HYDROGEN PRODUCTION VIA ETHANOL STEAM REFORMING OVER
ALUMINA SUPPORTED RHENIUM-NICKEL CATALYST

By
MR. Peat KHEMNARONG

A Thesis Submitted in Partial Fulfillment of the Requirements
for Master of Engineering (CHEMICAL ENGINEERING)
Department of CHEMICAL ENGINEERING
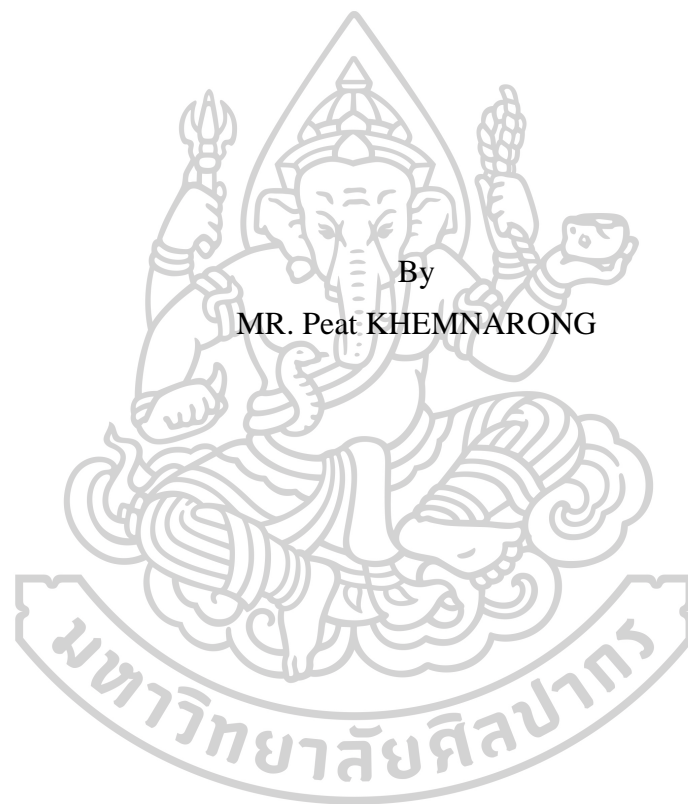Graduate School, Silpakorn University
Academic Year 2021
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ตัวรองรับอลูมิน่าเป็นตัวเร่งปฏิกิริยา

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59404204 : Major (CHEMICAL ENGINEERING)

Keyword : Ethanol Steam reforming, Hydrogen, Re-Ni catalyst, Anti-coke formation

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Renewable hydrogen was regarded as an ideal energy carrier for the future due to its high energy content, cleanliness, and abundance. Among the various renewable sources, ethanol is a promising candidate since it is simply produced by fermentation of biomasses and has reasonably high hydrogen content. Supported Ni catalysts widely used in ethanol steam reforming (ESR); however, it was seriously suffered by higher methane formation and rapid deactivation due to carbon deposition. In this study, small amount of rhenium (Re) was promoted on Ni/Al_2O_3 catalysts to perform the hydrogen production from ESR in the temperature range of 450-650 ^{o}C to evaluate the effects of Re addition on the catalyst activity and stability. The catalysts were prepared by wetness impregnation method and calcined at 600 ^{o}C in air for 6 h then characterized by various techniques such as N_2 physisorption (BET method), XRD, SEM-EDX and, H_2-TPR. The characterization showed that both Re and Ni particle were highly dispersed on the catalysts surface. The experimental results indicated that 3%Re-Ni/Al_2O_3 catalyst provides considerably higher reforming activity and excellent resistance towards carbon deposition in comparison with Ni/Al_2O_3. Promoting a small proportion of Re (3 wt.%) on Ni/Al_2O_3 causes the significant influence by greatly reduced the CO formation from a high of up to 20% to less than 10% throughout the reaction time, and also indicated a rather stable catalytic performance for over 60 h time-on-stream without any deactivation.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Renewable energy resources have shown a great attention at present global scenario due to three vital factors: population, per capita energy consumption, and economic growth [1] which leads to progressive depletion of conventional fossil fuels (coal, petroleum, natural gas) since, the majority of the energy consumed today comes from non-renewable fossil fuels. This has not only depleted fossil fuel stocks, especially crude oil, but has also resulted in significant environmental pollution. [2-4]. Extensive research attempts are being made to develop alternative renewable energy sources [5].

Unlike fossil fuels, hydrogen gas is a clean source of energy that could be utilized without releasing any carbon-based pollutants into the environment [6]. Furthermore, it has the largest energy content per unit weight (i.e., 120.7 kJ/g). Hydrogen, when produced from renewable biomass sources, has been regarded as an ideal energy carrier for the sustainable energy development [6, 7]. Hydrogen can be used in fuel cells to produce electricity very efficiently and cleanly [8]. Therefore, it is expected that in the nearly future, hydrogen will be used in a large extent. Currently, the most common method for hydrogen production is steam reforming of non-renewable hydrocarbons, however, most of the time, this process not pay that much attention to the follow-up costs of the environmental impact [9]. Alcohols are the best candidates among the several families of oxygenated fuels. Methanol has attracted the interests regarding the beneficial usage in fuel cells. [10, 11] however, it has a consequence on both the health and environmental issues concerned with its use. Compared to methanol, ethanol is more attractive as it is a cheap, non-toxic, and widely available biofuel that can be produced renewably from biomass, whereas the significant proportion of methanol is synthesized from fossil fuels via the syngas-to-methanol route. [12].

The potential in application of hydrogen produced from biomass in fuel cells has greatly attracted the interest among several researchers since, the utilization of bio-fuels for hydrogen production has long - term environmental benefits considering the CO_2 generated is consumed for biomass growth and thus offering a carbon dioxide neutral energy supply [13]. Up to date, steam reforming (SR), partial oxidation (POX) and oxidative steam reforming (OSR) were proposed to be efficient processes for hydrogen production from ethanol [14]. Among the numerous pathways for hydrogen production from ethanol, ethanol steam reforming is the most investigated process due to its highest hydrogen yield, lower reaction rates and a marked endothermicity (Eq. (1))

$$CH_3CH_2OH+3H_2O \rightarrow 6H_2+2CO_2 \qquad \Delta H298°=174.2 \ kJ/mol \qquad (1)$$

The selection of catalysts has an important role in the reforming process, as it may advance to different reaction pathways. Since, the core of ethanol steam reforming is the surface reaction, the general requirements for catalytic surfaces are: (i) C–C bond breaking to produce CO_x (CO and/or CO_2) and CH_4 rather than promote the C–O bond formation; (ii) reforming of these C_1 intermediates (CO, CH_4) to generate H_2 and CO_2; (iii) activate water/oxygen to produce highly mobile oxygen and to inhibit coke formation. Based on the above considerations, active metals mainly enhanced the C–C bond cleavage and the diffusion/transformation of the intermediates took place over the metal–support interface [15]. Currently, the active metals with supported chosen for this reaction can be divided into two groups: noble metals which include Rh, Pt, Pd, and Ru, and nonnoble metals such like Ni, Cu and Co. [16]. Among the numerous active phases, the noble metal group (Rh, Pd, Pt, and Ru) exhibits an outstanding result by showing high activity and selectivity of hydrogen in the ESR [6, 17, 18]. Nevertheless, the high cost of noble metal catalysts made it far from commercial use. Therefore, the most researched catalysts for hydrogen production via the ESR route which are much cheaper and widely available are Ni- and Co-based materials [19-21]. The Ni-based catalyst was very well known for its high activity for C-C bond cleavage and high performance in H_2 production [22-24].

Nickel-based catalysts is industrially used for hydrogen production via methane steam reforming due to their high activity for C-C bond cleavage and low cost, which currently takes up about 80% of hydrogen capacity worldwide. However, Ni based catalysts seriously suffered from rapid deactivation from heavy coke formation as well as Ni particles sintering. In order to improve the catalysts stability, the method of modifying the support or Ni species were developed [17, 25]. Another disadvantage for Ni based catalysts was the high CO production owing to the lack of WGS reaction. Therefore, the addition of the dopants to the support is the most common way to prevent carbon deposition, Ni particles sintering as well as decreasing the CO formation. There was evidence that the addition of Re could enhance the catalytic activity, selectivity, and long-term stability in various reactions by raising the metal dispersion which results in preventing agglomeration of particles and also facilitate water dissociation leading to improving the water gas shift activity [26-28].

Obviously, the catalytic stability associated with the resistance to coke deposition still is the main challenge of the catalyst for ethanol steam reforming, which greatly relies on the development of new catalysts and process design. Given this background, the objective of the present study was to develop a highly efficient, more stable and cost-effective catalyst for SRE.

1.2 Objective of research

To investigate the effect of Re loading amount over Ni/Al$_2$O$_3$ catalysts and reaction temperature on hydrogen production performance via steam reforming of ethanol.

1.3 Scope of research

The catalytic stability and performances of hydrogen production from ethanol steam reforming over Re-Ni/Al$_2$O$_3$ catalysts prepared by wetness impregnation method with different Re loading amount of 1, 3, 5 wt% have been investigated in various

temperature of 450, 550, 650 $^{\circ}$C. Catalyst properties will be characterized using XRD, BET, SEM-EDX, and H_2-TPR techniques.

CHAPTER 2
THEORY

2.1 Renewable energy

The continuous growth in global population and civilization advancement have resulted in an exponential rise in energy demand. Energy sources are classified into three main categories: fossil fuels, nuclear resources, and renewable energy sources. [29]. Although fossil fuels are not sustainable and caused serious environmental and health problems, they are still the main contributor to the energy sector. The utilization of fossil fuels also resulted in the depletion of ozone, climate changes, environmental problems, and increasing health issues for all living organisms on earth. The increasing in CO_2 emissions cause a significant increase in the average CO_2 level in the atmosphere, which was 280 ppm in the pre-industrial age and has now risen to 390 ppm [30]. To protect the environment and prevent possible climate change, sustainable and clean technologies known as renewable energy technologies have been developed.

Renewable energy is energy that has been derived from earth's natural resources that are not finite or exhaustible and are naturally replenished overtime on a human timescale. Renewable energy sources potentially supply pollution-free energy while emitting zero or almost zero percent of greenhouse gases. Nowadays, newly developed and less-expensive technologies of capturing and utilizing renewable energy from diverse renewable sources such as solar energy, wind energy, geothermal energy, marine energy, biomass energy, biofuels, and many more have been discovered. However, various renewable energy technologies currently in use in the twenty-first century, and many of these technologies are still under development. Renewable energy supplied an estimated 19% of worldwide final energy consumption in 2012, and rising to 23.7 percent in 2014.[31]. Recently, hydrogen fuel cells have received a lot of interest in the energy aspect. A fuel cell, as an electrochemical device, could very well convert chemical energy into electricity. Fuel cells provide a number of advantages, with a

relatively high efficiency. Conventional fuel cells have efficiencies ranging from 40% to 50%, whereas internal combustion engines have efficiencies ranging from 20% to 35%. Fuel cells, on the other hand, produce just water and heat as byproducts of the process, with no greenhouse gases released (CO_2, NO_x, SO_x, etc.) and zero harmful emissions. Hydrogen production in a mobile device, such as proton exchange membrane (PEM) and fuel cells, with high power density, moderate temperature operation, and no pollutants emission, is a promising energy source for portable applications. However, hydrogen does not naturally exist in sufficient quantities, although it has been regarded as an ideal energy carrier to favor sustainable energy development.

