ปฏิกิริยาคาร์บอนไดออกไซด์เมทาเนชันบนตัวเร่งปฏิกิริยาฐานนิกเกิลสปิเนล

นางสาวชัญญา ธรรมมา

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CO_2 methanation over $NiAl_2O_4$ spinel - based catalysts

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ชัญญา ธรรมมา : ปฏิกิริยาคาร์บอนไดออกไซด์เมทเนชันบนตัวเร่งปฏิกิริยาฐานนิกเกิลสปิเนล (CO_2 methanation over $NiAl_2O_4$ spinel - based catalysts) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. จูงใจ ปั้นประณต, 101 หน้า.

ในงานวิจัยนี้ศึกษาการเตรียมตัวเร่งปฏิกิริยาฐานนิกเกิลออกไซด์/นิกเกิลสปิเนล ที่มีอัตราส่วนโมล Ni/Al = 1/2 ด้วยวิธีตกตะกอนร่วม ที่อุณหภูมิการตกตะกอน 30 และ 80 องศาเซลเซียส และอุณหภูมิการเผา 500, 700, 900 และ 1200 องศาเซลเซียส วิเคราะห์คุณลักษณะของตัวเร่งปฏิกิริยาด้วยเทคนิค เช่น การดูดซับด้วยแก๊สไนโตรเจน การเลี้ยวเบนของรังสีเอ็กซ์ การรีดักชันแบบโปรแกรมอุณหภูมิด้วยไฮโดรเจน กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด พบว่าตัวเร่งปฏิกิริยานิกเกิลออกไซด์บนตัวรองรับนิกเกิลสปิเนลที่เตรียมด้วยอุณหภูมิตกตะกอน และเผา ที่อุณหภูมิ 80 และ 900 องศาเซลเซียส ตามลำดับ แสดงประสิทธิภาพที่ดีที่สุด ในการทดสอบในปฏิกิริยาเมทเนชันที่อุณหภูมิ 350 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง โดยให้ค่าการเปลี่ยนของคาร์บอนไดออกไซด์เป็นมีเทน 92 เปอร์เซ็นต์ โดยปราศจากการเกิดคาร์บอนมอนอกไซด์ ปริมาณสัดส่วนที่เหมาะสมของนิกเกิลออกไซด์และนิกเกิลอะลูมิเนท ที่ 24.7 และ 75.3 เปอร์เซ็นต์โดยน้ำหนัก ส่งผลต่อการลดการรวมตัวกันของโลหะกัมมันต์ เพิ่มความเสถียรของตัวเร่งปฏิกิริยา อีกทั้งยังส่งผลให้อุณหภูมิในการรีดิวซ์ของนิกเกิลออกไซด์ลดลง นอกจากนี้การเผาตัวเร่งปฏิกิริยาที่อุณหภูมิสูง ส่งผลให้ปริมาตรรูพรุนใหญ่ขึ้น ซึ่งช่วยให้แก๊สตั้งต้นเข้าถึงตำแหน่งกัมมันต์ได้ดีในระหว่างการทำปฏิกิริยา เมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยาที่ไม่ได้เติมโลหะมีค่าพบว่า ตัวเร่งปฏิกิริยาที่สนับสนุนด้วยรูเทเนียมบนตัวเร่งปฏิกิริยานิกเกิลออกไซด์บนตัวรองรับนิกเกิลอะลูมิเนท แสดงประสิทธิภาพที่สูงกว่าตัวเร่งปฏิกิริยาที่ไม่สนับสนุนด้วยโลหะมีค่า ในการทดสอบในปฏิกิริยาเมทเนชัน ที่อุณหภูมิต่ำ ประมาณ 250-300 องศาเซลเซียส โดยปราศจากการเกิดคาร์บอนมอนอกไซด์ ซึ่งผลจากการเติมรูเทเนียม ทำให้ผลึกของโลหะนิกเกิลมีขนาดลดลง การกระจายตัวบนตัวรองรับดีมากขึ้น และช่วยเพิ่มความสามารถในการรีดิวซ์ ซึ่งเป็นผลดีต่อความว่องไวของตัวเร่งปฏิกิริยา

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CHANYA THAMMA: CO_2 methanation over $NiAl_2O_4$ spinel - based catalysts. ADVISOR: PROF. JOONGJAI PANPRANOT, Ph.D., 101 pp.

In the present work, a series of $NiO/NiAl_2O_4$ catalysts were prepared by co-precipitation method with molar ratio of Ni/Al equal 1/2 at different precipitation temperatures (30 and $80^{o}C$) and calcination temperatures (500, 700, 900, and $1200^{o}C$). The catalyst properties were characterized by using N_2 physisorption, X-ray diffraction, H_2 – TPR, SEM, and TEM. The $NiO/NiAl_2O_4$ precipitated at $80^{o}C$ and calcined at $900^{o}C$ showed the best activity in CO_2 methanation at $350^{o}C$ with conversion 92% and 100% methane selectivity without CO formation. The optimal of NiO and $NiAl_2O_4$ composition at 24.7% and 75.3%wt could provide a stabilizing effect preventing the metal aggregation and to lowering the reduction temperature of NiO. Moreover, the higher calcination temperature led to larger total pore volume was good to provide sufficient exposed metallic active sites for gas reactants. Compared the unpromoted catalyst, the Ru promoted $NiO/NiAl_{80}$ – 900 catalyst exhibited higher activity at low temperature ($250\text{-}300^{o}C$) without CO formation due to the decrease of crystallite size of Ni metal resulting in high dispersion and enhanced reducibility of catalyst, which had a positive effect for catalytic activity.

Department: Chemical Engineering   Student's Signature ....

Field of Study: Chemical Engineering   Advisor's Signature ....

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จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

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CHAPTER I

INTRODUCTION

1.1 Motivation

In recent years, the increasing energy demand required for our society development, the usage of carbon-based sources fossil fuel has increased enormously. However, many renewable and environmentally friendly sources of energy pose challenge. Solar energy can be successfully harnessed only in regions which have a highly amount of sunshine, wind turbines can be used to generate electricity only in area with sufficient amount and power of the wind. On the other hand, the biogas upgrading to biomethane can be produced just about everywhere. However, the biogas produced form anaerobic digesters contains 40-75% methane, 25-55% carbon dioxide and other traces gas (N_2, O_2, H_2S and H_2) 0.1-3% [5]. The biomethane has many environment benefits to the natural gas replacement for sustainable and environmentally friendly sources of energy including compressed natural gas (CNG), liquid natural gas (LNG), and diesel replacement (bio-CNG and bio-LNG for transport fuel usage).

At the present, CO_2 methanation is a practical way to convert biogas into high methane concentration. The CO_2 hydrogenation to methane has many several positive effects due to very simple reaction that can be operated under atmospheric pressure. However, the formation of methane from CO_2 at low temperature has become an interesting topic to study in many studies, although the conversion was still very low [3].

Ni based catalyst is the most widely studied materials because of their low cost, easily availability with reducible oxide material and possible practical application for this reaction [3]. However, Ni catalyst may be easily deactivated even at low temperature due to the sintering of Ni particle [6].

Many supported Ni catalyst has been investigated on various oxide supports (TiO_2, CeO_2, SiO_2, and ZrO_2). Ni/γ-Al_2O_3 shows high catalytic activity but is the easily deactivaties at high temperature due to carbon deposition ,sintering of Ni metal active site resulting to poor stability [7, 8]. Moreover, nickel and alumina easily form the

strong interaction between NiO and γ-Al$_2$O$_3$ to NiAl$_2$O$_4$ spinel phase catalyst resulting to low catalytic activity in CO methanation reaction[9, 10]. In the same way, in the study about Mn-promoted Ni/Al$_2$O$_3$ catalysts for CO$_2$ methanation, it was found that the formation of NiAl$_2$O$_4$ inhibited and decreased the catalytic activity [11]. On the other hand, Mahesh M. Nair et.al reported that in dry reforming of methane the formation of NiAl$_2$O$_4$ may improve coke resistance and enhance stability[12]. In the same way, in the hydrogenation of acetylene over Ni/NiAl$_2$O$_4$ catalyst, the formation of NiAl$_2$O$_4$ can provide a stabilizing effect resulting in the inhibition of metal aggregation and enhance control over sintering or lowering coking rate formation [13].

Thus, there are some contradiction about effect of NiAl$_2$O$_4$ spinel phase in CO$_2$ methanation and steam reforming of methane. CO$_2$ methanation is the highly exothermic reaction that the deactivation occurs due to sintering or carbon deposition on surface of catalyst during operating at high temperature corresponding to low stability and very poor of catalytic activity. Also, the catalysts used in CO$_2$ methanation reaction, coke or sintering resistance properties is needed. Meanwhile, in a previous work that studied about steam reforming reaction over NiAl$_2$O$_4$ based catalyst, the formation of NiAl$_2$O$_4$ can improve the coke formation rate, inhibit the deactivation cause of sintering, and enhance the stability resulting in high catalytic performance.

Although, Ni based catalyst may be easily deactivation due to sintering. Many strategies have been investigated to enhance the stability and catalytic activity of Ni based catalyst. The effect of promoted catalyst is interesting to study. In a previous work, Ru/γ-Al$_2$O$_3$ showed high stability and high activity for CO$_2$ methanation (96%methane yield at 300°C) [14]. Furthermore, Maria Mihet and Mihaela D. Lazar reported about the effect of noble metal promotion over Ni/γ-Al$_2$O$_3$. The enhancement of CO$_2$ conversion and CH$_4$ selectivity were found in the Pt and Pd promoted of Ni/γ-Al$_2$O$_3$ at the 180-270°C and all the catalysts exhibited high stability over the investigated time range (240 min) [15].

Therefore, this work aims to investigate a series of NiAl$_2$O$_4$ based catalysts prepared by co-precipitation method in the CO$_2$ methanation. The effects of precipitation temperature and calcination temperatures on the characteristics and catalytic performances of the NiAl$_2$O$_4$ spinel were focused in part I. Furthermore, in part II the effect of promotion by Ru, Rh and Pd over NiAl$_2$O$_4$ based catalysts were investigated. The prepared catalysts were characterized by multi-techniques such N$_2$

physisorption (BET), X-ray Diffraction (XRD), temperature program reduction (TPR), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM).

1.2 Objective of research

The objectives of this research are to investigate

(i) The effect of preparation and calcination temperatures of $NiAl_2O_4$ spinel based catalysts in CO_2 methanation.

(ii) The effect of spinel phase formation compared with Ni supported commercial Al_2O_3 in CO_2 methanation.

(iii) The effect of noble metal (Ru,Rh,Pd) promotion on $NiAl_2O_4$ catalyst in CO_2 methanation.

1.3 Scope of research

(i) The $NiAl_2O_4$ catalysts were prepared by co-precipitation method with molar ratio of Ni/Al is 1/2. The temperatures of precipitation was 30^oC and 80^oC and the calcination temperature was 500,700 and 900^oC.

(ii) The activity comparison of $NiAl_{80}$ – 900 catalyst with 20 and 36.5% wt Ni loading onto Al_2O_3 commercial supported catalysts that prepared by impregnation method.

(iii) The noble metal (Ru,Rh,Pd) loading was 1%wt as promoter on $Ni-Al_2$ 900 catalyst.

(iv) The catalysts were characterized by using N_2 physisorption (BET), X-ray diffraction (XRD), temperature program reduction (TPR), temperature program desorption (TPD), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM).

(v) The catalytic performances were tested in CO_2 methanation reaction. Prior to catalytic testing the catalysts were pretreated in H_2 at 450^oC for 2.30 h with H_2 at flow rate of 30 cm^3/min. The reaction temperature was 350^oC under atmospheric pressure with gas mixed ratio of $CO_2:H_2:N_2$ are 10:1:4 with total flow rate 40 cm^3/min.

The composition of outlet gas was analyzed by pulse inlet to GC-TCD with molecular sieve and Porapack Q columns. .

(vi) Both $NiAl_2O_4$ and $1wt\%Ru/NiAl_2O_4$ catalysts were tested in temperature profiles at 250-350°C and each temperature was kept for 1 h.

1.4 Contribution of Research

1.4.1 Knowledge of preparation and properties of $NiAl_2O_4$ based catalyst by using co-precipitation method.

1.4.2 Knowledge about the best reaction conditions for CO_2 methanation reaction and the effect of catalyst properties on the catalytic performance.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 The CO_2 methanation reaction mechanism

Catalytic hydrogenation of carbon dioxide to methane, also called the Sabatier reaction, is an important catalytic process.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad (\Delta H_{298K} = -252.9 \text{ kJ/mol}, \Delta G_{298K} = -130.8 \text{ kJ/mol})[8]$$
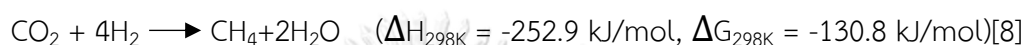
The mechanism of CO_2 methanation is difficult to establish. There are arguments of opinion on the nature of the intermediate compound involved the rate determining step of the process and on the formation of methane scheme. The mechanism of CO_2 methanation have been classified into two main categories. The first step is the CO_2 convert to CO as the intermediate prior to formation of methane as the same CO methanation reaction. And the second one is the direct hydrogenation of CO_2 to methane without CO formation as the intermediate. It has been proposed that the rate-limiting step is either the formation of the intermediate CH_xO and its interaction with hydrogen or the formation of surface carbon in CO dissociation and its hydrogenation[3, 8]. Similarly, Wu, H.C. et.al [16] revealed the reaction path way of CO_2 methanation over Ni/SiO_2 catalyst. The reaction path way may be classified into two pathways. The fist pathway is the consecutive, the conversion of CO_2 to CO as intermediate prior methane formation. The other one is the parallel path way, the mixed of both consecutive pathway and the direct CO_2 hydrogenation to methane without CO formation.

The reaction mechanism shown in scheme 2.1 includes to the formation step of formate through carbonate species. The intermediates of reaction involved carbon monoxide and formate were the key intermediate formed and its hydrogenation led to methane formation. In addition, the bounding more strongly on the support and in equilibrium with the active formate species on the metal-support interface. The hydrogenation of the adsorbed carbon monoxide involved six adsorbed hydrogens. A pathway involving hydrogen carbonate was presented for the formation of the interfacial formate because DRIFTS experiments indicated that this species was formed

on the support during the reaction and its transient response was consistent with the response of a carbon monoxide precursor [17].
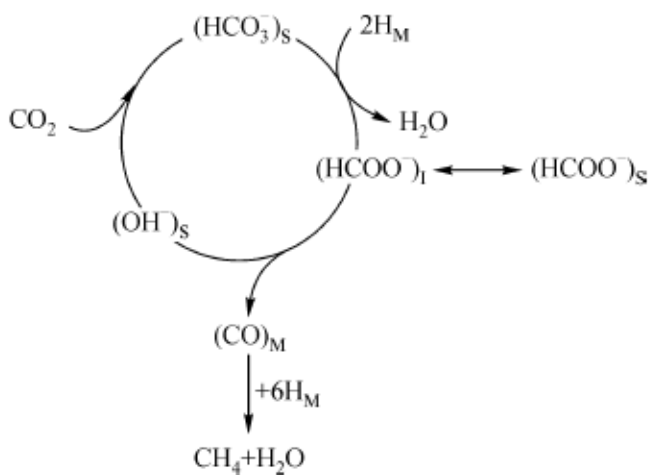
S: the support, M: the metal, I: the metal-support interface

Scheme 2.1 The proposed reaction mechanism of CO_2 methanation [17]

Choe et al. [1] investigated the elementary reaction step and activation energies for CO_2 methanation on Ni (111) surface. The elementary reaction steps considered are:

$$CO_{2ads} \longrightarrow CO_{ads} + O_{ads} \qquad \text{Step 1}$$

$$CO_{ads} \longrightarrow C_{ads} + O_{ads} \qquad \text{Step 2}$$

$$2CO_{ads} \longrightarrow C_{ads} + CO_{2gas} \qquad \text{Step 3}$$

$$C_{ads} + H_{ads} \longrightarrow CH_{ads} \qquad \text{Step 4}$$

$$CH_{ads} + H_{ads} \longrightarrow CH_{2ads} \qquad \text{Step 5}$$

$$CH_{2ads} + 2H_{ads} \longrightarrow CH_{4gas} \qquad \text{Step 6}$$
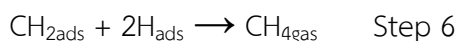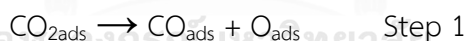
This elementary steps considered to two mechanisms that are carbon formation and carbon methanation. Step 1 assumed CO as the intermediate on the surface in the CO_2 methanation proceed. Step 2 for the CO dissociation is irreversible owing to rapid removal of surface O by hydrogenation, while step 3 for CO dissociation is attributed

to the disproportion, and lastly step 6 for desorption of methane is irreversible. Step 4 and step 5 are steps occurring after the rate-determining steps.

Table 2.1 shows the calculated activation energies. The dissociation reactions of carbon dioxide and carbon monoxide shown in step 1, step 2, and step 3, and calculated activation energies are 1.27 eV, 2.97 eV and 1.93 eV, respectively. The calculated carbon hydrogenation is shown in step 4, step 5, and step 6, with activated energies of 0.72 eV, 0.52 eV, and 0.50 eV, respectively. Although, the rate-limiting step is the CO dissociation elementary step as step 2 and the calculated activation energy is 2.97eV.

Table 2.1 Calculated activation energies for methanation of carbon dioxide on the Ni_{25} cluster surface [1].

Activation Energies (Ea (eV))		
$CO_{2ads} \longrightarrow CO_{ads} + O_{ads}$	Step 1	1.27 eV
$CO_{ads} \longrightarrow C_{ads} + O_{ads}$	Step 2	2.97 eV
$2CO_{ads} \longrightarrow C_{ads} + CO_{2gas}$	Step 3	1.93 eV
$C_{ads} + H_{ads} \longrightarrow CH_{ads}$	Step 4	0.72 eV
$CH_{ads} + H_{ads} \longrightarrow CH_{2ads}$	Step 5	0.52 eV
$CH_{2ads} + 2H_{ads} \longrightarrow CH_{4gas}$	Step 6	0.50 eV

Qiushi Pan et al. [4] has investigated the in situ FTIR spectroscopic of CO_2 methanation mechanism on $Ni/Ce_{0.5}Zr_{0.5}O_2$ to identify the adsorption species and any intermediate species. They found that CO_2 perfers to adsorb on surface oxygen sites adjacent to Ce (III) more than those one that adjacent to Ce (IV)/Zr or hydroxyl surface sites. There are five adsorption species for CO_2 adsorption on catalyst surface and monodentate carbonates formed on Ce (III) are easier to be hydrogenated than those on Ce (IV). Formate species is the main intermediate species and Ce (III) sites were proposed to be active sites for the hydrogenation. The identification confirms that the adsorption and hydrogenation of formic acid as the intermediate species during reaction and for the first time found the CH_2OH species and further to the intermediates in the reaction. The mechanism presented in Fig.2.1.
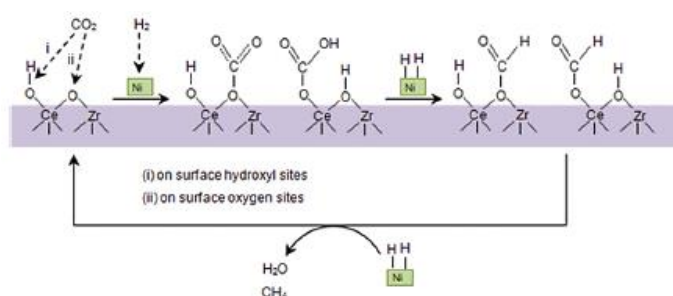
Figure 2.1 Proposed reaction pathway for CO_2 methanation on a $Ni/Ce_{0.5}Zr_{0.5}O_2$ catalyst [3, 4].

M.A.A. Aziz et al. [3, 18] has reported about the plausible mechanism of CO_2 methanation on metal promoted mesostructured silica nanoparticles (M/MSN). The mechanism shows in Fig.2.2 revealed that the CO_2 and H_2 was adsorbed onto the metal sites and subsequently, dissociated to form CO, O and H atoms and migrated onto the MSN surface. Whilst there are the interaction between CO and oxide surface of the MSN to form (i) bridged carbonyl and (ii) linear carbonyl. In addition, (iii) bidentate formate was formed through the interaction with atomic hydrogen. Meanwhile, the O atom spilt over onto the MSN surface and was stabilized in the oxygen vacancy site near the metal site. Afterward, the hydroxyl was formed on the MSN surface due to the adsorbed oxygen was reacted with atomic hydrogen and the further reaction, the hydroxyl was reacted with another atomic hydrogen to form a water molecule. Finally, the adsorbed carbon species was further hydrogenated to methane and a water molecule as a byproduct. However, the work reported by M.A.A. Aziz et.al are in good agreement with the previous work [4, 19] that the main intermediate for CO_2 methanation reaction is the bidentate formate species.
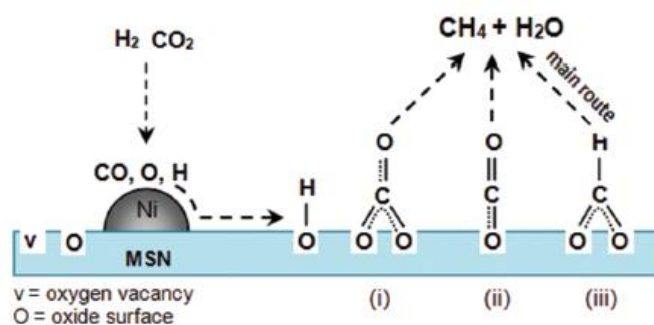
Figure 2.2 Plausible mechanism of CO_2 methanation on Ni/MSN;
(i) bridged carbonyl, (ii) linear carbonyl and (iii) bidentate formate.

2.2 Characterisation of methanation catalysts

The development of thermally stable catalysts with high activities at low temperatures is a challenge. The suitable catalysts is determined by different qualities such as stability, selectivity, costs of catalyst, etc. The previous work are most discusses the following types of noble and non-noble metal-based catalysts – ruthenium (Ru), rhodium (Rh), palladium (Pd), platinum (Pt), nickel (Ni), iron (Fe), cobalt (Co) and molybdenum (Mo), respectively. In Table 2.2 basic characteristics of the most investigated CO_2 methanation catalysts are summarized.

Table 2.2 Characteristics of methanation catalysts

Methanation catalyst	Advantages	Disadvantage
Ruthenium (Ru) [3, 6-8, 14, 20-24]	- The most active metal for CO_2 methanation than Ni - Good result of CH_4 yield at low temperature without CO co-production - The most stable in CO_2 methanation process than Ni - Higher chemical activity than Ni - Easily reduced to the metallic state at low temperature - No obvious sintering of the active Ru particles happened (200-800**°**C)	- About 3 times more expensive than Ni (costs dated by 2018 Ru 20 USD/lb Ni 6.21 USD/lb *) - High the Ru loading (>2.2wt%) affect to site-blocking mechanism
Rhodium (Rh) [3, 7, 8, 24-29]	- The activity shows lower than Ru and Ni - Can produce methane at low temperature (below 500°C)	- Not occur the direct path way - The CO formation at high temperature (>500°C)

Methanation catalyst	Advantages	Disadvantage
Palladium (Pd) [3, 6-8, 24, 30-33]	- High methane selectivity - Beneficial impact on the stability of the nanoparticle against sintering	- The CO_2 conversion exhibited lower than Ru,Ni - Easily deactivated from carbon deposition
Platinum (Pt) [6, 8, 24, 34]	- Highly selectivity than Ni - Effective reduction at low temperature	- Lower activity than Ru and Ni
Iron (Fe) [24, 35-41]	- High activity - Environmentally friendly –long lifetime - Fe is lower price than Ni - Operating at high temperature (700-950°C)	- Favor to produce long chain hydrocarbon - Very low CH_4 selectivity
Cobalt (Co) [24, 42-44]	Similar selectivity to Ni	- Low CO_2 conversion - More expensive than Ni - Not widely used for commercial application as nickel catalysts

Methanation catalyst	Advantages	Disadvantage
Molybdenum (Mo) [24, 35, 45]	- Sulfur tolerant properties - High selectivity toward C_{2+} hydrocarbon than Ni	- Lower activity compared to Ru,Fe,Co,Ni
Nickle (Ni) [2, 3, 6-9, 14, 16, 46-52]	- Low price - Commercial catalyst - Easily availability with reducible oxide material - High activity and selectivity of methane Operating temperature 300-600°C	Easily deactivated at low temperature due to the sintering of Ni particle (short lifetime of catalyst)

2.3 The Ni based catalysts

Hydrogenation of CO_2 to methane has been widely investigated on Ni based catalysts because Ni metal material is commercially, low cost and easily availability. The Ni based catalyst is practical in this reaction and has high potential to convert CO_2 to methane in the range of reaction temperature 100 – 700°C. In addition, the catalytic activity of Ni based catalysts is dependent on various parameters such as the Ni loading, the support and the promoters.

