdot 100 \cdot 100 = 1.6 \end{aligned}$$

$$\begin{aligned} \text{Active site (molecule of CO/g)} &= S_f \cdot (V_{ads}/V_g) \cdot (6.02 \cdot 10^{23}) \\ &= 1 \cdot (0.62/22414) \cdot (6.02 \cdot 10^{23}) \\ &= 1.66 \cdot 10^{19} \text{ molecule CO/g} \end{aligned}$$

APPENDIX E

CALCULATION FOR CONVERSION SELECTIVITY AND YIELD

The conversions of CO₂ and CH₄ are defined in Equation (F.1) and (F.2) and the selectivity of H₂ and CO are defined in Equation (F.3) and (F.4), respectively

$$X_{CH_4} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100 \quad (\text{Eq.F.1})$$

$$X_{CO_2} = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100 \quad (\text{Eq.F.2})$$

$$S_{H_2} = \frac{[H_2]_{out}}{[H_2]_{out} + [CO]_{out}} \times 100 \quad (\text{Eq.F.3})$$

$$S_{CO} = \frac{[CO]_{out}}{[H_2]_{out} + [CO]_{out}} \times 100 \quad (\text{Eq.F.4})$$

$$Y_{H_2} = \frac{[CH_2]_{out}}{2[CH_4]_{in}} \times 100 \quad (\text{Eq.F.5})$$

$$Y_{CO} = \frac{[C_{CO}]_{out}}{[C_{CH_4}]_{in} + [C_{CO}]_{in}} \times 100 \quad (\text{Eq.F.6})$$

APPENDIX G

LIST OF PUBLICATION

Sutarat Thongratkeaw¹, Suphot Phatanasri^{2*}

“COMPARISON OF MONO METALLIC AND BIMETALLICS Co, Ni CATALYSTS
FOR CO₂ REFORMING OF METHANE”

The Thai Institute of Chemical Engineering and Applied Chemistry (TIChE) Conference
International 2014

“Changes: Cleaner Energy, Leaner Processes, Better Living”

December 18 - 19, 2014, Furama Hotel, Chiang Mai, Thailand



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