2.2 Hydrogen production technology

Hydrogen as a fuel has regarded as a promising energy carrier and an alternative to fossil fuels due to its high energy density (120 MJ/kg) compared to gasoline (44 MJ/kg) and liquefied natural gas (49.4 MJ/kg) [32]. The use of hydrogen not only minimizes greenhouse gas emissions, but could also lessen other harmful emissions that affect the environment and contribute to global warming. Currently, hydrogen is mostly used in oil-refining industry and synthetic nitrogen fertilizer production. However, since hydrogen is considerably more expensive to produce than conventional fossil fuels, it is only utilized for a small portion of energy production. The average cost of hydrogen production exceeds that of fossil fuels by at least five times ($16.26/Gasoline Gallon Equivalent (GGE) against $3.09/GGE) [33]. Regarding to the devastating effects of climate change from excessive usage of fossil fuels, hydrogen is increasingly promoted as an appealing option for long-term energy management.
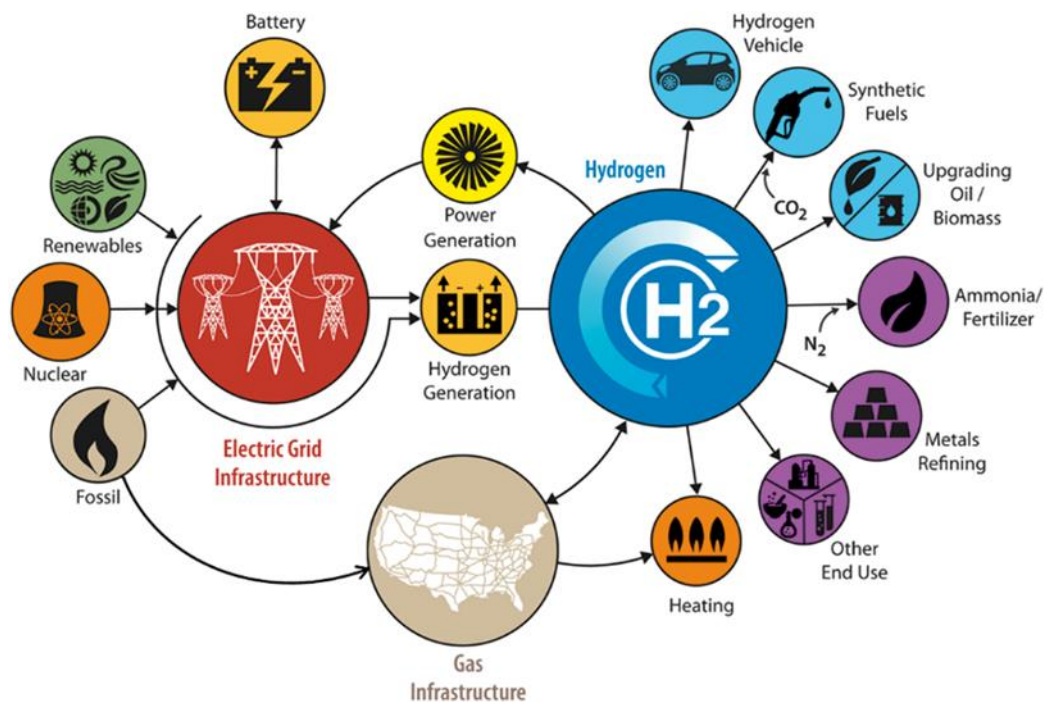
[1]**Figure 2.1** The H_2@Scale Vision-Hydrogen can be produced from diverse domestic resources and is a central input to many important ends uses in the industrial, chemical, and transportation sectors.

The lack of logistics and appropriate infrastructure is a significant barrier in the storage and transportation of liquid hydrogen. Steel alloys, for example, are not ideal for storing liquid hydrogen. The use of hydrogen as a fuel for mobile and remotely applications would demand numerous research efforts in the development of noncorrosive, diffusion-resistant materials capable of safely and properly preserving liquid hydrogen. The hydrogen would be stored in underground reservoirs as part of this project[36]. However, before hydrogen could be used in liquid form, a suitable technology with favorable economic and environmental implications must be developed.

According to the International Renewable Energy Agency (IRENA), H_2 is created from a variety of sources. The vast majority of hydrogen (95%) is generated from fossil fuels such oil, natural gas, and coal [37]. The largest part of the industrially

---

[1] 34.   Miller, E.L., et al., *US Department of Energy hydrogen and fuel cell technologies perspectives.* MRS Bulletin, 2020. **45**(1): p. 57-64.

produced H_2 is obtained from methane steam reforming, while gasification of oil and coal follows shortly afterwards. These techniques of synthesizing H_2 release greenhouse gases, which are believed to be the main causes of climate change [38]. Electrolysis yields only a little portion of the world's H2 supply, roughly 4%. Although electrolysis looks to be a clean technique of producing hydrogen, it still demands a considerable amount of energy. If the required energy to separate water atoms into H_2 and oxygen (O_2) atoms originates from fossil fuels, the process is still far from carbon-neutral. As a matter of fact, a fully developed hydrogen economy is essential to prevent global warming and play a vital role in providing sustainable future with great environmental, economic, and societal advantages.

2.3 Ethanol steam reforming

Currently, hydrogen production methods are getting more efficient, affordable, and environmentally friendly and less fossil fuel dependent as the innovative hydrogen production pathways and systems are developed [39]. Numerous feeds that contain the hydrogen atom in its composition can be used to produce hydrogen. The conventional process for producing hydrogen is primarily focused on the reforming of natural gas or naphtha. However, producing hydrogen through renewable energy sources rather than fossil fuels offers countless ecological benefits because fossil fuel is not a sustainable energy source. Biofuels are one of the most outstanding renewable sources with mass acceptance for hydrogen generation.

From the several feedstocks available, alcohols are absolutely fascinating alternatives since they decompose efficiently in the presence of water and produce a hydrogen-rich mixture at a lower temperature. Methanol steam reformation has recently received a lot of attention. The greatest drawback is its high toxicity. Among the different processes proposed, steam reforming of ethanol for hydrogen production is incredibly attractive because ethanol can be produced renewably by fermentation of biomass sources such as energy plants, agro-industrial wastes, forestry residue materials, and organic fraction of municipal solid waste. This is renowned as bioethanol, which is a mixture of ethanol and water with a molar ratio of 1:13 (about

12 wt percent ethanol). With its relatively high hydrogen content, availability, low toxicity, convenience of transportation, and storage and handling safety, bioethanol is promising alternatives. As a result, it lends itself well to a distributed-production approach and can be utilized for on-demand hydrogen production both automotive and distributed power generating applications [40]. More significantly, ethanol is CO_2 neutral because the CO_2 generated by steam reforming is consumed by biomass growth, resulting in a nearly closed carbon loop that does not contribute to greenhouse gas emissions.

Due to the obvious growing interest in ethanol, a lot of investigations on hydrogen production from ethanol have been performed. Different technologies, such as steam reforming, partial oxidation, and autothermal reforming, can be used to produce hydrogen from ethanol. Steam reforming of ethanol has been considered as the most effective approach. However, this process has several drawbacks, such as the formation of byproducts and rapid catalyst deactivation. Furthermore, it is a highly endothermic process, requiring the addition of heat for energy.

The reactions involved for producing hydrogen from ethanol include (i) steam reforming (ii) high temperature water-gas shift reaction (iii) low temperature water gas shift reaction and (iv) selective carbon monoxide oxidation.

The overall reactions are as follows:

Steam reforming

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad , \Delta H^0_{298K} = 174 \text{ k}J/mol \qquad (2.1)$$

Water-gas shift

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad , \Delta H^0_{298K} = -41 \text{ k}J/mol \qquad (2.2)$$

Selective CO oxidation

$$CO + \frac{1}{2}O_2 \leftrightarrow CO_2 \quad , \Delta H^0_{298K} = -283 \text{ k}J/mol \qquad (2.3)$$
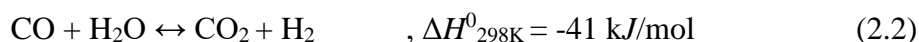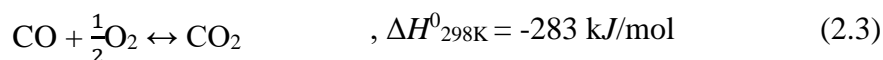
Many side reactions in the steam reforming process yield considerable amounts of CO and CH_4. Since CO can damage the fuel cell, this must be suppressed to less than 10 ppm. Water-gas shift reactors are therefore applied to lessen the outlet CO concentration while producing more H_2. Even after the low temperature shift reactor, the CO concentration is approximately 1%, which is lowered further by selective oxidation. The major difficulty is to provide develop highly active, selective, and long-lasting catalysts for the reactions involved.

CHAPTER 3
LITERATURE REVIEWS

In this chapter, several researches related to the background of hydrogen production from steam reforming of ethanol, methanol and other candidates over various catalysts and conditions has been reviewed, which leaded to greater understanding the neutral of the steam reforming reaction

The selection of different raw materials and reaction for hydrogen production depends on technical, economical or even political factors. Many hydrocarbons, notably gasoline, natural gas, methanol, propane, and ethanol, can be used to synthesize hydrogen. However, the majority of hydrogen energy is still produced from non-renewable natural gas via reforming processes that are still dependent on a fossil fuel system.

The most energy-efficient technology currently available is steam reforming of natural gas to create H_2 [14]. Furthermore, the reforming process could generate H2 both from the hydrocarbon fuels and water. Although the reaction is fast, H2 synthesis is limited by thermodynamic equilibrium. Moreover, when applied to large-scale production, catalytic steam reforming of natural gas is the most cost-effective technique when compared to the other technologies [41].

Recently, the rising concern with the reduction of greenhouse gas emissions and atmospheric pollution increased the interest in clean and renewable feedstocks. Based on the sustainable development, the steam reforming of ethanol is a promising choice in H_2-based energy systems due to it renewability, availability, low toxicity and it could be easily decomposed in the presence of water to form a hydrogen-rich gas mixture. In addition, the steam reforming of ethanol for hydrogen production is thermodynamically feasible [42]. Stoichiometrically, the overall steam reforming reaction of C_2H_5OH could be represented as follows [43].