2.3.1 The effect of Ni loading

Table 2.3 Summary of research on the effect of Ni content in CO_2 hydrogenation

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
H.C.Wu et al 2015 [12]	The mechanism, reaction pathway and selectivity promoted by different Ni particle sizes	0.5Ni/SiO$_2$ 10Ni/SiO$_2$	-The catalysts were prepared by impregnation method and calcined at 500°C. -The reaction carried out at 400°C 1 atm.	- 0.5Ni/SiO$_2$ shows the smaller crystallite size and proceed consecutive pathway. - 10Ni/SiO$_2$ shows larger crystallite size and proceed both of consecutive and parallel pathway.
M. V. Gabrovska et al 2015 [18]	The effect on magnesium promoted on the properties and catalytic activity of Ni-Al LDHs with TKl structure	1.5NiAl 3.0NiAl 1.5NiMgAl 3.0NiMgAl	- The catalysts were prepared by co-precipitation method. - Reduction temperature	- 3.0NiMgAl show the highest conversion during 220-260°C. - The highly reduction temperature (530 and 600°C) resulted

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
			various 400-600°C. - The reaction condition operated at 200-400°C 1 atm.	to sintering deactivation.
Soudabeh Rahmani et al 2014 [19]	The effect of Ni loading on catalytic activity and stability of catalysts supported on γ-Al$_2$O$_3$	10Ni/Al$_2$O$_3$ 15Ni/Al$_2$O$_3$ 20Ni/Al$_2$O$_3$ 25Ni/Al$_2$O$_3$	- The catalysts were prepared by impregnation method and calcined at 450°C for 3 h. - Reduction temperature was 450°C for 2h. - The catalytic tests were carried out at	- The 20Ni on γ-Al$_2$O$_3$ supported catalyst showed the highest activity (82.4%) and selectivity (100%) at 350°C.

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
			different temperatures ranging from 200 to 500°C	
I. Grac¸a et al 2014 [20]	The effect of Ni content (2, 5, 10, and 14) supported on HNaUSY zeolite	2.0Ni/HNaUSY 5.0Ni/HNaUSY 10Ni/HNaUSY 14Ni/HNaUSY	- The catalysts were prepare by incipient wetness impregnation method. - Pre-reduced in-situ at 470°C during 1 h. - The activity testing at 250-450°C and GHSV was 43000 h^{-1}. -The reaction carried out at 400°C 1 atm.	- The 14Ni/HNaUSY zeolite catalyst showed the highest CO_2 conversion (65.5%) and CH4 selectivity (94%) at 400°C.

Ni loading has affected of path way to achieve the reaction including the yield of methane and CO as by product.

H.C.Wu et al. 2015 [16] has investigated the effect of Ni content of 0.5wt% and 10wt% on SiO_2 supported catalysts and focused on the path way to produce CO and CH_4 in CO_2 methanation reaction. The 0.5wt% and 10wt% Ni loadings revealed the different effects in Ni particle size and the kinetic parameters of reaction. Figure 2.3 shows the formation path way of CO and CH_4. 0.5%wt Ni loading shows the smaller clusters and preference for consecutive pathway in the presence of CO as intermediate while both of consecutive and parallel reaction pathways were observed on the large Ni particles with 10%wt Ni loading. Lower Ni loading (0.5%wt) catalyst shows a higher catalytic activity for CO_2 hydrogenation with high CO selectivity. On the other hand, the selectivity is switched to favor CH_4 formation when Ni loading increased to 10wt% with 9 nm of particles. Small Ni particle size favored the consecutive pathway due to low H_2 coverage on Ni surface that led to dissociation of m-HCOO intermediates resulting to CO formation and high CO selectivity. In addition, the CO_2 hydroganetion on large Ni particles may be described to both of consecutive and parallel pathways. The part of parallel reaction may competitively hydrogenated the m-HCOO intermediate to CO or CH_4. The active site for H_2 adsorption in the 10wt% Ni/SiO_2 catalyst was more than the 0.5wt% Ni/SiO_2 catalyst resulting in higher H_2 coverage in the Ni surface proceeding to enable in the parallel pathway. The sites corresponding to corner or step position are attended as the primary active sites for CO_2 hydrogenation on both of Ni/SiO_2 catalysts.
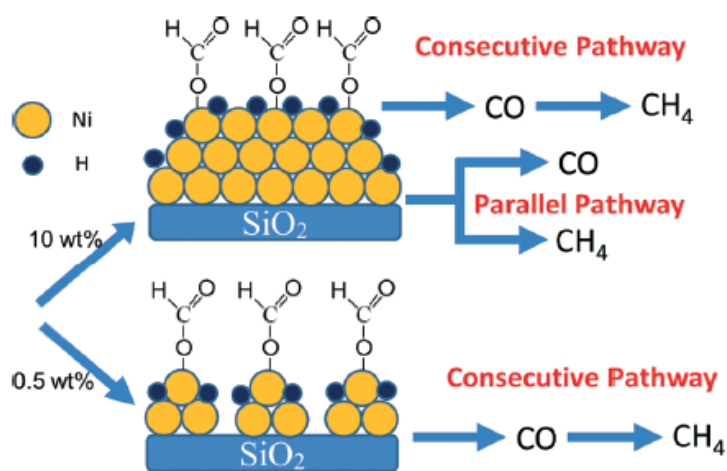
Figure 2.3 Proposed mechanism for CO_2 hydrogenation on Ni/SiO_2

M. V. Gabrovska et al.2015 [46] studied about the effect of Ni content on Ni-Al layered double hydroxides (LDHs) for CO_2 methanation by the variation of Ni^{2+}/Al^{3+} molar ratio (3, 1.5 and 0.5). After reduction at 400 and 450°C, the high nickel loading catalyst (3.0NiAl) revealed the highest conversion and a tendency to be more active than low Ni metal loaded (1.5NiAl and 0.5NiAl). The catalytic activity was ascribed to the larger specific surface areas and smaller particle sizes of Ni metal due to higher Ni dispersion. However, the pretreatment of catalyst at high temperature (530 and 600°C) induced to the sintering deactivation of nickel metal particles via the decreasing of methanation activity.

Soudabeh Rahmani et al. 2014 [52] studied the effect of Ni loading on catalytic activity and stability of catalysts supported on γ-Al_2O_3 in CO_2 methanation reaction. The nickel content affected to CO_2 conversion and CH_4 selectivity, the catalytic activity were increased with increasing in Ni loading from 10 to 20 wt%. But further increasing in Ni content resulted in the bigger crystallite size and lower surface area of catalyst and caused the decrease in conversion as seen in Fig.2.4. The 20wt%Ni on γ- Al_2O_3 supported catalyst showed the highest activity and selectivity among all the studied samples.
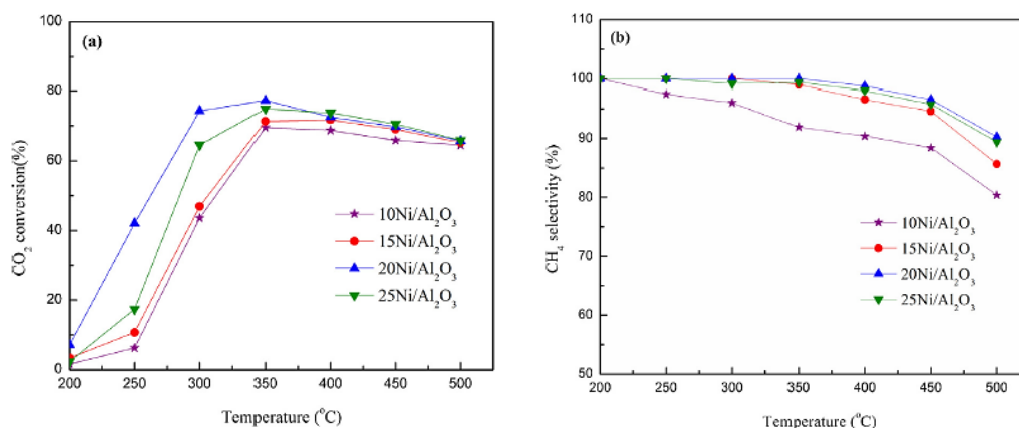
Figure 2.4 (a) Effect of Ni content on CO_2 conversion and (b) CH_4 selectivity, GHSV = 9000 ml/g_{cat} h, H_2/CO_2 molar ratio = 3.5

I. Grac¸a et al. 2014 [51] investigated the effect of Ni contents (2, 5, 10, and 14) on HNaUSY zeolite for CO_2 methanation reaction. The enhancement of CO_2 conversion corresponded to an increase of the Ni content. The 14%Ni/HNaUSY zeolite catalyst showed the highest CO_2 conversion (65.5%) and CH_4 selectivity (94%) at 400°C and GHSV 43000 h^{-1} due to the higher amount of Ni^0 species after reduction. The resulting catalytic activity is shown in Figure 2.5.
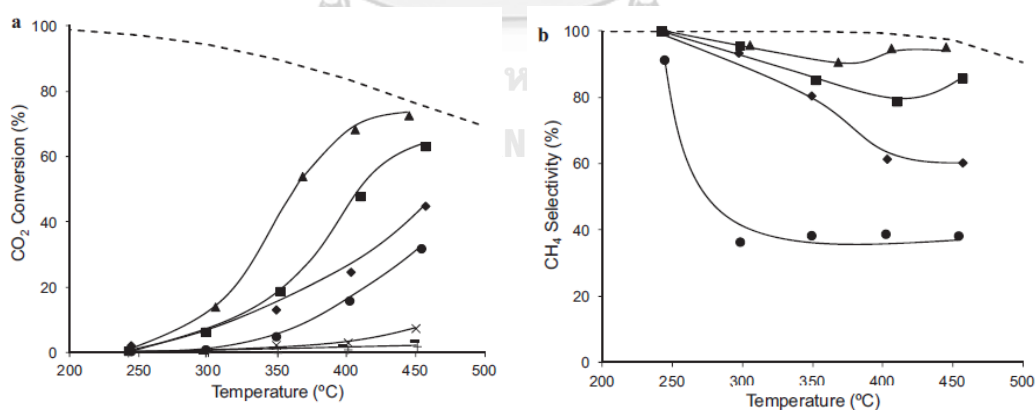
Figure 2.5 (a) CO_2 conversion and (b) CH_4 selectivity vs. temperature, at GHSV = 43,000 h^{-1}, for the USY (+), 10%NiO + USY (×), 2%NiUSY$_{Ex}$ (–), 2%NiUSY$_{Imp}$ (●), 5%NiUSY$_{Imp}$ (◆), 10%NiUSY$_{Imp}$ (■) and 14%NiUSY$_{Imp}$ (▲) catalysts. Dashed line thermodynamic equilibrium conversion values.

2.3.2 The effect of supported catalysts

Table 2.4 Summary of research of supported on Ni catalysts

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
Thien An Le et al. 2017 [2]	- The effect of metal oxide supported catalysts - The effect of difference CeO_2 surface area	Ni/CeO_2 (230) Ni/CeO_2 (140) Ni/CeO_2 (55) Ni/CeO_2 (19) Ni/γ-Al_2O_3 Ni/SiO_2 Ni/TiO_2 Ni/ZrO_2	- The catalysts were prepared by wet-impregnation method with 10wt% Ni loading. - Reduction temperature was $500^{\circ}C$. - The activity testing at 150-$400^{\circ}C$ 1 atm.	- The Ni/CeO_2 (230) catalysts was revealed the best performance at low temperature (200-300$^{\circ}C$). - The conversion of CO_2 were increased with the increasing of CeO_2 surface.
Hiroki Muroyama et al. 2016 [53]	The catalytic activity over Ni catalysts supported on various metal oxides	Ni/Y_2O_3 Ni/Al_2O_3 Ni/Sm_2O_3 Ni/ZrO_2 Ni/CeO_2 Ni/La_2O_3	- The catalysts were prepared by the impregnation method with 10wt%Ni loading and calcined at $600^{\circ}C$ for 2h.	- The Ni/Y_2O_3 (low s.v) shows the highest activity and CH_4 yield at $250^{\circ}C$.

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
			- Reduction temperature was 600°C for 3 h. - The activity testing at 200-450°C with GHSV were 20,000 and 30,000 l kg^{-1} h^{-1}.	- The Ni/Al$_2$O$_3$ shows high stability within 75% CO$_2$ conversion for 48 h.

The CO_2 methanation reaction over supported Ni catalysts has been studied by Thien An Le and et al. 2017 [2] Their studies showed the comparative of some selected supports such as γ- Al_2O_3, SiO_2, TiO_2, CeO_2 and ZrO_2. Figure 2.6 showed the catalytic activity in the order; Ni/CeO$_2$ (230) > Ni/SiO$_2$ > Ni/ZrO$_2$ > Ni/γ-Al$_2$O$_3$ > Ni/TiO$_2$ at 350-400 °C. Furthermore, the Ni/CeO$_2$ (230) catalysts revealed the best performance at low temperature (200-300°C). The smallest Ni particle size related to high Ni dispersion as long as the Ni species were completely reduced.
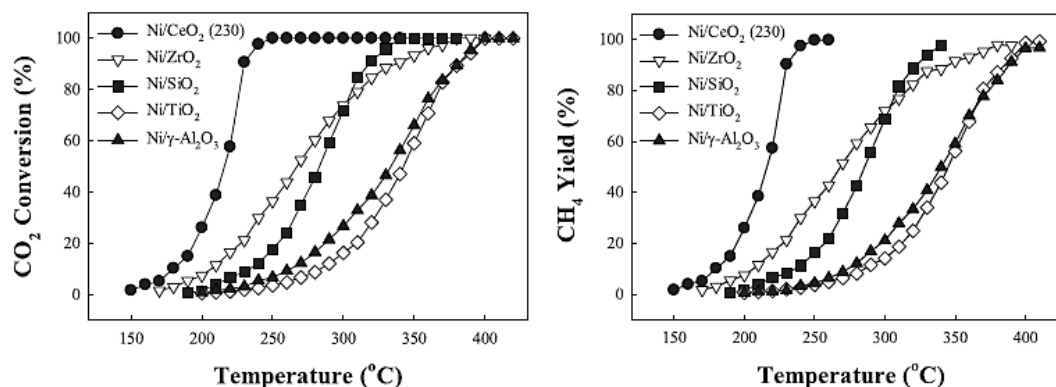
Figure 2.6 Catalytic performance of supported Ni catalysts for CO_2 methanation. Reaction conditions: 1 mol% CO_2, 50 mol% H_2, 49 mol% He, F/W = 1000 mL/min/g_{cat}

In addition, they have found that the surface area of CeO_2 affected to the catalytic activity. The physicochemical properties of Ni/CeO_2 catalysts with different surface areas are shown in Table 2.4. The decreasing of Ni/CeO_2 surface area follows in the order Ni/CeO_2 (230) > Ni/CeO_2 (140) > Ni/CeO_2 (55) > Ni/CeO_2 (19).

Table 2.5 Physicochemical properties of Ni/CeO_2 catalysts with different surface areas [2].

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)[a]	Crystallite size (nm)[b]		H_2 consumption (mmol H_2/g)[c]
				CeO_2	Ni	
Ni/CeO_2 (230)	117	0.13	4.4	9	n.d	2.4
Ni/CeO_2 (140)	94	0.22	9.3	8	9	2.5
Ni/CeO_2 (55)	44	0.22	20.1	18	21	2.3
Ni/CeO_2 (19)	15	0.15	39.9	37	27	2.2

[a] Average pore diameter was determined in BJH model.

[b] Crystallite size of Ni was determined by Scherrer formula for supported Ni catalysts reduced at 500°C.

[c] H_2 consumption was detected based in the H_2-TPR.

The catalytic activity of Ni/CeO_2 with different CeO_2 surface areas are shown in Figure 2.7. The conversion of CO_2 increased with increasing of CeO_2 surface, which may be due to the higher Ni dispersion and interaction between Ni and ceria which were responsible for the high catalytic activity.
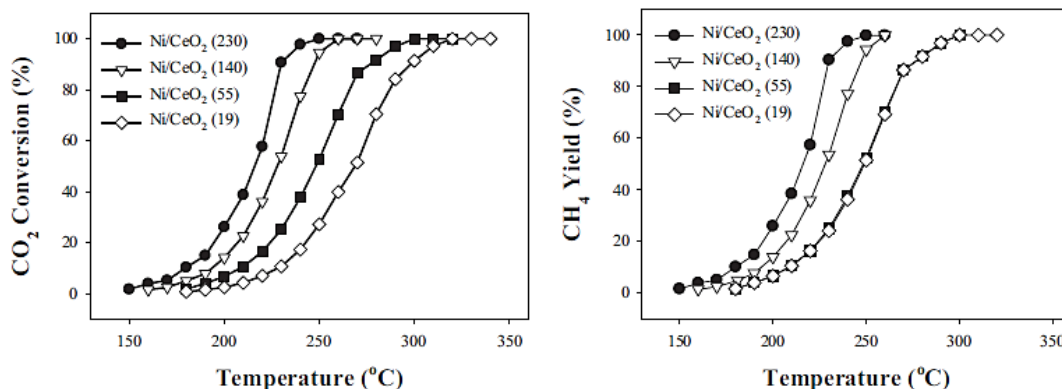
Figure 2.7 Catalytic performance of Ni/CeO$_2$ with different surface areas for CO$_2$ methanation. Reaction conditions: 1 mol% CO$_2$, 50 mol% H$_2$, 49 mol% He, F/W = 1000 mL/min/g$_{cat}$.

In the same way, Hiroki Muroyama et al. 2016 [53] investigated the CO$_2$ methanation over Ni catalysts supported on various metal oxides such as Y$_2$O$_3$, Al$_2$O$_3$, Sm$_2$O$_3$, ZrO$_2$, CeO$_2$ and La$_2$O$_3$. After reduction at 600°C, for most of the catalysts, the CO$_2$ conversion drastically increased at 225-250°C and reached a maximal value at 300-350°C. The order of CO$_2$ conversion and CH$_4$ yield at 250°C followed: Ni/Y$_2$O$_3$ > Ni/Sm$_2$O$_3$ > Ni/ZrO$_2$ > Ni/CeO$_2$ > Ni/Al$_2$O$_3$ > Ni/La$_2$O$_3$, be partly revealed to the basic properties of catalysts.
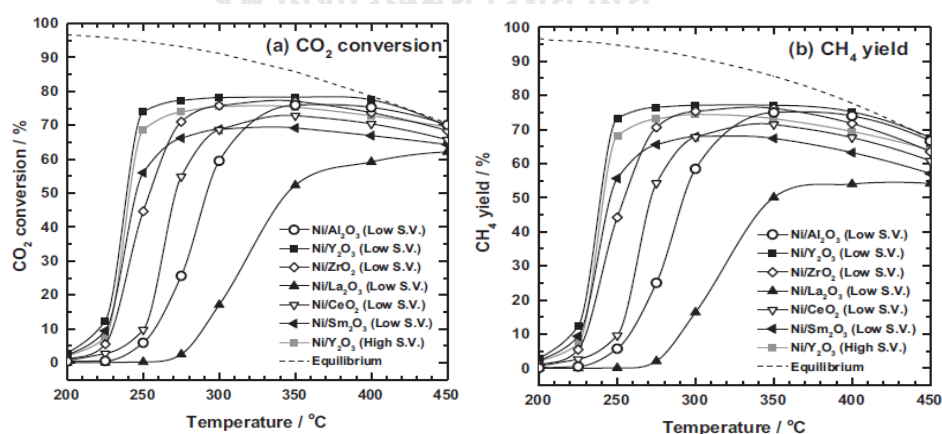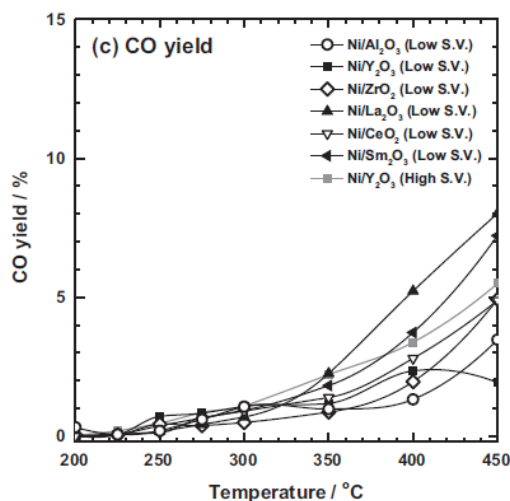
Figure 2.8 (a) CO_2 conversion, and (b) CH4 and (c) CO yields in CO_2 methanation over 10 wt. % Ni/metal oxide catalysts (Al_2O_3, Y_2O_3, ZrO_2, La_2O_3, CeO_2, and Sm_2O_3). Reaction gas: 10% CO_2–40% H_2–50% N2. Low S.V.: 20,000 l kg^{-1} h^{-1}. High S.V.: 30,000 l kg^{-1} h^{-1}.

In addition, the CO_2 desorption behavior of Ni catalysts has a positive effect on the catalytic activity for CO_2 methanation. The comparative species formed on the surface during CO_2 methanation for Ni/Y_2O_3, Ni/Al_2O_3 and Ni/La_2O_3 catalysts were detected. The CO species on Ni surface was confirmed on Ni/Al_2O_3 that proceeded via the formation of CO intermediate. Only carbonates were observed over Ni/La_2O_3 even under the methanation condition. On the other hand, On Ni/Y_2O_3 the carbonate-like species were observed, which convertd to formate species by introducing H_2 to the CO_2 atmosphere while the formate species were decomposed in the H_2 atmosphere. Also, the decomposition of formate species affected to promote the high catalytic activity over Ni/Y_2o_3 catalyst.

Furthermore, the stability tests for the Ni/Y_2O_3, Ni/Sm_2O_3 and Ni/Al_2O_3 catalysts were carried out at 300°C and 20,000 $kg^{-1}h^{-1}$. Figure 2.9 shows the time on stream of CO_2 conversion, CH_4 and CO yields over the Ni/Y_2O_3, Ni/Sm_2O_3 and Ni/Al_2O_3 catalysts. The high stability was exhibited on Ni/Al_2O_3 catalyst within 75% CO_2 conversion for 48 h. For Ni/Y_2O_3 catalyst, the conversion of CO_2 slightly dropped form 77.0% to 74.2% with time and the CO yields were within 0.05% which were quite lower than Ni/Al_2O_3.