$$C_2H_5OH + 3H_2O \rightarrow CO_2 + 6H_2 \qquad\qquad (3.1)$$
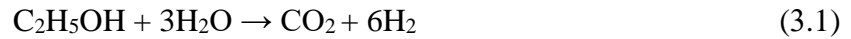
According to Haryanto, Fernando [35] there are several reaction pathways that could
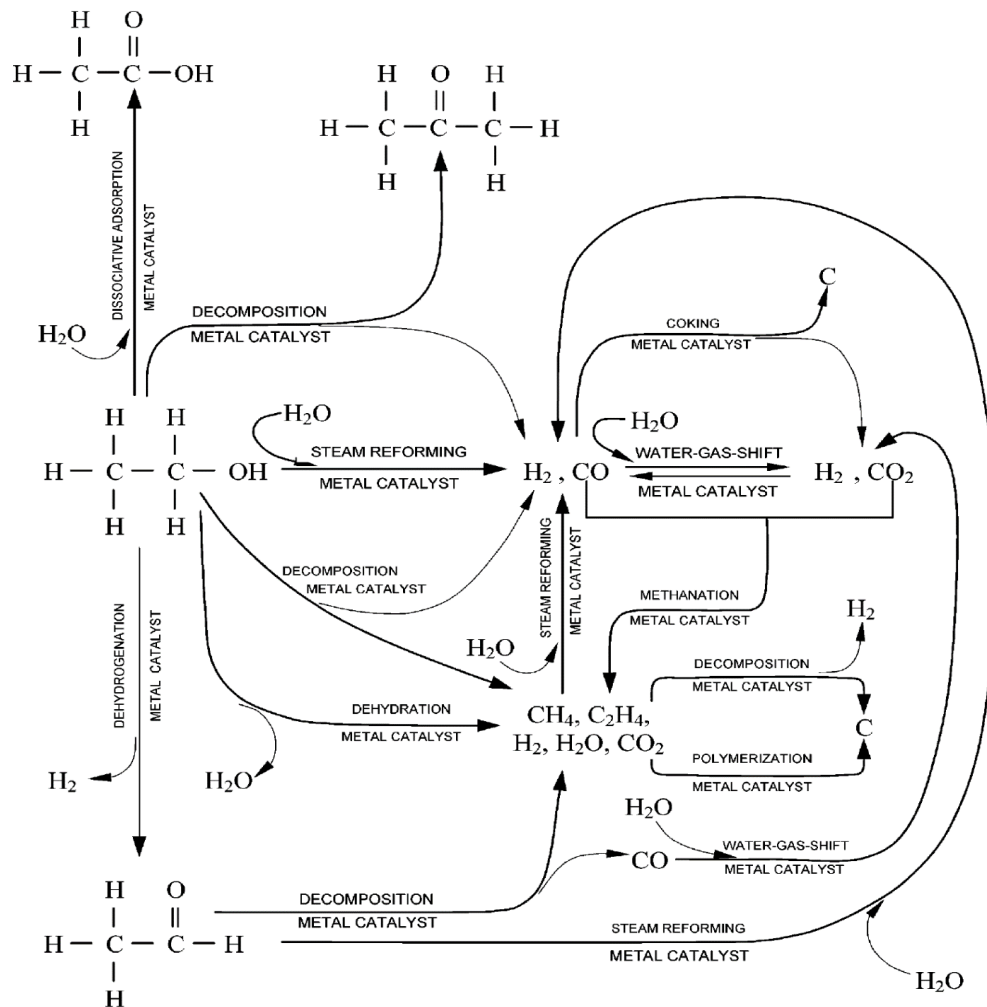
occur in the ethanol steam reforming process, depending on the catalysts used.

[2]**Figure 3.1** Reaction pathways that can occur during ethanol steam reforming over metal catalysts.

[2] 35.   Haryanto, A., et al., *Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review.* Energy & Fuels, 2005. **19**(5): p. 2098-2106.

Figure 3.1 showed some reactions pathways could occurs while ethanol steam reforming reaction is performed. A detail of the reactions is given below:

(1) C_2H_5OH dehydration to ethylene (C_2H_4) and water, followed by polymerization of C_2H_4 to form coke:

Dehydration:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (3.2)$$

Polymerization:

$$C_2H_4 \rightarrow coke \qquad (3.3)$$

(2) C_2H_5OH decomposition or cracking to CH_4, followed by steam reforming:

Decomposition:

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \qquad (3.4)$$

Steam reforming:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (3.5)$$

(3) C_2H_5OH dehydrogenation to acetaldehyde (C_2H_4O), followed by decarbonylation or steam reforming of C_2H_4O:

Dehydrogenation:

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \qquad (3.6)$$

Decarbonylation:

$$C_2H_4O \rightarrow CH_4 + CO \qquad (3.7)$$

Steam reforming:

$$C_2H_4O + H_2O \rightarrow 2CO + 3H_2 \tag{3.8}$$

(4) C_2H_5OH decomposition into acetone (CH_3COCH_3), followed by steam reforming:

Decomposition:

$$2C_2H_5OH \rightarrow CH_3COCH_3 + CO + 3H_2 \tag{3.9}$$

Steam reforming:

$$C_2H_4O + H_2O \rightarrow 2CO + 3H_2 \tag{3.10}$$
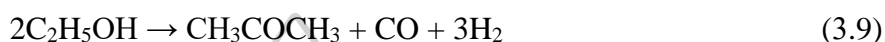
(5) C_2H_5OH Steam reforming of C_2H_5OH to syngas ($CO + H_2$):

$$2C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \tag{3.11}$$

(6)   Water gas shift:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3.12}$$

(7)   Methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3.13}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{3.14}$$

(8)   Coking from the decomposition of CH_4:

$$CH_4 \rightarrow 2H_2 + C \tag{3.15}$$

(9)   Coking from the Boudouard reaction:

$$CO_2 \rightarrow O_2 + C \tag{3.16}$$

(10)   Dissociative adsorption of water to form acetic acid (CH_3COOH):

Water adsorption:

$$C_2H_5OH + H_2O \rightarrow CH_3COOH + H_2 \tag{3.17}$$

The reforming process intended to produce H_2 as high as possible from C_2H_5OH cracking in the presence of water over catalyst. However, the overall reaction is highly complex with so much products involved. Consequently, reducing undesired intermediate products is important key to achieve high yield of hydrogen.

Both the reaction conditions selected (e.g., reaction temperature, residence time, feed composition) and the choices of catalyst used are essential control variables of hydrogen production from ethanol. High temperatures, long residence times, and a high steam to ethanol ratio are necessary to achieve a high hydrogen yield.. Pereira, Ramírez de la Piscina [44] investigated the thermodynamic analysis of ethanol steam reforming process, which resulting in high values of equilibrium constant for temperature above 323 °C and an increasing temperature prevents methane formation. da Silva, de Souza [45] found that increasing space time could promoted ethanol conversion and hydrogen selectivity despite minimizing intermediate product production. Generally, raising the amount of water in the reactants enhances ethanol conversion and H_2 production. The increase in CO_2 concentration, combined with the reduction in CO, indicated that adding water accelerated the WGS reaction. The presence of oxygen in the input might facilitate in the initial conversion of ethanol. However, H_2 concentration declined due to the partial oxidation. Moreover, the coke formation significantly declines with the increase in H_2O/Ethanol or O_2/ethanol ratios considering the contribution of the carbon gasification by H_2O or O_2.

Chiou, Siang [46] reviewed the possible pathways of ethanol steam reforming over Pt, Ir and Co supported by ceria catalysts prepared by deposition-precipitation methods and investigated for their suitability at a temperature range of 250-500 °C under an H_2O/EtOH molar ratio of 13. They proposed that at low temperatures, ethanol dehydrogenation was the primary reaction, and that as temperature rises, two competing pathways were pursued as showed in Figure 3.2. Thus, the steps for catalytic surface in ethanol steam reforming are (i) dehydrogenation of ethanol; (ii) the carbon-carbon bond (C-C bond) breaking of C_2 intermediates to produce CO and CH_4; and (iii) the C1 products with water reforming to generate additional hydrogen.

The world's present energy demands, as well as those projected in the next years, would accelerate the development of pollution-free alternative energy sources. In this respect, hydrogen derived from natural resources, particularly oxygenated molecules, would perform as a versatile energy carrier. Kubacka, Fernández-García [47] particularly reviewed WGS and reforming reaction of oxygenated hydrocarbons over Cu, Ni and Co catalysts over the last five year to give a comprehensive update of various developments in the field of hydrogen production from oxygenated molecules using base metal catalysts. The report presented an overview of the water gas shift and steam reforming processes, as well as their connection to other process and techniques including such partial oxidation, autothermal, supercritical water reforming, CO_2-sorption-assisted, and thermochemical looping, in providing a more comprehensive view of the most interesting results.
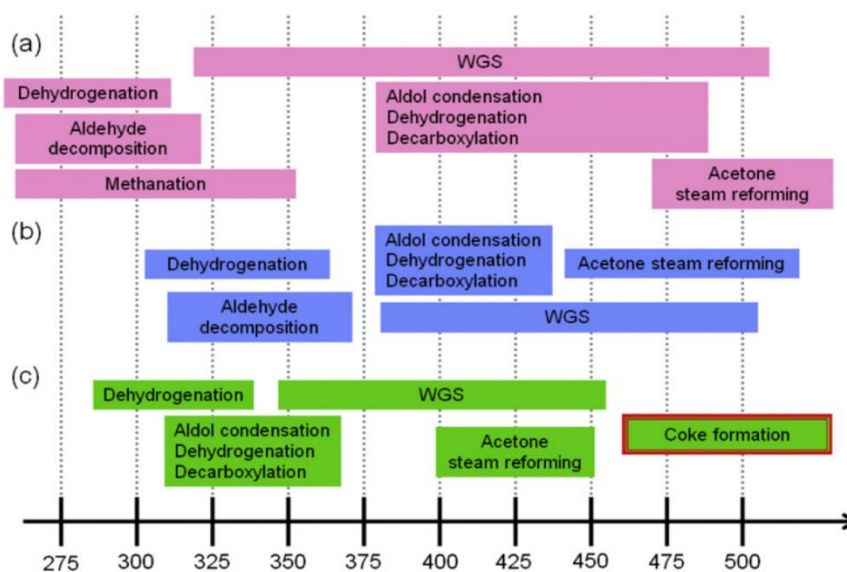
[3]**Figure 3.2** A) Reaction routes of SRE on M/CeO_2 catalysts. (B) Temperature window of SRE reaction over M/CeO_2 catalysts: (a) Pt/CeO_2 (b) Ir/CeO_2 (c) Co/CeO_2.

Lorenzut, Montini [48] studied hydrogen production by steam reforming of alcohols (methanol and ethanol) over a series of $Cu/ZnO/Al_2O_3$ catalysts prepared by different coprecipitation procedures. This demonstrating good performances in the hydrogen production through the steam reforming of alcohols.

Ethanol steam reforming and water gas shift reaction are both reversible. The selection of the catalysts that could increase reaction rate which lead system tends toward thermodynamic equilibrium is an important task to achieve the desired result. There have been several attempts to develop potential catalysts that enhance the ethanol steam reforming process with less byproducts. However, the main challenge for the steam reforming of ethanol to produced hydrogen has remained the development of efficient catalysts which resulting in a high yield of hydrogen and suitable stability.

[3] 46.   Chiou, J.Y.Z., et al., *Pathways of ethanol steam reforming over ceria-supported catalysts.* International Journal of Hydrogen Energy, 2012. **37**(18): p. 13667-13673.

Group 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Period

1   1   2
   H   He

2   3 4   5 6 7 ⑧ 9 10
   Li Be   B C N (O) F Ne

3   11 12   13 14 15 16 17 18
  (Na)(Mg)   (Al)(Si) P S (Cl) Ar

4   19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36
  (K) Ca Sc (Ti)(V) Cr Mn (Fe)(Co)(Ni)(Cu)(Zn) Ga Ge As Se Br Kr

5   37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54
  Rb Sr Y (Zr)(Nb) Mo Tc (Ru)(Rh)(Pd) Ag Cd In Sn Sb Te I Xe

6   55 56 * 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86
  Cs Ba   Lu Hf Ta W Re (Os)(Ir)(Pt)(Au) Hg Tl (Pb) Bi Po At Rn

7   87 88 ** 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118
  Fr Ra   Lr Rf Db Sg Bh Hs Mt Ds Uuu Uub Uut Uuq Uup Uuh Uus Uuo

*Lanthanoids * 57 58 59 60 61 62 63 64 65 66 67 68 69 70
    (La)(Ce) Pr Nd Pm (Sm) Eu Gd Tb Dy Ho Er Tm Yb

**Actinoids ** 89 90 91 92 93 94 95 96 97 98 99 100 101 102
    Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No

[4]**Figure 3.3** Elemental compounds that were tried as catalysts in ethanol steam reforming reaction (denoted by circles).

Figure 3.3 showed lists of elemental compounds that had been attempted as catalysts for the ethanol reforming process. Most of attempts were studied on metals, both base and noble compounds. Deluga, R Salge [49] suggests that metals were not only one factor assisted H_2 production. This study imply that the performance of metal catalysts could be improved by using suitable supported materials.

Ni-based catalysts have been frequently utilized as non-noble transition metal catalysts for ESR because to their strong activity for C-C bond cleavage and CH_4 steam reforming. However, it generates more byproducts like coke and CH_4 than Co-based catalysts. Various preparation techniques, Ni precursors, and supports have been extensively researched in order to create Ni catalysts with a well dispersion of small Ni particles, since size of the Ni particles is a key factor that influences activity, selectivity, and carbon deposition. Diverse supports for Ni catalysts have been studied. For its greater surface area and stability, Al_2O_3 support has been extensively used for the ESR among Ni-based catalysts. However, the acidic site of Al_2O_3 support favors the generation of ethylene, a coke precursor that promotes coke deposition. The

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[4] 49.   Deluga, G.A., et al., *Renewable Hydrogen From Ethanol by Autothermal Reforming*. Vol. 303. 2004. 993-7.

modification of basic oxides (La_2O_3 and ZrO_2) to the Al_2O_3 support efficiently neutralizes the acidic sites and inhibits coke formation.

Maria et al. [50] The mechanistic characteristics of ethanol steam reforming on Pt, Ni, and PtNi catalysts supported on γ-Al_2O_3 were investigated using adsorbed species and gas phase products generated on catalysts during temperature-programmed ethanol desorption and during the ethanol steam reforming process. PtNi and Ni catalysts are more stable than Pt monometallic counterparts, according to DRIFTS-MS investigations of ethanol decomposition and ethanol steam reforming reactions. The first reaction pathways of ethanol steam reforming over the examined catalysts are ethanol dehydrogenation and acetaldehyde breakdown, according to ethanol TPD data on Ni, Pt, and NiPt catalysts. Carbon deposits rapidly deactivate the active sites necessary for acetaldehyde decomposition in the first minutes on-stream. Once the acetaldehyde decomposition pathway is inactive for Ni and PtNi catalysts, a second reaction pathway consisting in the decomposition of acetate intermediates produced on the surface of the alumina support becomes the primary reaction pathway functioning in steam reforming of ethanol. Considering the variations in ethanol decomposition pathways, the better stability observed for PtNi catalyst is proposed to be attributed to a cooperative effect between Pt and Ni activities, along with Ni enhanced ability to gasify the methyl groups produced by acetate species decomposition. Monometallic catalysts, on the other hand, are expected to dehydrogenate these methyl groups, resulting in coke and metal particle deactivation.

CHAPTER 4

METHODOLOGY

4.1 Chemicals

Table 4.1 The chemicals used to prepare the catalysts

Chemicals	Formula	Grade	Manufacture
Ammonium perrhenate	(H_4NO_4Re)	≥99%	Sigma-Aldrich
Nickel(II) nitrate	($Ni(NO_3)_2$)	Assay 97.0%	UNILAB
Ethanol	(C_2H_5OH)	AR, 99.9%	Qrec
Nitrogen	N_2	UHP, 99.999%	Linde
Hydrogen	H_2	UHP, 99.995%	Linde
Argon	Ar	UHP, 99.995%	Alternative
Air zero	21%O_2 in N_2	HP, 99.995%	Linde
Liquid nitrogen	$N_{2,liq}$	-	-

4.2 Catalyst preparation

The catalysts were prepared by the wetness impregnation method. The deionized water as solvent, commercially γ-alumina, nickel(II) nitrate ($Ni(NO_3)_2$) and ammonium perrhenate (H_4NO_4Re). Prior the preparation, γ-alumina support was preheated in water bath at 80 ºC. Calculated amount of nickel nitrate and ammonium perrhenate were dissolved in deionized water and gradually dripped on the preheated alumina. The precursor solution was stirred and heated at 80ºC. After evaporate the

remaining water, the catalysts were dried overnight at 105 $^{\circ}$C and then calcined at 600 $^{\circ}$C in the presence of air with a heating rate of 10°C/min to achieve 1, 3 and 5% Re-Ni/Al$_2$O$_3$ catalysts.

4.3 Catalysts Characterization

4.3.1 Nitrogen Physisorption (BET)

The internal surface area was determined by isotherm measurement of physical adsorption or BET method (Bruna Emmett Teller Method). BET surface areas were measured by nitrogen physisorption at -196 $^{\circ}$C using BELSORP II (surface area and porosity analyzer). The catalysts were pre-treated in nitrogen gas flow at 350 $^{\circ}$C for 4 h to remove the adsorbed water. The pore size distribution was measured by BJH method.

4.3.2 X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of catalysts were obtained using X-ray diffractometer SIEMENS D-5000 coupled with a computer using Diffract ZT (version 4.2) for fully control of the XRD analyzer. The instrument was operated using Cu Kα radiation. The scans were performed over the 2θ ranges from 20° to 80°. The crystallite sizes were estimates from XRD data according to the Scherrer equation.

4.3.3 Temperature Programmed Reduction (TPR)

The temperature programmed reduction was used to determine the reducibility and reduction behavior of each catalyst. The hydrogen consumption was measured using a Micrometritics Autochem II 2910 instrument. The pre-mixed of 10%H$_2$ in N$_2$ and pure nitrogen in ultra-high purity grade were used as a probe molecule gas and a carrier gas, respectively. 100 mg of each catalyst sample was placed in a quartz tubular reactor. To eliminate the adsorbed water, the catalyst sample was heated up to 250 $^{\circ}$C under N$_2$ atmosphere at a flow rate of 30 ml/min with a heating rate of 10 $^{\circ}$C/min and was held for 1 h. After pre-treatment, the system was cooled down to ambient temperature. The reduction step was performed under 10%H$_2$ in N$_2$ flow at 30 ml/min and heating from room temperature to 800 $^{\circ}$C at a heating rate of 10 $^{\circ}$C/min. Effluent

gas was passed through a cooling trap to condense water produced during the reduction. H_2 consumption was measured by thermal conductivity detector.

4.3.4 Scanning Electron Microscope - Energy Dispersive X-ray (SEM-EDX)

The morphological characterization of the samples was analyzed using the scanning transmission electron microscope (Hitachi S3400). The element distribution was obtained by energy dispersive X-ray microscopy.

4.4 Catalytic Evaluation

Steam reforming experiments were performed at ambient pressure in a fixed-bed quartz reactor (6 mm ID, 500 mm length) placed in a temperature-controlled oven. Prior to the reaction, 100 mg of each catalyst was reduced with a mixed stream of 20% H_2 in N_2 (70 ml/min) at 500 $^{\circ}$C for 150 min. After purging the reactor with N_2 flow (55 ml/min) for 60 min, the temperature was then ramp to the reaction temperature. A liquid mixture of ethanol/water (1.5 ml/h, 1:3 molar ratio) was introduced into the system by a syringe pump (NE-300 Just Infusion™). Inlet line was heated at 140 $^{\circ}$C to vaporize the liquid mixture with N_2 flow as carrier gas (55 ml/min). The condensable products were trapped with ice-salt cold trap, the dry gasses (non-condensable gas products) were then analyzed using an on-line gas chromatography (SRI-8610 C, USA) equipped with two columns (Molecular Sieve 5A and Silica Gel) and a thermal conductivity detector (TCD).
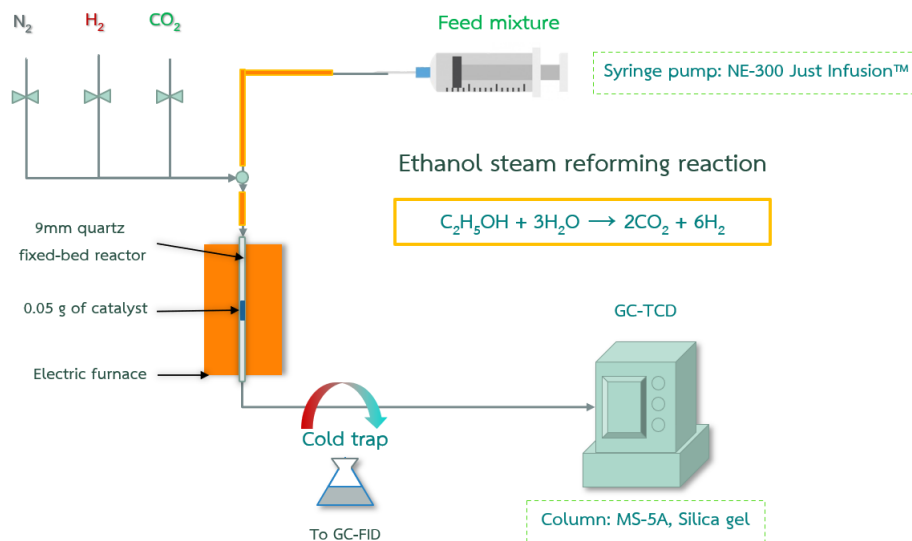

Figure 4.1 Schematic diagram for ethanol steam reforming reaction system.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Physicochemical Characterization

Table 5.1 demonstrated the physical properties of support and Re-Ni/Al$_2$O$_3$ catalysts. All catalysts exhibited type-IV isotherms of a mesoporous structure (Figure 5.1-5.5). A significant dropped in surface area (S$_{BET}$) from 164.25 m^2/g to 125.91 m^2/g was observed upon loading Ni to the alumina support. The surface area was further slightly decreased after Re was introduced to the catalysts. This reasonably caused from partial blocking of the mesoporous structure by the added-up metal species.

Table 5.1 BET surface area, average particle size and mean pore diameter of the catalysts.

Catalysts	BET Surface area (m^2/g)	Average pore diameter (nm)
Al$_2$O$_3$	164.25	5.98
10Ni/Al$_2$O$_3$	125.91	6.32
1Re-10Ni/Al$_2$O$_3$	128.14	6.06
3Re-10Ni/Al$_2$O$_3$	119.70	6.55
5Re-10Ni/Al$_2$O$_3$	115.38	6.38

Table 5.2 Crystalline size and reducibility the catalysts.