Conversely, Ni/Sm_2O_3 significantly decreases in CH_4 and CO yields. The degradation of catalysts may be derived from the carbon deposition and sintering of Ni particles.
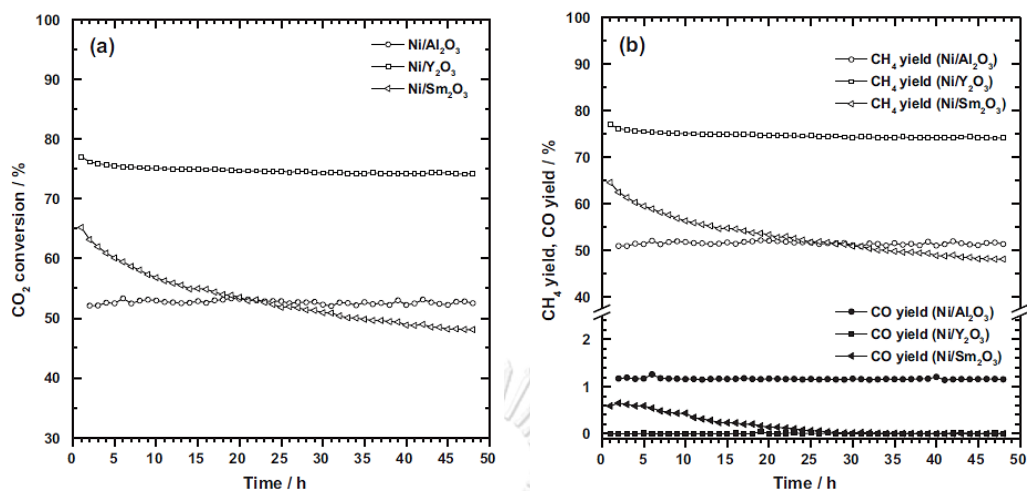
Figure 2.10 Time courses of (a) CO_2 conversion, and (b) CH4 and CO yields in CO_2 methanation over 10 wt.% Ni/Al_2O_3, Ni/Y_2O_3, and Ni/Sm_2O_3. Reaction gas: 10% CO_2– 40% H_2–50% N_2. S.V.: 20,000 $l\ kg^{-1}\ h^{-1}$.

2.3.3. The effect of promoters on Ni based catalysts

The promoter of catalyst may be classified into two types. The first one, electron promoter to change the electron mobility of catalyst. Second one, structure promoter to inhibit the migration of active site under the high temperature of reaction including to improve the dispersion and thermal stability of catalyst by changing the chemical component, crystal texture, pore structure, dispersion state, and mechanical strength of catalyst [54].

2.3.3.1 Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Platinum (Pt)

Table 2.6 Summary of research of noble metal promoters

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
Maria Mihet and Mihaela D. Lazar 2016 [15]	The effect of noble metals (Pt, Pd and Rh) promoted on Ni/ γ-Al$_2$O$_3$ catalyst in the reduction of CO$_2$ by H$_2$ to methane	Ni-Pt/ γ-Al$_2$O$_3$ Ni-Pd/ γ-Al$_2$O$_3$ Ni-Rh/ γ-Al$_2$O$_3$ Ni/ γ-Al$_2$O$_3$	- The catalysts were prepared by impregnation method with 10wt% Ni, 0.5wt% promoter and calcined at 550°C for 3 h. - Reduction temperature was 550°C for 3 h. - The catalytic testing were carried out 30-300°C 1 atm.	- The Ni-Pd/ γ-Al$_2$O$_3$ and Ni-Pt/ γ-Al$_2$O$_3$ shows the high CO$_2$ conversion and CH$_4$ selectivity in the range of temperature are 180-270°C. - The Ni-Pd / γ-Al$_2$O$_3$ shows the high stable CO$_2$ conversion of 74.6% and 96.6% CH$_4$ selectivity at 250°C

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
Yi Liu et al. 2018 [24]	The effect of noble metal promoter (Ru,Pt,Pd) on 20wt%Ni/SiO$_2$ catalyst during CO methanation reaction	Ni-Ru/SiO$_2$ Ni-Pt/SiO$_2$ Ni-Pd/SiO$_2$	- The catalysts were prepared by aqueous incipient wetness impregnation method with 10wt% Ni, 0.5wt% promoter and calcined at 400°C for 2 h. - Reduction temperature was 400°C for 10 h. - The activity testing at 200-280°C with GHSV was 40,000 cm^3 g^{-1} h^{-1}.	- The Ni-Ru/SiO$_2$ shows the dramatically improvement of catalytic activity at 275°C.

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
Wenlong Zhen et al. 2014 [25]	The long term stability testing on 10Ni-1.0Ru/ γ-Al$_2$O$_3$	10Ni-1.0Ru/ γ-Al$_2$O$_3$	- The catalysts were prepared by impregnation method with 10wt% Ni, 1.0wt% Ru and calcined at 450°C for 5 h. - Reduction temperature was 450°C for 2 h. - The activity testing at 400°C 1 atm with GHSV was 9000 h^{-1}	- The 10Ni-1.0Ru/ γ-Al$_2$O$_3$ catalyst performed the high catalytic activities, selectivity and no deactivation up to 100h in long term stability testing at 400°C 1 atm

Maria Mihet and Mihaela D. Lazar (2016) [15] investigated the presence of Pt,Pd or Rh promotion on Ni/ γ-Al$_2$O$_3$ during CO_2 methanation. The addition of 0.5wt% noble metal promoter resulted in an increase of NiO reducibility (Ni-Rh > Ni-Pt > Ni-Pd > Ni), enhanced metal dispersion and increased H_2 chemisorption capacity (Ni-Pt > Ni-Rh > Ni-Pd >Ni) with no significant influence upon the support intrinsic activity given by the CO_2 adsorption capacity. The catalytic testing were carried out 30-300°C under atmospheric pressure. The Pt and Pd promoted on Ni/ γ-Al$_2$O$_3$ catalysts can enhance CO_2 conversion and CH_4 selectivity in the range of temperature are 180-270°C, while Ni-Rh/ γ-Al$_2$O$_3$ showed lower activity than Ni/ γ-Al$_2$O$_3$ as shown in Figure 2.11.
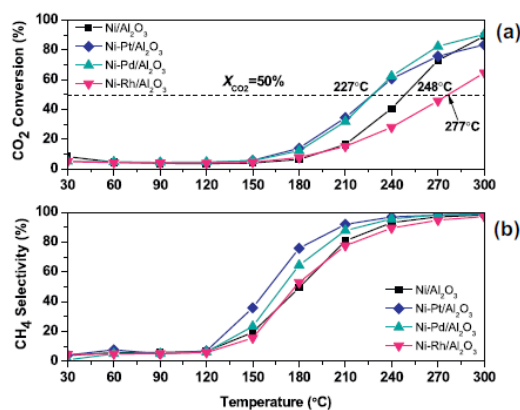
Figure 2.11 (a) CO_2 conversion, and (b) CH_4 selectivity profiles obtained on Ni/γ-Al_2O_3, Ni-Pt/ γ-Al_2O_3, Ni-Pd/ γ-Al_2O_3, and Ni-Rh/ γ-Al_2O_3 (CO_2:H_2= 1:4, GHSV = 5700 h^{-1}).

Considering the stability exhibited in Figure 2.12, all the catalysts showed stable catalytic performance over time range studied. The Ni-Pd / γ-Al_2O_3 revealed the most efficient catalyst with stable CO_2 conversion of 74.6% and 96.6% CH_4 selectivity at 250°C, Furthermore, during temperature programed reaction tests the maximum values of 90.5% CO_2 conversion and 98.7% CH_4 selectivity were obtained at 300°C.
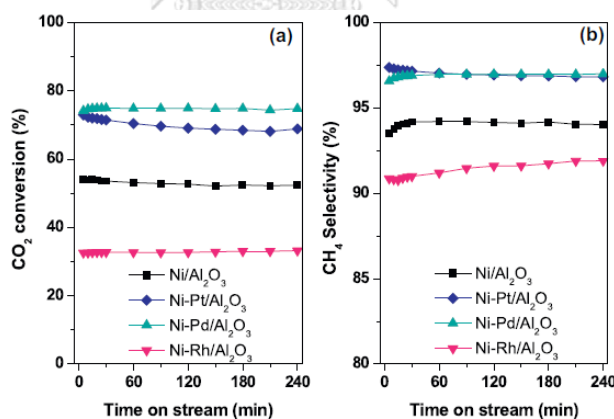
Figure 2.12 Effect of time on stream on the (a) conversion of CO_2, and (b) CH_4 selectivity in the methanation reaction over Ni/ γ-Al_2O_3, Ni-Pt/ γ-Al_2O_3, Ni-Pd/ γ-Al_2O_3, and Ni-Rh/ γ-Al_2O_3 at 250°C (CO_2:H_2= 1:4, GHSV = 5700 h^{-1}).

Yi Liu et al. (2018) [55] investigated the effect of noble metal promoter (Ru,Pt,Pd) on 20wt%Ni/SiO_2 catalyst during CO methanation. They found that the addition of 0.5wt% of promoter showed the dramatically improvement of catalytic activity in the order Ru>Pt>Pd at the same temperature (275°C) comparable with

20Ni/SiO$_2$ catalyst, which may be due to the presence of Ru had decreased the crystallite size of Ni particle resulting to higher dispersion including the enhanced reducibility by hydrogen spillover.

In the same way, the positive effect by adding Ru promoter on 10wt%Ni/γ-Al$_2$O$_3$ catalyst for CO$_2$ methanation were studied by Wenlong Zhen et al. 2014 [56] On 10Ni-1.0Ru/γ-Al$_2$O$_3$ catalyst high catalytic activities, selectivity and no deactivation up to 100h in long term stability testing at 400°C 1 atm were established and were attributed to the easily reduced to the metallic state. For the possible reaction mechanism was revealed, the dissociation of CO$_2$ was activated in Ru surfaces to form carbon species (CO$_{ads}$) and further to react with activated H on Ni active site to form methane. In addition, Abe et al. 2009 [57] revealed 0.8wt%Ru/TiO$_2$ catalyst (Ru diameter 2.5nm) showed 100%yield CH$_4$ at 160°C and this catalyst showed no deactivation over at least 170 h testing.

2.3.3.2 Other metal promoter

Table 2.7 Summary of research of other metal promoters

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
Zhenhua Li et al. 2014 [58]	The comparative of catalytic performance between Ni-Mg/Al_2O_3 and Ni/Al_2O_3	NiMg8 11Ni/Al_2O_3	- 11Ni/Al_2O_3 was prepared by incipient wetness impregnation method and calcined at 600°C for 5 h - NiMg8 (Ni/Mg = 1/8) was prepared by co-precipitation method and calcined at 650°C for 8 h. - Reduction temperature was 800°C for 4 h. - The catalytic testing were operated at 600°C for 5 h.	- The NiMg8 (Ni/Mg = 1/8) described the higher performance than Ni/Al_2O_3 catalyst

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
Lu et al. 2016 [59]	The effect of metal (La, Ce, Fe or Co) doped nickel catalysts supported on zirconia modified clays during CO methanation	Ni-La/ZrO_2 Ni-Ce/ZrO_2 Ni-Fe/ZrO_2 Ni-Co/ZrO_2	- The catalysts were prepared by the incipient wetness co-impregnation method with 15wt%Ni, 1wt% promoter and calcined temperature programmed from 25°C to 500 °C at a heating rate of 2 °C/min. - Reduction temperature was at 500 °C for 3 h. - The activity testing were operated at 300-500°C	- The adding of metal promoter resulted to positive effect and improve better propertied of methanation catalyst. - The Fe and CO promoters preferred to beneficial for CO_2 methanation - The La and Ce promoters preferred to beneficial for CO methanation

Researchers	Objective of research	Methodology		Results
		Catalysts	Preparation method and reaction condition	
Javier Barrientos et al. 2017 [60]	- The effect of metal oxides promoted (Zr, Mg, Ba or Ca) nickel catalysts supported on alumina during CO methanation - To study the rate of polymeric carbon formation and the thermal sintering under accelerated ageing tests	Ni-Zr/Al$_2$O$_3$ Ni-Mg/Al$_2$O$_3$ Ni-Ba/Al$_2$O$_3$ Ni-Ca/Al$_2$O$_3$	- The catalysts were prepared by Impregnation method with 30wt%Ni and 5wt%promoters and calcined at 500°C for 3 h. - Reduction temperature was 500°C for 4h. - The rate of carbon formation testing were operated at 300°C for 24 h. - The accelerated ageing testing were aged at 690°C in a H$_2$O/H$_2$ atmosphere for 7 days	- None of all promoter has satisfactory effect on the thermal resistance in accelerated ageing condition. - The Zr promoter can inhibited the rate of polymeric carbon formation conversely with La promoted.

Zhenhua Li et al. 2014 [58] revealed the H$_2$-TPR results that the dispersed NiO interacting with MgO promoter and the support that inhibited the agglomeration of Ni metal active sites resulting in an improved activity and stability of catalyst at high temperature (up to 973K) in methanation reaction. Furthermore, MgO has positive effect to improve resistance of carbon deposition and minimize Ni particle sintering

[32]. In addition, The Ni/Al hydrotalcite- like with adding Mg as promoter and the catalyst designation NiMg8 (Ni/Mg = 1/8) described the higher performance than Ni/Al$_2$O$_3$ catalyst. Addition of Mg promoter can enhance activity and improve stability for the methanation of syngas corresponding to the minimize rate of carbonaceous deposits formation due to a higher extent of Ni dispersion in the NiMg8 catalyst [58].

Lu et al. 2016 [59] investigated the effect of metal (La, Ce, Fe or Co) doped nickel catalysts supported on zirconia modified clays. They found that doping metal promoter may promote NiO dispersion, increase the reducibility of Ni species and enhance the thermal stability for CO$_2$ methanation. In addition, doping of Fe and Co shows the positive effect on CO$_2$ methanation while La and Ce preferred proceed the beneficial in CO methanation.

Javier Barrientos et al. 2017 [60] studied about the effect of metal oxides promoted (Zr, Mg, Ba or Ca) nickel catalysts supported on alumina. The CO methanation was carried out under low temperature (300°C) in order to study the rate of polymeric carbon formation and the thermal sintering under accelerated aging test conditions. Apparently, none of the promoter has satisfactory effect on the thermal resistance due to the Ni metal surface area was loss corresponding to sintering and pore collapse. However, the Zr promoter can inhibited the rate of polymeric carbon formation while Ca promoter has adverse effect on carbon formation.

2.4 The NiAl$_2$O$_4$ spinel catalyst on steam reforming reaction

N. Sahli et al. [61] studied the NiAl$_2$O$_4$ catalyst that prepared by using sol-gel method (propionic acid) during CO$_2$ reforming of methane. They found the spinel structure was unaltered of nickel to aluminum ratio higher than 0.5 and the excess of nickel may give the large particle size of NiO on spinel phase. For the ratio of nickel to aluminum higher than 0.5, free NiO was observed on spinel and the reduction of nickel preferred to proceed at low temperature while the Ni/Al ratio lower than 0.5 revealed the formation of Al$_2$O$_3$ and NiAl$_2$O$_4$ and high surface area was obtained. To get high performance, coke formation on small metallic particles and the growing of Ni particle needed to be limited. In addition, the substochiometric spinel structure showed properties that proceeded as the active catalyst following the high stability of structure at low temperature, high dispersion of NiO into the spinel. The growing Ni particles

were limited probably due to the interaction between nickel metal out of structure and Ni oxide of structure.

Cristina Jiménez-González et al. 2013 [13] investigated two series of nickel aluminates supported (15wt% and 70wt% of $NiAl_2O_4/Al_2O_3$) and unsupported ($NiAl_2O_4$) catalysts. The Ni^{2+} was detected on surface nickel of $NiAl_2O_4/Al_2O_3$ calcined at 850^oC. Furthermore, the Ni surface composition of all the catalysts was the mixture of NiO and $NiAl_2O_4$ structures. The distribution of nickel between NiO and $NiAl_2O_4$ species depended on Ni loading and the preparation method. The nano-structural and chemical properties of supported catalysts were modified by the interaction among the phases lying on the carrier after reduction at high temperature. Considering the relationship between the Ni particle size and $NiO/NiAl_2O_4$ ratios, low $NiO/NiAl_2O_4$ ratio resulted in the smallest Ni particle size (6nm)   leading to the highest dispersion that observed on $70\%NiAl_2O_4/Al_2O_3$ catalyst. These interesting results allowed us to conclude. Conversely, the previous literature data reported the small metallic Ni particle size was controlled by the $NiO/NiAl_2O_4$ ratio initially present in the calcined samples. Moreover, in this work, several Ni contents from 15% to 70% were modulated the surface acidity of $NiAl_2O_4$ supported catalysts and no dramatic loss of active sites. For the catalytic activity results on steam reforming of methane, the $70\%NiAl_2O_4/Al_2O_3$ catalyst showed a higher activity and hydrogen yield than the other investigated nickel based catalysts. The stability improvement and the resistance towards sintering and carbon formation corresponded to the higher dispersion and smaller Ni crystallite size. Also, the dispersion of nickel aluminate phase on high surface area transition alumina provided better textural and nano-structural stability than pure $NiAl_2O_4$.

CHAPTER III

MATERIALS AND METHODOLOGY

This chapter explains about the details of co-precipitation method and conditions of catalyst preparation including precipitation and calcination temperatures. It is divided into three parts consisting of catalyst preparation, catalyst characterization and catalytic reaction test. The first part describes the preparation method of catalysts by co-precipitation method. Second part shows the details of characterization techniques such as N_2 physisorption (BET), X-ray diffraction (XRD), temperature program reduction (TPR), temperature program desorption (TPD), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). And finally, the reaction test for CO_2 methanation is exhibited in the third part.

Part I: Catalysts preparation

3.1 Materials

The chemicals used in the catalyst preparation were analytical grades as shown in Table 3.1.

Table 3.1 List of chemicals prepared catalysts by co-precipitation method.

Chemicals	Formula	Assay (%)	Manufacture
Nickel(II)nitrate hexahydrate	$Ni(NO_3)_2 \cdot 6H_2O$	99.99	Sigma-Aldrich
Aluminium nitratrate	$Al(NO_3)_3 \cdot 9H_2O$	98	Ajax Finechem
Ruthenium (III) nitrosyl nitrate solution	$Ru(NO)(NO_3)_3$	75	Sigma-Aldrich
Tetramminepalladium (II) chloride monohydrate	$Pd(NH_3)_4Cl_2 \cdot H_2O$	39	Alfa Aesar
Rhodium (III) Chloride hydrate	$RhCl_3 \cdot xH_2O$	38.5-45.5	Alfa Aesar
Aluminum oxide	Al_2O_3	-	Fluka

3.2 Catalysts preparation by co-precipitation method

3.2.1 $NiAl_2O_4$ spinel catalysts preparation

$NiAl_2O_4$ catalysts were prepared by co-precipitation method with molar ratio of Ni/Al was 1:2. Nickel nitrate (Ni $(NO_3)_2 \cdot 6H_2O$) and aluminium nitrate (Al $(NO_3)_3 \cdot 9H_2O$) were used as the metal precursors. Firstly, nickel nitrate and aluminium nitrate were diluted in DI water with concentration of solution 0.5 molar and then adjust pH of solution by adding NH_4OH from pH 4 to 8.5 and stirring until precipitated. The temperature of co-precipitation were varied at 30 and 80°C After that the precipitate powder were filtrated and dried at 110°C for 12 h in air and calcined at temperature 500, 700, 900 or 1200°C for 5 h. The preparation conditions and the nomenclature of the prepared catalysts are shown in Table 3.2

Table 3.2 Co-precipitation and calcination conditions of the prepared catalysts

No	Co-precipitation temperature (^{o}C)	Calcination temperature (^{o}C)	Catalysts nomenclature
1	30	500	$NiAl_{30}$ – 500
2	30	700	$NiAl_{30}$ –700
3	30	900	$NiAl_{30}$ – 900
4	80	500	$Ni-Al_{80}$ – 500
5	80	700	$Ni-Al_{80}$ – 700
6	80	900	$Ni-Al_{80}$ – 900
7	80	1200	$Ni-Al_{80}$ – 1200

3.2.2 Ni/Al_2O_3 catalyst preparation

36.5Ni/Al_2O_3 was also prepared by impregnation method with a similar molar ratio of Ni/Al   1:2 using nickel nitrate (Ni $(NO_3)_2 \cdot 6H_2O$) and Al_2O_3 commercial (Fluka s.f. 155 sq.m/g) as precursor of metal and support, respectively. The catalyst was dried at 110°C overnight and calcined at 550°C for 5 h.

20Ni/Al_2O_3 was also prepared by impregnation method with 20wt% of Ni loading onto the Al_2O_3 commercial support catalyst (Fluka s.f. 155 sq.m/g). The catalyst was dried at 110°C overnight and calcined at 550°C for 5 h.

3.2.3 Promoted catalysts preparation

The various metal catalysts were promoted on $NiO/NiAl_2O_4$ catalyst that precipitated at 80^oC and calcined at 900^oC. The Ru (NO) $(NO_3)_3$, Pd $(NH_3)_4Cl_2 \cdot H_2O$ and $RhCl_3 \cdot xH_2O$ were used us metal precursor with metal loading 1%wt. The catalyst was dried at 110^oC overnight and calcined at 350^oC for 2 h.

Part II: Catalysts characterization

3.3 Catalysts characterization

3.3.1 N_2 physisorption (BET)

BET surface area, total pore volume and average pore size diameter were calculated from the nitrogen adsorption isotherms at 77 K using a BEL-SORP automated system. The surface area was calculated according to Brunauer – Emmett – Teller (BET). Pore volume and average pore size diameter were calculated by Barrett – Joyner – Halenda (BJH) analysis.

3.3.2 X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns was the technique for examine the crystallite phase and elemental distribution of the catalyst particle. The XRD pattern were performed by using SIEMENS XRD D5000 X-ray diffractometer with CuK_α radiation. The scanning were recorded over a range of 2θ angles from 10° to 80°. The average crystallite size of catalysts were calculated from line broadening according to the Scherrer's equation.

3.3.3 Temperature program reduction (TPR)

TPR measurements were carried in quartz u- tube reactor to determine the behavior of reduction temperature of the catalysts. Prior the measurement, the samples were pretreated by N_2 with flow rate 30 cm^3/min at 200^oC for 1 h then cooled down to the room temperature. After that, flowing the carrier gas (10%H_2/Ar) through the catalysts samples at 30 cm^3/min and temperature ramping from 300^oC to 800^oC with the temperature rating 10^oC/min.

3.3.4   Scanning Electron Microscopy (SEM)

The morphologies of all catalysts sample were performed by using JEOL mode JSM-5800L V. scanning electron microscopy.

3.3.5 Transmission Electron Microscopy (TEM)

The transmission electron microscope of TECNAI F20 G with field emission gun operating at voltage rang of 50-200 kV and optical point resolution of 0.23 nm was performed for TEM analysis. This TEM technique provide morphology images (TEM images) and crystallite size.

Part III: Catalytic activity

3.4 Catalytic activity

3.4.1 Materials

The catalytic activity of the prepared catalysts were evaluated in CO_2 methanation reaction at 350°C for 3 h under atmospheric and the molar gas mix ratio of CO_2:H_2:N_2 1:10:4 with the total flow rate is 40 cm^3/min. Approximately 0.1 g catalyst was packed in 9 mm diameter of the tubular quartz reactor. Prior to the reaction test, the samples were pretreated in pure H_2 at 450°C for 2.30 h with flow rate is 30 cm^3/min. The composition of outlet gas was analyzed by pulse inlet to GC-TCD with molecular sieve and Porapack Q columns.

3.4.2 Apparatus

A flow diagram of the system for testing the catalytic activity is shown in Figure 3.1. An apparatus consisted of a quartz tubular reactor, an automation temperature controller, an electrical furnace, a gas controlling system and gas chromatography that was thermal conductivity detector (TCD). The instruments used in this system were listed and explained as follows:

Table 3.3 The operating conditions of TCD gas chromatographs for the catalytic activity test.

Gas chromatograph	Shimadzu GC-14B
Detector	TCD
Column	Porapak Q (2m) , Molecular sieve
Carrier gas	Helium
Carrier gas flow	30 ml/min
Injector temperature	$100^{o}C$
Detector temperature	$70^{o}C$
Column temperature	$70^{o}C$
Analysis gas	CO_2 , CH_4 , CO

1. Pressure Regulator 2. On - Off Value 3. Gas Filter

4. Metering Valve 5. Check valve 6. Three - way Valve

7. Inlet sampling 8. Catalyst bed 9. Furnace

10. Temperature Controller 11. U-tube water Trap 12. Outlet sampling

13. Bubble flow meter 14. GC-TCD 15. Thermocouple

16. Gas CO_2 mixed H_2 17. Pure H_2 gas 18. Inert N_2 gas
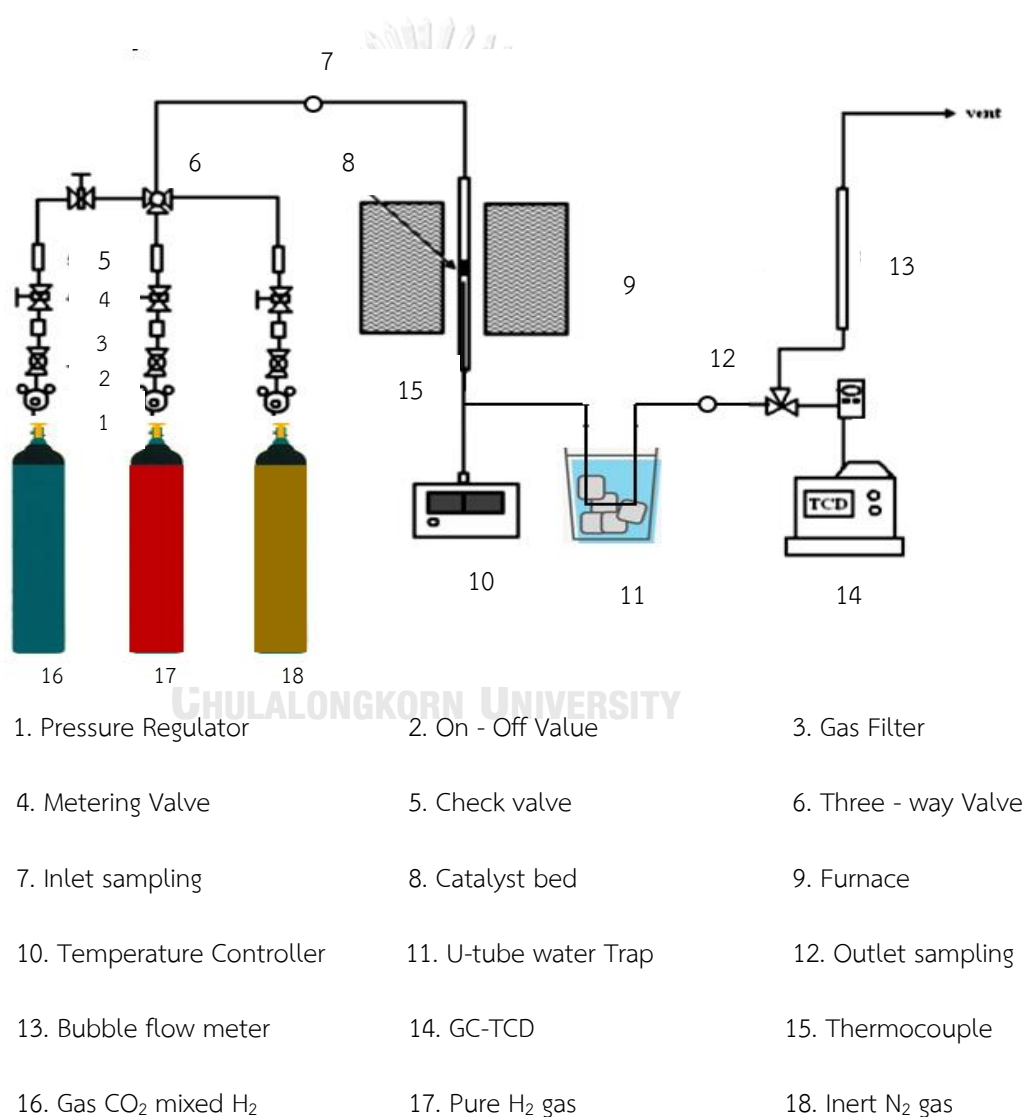
Figure 3.1 Schematic diagram of the reaction line for testing the CO_2 methanation analyzed by GC – TCD equipped with molecular sieve and Porapack Q columns.

CHAPTER IV

RESEARCH METHODOLOGY AND RESEARCH PLAN

4.1 Research methodology

In this work, the research were divided into three parts according to

4.1.1 The effect of preparation and calcination temperatures of $NiO/NiAl_2O_4$ spinel catalyst during CO_2 methanation reaction

```
┌─────────────────────────────────────────────┐
│  The NiO/NiAl₂O₄ catalysts were prepared     │
│  by co-precipitation method with Ni/Al       │
│  molar ratio was 1/2                          │
└─────────────────────────────────────────────┘
```

The $NiO/NiAl_2O_4$ catalysts were prepared by co-precipitation method with Ni/Al molar ratio was 1/2

The precipitation was kept at 30°C

The precipitation was kept at 80°C

The precipitated powder were calcined at 500, 700, 900 °C in air for

The precipitated powder were calcined at 500, 700, 900°C in air for 5 h

Pretreated in H_2 at 450°C for 2.30 h

The catalytic activity tested in CO_2 methanation at 350°C under atmospheric pressure for 3 h

Discussion and conclusion

The catalysts were characterized by

➢ BET
➢ XRD
➢ H_2 − TPR
➢ SEM
➢ TEM

4.1.1.1 The effect of spinel phase formation compared Ni support on commercial Al_2O_3

Ni metal with 20 and 36.5wt% loading impregnated on Al_2O_3 commercial supported catalyst

↓

The powder catalyst was calcined at 550^oC in air for 5 h

Pretreated in H_2 at 450^oC for 2.30 h

The catalytic activity tested in CO_2 methanation at 350^oC under atmospheric pressure for 3 h

Discussion and conclusion

The catalysts were characterized by

➢ BET
➢ XRD
➢ H_2 – TPR
➢ SEM
➢ TEM
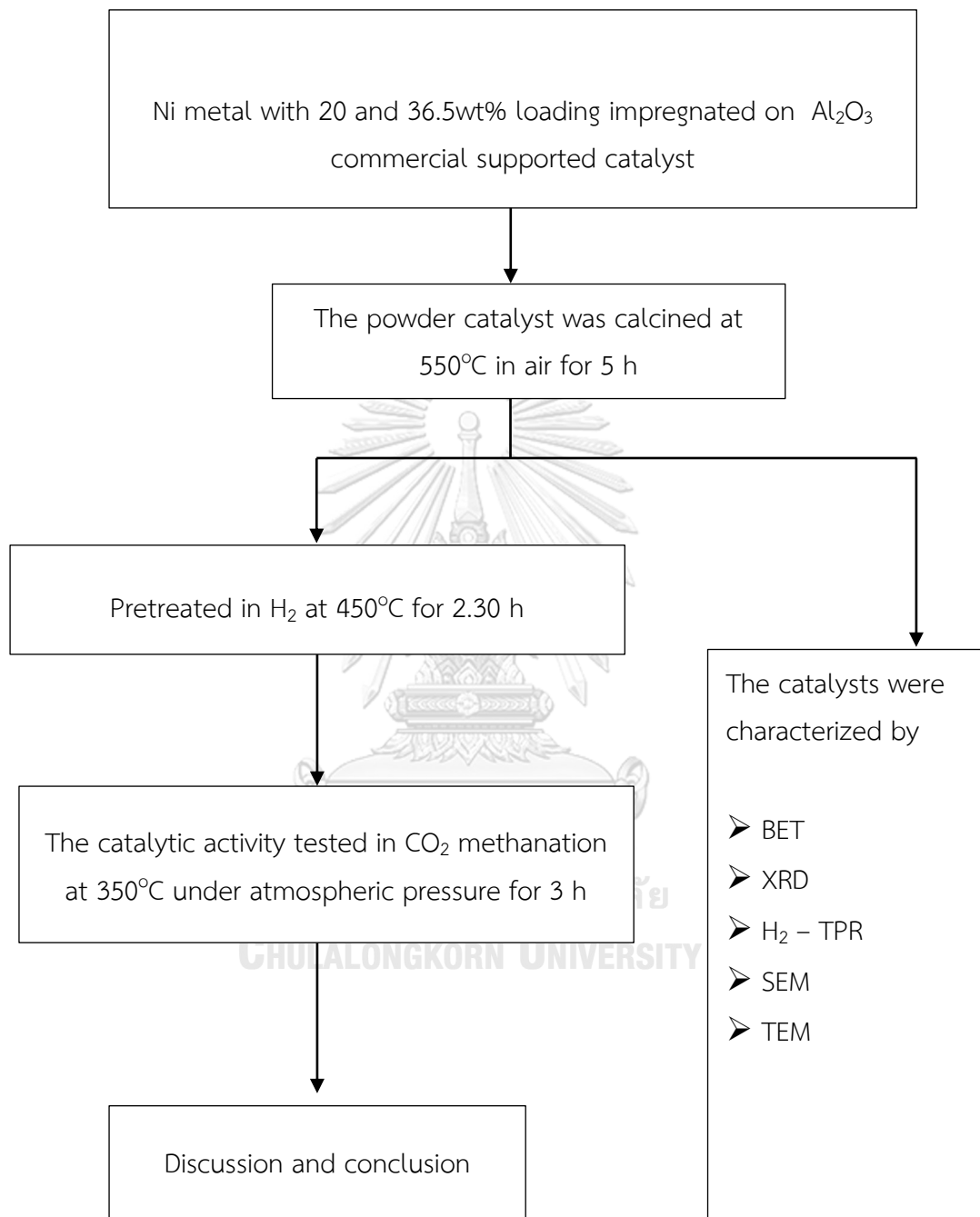
4.1.2 The effect of noble metal loading support on $NiO/NiAl_2O_4$ spinel catalyst during CO_2

```
┌────────────────────────────────────────────────────────┐
│                                                        │
│   Noble metal (Ru,Rh,Pd) with 1wt% loading            │
│   impregnated on Ni-Al_80 900 catalyst                │
│   (NiO/NiAl_2O_4 was precipitated at 80°C and         │
│   calcined at 900°C)                                   │
│                                                        │
└────────────────────────────────────────────────────────┘
                          │
                          ▼
        ┌──────────────────────────────────────┐
        │  The powder catalyst was calcined at  │
        │        350°C in air for 2 h           │
        └──────────────────────────────────────┘
                    │                    │
                    ▼                    ▼
┌──────────────────────────────┐   ┌──────────────────────┐
│ Pretreated in H_2 at 450°C   │   │ The catalysts were   │
│        for 2.30 h            │   │ characterized by     │
└──────────────────────────────┘   │                      │
                 │                  │  ➢ BET               │
                 ▼                  │  ➢ XRD               │
┌──────────────────────────────┐   │  ➢ H_2 – TPR         │
│ The catalytic activity tested │   │  ➢ SEM               │
│ in CO_2 methanation at 350°C  │   │                      │
│ under atmospheric pressure    │   └──────────────────────┘
│ for 3 h                       │
└──────────────────────────────┘
                 │
                 ▼
┌──────────────────────────────┐
│  Discussion and conclusion   │
└──────────────────────────────┘
```

4.1.2.1 The effect of reaction temperature over Ru-NiO/NiAl$_2$O$_4$ catalyst during CO$_2$ methanation

The 1%wtRu-NiO/Ni-Al$_{80}$ 900 catalyst

The powder catalyst was calcined at 350°C in air for 2 h

Pretreated in H$_2$ at 450°C for 2.30 h

The catalytic activity tested in CO$_2$ methanation at 250-350°C under atmospheric pressure and each temperature was kept for 1 h

Discussion and conclusion
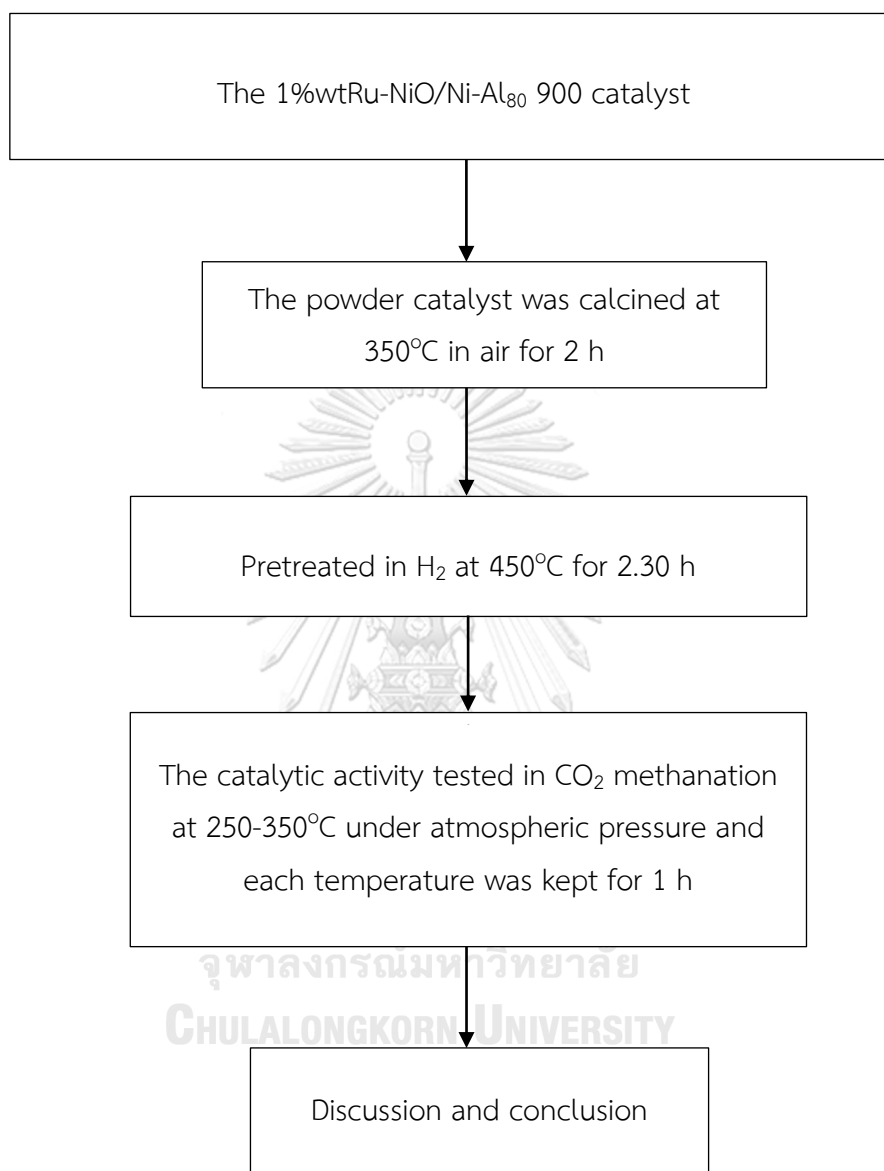
CHARTER V

RESULTS AND DISSCUSSION

Part I: The effect of preparation and calcination temperatures of NiO/NiAl$_2$O$_4$ spinel catalysts during CO$_2$ methanation reaction

5.1 Characterization of NiO/NiAl$_2$O$_4$ spinel catalysts

5.1.1 N$_2$- physisorption (BET)

The adsorption-desorption isotherm of the NiO/NiAl$_2$O$_4$ spinel catalysts are shown in Figure 5.1. All the catalysts exhibited type IV isotherm that indicated mesoporous structure with pore size 2-50 nm with significantly reduced hysteresis loops.
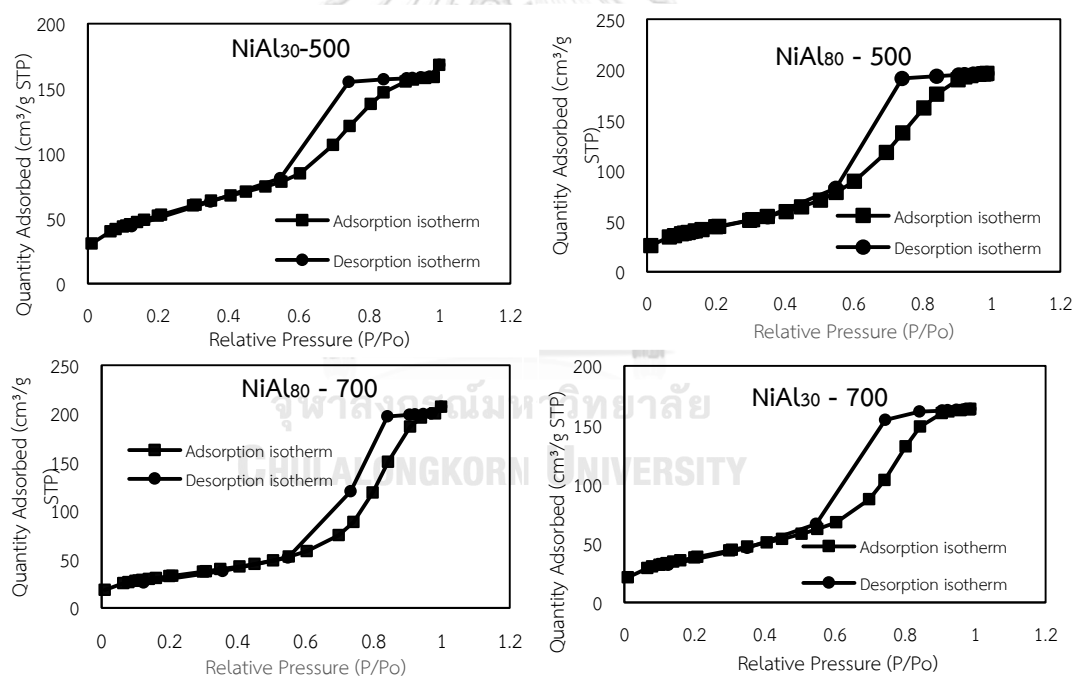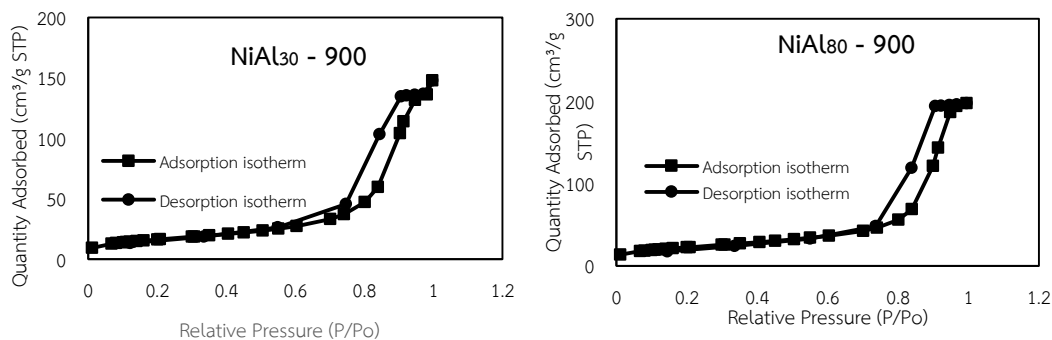
Figure 5.1 Adsorption-Desorption Isotherm of all NiO/NiAl$_2$O$_4$ – spinel based catalysts

The results of surface area, pore volume and average pore size diameter are summarized in Table 5.1. For the catalysts prepared by precipitation at temperature 30°C, the NiAl$_{30}$ – 500 had the higher BET surface area (190.2 m^2/g) than NiAl$_{30}$-700 (138.8 m^2/g). The lowest surface area 58.7 m^2/g was found for NiAl$_{30}$ – 900. In the same way, the total pore volume had slightly decreased from 0.27 to 0.23 cm^3/g with increasing calcination temperature from 500 to 900°C. In contrast, the average pore diameter decreased with increasing calcination temperature in the order to NiAl$_{30}$ – 900 (9.7 nm) > NiAl$_{30}$ – 700 (4.8 nm) > NiAl$_{30}$ – 500 (4.4 nm). In addition, the catalysts prepared at precipitation temperature 80°C revealed the similar trend of surface area and total pore volume to the catalysts that precipitated at 30°C. From Table 5.1, the NiAl$_{80}$ – 500 had the highest surface area 161.4 m^2/g subordinated to NiAl$_{80}$ – 700 with the surface area 118.4 m^2/g and the lowest surface area 80.6 was NiAl$_{80}$ – 900. The total pore volume of NiAl$_{80}$ – 500, NiAl$_{80}$ – 700 and NiAl$_{80}$ – 900 were around 0.31-0.32 cm^3/g that described the similarity when the calcination temperature increased. On the other hand, the average pore diameter increased with increasing calcination temperature in the order of NiAl$_{80}$ – 500 (4.8 nm) < NiAl$_{80}$ – 700 (6.5 nm) < NiAl$_{80}$ – 900 (10.8 nm)

For the NiAl$_{80}$ – 1200 catalyst the BET surface area dramatically decreased to 2.33 m^2/g due to the migration of nanoparticles with very low total pore volume. The catalyst exhibited a similar pore diameter to NiAl$_{30}$ – 500 catalyst.

The surface area of 36.5Ni/Al$_2$O$_3$ catalyst was similar to NiO/NiAl$_2$O$_4$ calcined around 700°C but the total pore volume decreased to 0.14 because of pore blocking from impregnated Ni particles on the commercial Al$_2$O$_3$.

However, both precipitation and calcination temperatures affected BET surface area as seen in Table 5.1. The surface area decreased as a result of higher crystallinity of spinel and/or the particle size increased from sintering and nucleation after calcined at high temperature. The total pore volume slightly decreased when the calcination temperature increased probably due to pore blocking of spinels after calcination. In addition, the average pore diameter increased with increasing preparation and calcination temperatures [62, 63]. However, the larger total pore volume and the bigger average pore diameter were revealed towards higher calcination temperature that phenomena related to benefit gas molecules diffusing into the holes [56].