Catalysts	Crystalline size (nm)	Reducibility (%)
Al$_2$O$_3$	-	-
10Ni/Al$_2$O$_3$	8.26	71.87
1Re-10Ni/Al$_2$O$_3$	6.09	92.77
3Re-10Ni/Al$_2$O$_3$	6.29	95.87
5Re-10Ni/Al$_2$O$_3$	6.50	95.43
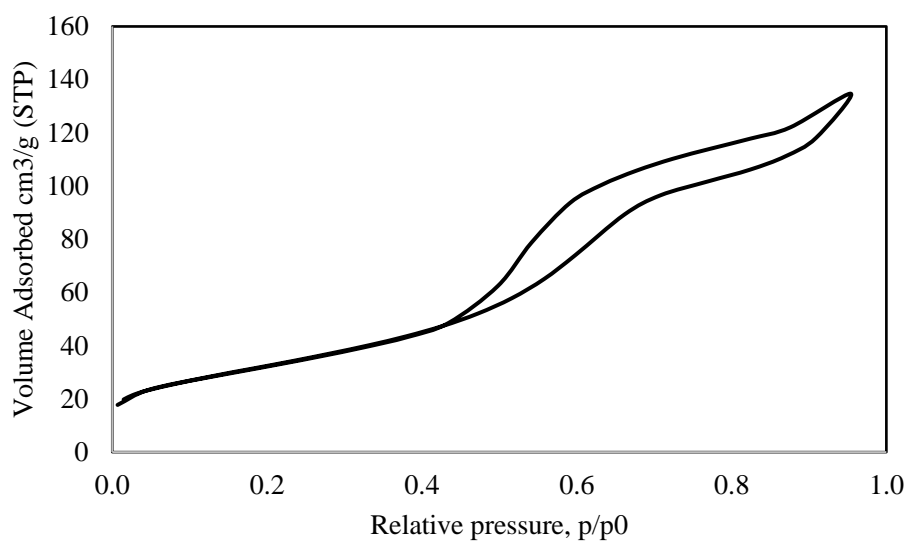
Figure 5.1 The N_2 adsorption/desorption isotherm of Al_2O_3.
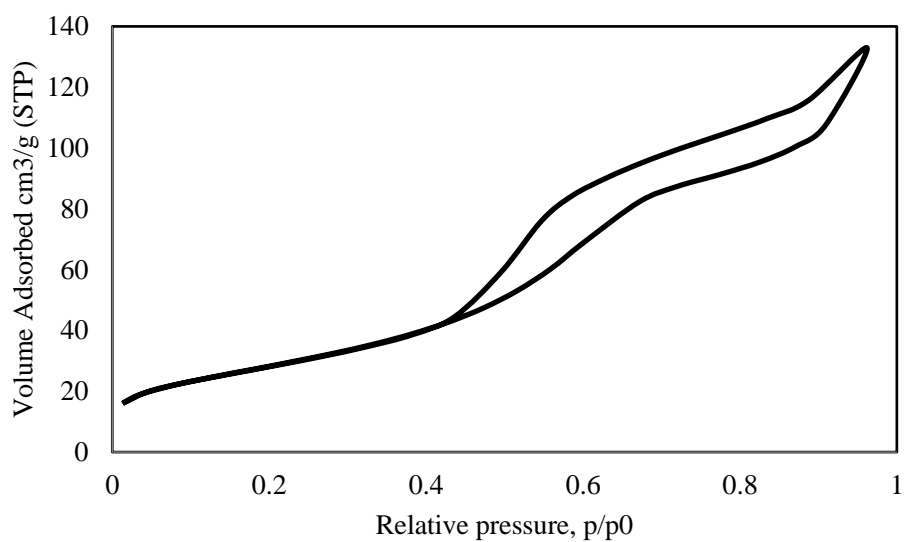
Figure 5.2 The N_2 adsorption/desorption isotherm of Ni/Al_2O_3.
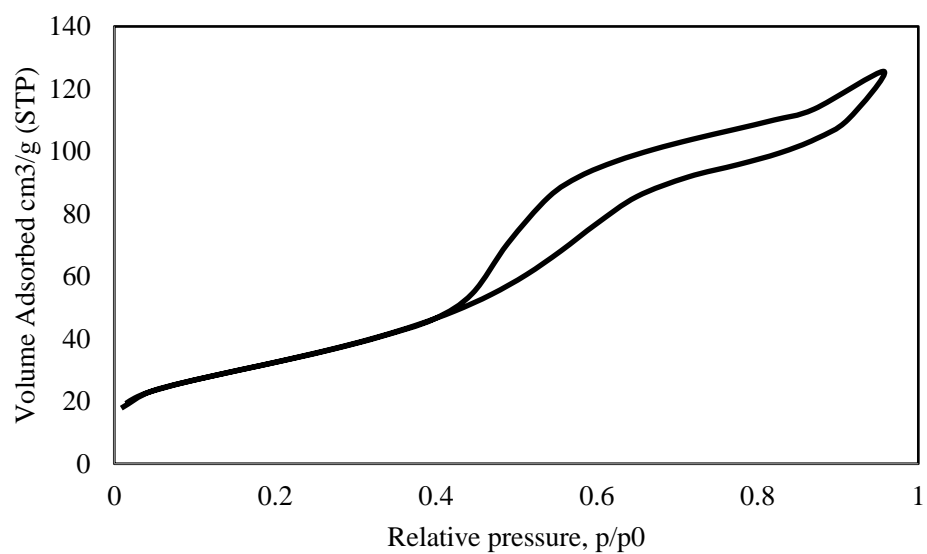
Figure 5.3 The N_2 adsorption/desorption isotherm of 1%Re-Ni/Al_2O_3.
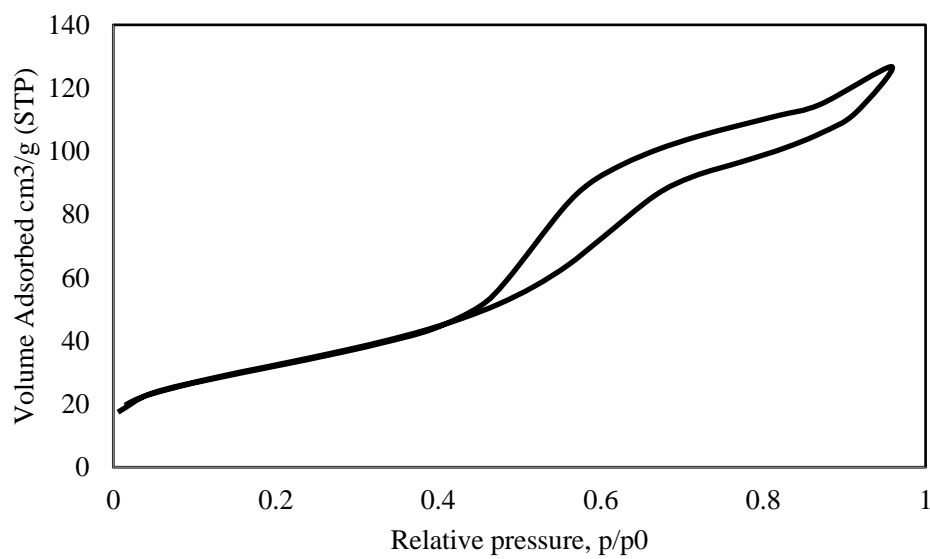
Figure 5.4 The N_2 adsorption/desorption isotherm of 3%Re-Ni/Al_2O_3.
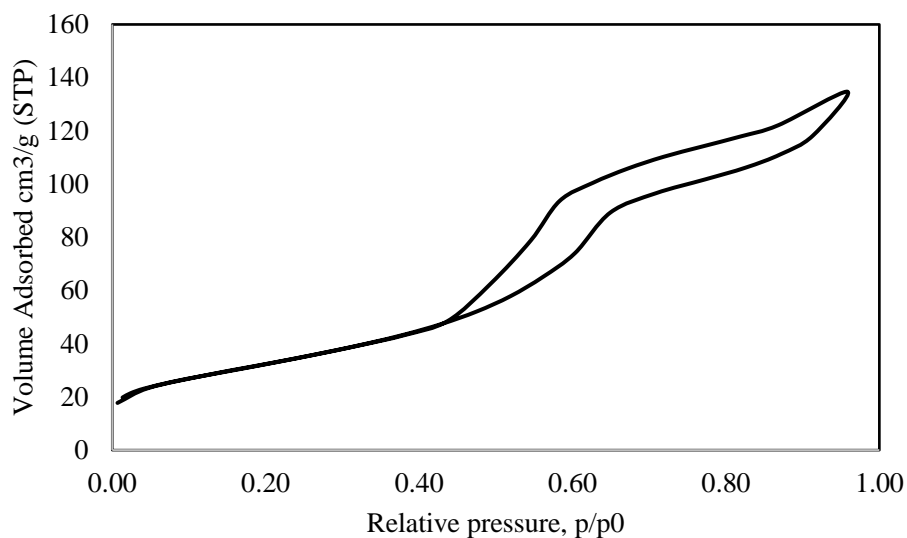
Figure 5.5 The N_2 adsorption/desorption isotherm of 5%Re-Ni/Al$_2$O$_3$.
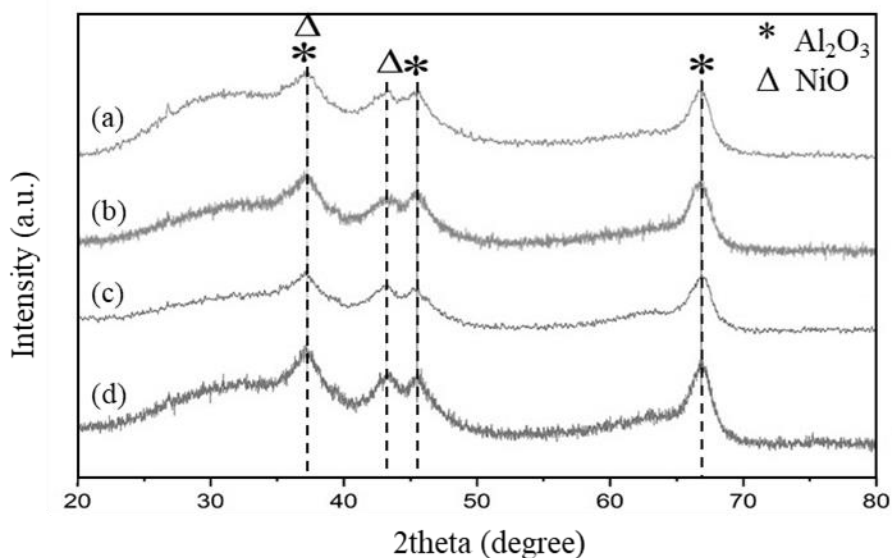
Figure 5.6 XRD diffraction patterns of (a) 5% Re-Ni/Al$_2$O$_3$, (b) 3% Re-Ni/Al$_2$O$_3$, (c) 1% Re-Ni/Al$_2$O$_3$, and (d) 10% Ni/Al$_2$O$_3$.

The XRD patterns of the samples were reported in Figure 5.6. The XRD spectra showed the diffraction peaks at $2\theta = 37.4°$, $46.07°$, and $66.9°$, corresponding to (311), (400), and (440) crystal planes of γ-Al$_2$O$_3$ with low crystallinity (JCPDS 29-0063), respectively [51]. The diffraction peaks located at $37.4°$ and $43.5°$ originating from NiO

(111) and NiO (200) crystal planes (JCPDS 44-1159) [52]. However, by introducing Re to the system, the positions of the characteristic diffraction peaks were remained unchanged and rhenium oxide was not observed in any rhenium doped sample, indicating a high dispersion of rhenium species over the surface of alumina or rhenium phase was amorphous. Similar results have been reported in the Re-based catalysts over Al_2O_3 support, where no evidence of rhenium oxides was observed [53]. Scherrer equation was further applied to estimate the crystalline size as shown in Table 5.2. The results revealed that bare Ni on alumina shows the crystalline size of 8.26 nm and by doping Re the crystalline size was slightly decreased to 6.09 nm then slightly increased along with the Re amount loaded into the catalysts for up to 6.50 nm at 5% Re. A scanning electron microscope was also used for the morphology observation of the synthesized catalyst. Figure 5.7-5.10 demonstrated the SEM images of prepared catalyst. EDX mapping ensured the high dispersion of active metal over the catalyst surface