Table 5.1. The BET surface area, total pore volume and average pore size diameter of all NiO/NiAl$_2$O$_4$ – spinel based catalysts

Catalyst	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Avg pore diameter (nm)
NiAl$_{30}$ – 500	190.2	0.27	4.4
NiAl$_{30}$ – 700	138.8	0.26	4.8
NiAl$_{30}$ – 900	58.7	0.23	9.7
NiAl$_{80}$ – 500	161.4	0.31	4.8
NiAl$_{80}$ – 700	118.4	0.32	6.5
NiAl$_{80}$ – 900	80.6	0.31	10.8
NiAl$_{80}$ – 1200	2.3	0.0024	4.2
20Ni/Al$_2$O$_3$	91.9	0.0937	4.1
36.5Ni/Al$_2$O$_3$	124.9	0.14	4.4

5.1.2 X-ray diffraction (XRD)

The XRD patterns of $NiO/NiAl_2O_4$ catalysts are shown in Figure 5.2. The crystalline phases were identified using JCPDS files. The patterns of $NiO/NiAl_2O_4$ precipitated at 30 and 80°C with calcination temperature 500°C and 700°C ($NiAl_{30}$ – 500, $NiAl_{80}$ – 500, $NiAl_{30}$ – 700 and $NiAl_{80}$ – 700) were similar. The nickel oxide phase were observed (NiO, JCPDS 89-7131) at 2θ degrees 37.5^o, 43.5^o and 63.1^o. There a partial transformation of nickel aluminate phase but this results were not clearly seen because there were the overlapping of NiO and $NiAl_2O_4$ at 2θ degrees 37.5^o and very small shoulder at 45.3^o, 65.8^o and 71.3^o [13, 61, 64, 65]. It is well known that under high calcination temperature, there are   sufficient energy of nickel ion to overcome the surface of alumina and integrate inti the alumina lattice to form spinel structure [64]. Interestingly, the corresponding patterns of $NiO/NiAl_2O_4$ calcined at highly temperature at 900°C ($NiAl_{30}$ – 900 and $NiAl_{80}$ – 900) were clearly observed which the high intensity of nickel aluminate phased ($NiAl_2O_4$, JCPDS 78-1601) at 2θ degrees 31.7^o, 45.3^o, 65.8^o and 71.3^o. For $NiO/NiAl_2O_4$ calcined at very high temperature 1200°C,the width of nickel aluminate peaks decreased indicating the increase in both crystallinity and crystallite size   but the presence of NiO phase was still observed [66].

The crystallite size of $NiO/NiAl_2O_4$ – spinels catalysts are shown in Table 5.2. For the $NiO/NiAl_2O_4$ prepared by precipitated at 30°C, the crystallite size of NiO increased from 7.4 to 8.4 nm and the crystallite size of $NiAl_2O_4$ also increased from 4.8 to 7.4 nm. The revelation of increased calcination temperature from 500 to 900 ^{o}C slightly increased crystallize size. In the same way, the higher precipitation temperature at 80°C had some effect to increase the crystallite size for both of NiO and $NiAl_2O_4$ as there was a slightly increasing of NiO crystallite size from 6.6 to 8.8 nm towards high calcination temperature from 500 to 900°C and dramatically increased to 36.6 nm when calcined at 1200°C. There were similar trend of the increasing crystallite size of $NiAl_2O_4$ from 9.4 to 14.4 nm with higher calcination temperature and dramatically increased to 37.3 nm when calcined at 1200°C probably to migration of nanoparticles corresponding to low surface area as shown in the results of N_2 – physisorption and decreasing of peaks width resulting in more crystallinity. Also, the crystallinity of $NiO/NiAl_2O_4$ – spinels catalysts prepared at higher calcination temperature was higher than lower calcination temperature [62, 66].
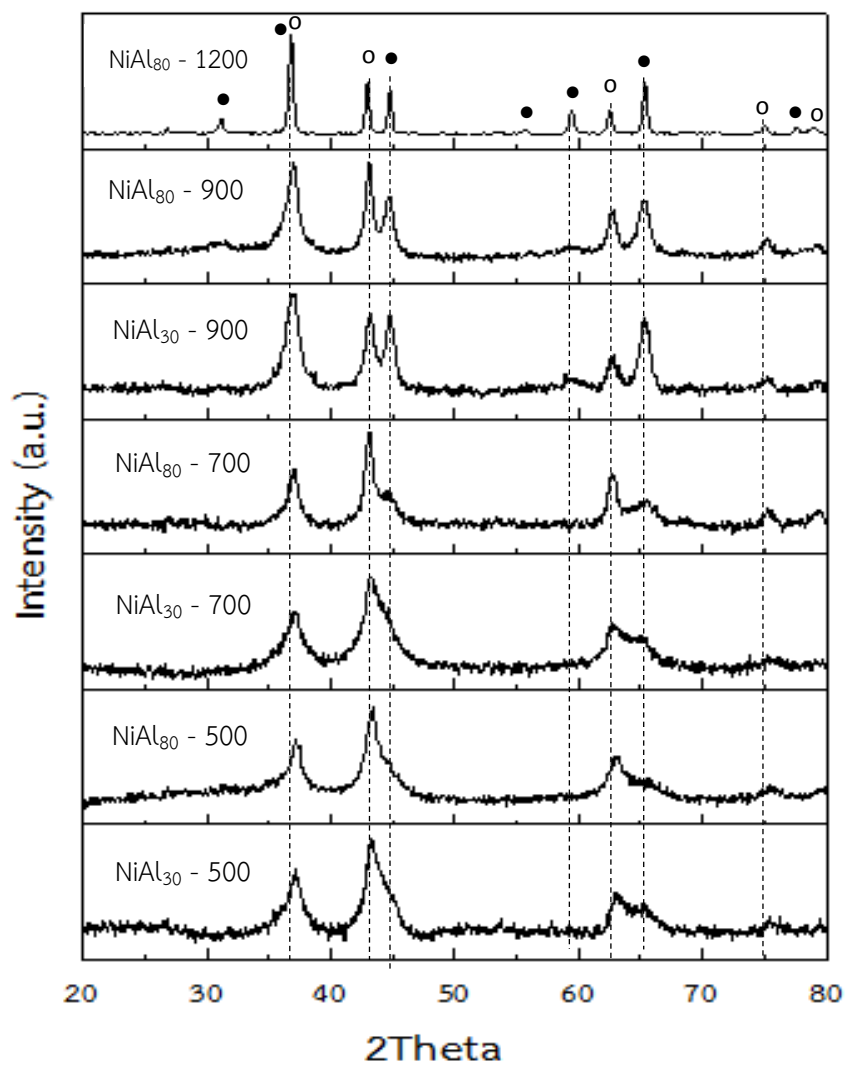
Figure 5.2 The XRD patterns of fresh $NiO/NiAl_2O_4$ spinel − based catalysts;

• $NiAl_2O_4$; ◦ NiO

Table 5.2 The average crystallite size and phase amount of $NiO/NiAl_2O_4$- spinel based catalysts

Catalyst	Average crystallite size of fresh catalyst (nm)[a]		Phase amount (Wt %)[b]		$NiO:NiAl_2O_4$ Weight ratio
	NiO	$NiAl_2O_4$	NiO	$NiAl_2O_4$	
$NiAl_{30} - 500$	7.4	4.8	81.4	18.6	4.4
$NiAl_{30} - 700$	8.2	5.5	70.1	29.9	2.4
$NiAl_{30} - 900$	8.9	7.4	26.5	73.5	0.4
$NiAl_{80} - 500$	6.6	9.4	78.8	21.3	3.7
$NiAl_{80} - 700$	7.3	11.3	55.9	44.1	1.3
$NiAl_{80} - 900$	8.8	14.2	24.7	75.3	0.3
$NiAl_{80} - 1200$	36.6	37.3	18.3	81.7	0.2

[a] Calculated by using Shcerrer equation

[b] Determine by Rietvield quantitative phase analysis in Material Analysis Using Diffraction (Maud) programmed.

From Table 5.2. The quantitative phase analysis by Rietveld method into Material Analysis Using Diffraction program were ascribed [66-69]. The calcination temperature affected to amount of NiO and $NiAl_2O_4$ phases in both of precipitation temperatures (30 and 80°C). $NiO/NiAl_2O_4$ catalysts calcined at 500°C and precipitated at 30°C had the highest quantitative of 81.4wt% NiO and lowest 18.6wt% $NiAl_2O_4$ compared with all the catalysts calcined at higher temperature (700, 900 and 1200°C), that resulting to highest $NiO:NiAl_2O_4$ weight ratio 4.4. In contrast, the increasing of calcination temperature at 1200°C of $NiO/NiAl_2O_4$ decreased the quantitative of

18.3wt% NiO while $NiAl_2O_4$ phase became highest at 81.7 wt%. However, the increasing of both precipitation and calcination temperatures affected to decrease the quantitative of NiO and improved the quantitative of $NiAl_2O_4$ phase formation that corresponding to $NiO:NiAl_2O_4$ weight ratio.
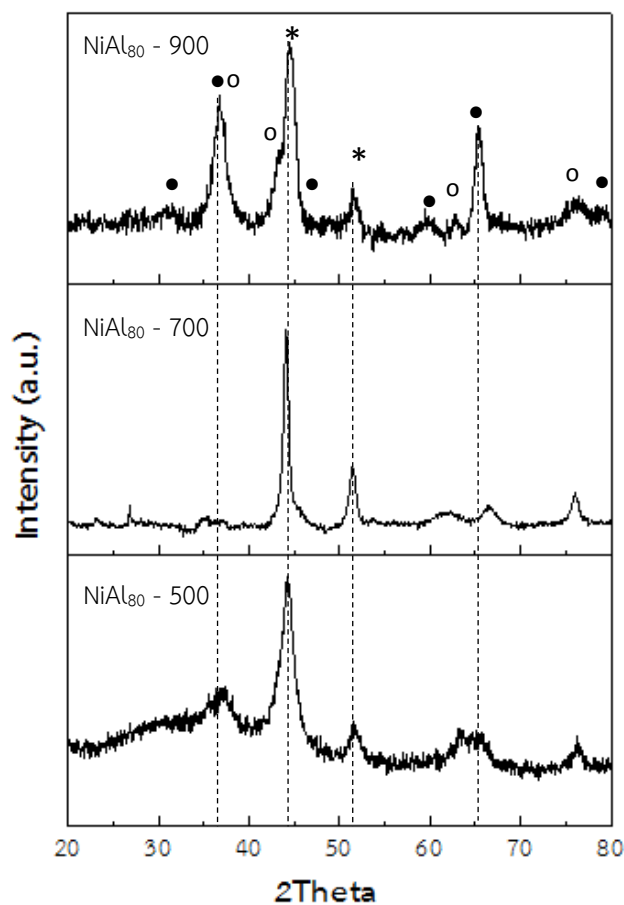
Figure 5.3 The XRD patterns spent $NiO/NiAl_2O_4$ spinel – based catalysts;

● $NiAl_2O_4$; o NiO ; * Ni metallic

Figure 5.3 showed the XRD patterns of spent of $NiO/NiAl_2O_4$ spinel- based catalysts. The merging of NiO and $NiAl_2O_4$ peaks at 2θ degrees 37°, $43-45^\circ$ and $62-67^\circ$ were observed in the pattern of $NiAl_{80}$ – 500 catalyst while the Ni metallic at 2θ degrees 52° was clearly observed. In the same way, the $NiAl_{80}$ – 700 catalyst exhibited the major peaks of Ni metallic (JCPDS 89-7128) at 2θ degrees 44.6° , 52° and 76.5° [13] while the combination of NiO and $NiAl_2O_4$ peaks were still observed at 2θ degrees around 37°, $61-65^\circ$ with a small shoulder peak around 45° with low intensity. In

contrast, the $NiAl_2O_4$ peaks were still clearly observed on $NiAl_{80}$ – 900 at 2θ degrees $31.7°$, $37.5°$, $60.2°$ and $65.8°$ except the peak at 2θ degrees $45.3°$ shows the small shoulder peak due to the combination peak with Ni metallic at 2θ degrees $44.6°$ and clearly Ni metallic at 2θ degrees $52°$ with low intensity. Moreover, the shoulder peak of NiO still was presented at 2θ degrees $37.5°$ (overlapping to $NiAl_2O_4$) and $43.5°$ (combined with Ni metallic peak).

Table 5.3 The average crystallite size of spent $NiO/NiAl_2O_4$- spinel based catalysts

Catalyst	Average crystallite size of spent catalyst (nm)[a]		
	NiO	Ni methallic	$NiAl_2O_4$
$NiAl_{80}$ – 500	7.3	6.1	17.8
$NiAl_{80}$ – 700	15.3	14.9	7.3
$NiAl_{80}$ – 900	6.1	6.7	10.4

[a] calculated by using Shcerrer equation.

However, there were difficultly defining species due to the combination and overlapping of peaks species so the calculation of crystallite size were investigated by using the Gaussian deconvolution [13, 50]. Table 5.3 shows the average crystallite size of spent $NiO/NiAl_2O_4$- spinel based catalysts. The increasing of crystallite size of NiO were observed on $NiAl_{80}$ – 500 and $NiAl_{80}$ – 700 spent catalyst which may be due to migration of NiO particles while the $NiAl_{80}$ – 500 catalyst ascribed the largest crystallite size of $NiAl_2O_4$ compared with spinel catalysts calcined at 700 and 900°C. On the other hand, the $NiAl_{80}$ – 900 spent catalyst revealed the decreasing of crystallite size of NiO and $NiAl_2O_4$ to 6.1 and 10.4 nm, respectively. The $NiAl_{80}$ – 500 and $NiAl_{80}$ – 900 catalysts revealed the similar crystallite size of Ni metallic around 6.1 and 6.7 nm, respectively probably the formation of $NiAl_2O_4$ corresponded to limitation of mobility

on the surface of support and resistance sintering [70], which was in good agreement with Paternina Berrocal et al. [65]. They suggested that the formation of large Ni crystallite was inhibited during reduction of the nickel aluminate phase. Also, crystallite size of Ni metallic for $NiAl_{80} - 700$ catalyst was increased to 14.9 nm maybe due to the agglomeration or sintering after reaction test, corresponding to the broad peak of the combination of NiO and $NiAl_2O_4$ peaks as seen in the XRD results.

In addition, the XRD patterns of fresh and spent Ni/Al_2O_3 catalysts are shown in Figure 5.4a and 5.4b. For both of $36.5Ni/Al_2O_3$ and $20Ni/Al_2O_3$ NiO and $\gamma - Al_2O_3$ phases was evidently observed with high intensity and sharp of peaks. The NiO phase of $36.5Ni/Al_2O_3$ catalyst were observed at 2θ degrees 37.5^o, 43.5^o, 63.1^o and 71.3^o (JCPDS 89-7131) while $\gamma - Al_2O_3$ phase were observed at 2θ degrees 31.6^o, 37.8^o and 67.1^o (JCPDS 79-1558) and the remaining peak were not clearly observed at 2θ degrees 45.7^o and 62°. In contrast, the small shoulder peak of $\gamma - Al_2O_3$ were observed on the $20Ni/Al_2O_3$ catalyst at 2θ degrees 45.7^o and 62°. After reaction test, Ni metallic phase were exhibited on both $36.5Ni/Al_2O_3$ and $20Ni/Al_2O_3$ catalysts at at 2θ degrees 44.6^o, 52° and 76.5^o (JCPDs 89-7128). The NiO peak were evidently disappeared on $36.5Ni/Al_2O_3$ catalyst while it was still observed small shoulder peak on $20Ni/Al_2O_3$ catalyst.

The crystallite size of fresh and spent Ni/Al_2O_3 catalysts are shown in Table 5.3. The $20Ni/Al_2O_3$ catalyst had larger crystallite size of both NiO and $\gamma - Al_2O_3$ (23.41 and 16.24, respectively) than $36.5Ni/Al_2O_3$. The $36.5Ni/Al_2O_3$ had the crystallite size of NiO and $\gamma - Al_2O_3$ around 16.2 and 13.8 nm, respectively that corresponded to the sharper peak as seen in the XRD pattern. For spent catalysts, crystallite size of NiO decresed because of the reduction of NiO to Ni metallic. The $20Ni/Al_2O_3$ catalyst revealed the larger the crystallite size of $\gamma - Al_2O_3$ than fresh catalyst to 20.5 nm. Neverless, the crystallite of $\gamma - Al_2O_3$ for $36.5Ni/Al_2O_3$ catalyst cannot be calculated due to the very sharp peak.
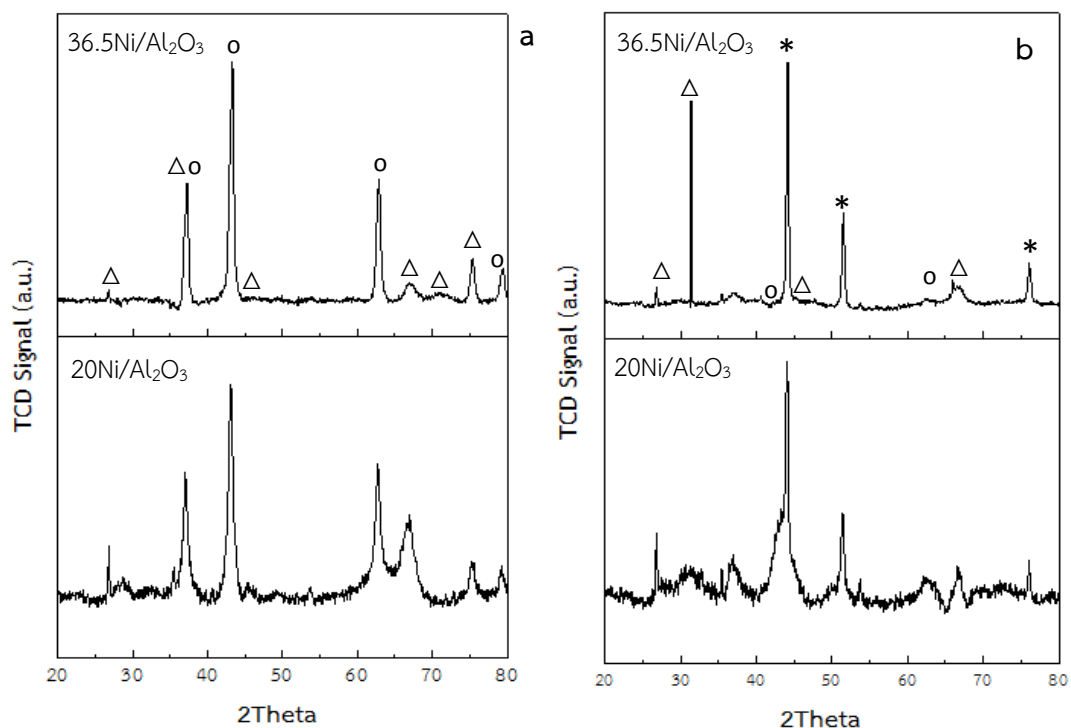
Figure 5.4 The XRD patterns of (a) fresh Ni/Al$_2$O$_3$ catalysts (b) spent Ni/Al$_2$O$_3$ catalysts;

△ γ- Al$_2$O$_3$; o NiO ; * Ni metallic

Table 5.4 The average crystallite size of fresh and spent Ni/Al$_2$O$_3$ catalysts

Catalyst	Average crystallite size of fresh catalyst (nm)[a]		Average crystallite size of spent catalyst (nm)[a]		
	NiO	γ – Al$_2$O$_3$	NiO	Ni metallic	γ – Al$_2$O$_3$
20Ni/Al$_2$O$_3$	23.41	16.24	8.76	5.88	20.45
36.5Ni/Al$_2$O$_3$	16.22	13.84	N/D	8.67	N/D

[a] calculated by using Shcerrer equation.

5.1.3 Temperature programed reduction (H_2 - TPR)

The reducibility of nickel species and the metal-support interaction were investigated proceeding H_2 – TPR experiment as shown in Figure 5.6a and 5.6b. In principle, the reducible NiO species are usually divided into three types: α, β and γ. The peak located low temperature (300-550°C) was assigned to α – type NiO species, which were free nickel oxides having a weak interaction with support. The medium temperature (550-700°C) expected to β – type NiO species with stronger interaction with alumina than α – type and finally, the high temperature (>700°C) related to γ – type NiO species which the stable nickel aluminate phase with spinel structure were ascribed [13, 50, 65].

Figure 5.5 shows the reduction profiles of the NiO/Al_2O_4 catalysts series and bulk NiO commercial. For bulk NiO commercial, clearly two distinct reduction peak were noted at 206 and 373°C. The types of reducible nickel species of all catalysts were applied by Gaussian-type.
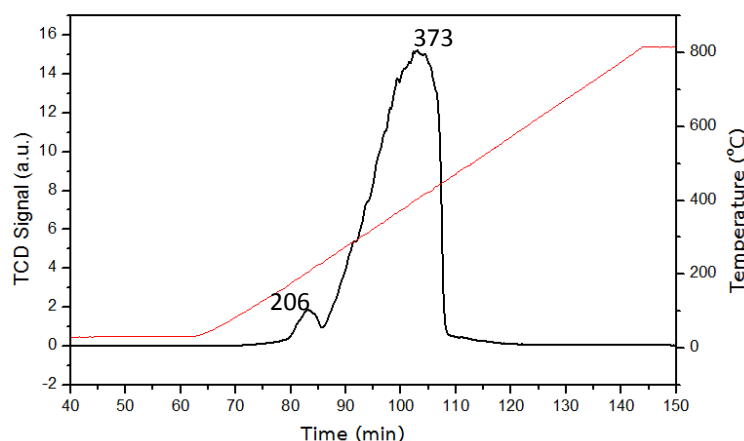
Figure 5.5 The H_2 – TPR profiled of NiO commercial catalysts plot against time

For the NiO/$NiAl_2O_4$ catalysts precipitated at 30°C and calcined under various calcination temperature (500, 700 and 900), there were three reduction peaks that related to presence of three types of NiO species. In the case of NiO/$NiAl_2O_4$ calcined at 500°C ($NiAl_{30}$ – 500), it exhibited initial reduction temperature at 511, 581 and 699°C which were lower than NiO/$NiAl_2O_4$ calcined at higher temperatures. Consequently, NiO/$NiAl_2O_4$ with calcination temperature at 700°C ($NiAl_{30}$ – 700), the initial reduction peaks were shifted toward higher temperature in order to 528, 586 and 740°C. In the

same way, the initial reduction peaks of $NiO/NiAl_2O_4$ calcined at 900 ($NiAl_{30} - 900$) were shifted toward higher temperature in order of 580, 707 and 814^oC, respectively.

Contrastingly, the increasing of precipitation to 80^oC of $NiO/NiAl_2O_4$ with various calcination temperatures (500, 700, 900 and 1200^oC), the similar trends of three reduction peaks were observed except for the $NiO/NiAl_2O_4$ calcined 1200^oC that had two reduction peaks. The $NiO/NiAl_2O_4$ calcined at 500^oC ($NiAl_{80} - 500$) had initial reduction temperature peak at 496^oC and the second and third peaks were exhibited at 563 and 680^oC, respectively. The increasing of calcination temperature to 700^oC, the reduction peaks were shifted toward higher temperature position in order to 572,617 and 765^oC. Interestingly, $NiO/NiAl_2O_4$ calcined at 900^oC ($NiAl_{80} - 900$) had initial reduction temperature at 426^oC that lower than $NiAl_{80} - 500$ (496^oC) and $NiAl_{80} - 700$ (572^oC) probably due to lower NiO/support interaction so the NiO can be reduced more easily [62]. Finally, $NiO/NiAl_2O_4$ calcined at 1200^oC ($NiAl_{80} - 1200$), broad peak around 573 to 729^oC were observed with very low intensity. The increasing of reduction temperature peak was due to very strongly interaction of NiO into nickel aluminate spinel structure and their dramatically larger crystallite sizes probably makes the reduction process more difficult [10].