Figure 5.7 SEM images of 10%Ni/Al$_2$O$_3$ in different magnification with EDX mapping.
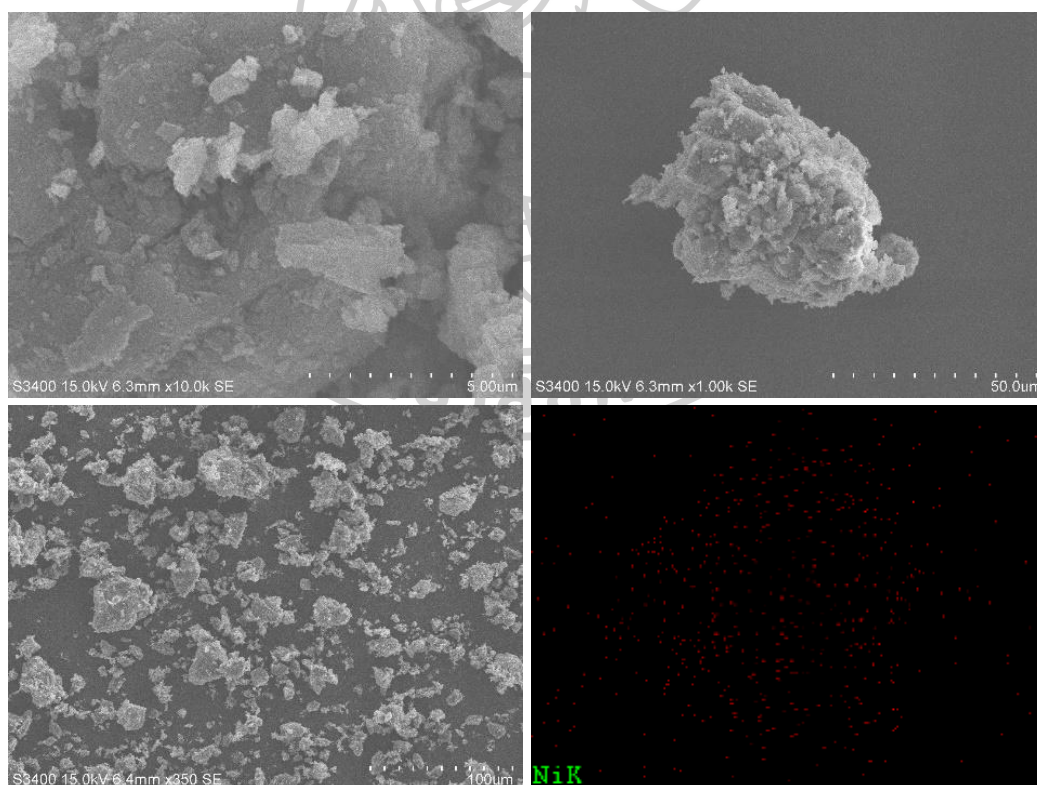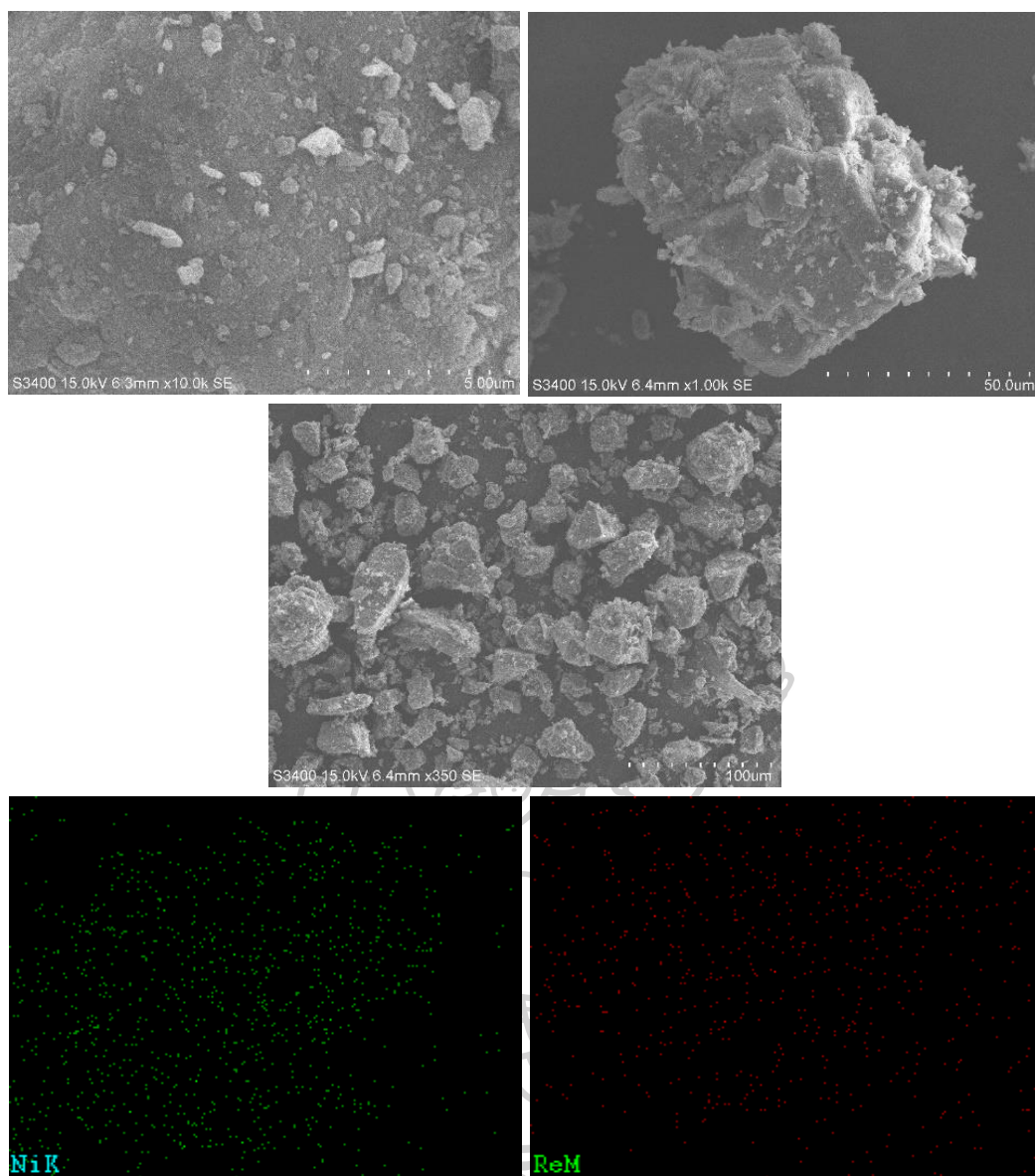
Figure 5.8 SEM images of 1%Re-Ni/Al$_2$O$_3$ in different magnification with EDX mapping.

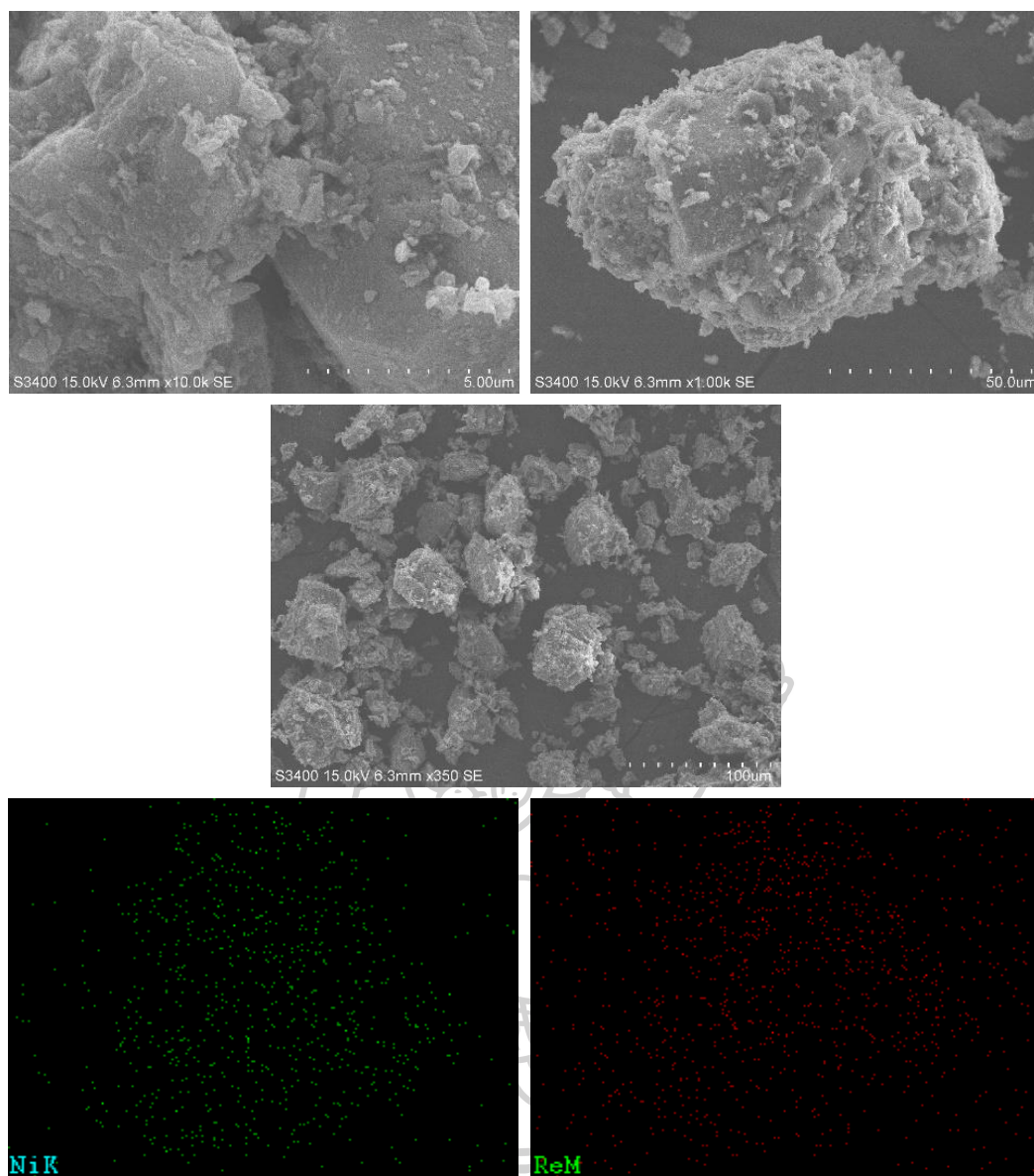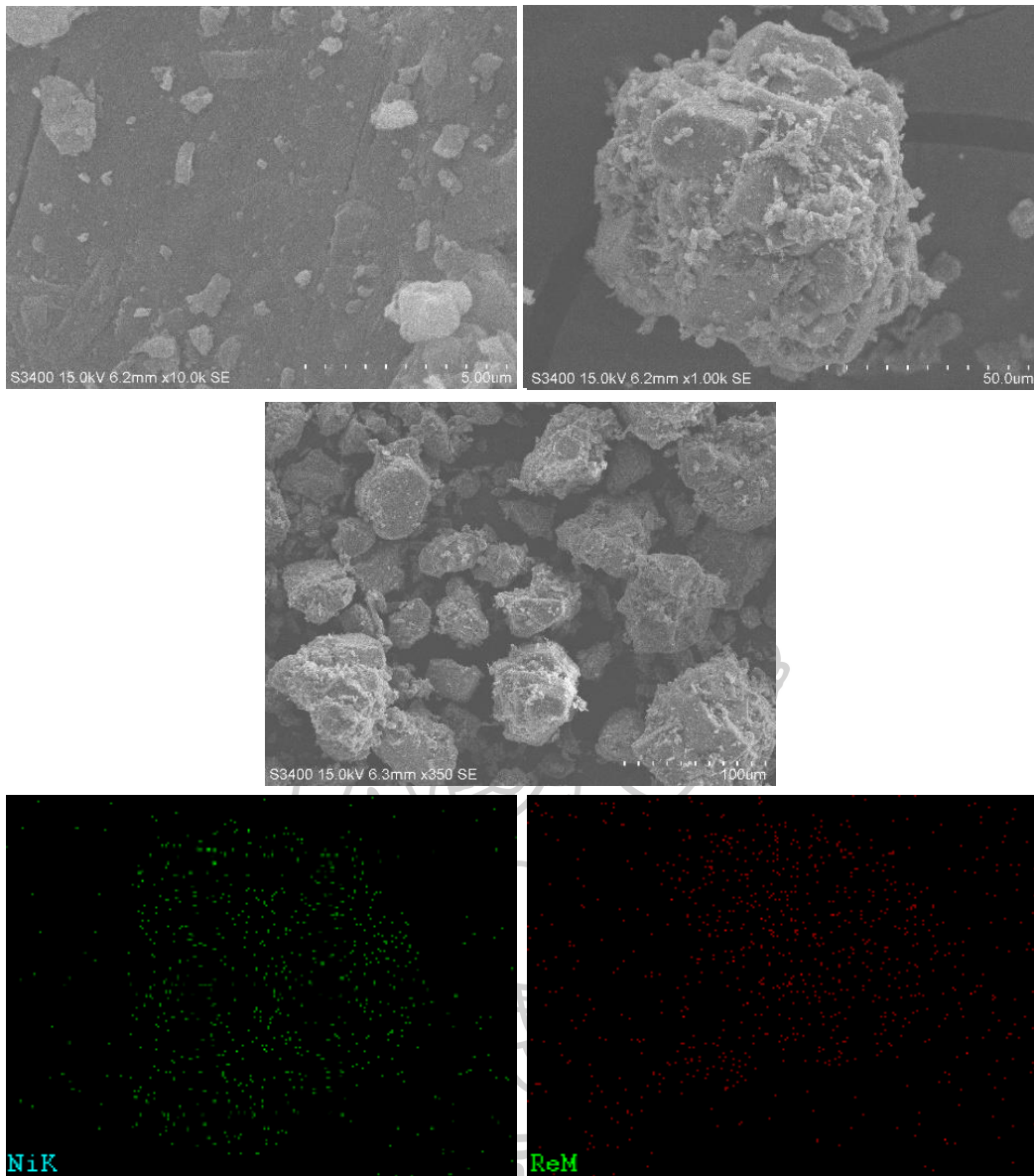**Figure 5.9** SEM images of 3%Re-Ni/Al₂O₃ in different magnification with EDX mapping.