By comparing of precipitation temperature, the spinel catalysts precipitated at higher temperature (80^oC) (except calcined 700), the reducing of NiO species started earlier probably due to different rates of NiO formation compared to the catalysts prepared at low temperature (30^oC) during calcination. Also, the presence of NiO particles interacted considerable with spinel phase and only small amount of NiO maybe more easily for reduction process [10, 71] as suggested by Yolanda C. et al. [10]. They reported the comparing of $NiAl_2O_4$ spinel with differential precipitation temperatures (25^oC and 75^oC) and observed that spinel precipitated at 25^oC shows initial reducing earlier at low temperature probably because the NiO favor proceed with the different precipitation rate of the nickel aluminum hydroxide at 25^oC.
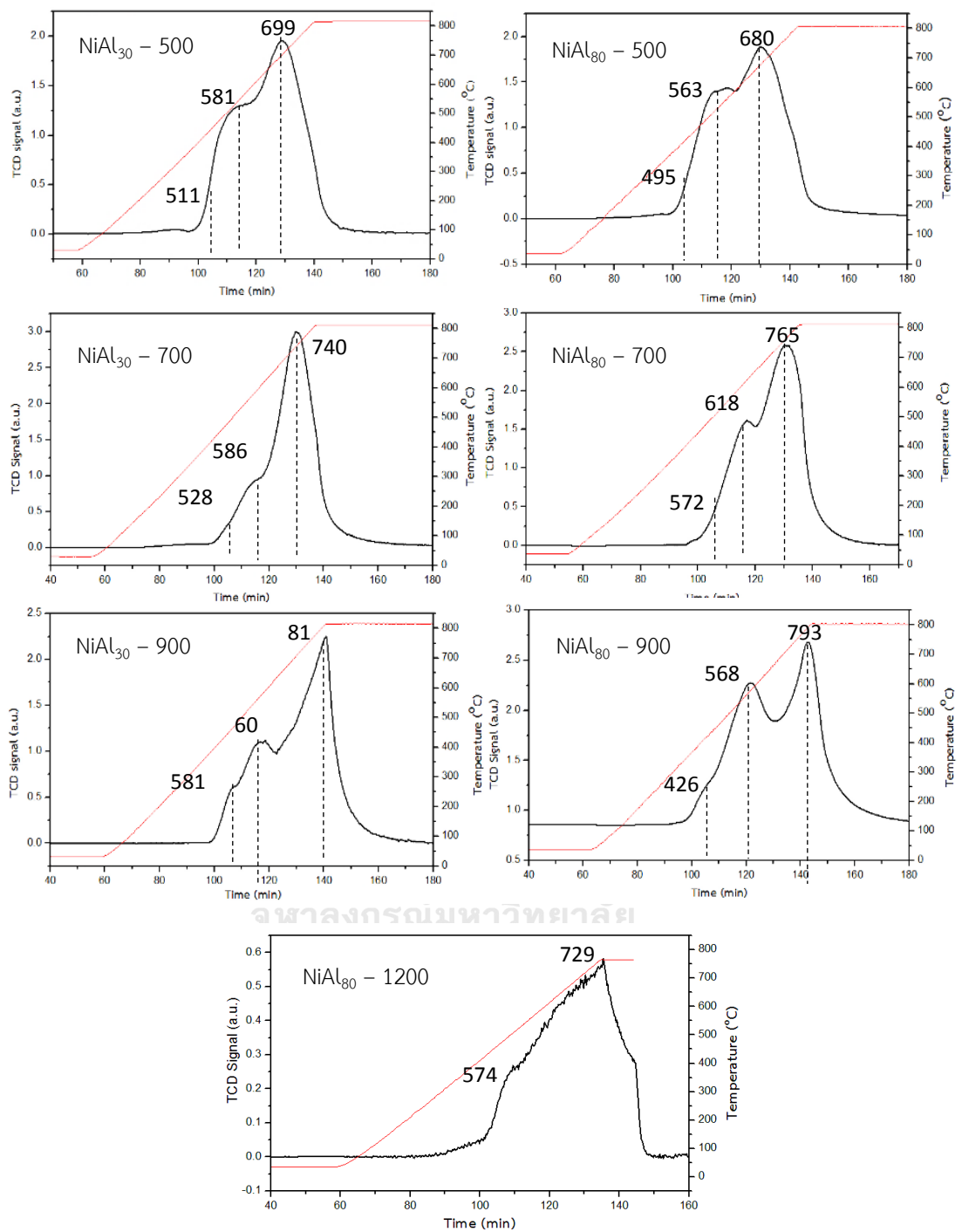
Figure 5.6 The H$_2$ – TPR profiled of NiO/NiAl$_2$O$_4$ – spinel catalysts plot against time

Moreover, the calcination temperature had a significant effect to the residual a amount of NiO from nickel interacted with alumina proceeding to nickel aluminate phase formation including to different crystallite size of particles. The increasing of calcination temperature related to more crystallite size and showed higher value of initial reduction temperature so the larger crystallite site can be more difficult to reduce [10, 72] except $NiO/NiAl_2O_4$ calcained at 900 and 1200°C, their peaks shifts to lower temperature probably lower content of NiO (as shown by XRD and quantitative phase analysis) and lower NiO/support interaction since they were more crystalline and can be reduced more easily [62, 65]. In addition, the serious aggregation resulting to the larger particle size that can be attributed to the weak interaction between the impregnated Ni species and the support [70].

In case of lower calcination temperature, the catalysts exhibited higher surface area and smaller particle size. Free NiO usually result in stronger interaction bonded to the support and is normally reduced at higher temperatures than large particles with poor metal-support interaction [70, 73, 74]
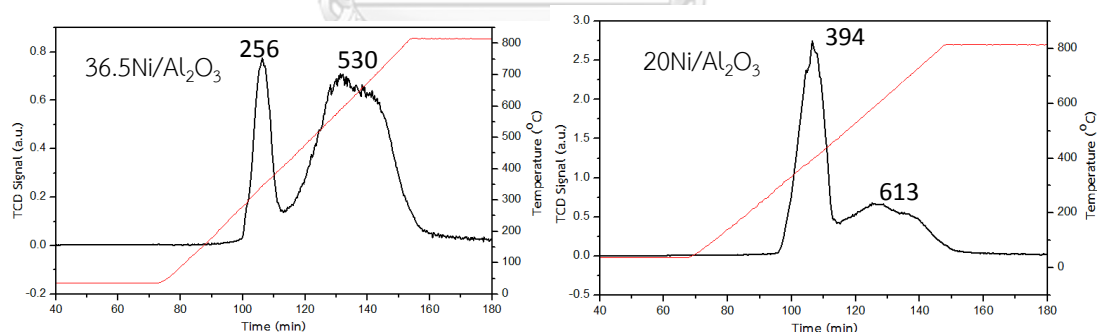
Figure 5.7 The H_2 – TPR profiled of $36.5Ni/Al_2O_3$ and $20Ni/Al_2O_3$ catalysts plot against time

Figure 5.7 shows the reduction profile of 36.5 wt% and 20 wt% of Ni loading on Al_2O_3 commercial support. The $20NiO/Al_2O_3$ catalyst exhibited clearly two distinct reduction peaks at 394 and 613°C without the strong interaction of NiO into $NiAl_2O_4$ spinel phase. Lower reduction temperature were observed on $36.5NiO/Al_2O_3$ catalyst which revealed two distinct peaks at 256 and 530°C. There were no observed γ-type

NiO at high temperature or the peak of spinel phase interaction. The reduction peak were shifted to lower temperature with higher Ni loading. Highly dispersed NiO exhibited a stronger interaction with the support, while the lower reduction temperature can be related to larger NiO particles having interactions of lower strength with the support. In addition, the increasing of Ni content ascribed to the decreasing metal – support interaction so the interaction of Ni species with alumina support became weaker at higher Ni content [52, 75].

Table 5.5 The summary of H_2 – TPR results

Catalyst	Peak position temperature (°C)		
	α – type NiO species	β – type NiO species	γ – type NiO species
$NiAl_{30}$ – 500	511	581	699
$NiAl_{30}$ – 700	528	586	740
$NiAl_{30}$ – 900	581	600	814
$NiAl_{80}$ – 500	496	563	680
$NiAl_{80}$ – 700	572	618	765
$NiAl_{80}$ – 900	426	568	793
$NiAl_{80}$ – 1200	-	574	729
$20Ni/Al_2O_3$	394	613	-
$36.5Ni/Al_2O_3$	256	530	-

5.1.5 Scanning Electron Microscopy (SEM)

The surface morphology of $NiO/NiAl_2O_4$ – spinel based catalysts were investigated by scanning electron microscopy and are shown in Figure 5.8. For $NiO/NiAl_2O_4$ calcined at $500^\circ C$ the higher dispersion was observed with smaller particle size and lower crystallite size corresponded to the XRD results. In addition, the lower surface area were observed on the catalysts which calcined at higher temperature due to nucleation of metallic particles and/or clustering of the nanoparticles including to more crystallite size.

The presence of Ni, Al and O was confirmed by means of energy dispersive X-ray analysis (EDX). The EDX spectrum revealed Ni, Al and O peaks.

NiAl₃₀ – 500

C:\student\Mild MM\15.spc 17-May-2018 11:52:05
LSecs : 30

Element	Wt%	At%
OK	23.55	45.03
AlK	24.69	28.00
NiK	51.76	26.97
Matrix	Correction	ZAF

NiAl₃₀ – 700

C:\student\Mild MM\14.spc 17-May-2018 11:47:02
LSecs : 30

Element	Wt%	At%
OK	22.68	43.23
AlK	27.17	30.72
NiK	50.15	26.05
Matrix	Correction	ZAF

NiAl$_{30}$ – 900

C:\student\Mild MM\18.spc 17-May-2018 12:03:45
LSecs : 30

Element	Wt%	At%
OK	23.84	45.02
AlK	26.07	29.19
NiK	50.09	25.78
Matrix	Correction	ZAF

NiAl$_{80}$ – 500

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LSecs : 30

Element	Wt%	At%
OK	24.93	47.07
AlK	23.61	26.44
NiK	51.46	26.49
Matrix	Correction	ZAF

NiAl$_{80}$ – 700

C:\student\Mild MM\5.spc 17-May-2018 11:19:00
LSecs : 30

Element	Wt%	At%
OK	29.58	53.53
AlK	20.23	21.72
NiK	50.19	24.75
Matrix	Correction	ZAF

Element	Wt%	At%
OK	21.75	42.50
AlK	25.28	29.29
NiK	52.98	28.21
Matrix	Correction	ZAF

Figure 5.8 The SEM images of NiO/NiAl$_2$O$_4$ spinel – based catalysts

5.1.6 Transmission Electron Microscopy (TEM)

The morphology of catalyst were investigated by using transmission electron microscopy (TEM). The TEM images of fresh NiAl$_{80}$ – 900 catalyst were displayed in Figure 5.9a. The irregular shape were observed and the average particle size was 7.5 nm. The spent NiAl$_{80}$ – 900 catalyst had the average particle size are smaller than fresh catalyst (3.2 nm) as seen in Figure 5.9b.
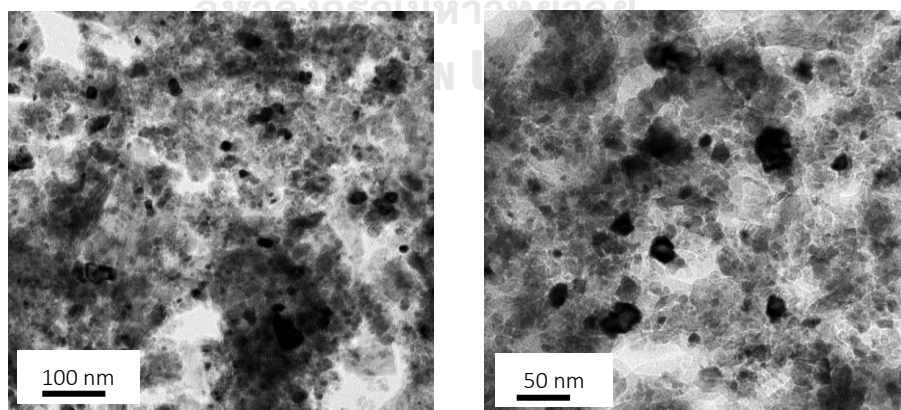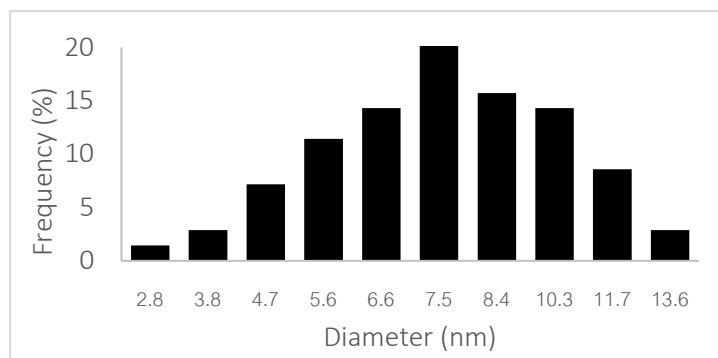
Figure 5.9a. The TEM images of fresh NiAl$_{80}$ − 900 catalyst
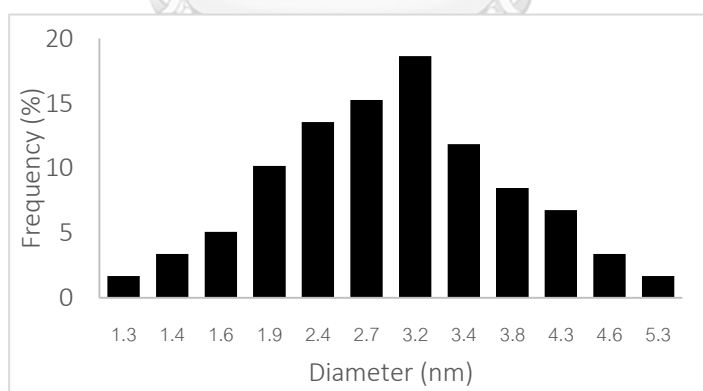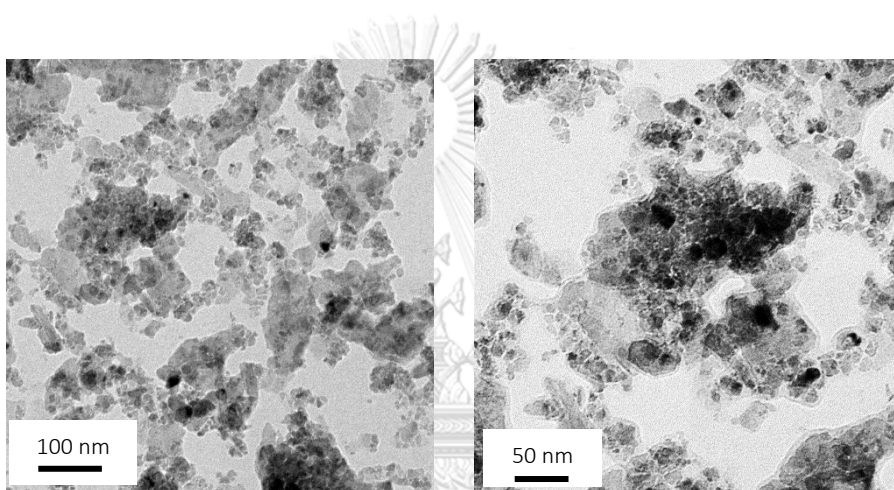
Figure 5.9b. The TEM images of spent NiAl$_{80}$ − 900 catalyst

The TEM images of the Ni/Al$_2$O$_3$ commercial catalysts with 20 and 36.5 %wt Ni loading are shown in Figure 5.10a, 5.10b, 5.11a and 5.11b, showing the metal distribution on the commercial Al$_2$O$_3$ supports. For the spent catalyst, sintering or agglomeration of metal particles with relatively larger size were observed.
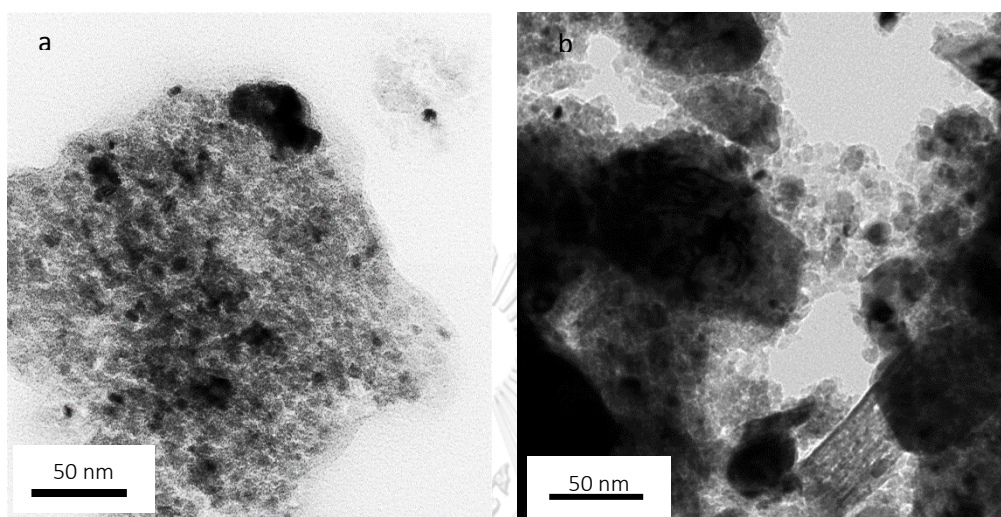
Figure 5.10 (a) The TEM image of fresh 20Ni/Al$_2$O$_3$ catalyst (b) The TEM image of spent 20Ni/Al$_2$O$_3$ catalyst.
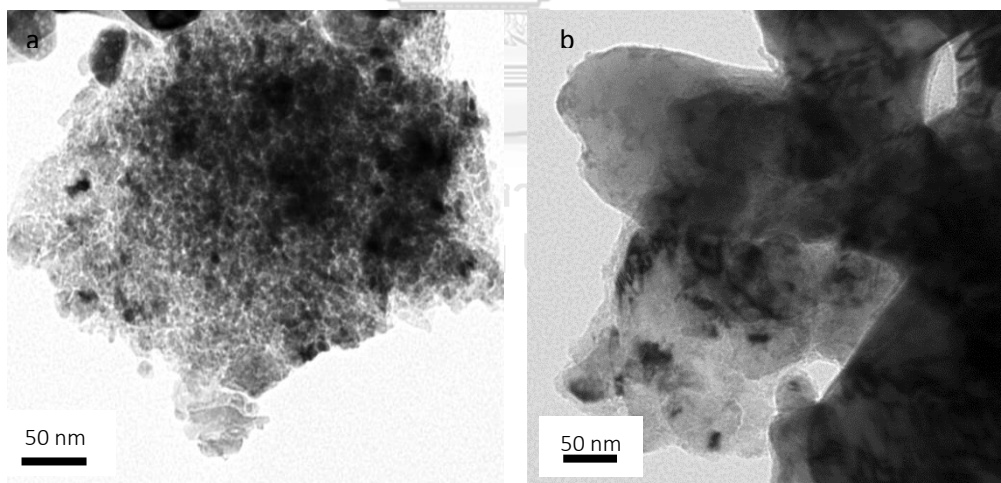
Figure 5.11 (a) The TEM image of fresh 36.5Ni/Al$_2$O$_3$ catalyst (b) The TEM image of spent 36.5Ni/Al$_2$O$_3$ catalyst.

5.2. Catalytic activity of $NiO/NiAl_2O_4$ catalysts

The catalytic activity tests for CO_2 methanation were carried out at 350°C for 180 min (3 h). The catalyst performances in terms of CO_2 conversion, CH_4 yield and CO yield are shown in Fig. 5.12. All the catalysts showed high stability during the 3 h time on stream and the outlet product showed no CO formation except $NiAl_{30}$ – 500, $NiAl_{80}$ – 1200 and $20Ni/Al_2O_3$ catalysts. The $NiAl_{80}$ – 900 catalyst exhibited the highest CO_2 conversion among of the catalysts studied at 92% and 100% methane selectivity without CO formation. For the $NiAl_{80}$ – 900 catalyst also showed slightly lower conversion of CO_2 than the $NiAl_{30}$ – 900 catalyst at 88% conversion. Interestingly, The CO_2 conversion of $NiAl_{30}$ – 500 (82%), $NiAl_{80}$ – 500 (82.5%), $NiAl_{30}$ – 700 (81.9%), and $NiAl_{80}$ – 700 (81%) were essentially similar at around 82% conversion but only $NiAl_{30}$ – 500 catalysts exhibited a slight of CO formation in 20 min after that the CO formation was disappeared. The $NiAl_{80}$ – 1200 catalyst showed the highest stability but the lowest conversion among all the catalysts studied at 23 % conversion with CO yield that slightly decreased during reaction operated.

By comparing the series of $NiO/NiAl_2O_4$ catalysts with the Ni/Al_2O_3 catalysts prepared by impregnation method with similar amount of Ni loading (36.5wt %) and another one with 20% Ni loading. The conversion of impregnated catalysts were lower than all the precipitated $NiO/NiAl_2O_4$ catalysts and only $20Ni/Al_2O_3$ catalyst revealed the CO formation during 180 min operated. The $36.5Ni/Al_2O_3$ catalyst exhibited 75% CO_2 conversion with 100% methane selectivity. For lower Ni content, $20Ni/Al_2O_3$ catalyst showed conversion of CO_2 at 68 % conversion with less CO yield around 1.3 % after reaction test for 180 min. The observation of CO formation on Ni/Al_2O_3 were intermediate during CO_2 methanation proceeded. The CO species were dissociated into carbon and oxygen species that proceed hydrogenated to form CH_4 and water. The dissociation of CO was reported to be the rate determining step on CO_2 methanation via the formation of CO intermediate [76] [77].

In general, CO_2 was dissociated over the catalyst support into carbon species (CO_{ads}) and oxygen species (O_{ads}), the H_2 was activated on the Ni surface to form the H_{ads} specied and finally reacted with CO_{ads} to generate CH_4 over the Ni surface [78]. The ability of H_2 activation would decrease as a result of thermal agglomeration of metallic Ni active so the selectivity of CH_4 would decreased due to lack of the H_{ads}

source. The previous work reported that 20wt% of Ni showed the highest activity and selectivity including stable performance during 10h of reaction but the conversion of CO_2 had decreased with increasing of Ni loading resulting in bigger crystallite size and lower surface area [52]. In this work, $36.5Ni/Al_2O_3$ catalysts showed higher conversion and selectivity without CO as byproduct probably due to the $36.5Ni/Al_2O_3$ can be reduced more easily at lower temperature as shown in the H_2 – TPR results.

The best catalytic performance were obtained on the $NiAl_{80}$ – 900 catalyst probably due to the lowest reduction temperature from H_2 – TPR results compared to all of spinel catalysts that can make the reduction more easily so that NiO was completely reduced to metallic Ni under reduction temperature conditions ($450^{\circ}C$ for 2.3h) before operated. The higher reduction rate of catalyst can improve the higher selectivity toward methane and higher activity [79]. Furthermore, the larger crystallite size of the bulk $NiAl_2O_4$ also showed high activity in the steam reforming of methane reaction that reported by Sahli. L et al.[61]

Although, the low surface area but the large total pore volume could provide sufficient exposed metallic active sites for reactants which accounted for its much higher catalytic [80].