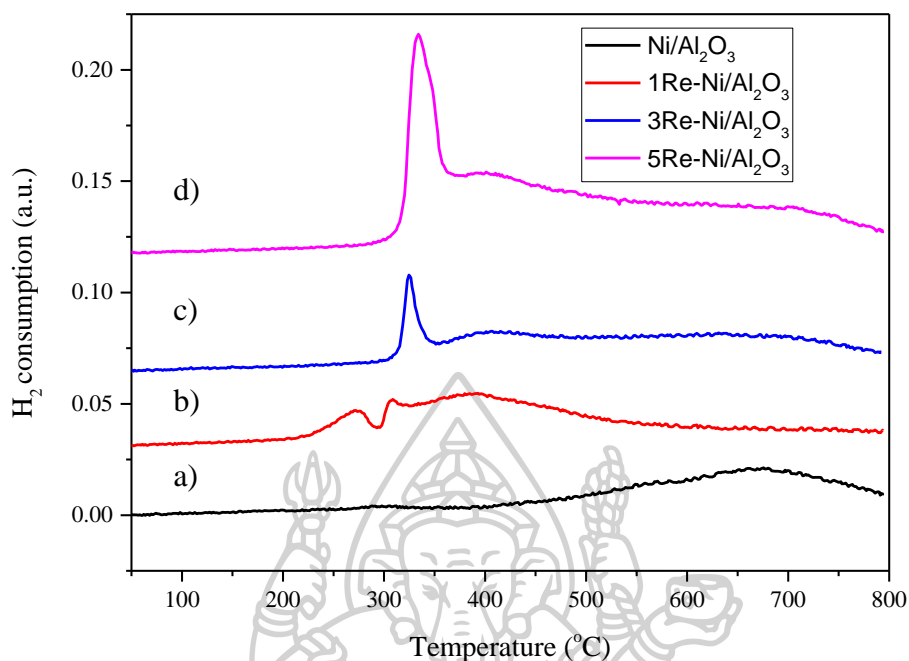**Figure 5.10** SEM images of 5%Re-Ni/Al$_2$O$_3$ in different magnification with EDX mapping.

Figure 5.11 H_2-TPR profiles of (a) 10%Ni/Al_2O_3, (b) 1% Re-Ni/Al_2O_3, (c) 3% Re-Ni/Al_2O_3, and (d) 5% Re-Ni/Al_2O_3.

The H_2-TPR curve of calcined samples was shown in Figure 5.11. The reduction pattern of monometallic sample shows single broad reduction peak in the temperature range of 400-800 °C corresponds to the reduction of NiO interacted with Al_2O_3 support. The low reducibility of this nickel catalyst is the result of phase transformation of nickel on alumina during calcination to form nickel aluminate (NiAl$_2O_4$) [51, 54]. Considering the Re-promoted samples, the first reduction process occurred around 270 °C for 1%Re-Ni/Al_2O_3, 320 °C for 3%Re-Ni/Al_2O_3 and, 330°C for 5%Re-Ni/Al_2O_3. This can be attributed to the reduction of rhenium oxides on the catalyst surface [55]. The following wide peak observed in these samples represent the reduction of NiO species in interaction with Re. This implied that the addition of Re shifts the reduction process of NiO to lowers temperature and increases the reducibility of the Re-promoted samples.

5.2 Catalytic activity and stability

The catalytic activity of different Re loading (0, 1, 3, and 5 wt.% Re) on Ni/Al_2O_3 catalyst was evaluated at ambient pressure with the temperature of 450, 550, and 650 ^oC. Almost complete conversion (>99.7%) with a trace amount of acetaldehyde can be obtained at the low temperature of 450 ^oC and totally converted at higher temperature for all catalyst loading. Figure 5.12-5.14 show the product distribution of $10\%Ni/Al_2O_3$ in ESR at 450, 550, and 650 ^oC respectively. H_2, CO, CO_2, and CH_4 were the major product during the entire reaction process.

For the low-temperature reaction at 450 ^oC, the H_2 concentration was maintained at ca. 57% with a high amount of CH_4 and CO at ca. 22% and 17% were observed. It is suggested that carbon-containing compounds were formed by additional reactions during the steam reforming of ethanol. Firstly, ethanol was dehydrogenated with desorption of acetaldehyde and H_2 ($C_2H_5OH \rightarrow C_2H_3CHO + H_2$) then the C−C bond breaking enhanced by the presence of metallic Ni leads to decomposition of acetaldehyde ($C_2H_3CHO \rightarrow CO + CH_4$) resulting in the formation of CH_4 and CO [56, 57].
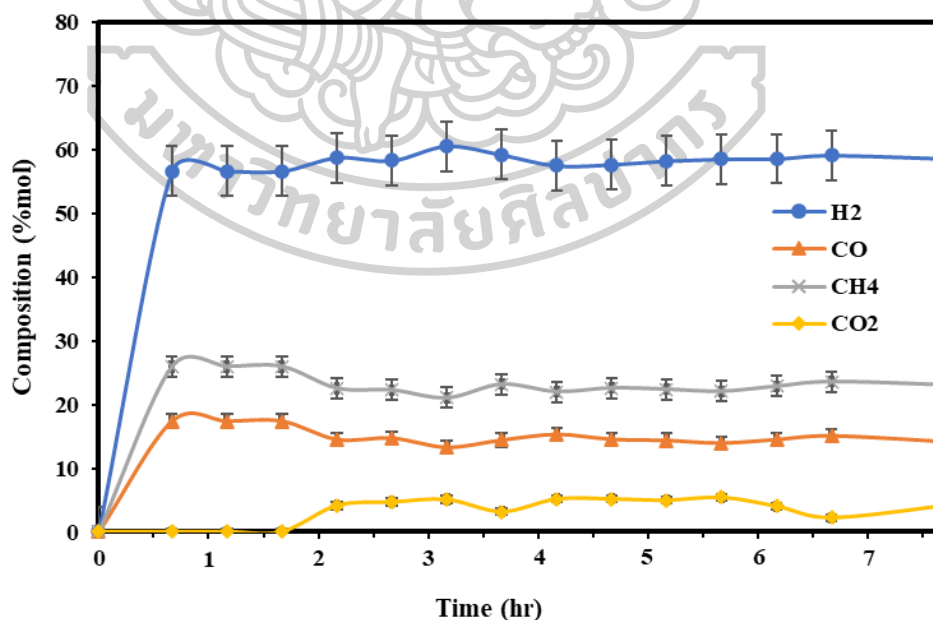

Figure 5.12 Product distribution of $10\%Ni/Al_2O_3$ in ethanol steam reforming reaction at 450 ^oC.
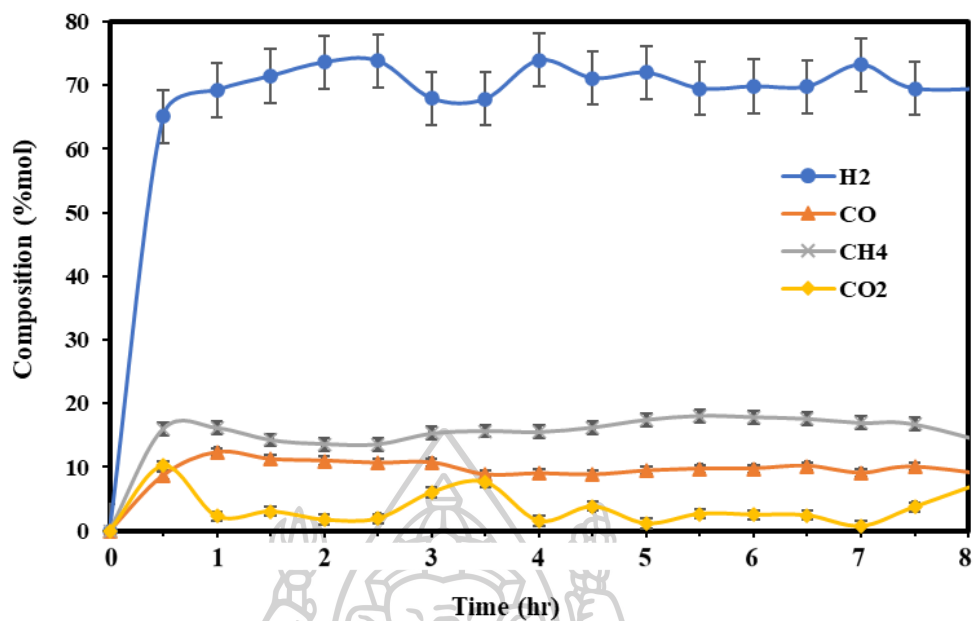
Figure 5.13 Product distribution of 10%Ni/Al$_2$O$_3$ in ethanol steam reforming reaction at 550 °C.

Figure 5.14 Product distribution of 10%Ni/Al$_2$O$_3$ in ethanol steam reforming reaction at 650 °C.
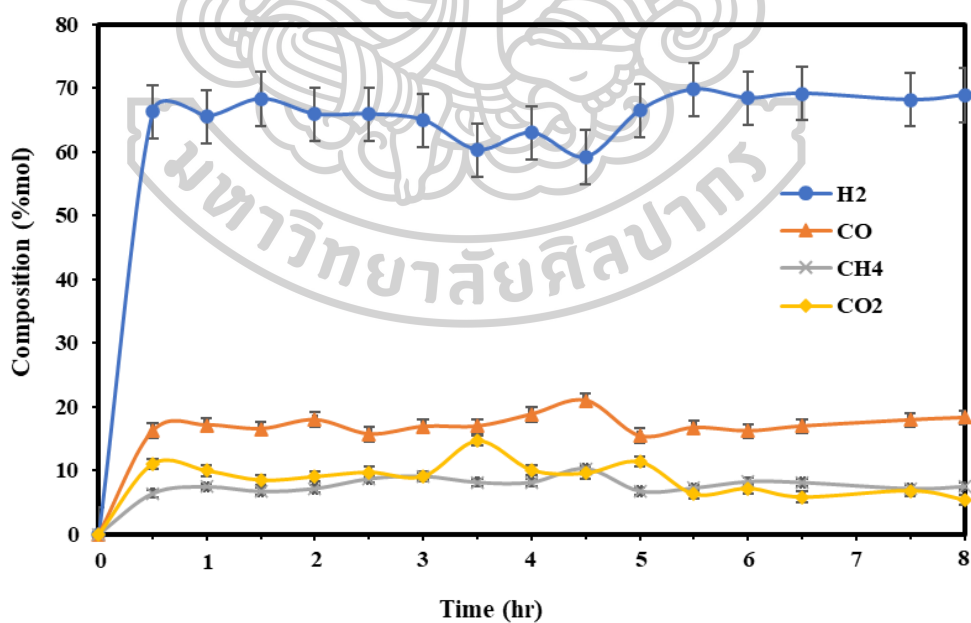
At 550 $^{\circ}$C the result was followed the same trend as in 450 $^{\circ}$C with a change in a higher amount of H_2 of up to ca. 67% in concentration while lowering CO and CH_4 production. By increasing the temperature to 650 $^{\circ}$C, the methane concentration decreased with an increased in the formation of CO and CO_2 which could be attributed to CH_4 reforming ($CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$) [58].

Interesting result was found upon performing ESR with the Re-containing catalysts. Figure 5.15-5.17 illustrated the product distribution of 1%Re-Ni/Al_2O_3, 3%Re-Ni/Al_2O_3, and 5%Re-Ni/Al_2O_3 in ESR at 650 $^{\circ}$C. Although the major products formed were similar to the bare Ni catalyst in 1%Re-Ni/Al_2O_3. However, the CO concentration was considerably suppressed to less than 5% in 3%Re-Ni/Al_2O_3 catalyst. This could be attributed to the higher reactivity of the water-gas shift reaction (CO + $H_2O \rightarrow H_2 + CO_2$) enhanced by the facilitative water dissociation of Re species [59]. Moreover, a more consistent flow of H_2 with a concentration of up to 72% was detected for over 60 h on steam without any sight of deactivation, indicating long-term stability of the catalyst. The remarkable catalytic activity and stability of the Re doped catalyst is implied from the formation of an alloy phase due to the strong interaction between Re-Ni and the addition of Re could further demote the surface reduction and hence the maintenance of active Ni by resisting the formation of Ni^{2+} [60-63].
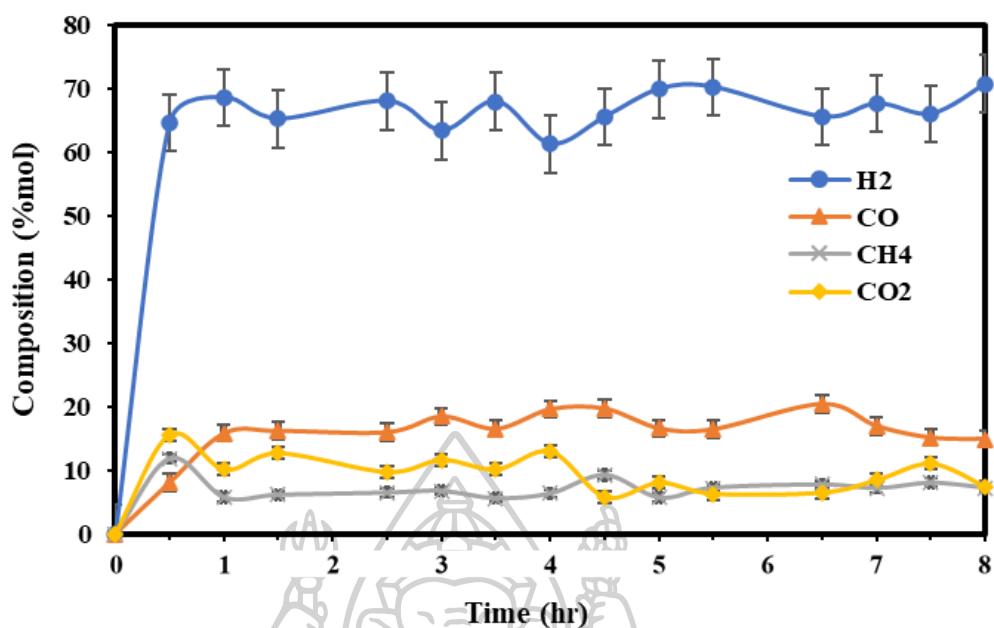
Figure 5.15 Product distribution of 1%Re-Ni/Al$_2$O$_3$ in ethanol steam reforming reaction at 650 $^{\text{o}}$
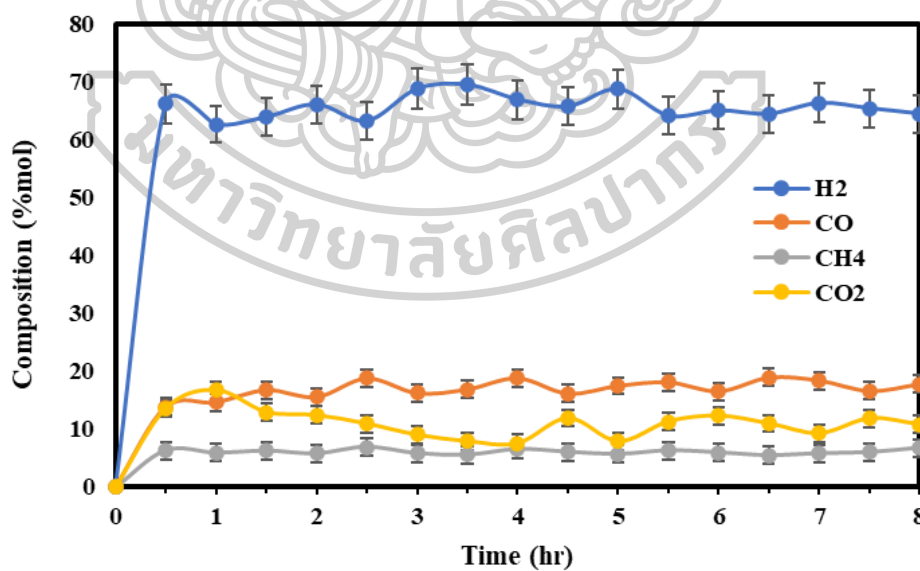
Figure 5.16 Product distribution of 5%Re-Ni/Al$_2$O$_3$ in ethanol steam reforming reaction at 650 $^{\text{o}}$C
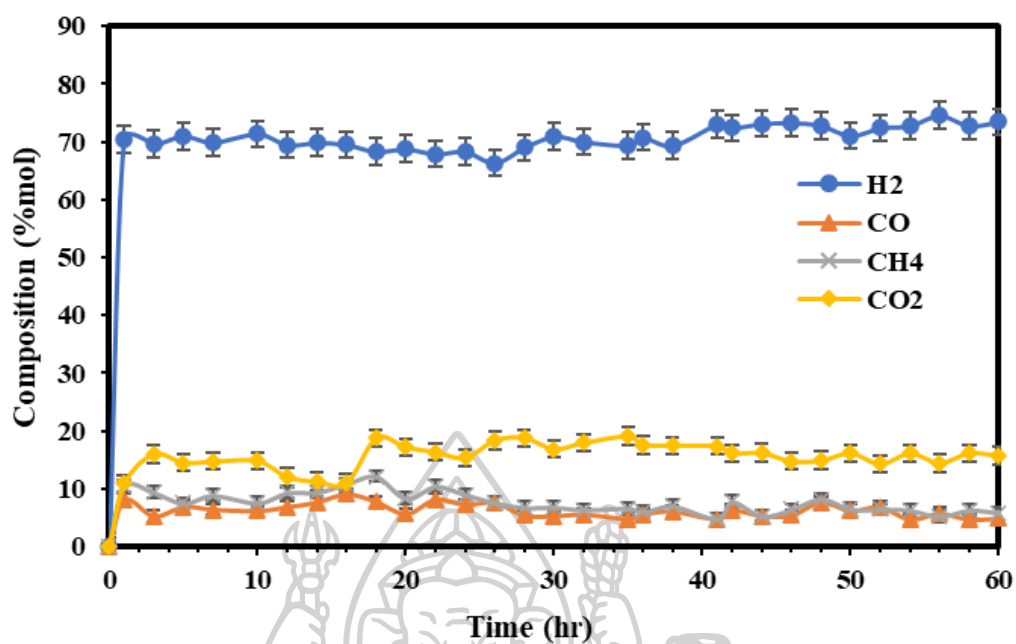
Figure 5.17 Product distribution of 3%Re-Ni/Al$_2$O$_3$ in ethanol steam reforming reaction at 650 °C on stability test for 60 h.

Table 5.3 Product distribution of the ethanol steam reforming reaction.

Catalyst	Concentration (%)			
	H$_2$	CO	CO$_2$	CH$_4$
10%Ni-450	57	17	4	22
10%Ni-550	67	12	5	16
10%Ni-650	66	18	10	6
1%Re-Ni-650	65	16	7	12
3%Re-Ni-650	72	5	17	6
5%Re-Ni-650	67	10	18	5

CHAPTER 6
CONCLUSION AND RECOMMENDATION

In this study, the bimetallic Re-Ni/Al_2O_3 catalysts were prepared by the wetness impregnation method to investigate the influence of Re addition on the catalytic performances of Ni/Al_2O_3 for ethanol steam reforming reaction. The catalysts were characterized by BET, XRD, H_2-TPR, and SEM-EDX techniques. The characterization results could confirm that Re-Ni/Al_2O_3 catalysts were successfully synthesized with a high dispersion of active metals over the catalyst surface. The presence of Re in bimetallic Re-Ni/Al_2O_3 catalyst caused the beneficial effect by significantly promoting the ESR reactivity from the suppression of CO formation during the reaction thus, increases the selectivity towards CO_2 and H_2. It is suggested that, during reaction, the NiO particles on the Al_2O_3 support are stabilized and the sintering process is effectively suppressed by the incorporation of Re. Moreover, the additional of a small amount of Re could facilitate the water dissociation resulting in higher WGS reactivity as well as promoting long-term stability with up to 60 h without any deactivation observed

As ethanol anhydrous AR grade was employed in the study; however, commercial hydrous ethanol is recommended for practical large-scale hydrogen production. Therefore, the effect of impurities in commercial hydrous ethanol on the Re-Ni/Al_2O_3 catalysts should be further studied.

Moreover, a series of post-run characterization technique such as TGA, XRD, SEM and TEM should be applied to approach more understanding toward the behavior of the catalyst throughout the reaction.

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