In addition, the formation of $NiAl_2O_4$ in optimal ratio with NiO form (24.67wt% NiO and 75.33%wt based on 36.5%wtNi loading) on the $NiAl_{80}$ – 900 catalyst showed the positive effect to conversion, selectivity, and stability. The presence of $NiAl_2O_4$ could probably exert a positive effect on Ni sintering. The particle size of Ni metal can changed to smaller size after reduced in pure H_2 at high temperature and resulted in high disposition on the $NiAl_2O_4$ support[6, 61]. In the CO_2 reforming of methane, an enhancement of CO_2 conversion and CH_4 yield over $NiAl_2O_4$ was attributed to the presence of spinel structure that was active and highly stable, high dispersion of NiO on the spinel, and the interaction of nickel metal and the support [71]. Moreover, in the hydrogenation of acetylene over $Ni/NiAl_2O_4$ catalyst, the formation of $NiAl_2O_4$ can provide a stabilizing effect resulting in the inhibition of metal aggregation and lowering coking rate formation[13]. Furthermore, the formation of $NiAl_2O_4$ can improve of coke resistance, and enhance stability of catalyst for dry reforming of methane reaction [64]. In the present work, the presence of both NiO and $NiAl_2O_4$ led to high activity in CO_2 methanation due probably to the formation of active substoichiometric spinel structure and high dispersion of Ni on $NiAl_2O_4$ upon reduction.
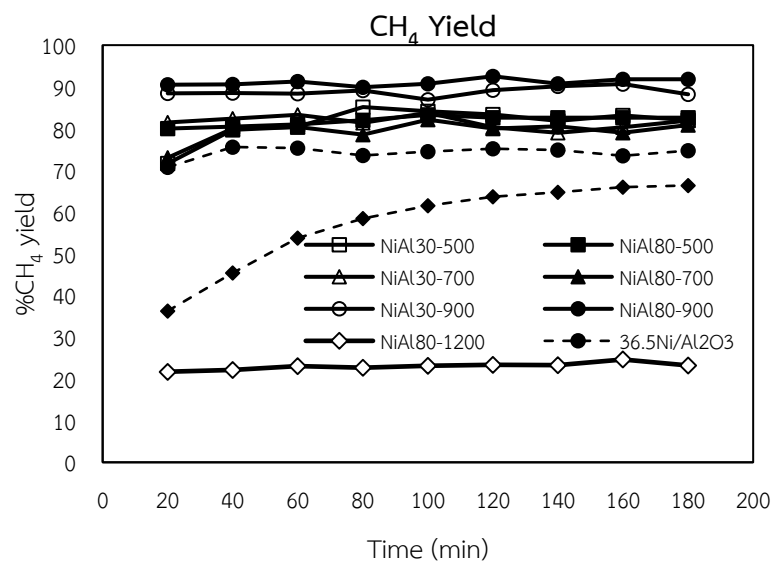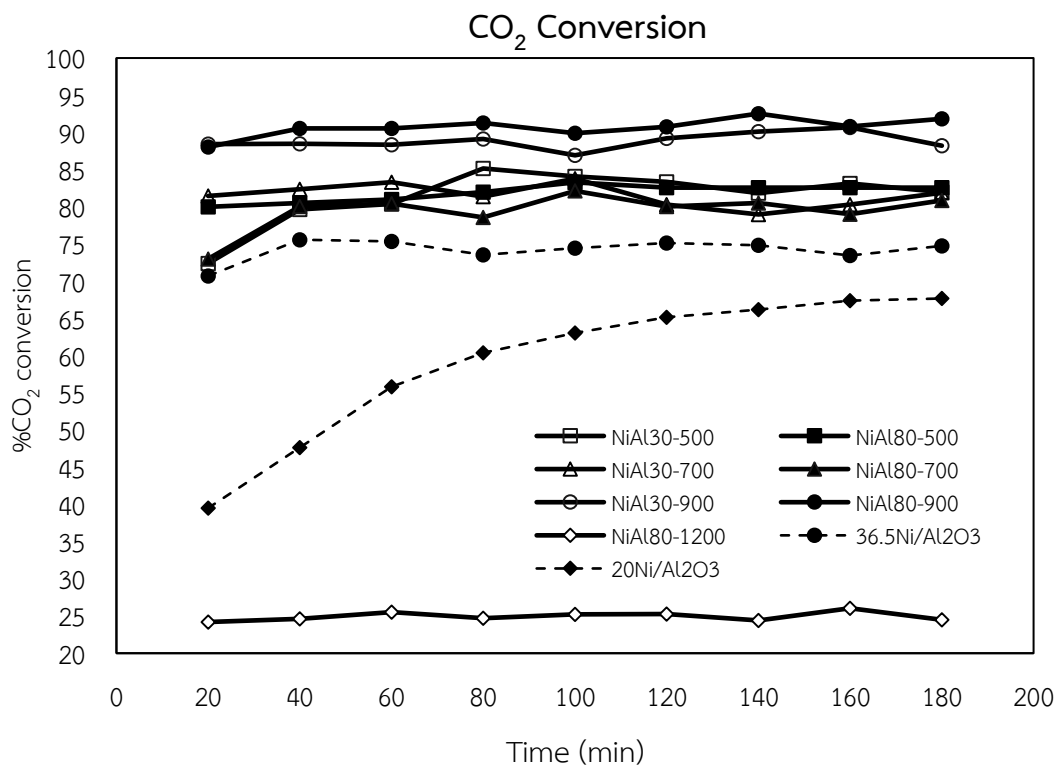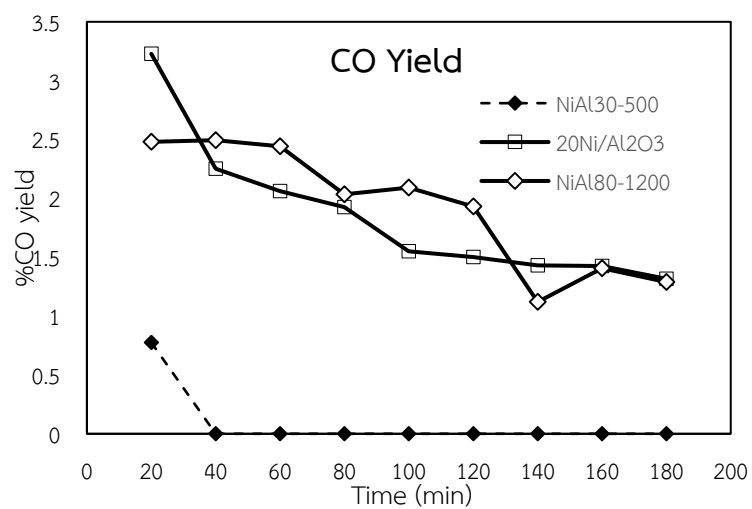
Figure 5.12 The activity of NiO/NiAl$_2$O$_4$-spinel based catalysts during CO$_2$ methanation reaction under atmospheric (1 atm) at 350°C for 180 min

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

Part II : The effect of noble metal loading on the NiO/NiAl$_2$O$_4$ spinel catalyst during CO$_2$ methanation

5.3 Characterization of metal-NiO/NiAl$_2$O$_4$ spinel catalysts

5.3.1 N$_2$ - physisorption (BET)

The adsorption-desorption isotherm of the metal doped onto NiO/NiAl$_2$O$_4$ spinel catalysts are shown in Figure 5.13. The type IV isotherms were exhibited indicated mesoporous (2-50 nm) with significantly reduced hysteresis loops for all catalysts. Also the doping of metal had no effect on the catalyst pore structure.
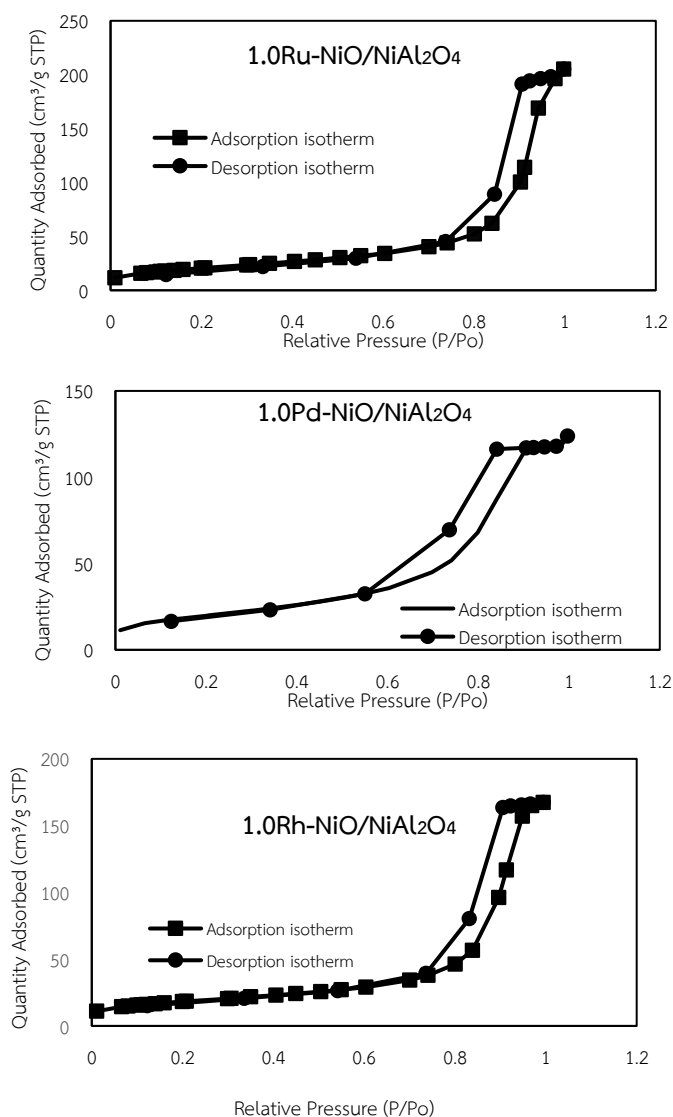
Figure 5.13 Adsorption-Desorption Isotherm of metal doped (Ru,Pd and Rh) into NiO/NiAl$_2$O$_4$ – spinel based catalysts

The results of surface area, pore volume and average pore size diameter summarized in Table 5.6. The BET surface area of unpromoted $NiAl_{80}$ − 900 catalyst decreased by adding noble metal in the order 1.0Ru-NiO/NiAl$_2$O$_4$ (75 m^2/g) > 1.0Pd-NiO/NiAl$_2$O$_4$ (71.5 m^2/g) > 1.0Rh-NiO/NiAl$_2$O$_4$ (65.4 m^2/g) because of pore blocking and/or agglutinated of metal into NiO/NiAl$_2$O$_4$. In addition, doping of Pd and/or Rh into NiO/NiAl$_2$O$_4$ catalysts had significant decreased to 0.19 and 0.26 cm^3/g, respectively. Interestingly, the total pore volume slightly increased to 0.32 cm^3/g by doping Ru metal. Moreover, the average pore diameter increased with Ru and Pd dopants to 12.3 and 11.4 nm, respectively. Opposite result was found for 1.0Rh-NiO/NiAl$_2$O$_4$ in which average pore diameter decreased to 6.7 nm.

Table 5.6 The BET surface area, total pore volume and average pore size diameter of metal doped onto NiO/NiAl$_2$O$_4$ − spinel based catalysts

Catalyst	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Avg pore diameter (nm)
$NiAl_{80}$ − 900	80.5	0.31	10.8
1.0Ru-NiO/NiAl$_2$O$_4$	75.0	0.32	12.3
1.0Pd-NiO/NiAl$_2$O$_4$	71.5	0.19	11.4
1.0Rh-NiO/NiAl$_2$O$_4$	65.4	0.26	6.7

5.2.2 X-ray diffraction (XRD)

The XRD patterns of metal doping (Ru,Rh and Pd) on $NiAl_{80}$ − 900 catalysts are shown in Figure 5.11a. The 1.0Ru-NiO/$NiAl_{80}$ − 900 catalyst exhibited three phases corresponding to NiO, NiAl$_2$O$_4$. The Ru metal dopant had no significant to gradate the XRD pattern of NiO and NiAl$_2$O$_4$ peaks. Also, the major XRD peaks of RuO$_2$ were not observed at 2θ degree 28.1°, 35.1°, 40.8° and 54.5° (PDF 70-2662) [81-83]. On the same way, the peak for rhodium oxide in RhO$_2$ and/or Rh$_2$O$_3$ phases from the XRD pattern of 1.0Rh-NiO/$NiAl_{80}$ − 900 were not detected probably to very small crystallite size less than 5 nm that the XRD cannot detect.

The XRD pattern of reduced catalysts at high temperature (450°C) are shown in Figure 5.14b. For 1.0Ru-NiO/NiAl$_{80}$ – 900 and 1.0Rh-NiO/NiAl$_{80}$ – 900 catalysts, there was the disappearance of NiO phased while presence of metallic Ni peaks at 2θ degree 44.6° , 52° and 76.5° (JCODS 89-7128) that evidenced completely reduced NiO into metallic Ni [13] and no observed the peak of Ru metallic may be the crystallite size decreased to less than 5 nm that XRD cannot detected. On the other hand, there was no clearly metallic Ni peak observed on 1.0Pd-NiO/NiAl$_{80}$ – 900 and NiO phase still presence. Similar, results of the XRD patterns of NiAl$_{80}$ – 900 catalyst were obtained. There were no clearly observation metallic Ni phase but the intensity of major NiO peak at 2θ degree 37° had decreased.
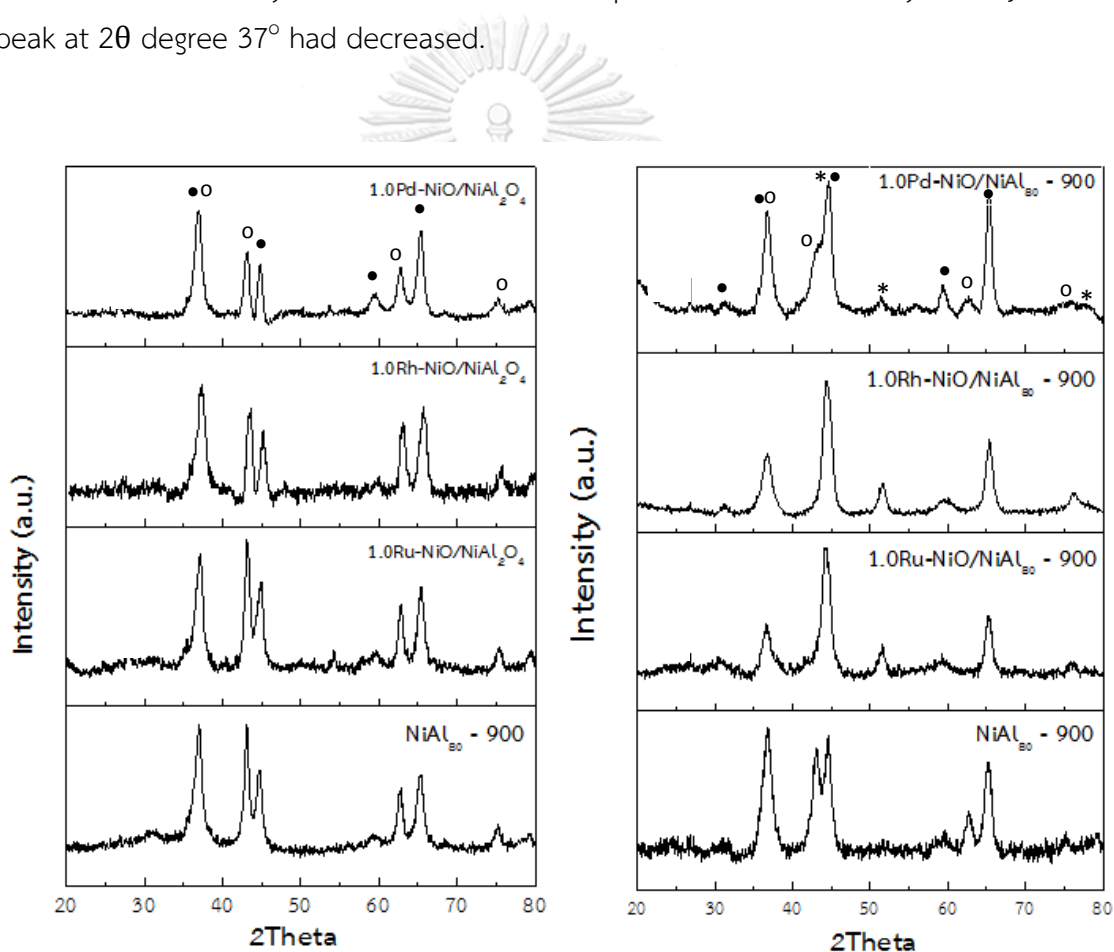

Figure 5.14. The XRD patterns of (a) fresh metal doping (Ru,Rh,Pd) on NiAl$_{80}$ – 900 catalysts and (b) reduced metal doping (Ru,Rh,Pd) on NiAl$_{80}$ – 900 catalysts ;

● NiAl$_2$O$_4$; ○ NiO; * Ni^0

The calculated crystallite size of Ni species are shown in Table 5.7. After doping Ru onto $NiAl_{80}$ – 900 the crystallite size of both NiO and $NiAl_2O_4$ were slightly decreased to 8.2 and 11.5 nm, respectively. In the same way, Rh metal dopant related to decrease the crystallite size of NiO and $NiAl_2O_4$ to 7.6 and 9.6 nm, respectively. Moreover, Pd metal dopant showed similar trend to decrease the crystallite size of NiO and $NiAl_2O_4$ to 8.3 and 9.1 nm, respectively.

Table 5.7 The average crystallite size and phase amount of metal doping (Ru,Rh,Pd) on $NiAl_{80}$ – 900 catalysts

Catalyst	Average crystallite size (nm)[a] of fresh catalyst		
	Nobel metal oxide form	NiO	$NiAl_2O_4$
$NiAl_{80}$ – 900	-	8.8	14.2
1.0Ru-NiO/$NiAl_2O_4$	N/D	8.2	11.5
1.0Rh-NiO/$NiAl_2O_4$	N/D	7.6	9.6
1.0Pd-NiO/$NiAl_2O_4$	N/D	8.3	9.1

[a] calculated by using Shcerrer equation.

5.2.3 Temperature programed reduction (H_2-TPR)

The reduction profiles of metal doping onto $NiAl_{80}$ – 900 catalysts are shown in Figure 5.15. The reduction temperature in unpromoted NiO/$NiAl_2O_4$ calcined 900°C was significantly decreased by Ru and Rh addition except Pd addition. The 1.0Ru-NiO/$NiAl_{80}$ – 900 catalyst had initial reduction temperature at 179°C corresponding the Ru species reduce to Ru oxide (RuO_2) in agreement with Masae K. et al [84], that reported the completely Ru oxide reduced below 200°C and the reduction of Ni species at 454°C. The higher reduction temperature at 775°C was attributed to the

reduction of nickel aluminate spinel [85]. For the 1.0Pd-NiO/NiAl$_{80}$ – 900 catalyst revealed two peaks of reduction at 421 that attributed to NiO reduction peak and NiAl$_2$O$_4$ spinel reduction peak at high temperature 745°C without palladium oxide reduction peak being observed. The 1.0Rh-NiO/NiAl$_2$O$_4$ catalyst exhibited the reduction peak at 246°C related to rhodium interact with nickel that higher than reduction peak of rhodium alone (exhibited around 112°C) [86]. The second peak of NiO reduction was exhibited at 436°C and the reduction peak of nickel aluminate spinel was evidenced at 781°C.
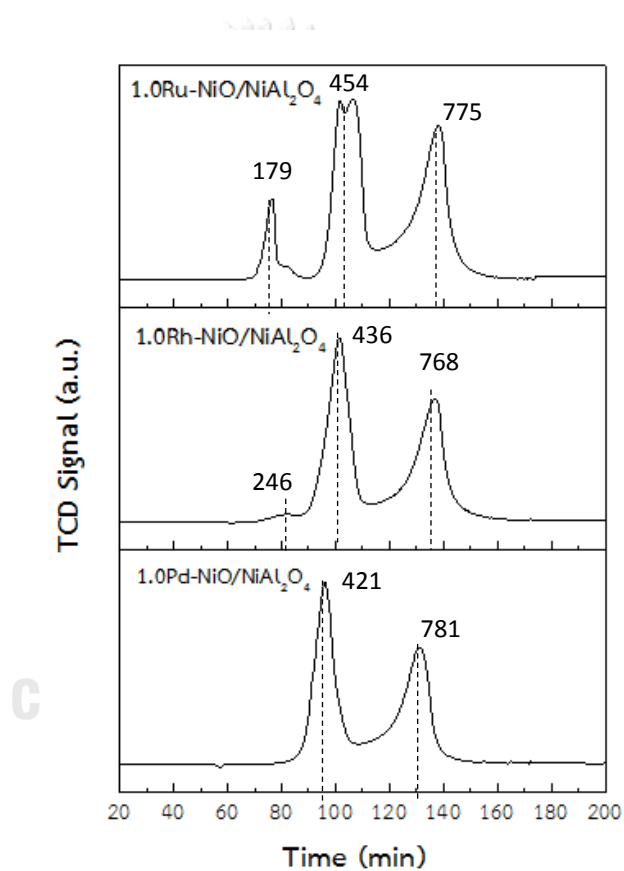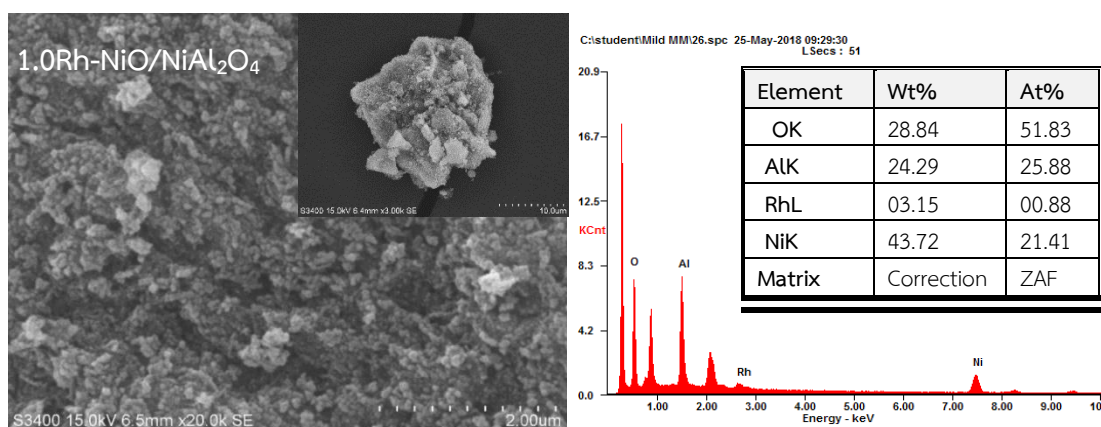

Figure 5.15 The H$_2$ – TPR profiled of metal doping onto NiAl$_{80}$ – 900 catalysts plot against time

5.2.5 Scanning Electron Microscopy (SEM)

The surface morphology of metal doping on $NiAl_{80}$ – 900 catalysts were investigated by scanning electron microscopy and are shown in Figure 5.16. For all the catalysts, the SEM – EDX results were similarly with the agglutination of nanoparticle cluster corresponding to decreasing of surface area which reported from N_2 – physisorption.

However, from XRD result the nobel metal phase were not detected but the X-ray analysis (EDX) confirmed the presence of noble metal. Moreover, The EDX spectrum revealed Ru, Rh, Pd, Ni, Al and O peak, indicating the presence of Ru ,Rh and/or Pd supported on $NiAl_2O_4$ phase.

1.0Ru-NiO/NiAl$_2$O$_4$

C:\student\Mild MM\19.spc 18-May-2018 09:42:06
LSecs : 30

Element	Wt%	At%
OK	25.58	48.00
AlK	23.73	26.41
RuL	01.56	00.46
NiK	49.13	25.12
Matrix	Correction	ZAF

1.0Rh-NiO/NiAl$_2$O$_4$

C:\student\Mild MM\26.spc 25-May-2018 09:29:30
LSecs : 51

Element	Wt%	At%
OK	28.84	51.83
AlK	24.29	25.88
RhL	03.15	00.88
NiK	43.72	21.41
Matrix	Correction	ZAF
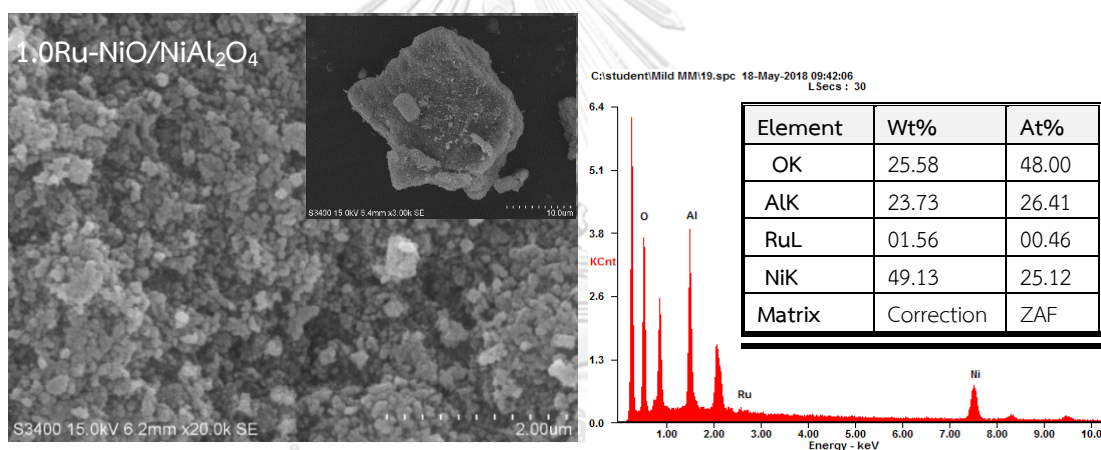
Figure 5.16 The SEM images of metal doping onto $NiAl_{80}$ – 900 catalysts

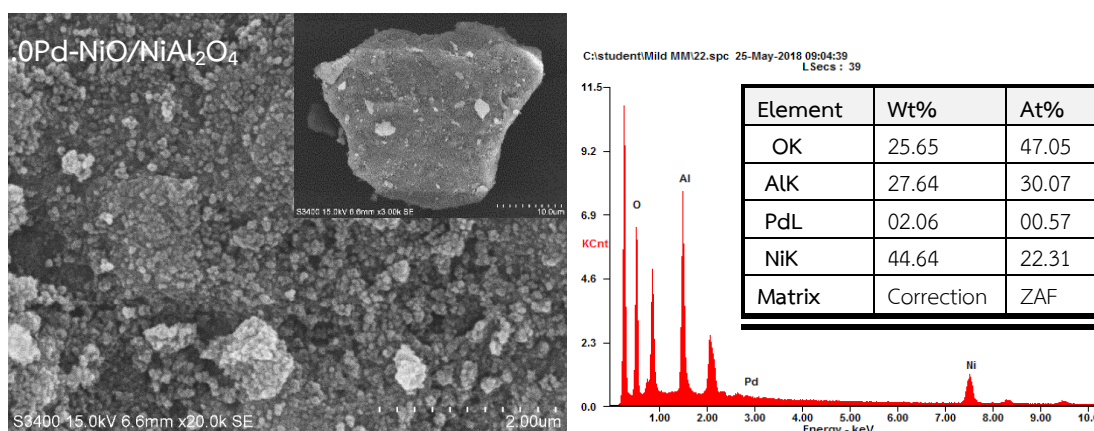## 5.4. Catalytic activity of noble metal doping on $NiO/NiAl_2O_4$ catalysts

The catalytic activity tests for CO_2 methanation were carried out at 350^oC for 180 min (3 h). The catalyst performances in terms of CO_2 conversion, CH_4 yield and CO yield are shown in Fig. 5.17. All metal doping catalysts exhibited 100% of methane selectivity corresponding to invisible CO formation during reaction test. The 1.0Ru-$NiO/NiAl_{80}$ – 900 catalyst showed the best stability and the highest conversion of CO_2 at 92% with 100% methane. The CO_2 conversion was closed to $NiAl_{80}$ – 900 catalyst activity. Meanwhile, the 1.0Rh-$NiO/NiAl_2O_4$ catalyst showed lower conversion of CO_2 at 49% conversion and finally the 1.0Pd-$NiO/NiAl_2O_4$ catalyst exhibited the lowest conversion at 11% among all the $NiO/NiAl_2O_4$ and Ni/Al_2O_3 series.

In addition, the activity had slightly decreased corresponding to presence of Rh and/or Pd promoter. For pure Pd/γ-Al_2O_3, the $CO_{(ads)}$ species are too strongly adsorbed, and the reaction is slow [33]. And the presence of NiO phase after reduction suggest an incomplete reduction of NiO to metallic active site, hence the lowest conversion of CO_2 was obtained.
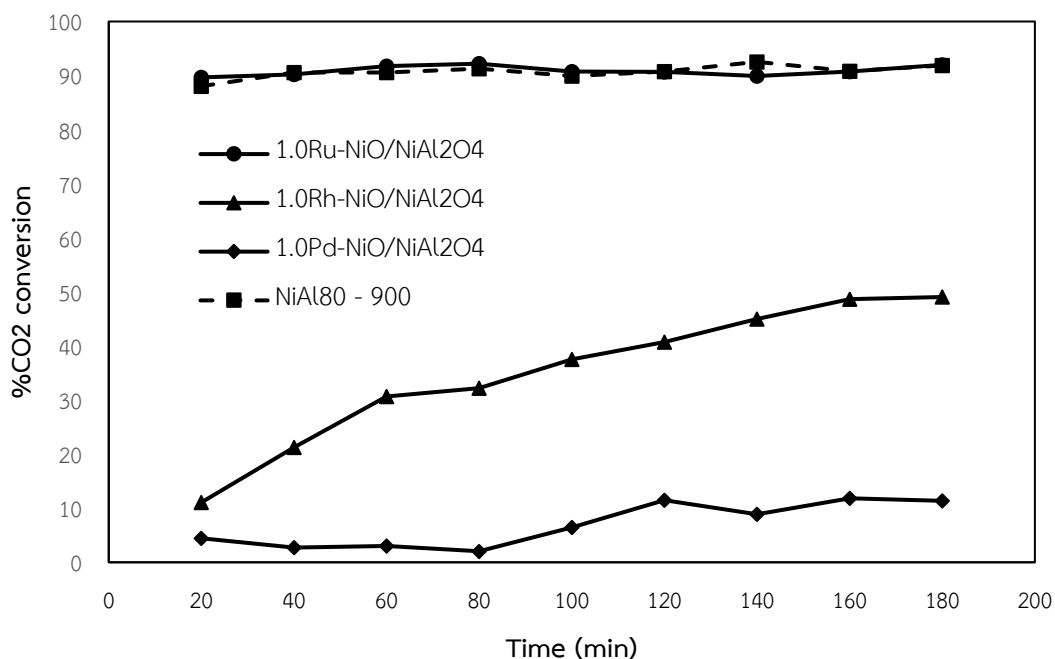
Figure 5.17 The activity of 1 wt% metal (Ru,Rh,Pd) doping into $NiO/NiAl_2O_4$-spinel based catalysts during CO_2 methanation reaction under atmospheric (1 atm) at 350°C for 180 min

However, the activities of 1.0Ru-$NiO/NiAl_{80}$ – 900 and $NiAl_{80}$ – 900 catalysts were similar during the reaction operated at 350°C. Neverless, the difference in activities testing for both of 1.0Ru-$NiO/NiAl_{80}$ – 900 and $NiAl_{80}$ – 900 catalysts were observed during the temperature profile reaction test from 250 to 350°C for each temperature kept for 1 h.

The 1.0Ru-$NiO/NiAl_{80}$ – 900 catalyst showed increased conversion of CO_2 form 19% at initial temperature 250°C to 43% and 74% at 275 and 300°C, respectively which exhibited higher performance than the $NiAl_{80}$ – 900 catalyst with 18 % CO_2 conversion at 250°C and slightly increased to 19% at 275°C and dramatically increased to 63% at 300°C.
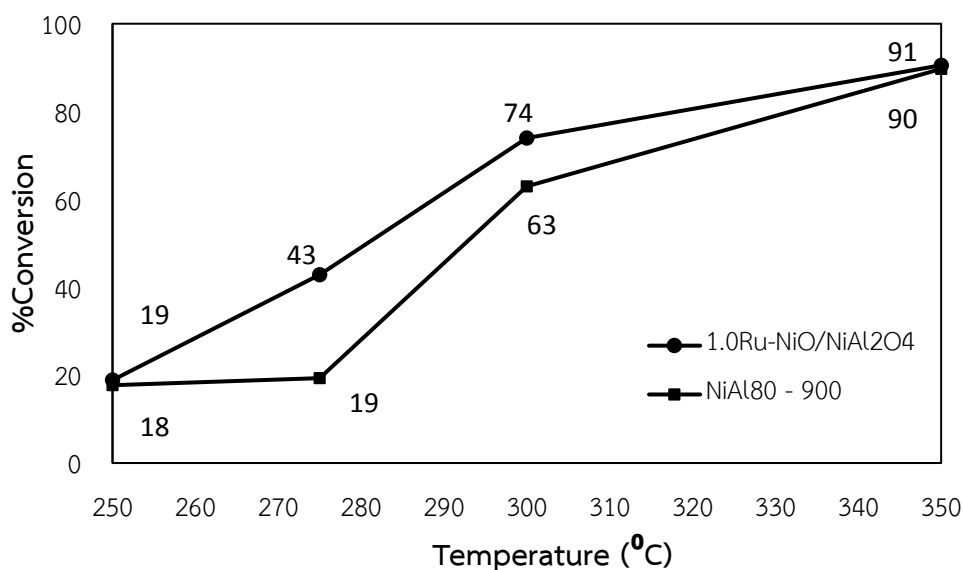
Figure 5.18 The activity of comparation of 1.0Ru-NiO/NiAl$_2$O$_4$ and NiAl$_{80}$ – 900 catalysts during CO$_2$ methanation reaction under atmospheric and temperature profile (250, 275 and 300°C) condition

In many previous works [6, 14, 20, 22], Ru metal was reported to be the most efficient catalyst for CO$_2$ methanation in terms of both conversion and selectivity. They showed the potentially a synergistic effect of the Ru containing with Ni as bimetallic catalyst that contributed to the high activity at lower temperatures. Thus, the results demonstrated that small amount of Ru can significantly improve the reaction rate at relatively low temperatures for Ni based catalysts as well as improved the selectivity of CH$_4$. The increase of the activity could be explained by the improved reducibility of Ni and the synergistic effect between Ni and Ru [87]. Furthermore, the adding of Ru decreased the crystallite size of Ni particles, resulting in higher dispersion including the enhanced reducibility by hydrogen spillover [55].

CHARTER VI

CONCLUSION

6.1 Conclusion

Among the various $NiO/NiAl_2O_4$ catalysts prepared by co-precipitation at different precipitation and calcination temperatures, the $NiO/NiAl_2O_4$ precipitated at 80^oC and calcined at 900^oC showed the best activity in CO_2 methanation at 350^oC with CO_2 conversion 92% and 100% methane without CO formation. The optimal of NiO and $NiAl_2O_4$ phase composition at 24.7%wt and 75.3%wt, could provide a stabilizing effect resulting in the inhibition of metal aggregation and the lower reduction temperature of NiO to metallic Ni. In addition, the calcination at higher temperature led to larger total pore volume, which was good to provide sufficient exposed metallic active sites for reactants.

Doping metal (Ru,Rh and Pd) onto $NiAl_{80}$ – 900 catalysts resulted in lower surface area and less of pore volume except for $1.0Ru-NiO/NiAl_{80}$ – 900 catalyst that retained similar physical properties as the unpromoted one.

Comparison to the unpromoted catalyst, the Ru promoted $NiO/NiAl_{80}$-900 exhibited higher activity at low temperature ($250 - 300^oC$) due to a decrease of the crystallite size of Ni particles resulting in higher dispersion and the enhanced reducibility due to hydrogen spillover and the synergistic effect between Ni and Ru. For the Rh- and Pd- promoted ones, poorer catalytic performances were obtained.

6.2 Recommendations

6.2.1 The $NiO/NiAl_2O_4$ spinel – based catalyst should be modified for higher activity at lower temperature (below 300^oC).

6.2.2 The effect of various ratios of Ni/Al for CO_2 methanation catalysts should be investigated.

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APPENDIX

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Preparation of NiO/NiAl2O4 catalysts by using Co-precipitation method

Preparation of NiO/NiAl$_2$O$_4$ catalysts by using Co-precipitation method with Ni/Al molar ratio 1/2 is presented as follows:

Precursor

- Nickel nitrate (Ni (NO$_3$)$_2$ • 6H$_2$O), MW = 290.79

- Aluminium nitrate (Al (NO$_3$)$_3$ • 9H$_2$O), MW = 212.996

Calculation

For concentration of (Ni (NO$_3$)$_2$ • 6H$_2$O) at 0.17 mol/lit

Using (Ni (NO$_3$)$_2$ • 6H$_2$O) = 0.17 mol/lit x 290.79 g/mol

= 49.43 g/lit

For concentration of (Al (NO$_3$)$_3$ • 9H$_2$O) at 0.34 mol/lit

Using (Al (NO$_3$)$_3$ • 9H$_2$O) = 0.34 mol/lit x 212.996 g/mol

= 72.418 g/lit

Based on total volume 1 lit (1000 ml)

For 1 liter using (Ni (NO$_3$)$_2$ • 6H$_2$O) 49.43 g

$\therefore$ 0.5 liter required (Ni (NO$_3$)$_2$ • 6H$_2$O) = $\dfrac{49.43 \times 0.5}{1}$ = 24.71 g

For 1 liter using (Al (NO$_3$)$_3$ • 9H$_2$O) 72.418 g

$\therefore$ 0.5 liter required (Al (NO$_3$)$_3$ • 9H$_2$O) = $\dfrac{72.418 \times 0.5}{1}$ = 36.209 g

Preparation of Ni/Al₂O₃ catalysts by using impregnation method

Preparation of Ni/Al$_2$O$_3$ catalyst by using Co-precipitation method with Ni/Al molar

ratio 1/2 is presented as follows:

Precursor

- Nickel nitrate (Ni (NO$_3$)$_2$ • 6H$_2$O), MW = 290.79

- Aluminum oxide (Al$_2$O$_3$), MW = 101.961

Based on 5 g of Al$_2$O$_3$ commercial supported catalyst

Find mole of Al$_2$O$_3$

$$\text{Mol of Al}_2\text{O}_3 = \frac{5 \text{ g}}{101.961 \text{ g/mol}}$$

$$= 0.049 \text{ mol Al}_2\text{O}_3$$

For   Al$_2$O$_3$ 101.961 g presence of Al = 26.98 X 2

$$\therefore \quad \text{Al}_2\text{O}_3 \ 5 \text{ g presence of Al} = \frac{26.98 \times 2 \times 5}{101.961}$$

$$= 2.646 \text{ g}$$

Find mole of Al and mole of Ni

$$\text{Mol of Al} = \frac{2.646 \text{ g}}{26.98 \text{ g/mol}}$$

$$= 0.098 \ \text{mol Al}$$

So, mol of Ni   =   0.098 X 0.5

$$= \ 0.049 \text{ mol Ni}$$

Find gram of Ni

Ni 0.049 mol :   0.049 mol X 58.69 g/mol

= 2.875 g Ni

Find (Ni (NO$_3$)$_2$ • 6H$_2$O) precursor requirement

Ni 58.69 g require (Ni (NO$_3$)$_2$ • 6H$_2$O) 290.79 g

So,   Ni 2.875 g require (Ni (NO$_3$)$_2$ • 6H$_2$O) = $\dfrac{290.79 \times 2.875}{58.69}$ = 14.24 g

Find %wt loading of Ni based on Al$_2$O$_3$ 5 g

For Al$_2$O$_3$ 5 g contained Ni 2.875 g

∴   Total amount of catalyst = 7.875 g

So, catalyst 100 g contained Ni = $\dfrac{100 \times 2.875}{7.875}$

= 36.5 g

∴ The molar ratio of Ni/Al = 1/2 equal 36.5%wt of Ni loading

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Preparation of metal dope onto NiAl$_2$O$_4$ catalysts by using impregnation method

Preparation of 1%wt metal dope onto NiAl$_2$O$_4$ catalysts by using impregnation method are presented follow:

Precursor

    - Ruthenium (III) nitrosyl nitrate solution (Ru (NO)(NO$_3$)$_3$) , concentration = 0.75 g in 50 ml solution

    - Tetramminepalladium (II) chloride monohydrate (Pd(NH$_3$)$_4$Cl$_2$ • H$_2$O) , assay Pd 39%

    - Rhodium (III) Chloride hydrate (RhCl$_3$ • xH$_2$O) , assay Rh 42 %

Support

    - NiAl$_2$O$_4$ prepared by co-precipitation method with Ni/Al molar ratio 1/2 precipitated at 80°C and calcined at 900°C (NiAl$_{80}$ – 900)

Calculation

    For 1%wt Ru loading on NiAl$_{80}$ – 900 catalyst

        Based on 1 g NiAl$_2$O$_4$ supported catalyst

            NiAl$_2$O$_4$ 99 g required Ru 1 g

        So,   NiAl$_2$O$_4$ 1 g required Ru 0.01 g

    Find the amount of precursor requirement

        From Ru 0.75 g contained in solution 50 ml

        So,   Ru 0.01 g required solution 0.67 ml

    For 1%wt Rh loading on NiAl$_{80}$ – 900 catalyst

        Based on 1 g NiAl$_2$O$_4$ supported catalyst

            NiAl$_2$O$_4$ 99 g required Rh 1 g

        So,   NiAl$_2$O$_4$ 1 g required Rh 0.01 g

Find the amount of precursor requirement

From $RhCl_3$ 100 g contained in Rh 42 g

So,   Rh 0.01 g required $RhCl_3$ = 0.0042 g

For 1%wt Pd loading on $NiAl_{80}$ – 900 catalyst
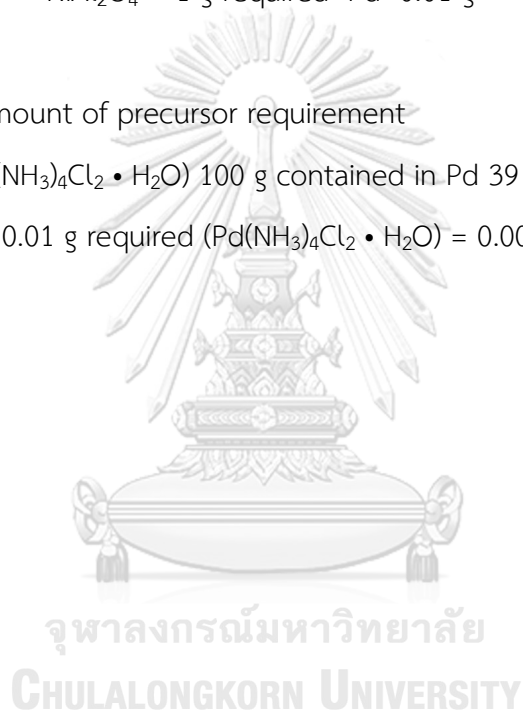
Based on 1 g $NiAl_2O_4$ supported catalyst

$NiAl_2O_4$ 99 g required Pd 1 g

So, $NiAl_2O_4$ 1 g required Pd 0.01 g

Find the amount of precursor requirement

$(Pd(NH_3)_4Cl_2 \bullet H_2O)$ 100 g contained in Pd 39 g

So,   Pd 0.01 g required $(Pd(NH_3)_4Cl_2 \bullet H_2O)$ = 0.0039 g

APPENDIX B

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye – Scherrer's equation

The crystallite size was calculated from the half – height width of the diffraction peak of XRD pattern using the Debye – Scherrer's equation.
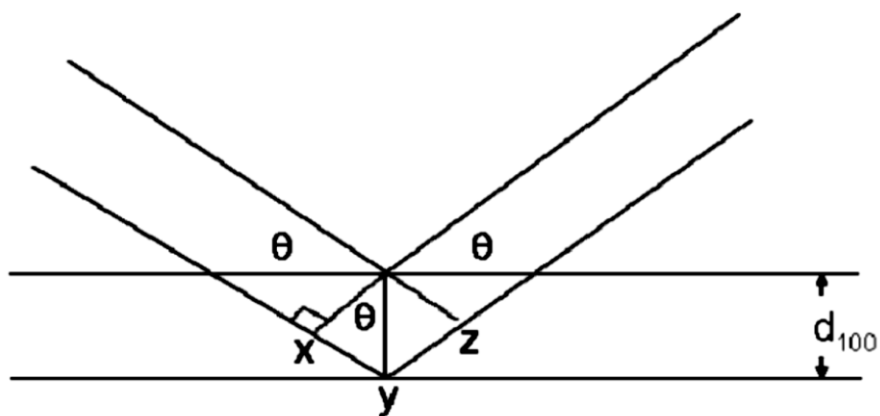

Figure B.1 Derivation of Bragg's Law for X-ray diffraction

$$xy = yz = d \sin \theta$$

Thus
$$xyz = 2d\sin \theta$$

But
$$xyz = n\lambda$$

Bragg's Law

So
$$d = \frac{n\lambda}{2\sin\theta}$$

The Bragg's Law was derived to B.1
From Scherrer's equation:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{B.1}$$

Where
D = Crystallite size, Å
K = Crystallite-shape factor = 0.9
λ = X-ray wavelength, 1.5418 Å for CuKα
θ = Observes peak angel, degree
β = X-ray diffraction broadening, radian

The X-ray diffraction broadening (β) is the pure width of powder diffraction free from all broadening due to the experimental equipment. α-alumina is used as a standard sample to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening (β) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta = \sqrt{B_M{}^2 - B_S{}^2} \qquad\qquad (B.2)$$

Where
B_M = The measured peak width in radians at half peak height.
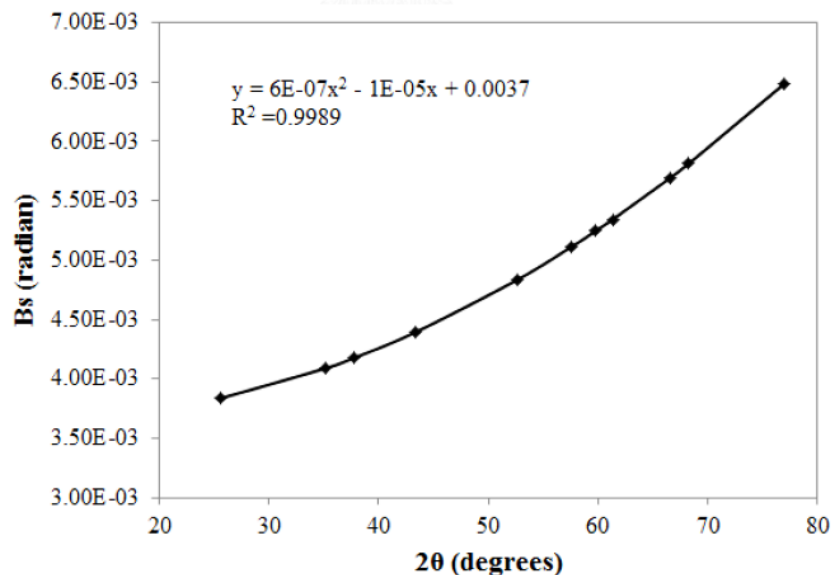B_S = The corresponding width of the standard material.

Figure B.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using α-alumina as a standard.

APPENDIX C

CALCULATON OF CO_2 CONVERSION AND SELECTIVITY

The catalyst performance for the CO_2 methanation was evaluated in terms of activity for CO_2 conversion reaction rate and selectivity

Activity of the catalyst performed in term of CO_2 conversion which is defined as moles of CO_2 converted from feed inlet:

$$CO_2 \text{ conversion (\%)} = \frac{[\text{area of } CO_2 \text{ in feed} - \text{area of } CO_2 \text{ in product}]}{\text{area of } CO_2 \text{ in feed}} \times 100 \qquad (D.1)$$

Which area of CO_2 peak obtained from GC solution program based plot on TCD (GC-14B)

Selectivity is product is defined as weight of product (A) form with respect to total area of product:

$$\text{Selectivity of A (mol\%)} = \frac{\text{area of A product}}{\text{total area of all product}} \times 100 \qquad (D.2)$$

VITA

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