

**Ni CATALYST SUPPORTED ON OPEN-CELL CERAMIC
FOAM FOR GLYCEROL STEAM REFORMING**

Miss Phichamon Sookjitsumran



**A Thesis Submitted in Partial Fulfillment of the Requirements
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ตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับเซรามิกโพรซนิตเซลล์เปิดในปฏิกิริยาอีฟอร์มมิงของกลีเซอรอล
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ปีการศึกษา 2562
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

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By Miss Phichamon Sookjitsumran
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Thesis Advisor Assistant Professor Palang Bumroongsakulsawat, Ph.D.

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..... Dean of the FACULTY OF
ENGINEERING
(Professor SUPOT TEACHAVORASINSKUN, D.Eng.)

THESIS COMMITTEE

..... Chairman
(Associate Professor ANONGNAT
SOMWANGTHANAROJ, Ph.D.)
..... Thesis Advisor
(Assistant Professor Palang Bumroongsakulsawat, Ph.D.)
..... Examiner
(Professor BUNJERD JONGSOMJIT, Ph.D.)
..... External Examiner
(Assistant Professor Suwimol Wongsakulphasatch,
Ph.D.)

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พินามณัฐ สุขจิตสำราญ : ตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับเซรามิกโฟมชนิดเซลล์เปิดในปฏิกิริยาไฮโดรเจนจาก
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งานวิจัยเรื่องนี้จัดทำขึ้นเพื่อศึกษาการวางตัวเร่งปฏิกิริยานิกเกิลบนเซรามิกโฟมสำหรับการผลิตไฮโดรเจนจาก
 ปฏิกิริยาไฮโดรเจนของกลีเซอรอลด้วยไอน้ำ โดยมีการศึกษาผลของปัจจัยต่างๆ ได้แก่ ผลของชนิดของเซรามิกโฟม (อะลูมินา
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 ให้ได้ค่าการเปลี่ยนแปลงกลีเซอรอลและผลได้แก๊สไฮโดรเจนสูงไปด้วย เนื่องจากมีปริมาณนิกเกิลบนโฟมมาก ส่วนการใช้อัตรา
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 ไฮโดรเจนลดลง เนื่องจาก ไหลผ่านเบดเร็ว กลีเซอรอลเข้ามามากขึ้น ตัวเร่งปฏิกิริยาไม่สามารถเปลี่ยนได้ทัน ดังนั้น การใช้
 ตัวเร่งปฏิกิริยาแบบโครงสร้าง (Structured catalyst) ที่มีความสูงเบดค่าหนึ่งจึงจำเป็นต้องหาอัตราป้อนสารตั้ง
 ต้นผ่านเบดที่เหมาะสมเพื่อให้ได้ประสิทธิภาพสูงสุด

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 CHULALONGKORN UNIVERSITY

สาขาวิชา วิศวกรรมเคมี
 ปีการศึกษา 2562

ลายมือชื่อนิสิต

ลายมือชื่อ อ.ที่ปรึกษาหลัก

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Phichamon Sookjitsumran : Ni CATALYST SUPPORTED ON OPEN-CELL CERAMIC FOAM FOR GLYCEROL STEAM REFORMING .
Advisor: Asst. Prof. Palang Bumroongsakulsawat, Ph.D.

This work studied of nickel catalyst on open-cell ceramic foam for hydrogen production from glycerol steam reforming. Effect of different foam materials (alumina and zirconia), different pore density (PPI) at 10, 20 and 30 PPI and different feed flow rate (0.04, 0.2 and 0.4 ml/min) on physical and chemical properties and catalyst performance in fixed-bed reactor (16 mm diameter, 500 mm length and 20 mm catalyst bed) were investigated. Fresh and used catalysts were characterized by various techniques including XRD, SEM-EDX, H₂-TPR, ICP, N₂ adsorption-desorption, TPO and TGA. Catalyst performance was observed in glycerol steam reforming in condition as follows; atmospheric pressure at 600 °C with molar ratio of feed (glycerol : water) at 1:9. From results of experiment, alumina foam showed higher glycerol conversion and H₂ yield than zirconia foam because of good adhesion and catalyst dispersion. Catalyst with high pore density provided high performance because of high amount nickel on foam. Feed flow rate affected glycerol conversion and H₂ yield. If feed flow rate was low, catalyst performance was high because low inlet glycerol and flowing through the bed slowly but entire bed if catalyst was not used. If feed flow rate was higher, glycerol conversion and H₂ yield were decreased because high amount of glycerol and flowing through the bed too fast caused catalyst cannot convert reactant to products in time. Therefore, using structured catalyst with certain bed height, it was necessary to find suitable feed flow rate for effective catalyst performance.

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CHAPTER I

INTRODUCTION

1.1 Motivation

Nowadays, more people are turning to use alternative energy because fossil energy causes air pollution which leads to global warming problem. Biodiesel is considered as renewable fuel which is derived from plants or animals. Transesterification, a reaction for production of biodiesel, produces by-product glycerol. Glycerol is generated along with biodiesel approximately in a mass ratio of 1:10 [1]. Therefore, attention has been paid to converting glycerol in valuable products. One of them is the production of hydrogen gas from glycerol. Hydrogen gas can be generated by many reactions such as pyrolysis, auto thermal reforming, aqueous phase reforming, dry reforming, and steam reforming (SR) [2]. Steam reforming reaction is chosen to study in this work. It is an endothermic reaction and has overall reaction as shown in Eq. (1).



According to stoichiometric, 7 moles hydrogen gas is produced from 1 mole of glycerol. Moreover, CO, CO₂ and CH₄ are by-product gases that is produced from side reaction.

Steam reforming is a reaction that has to use catalyst for increasing performance and gas products. Generally, there are two types of catalyst used in SR reaction; non-noble (Ni, Co) and noble metal (Pt, Ru, Rh). Mostly, pure noble metal is not popular for catalyst because its cost is not economical. Only small amount of noble metal is used for doping to increase catalyst activity and stability. Nickel is popular non-noble metal for SR reaction because it is cheap and gives high activity. But it also has main disadvantage, rapidly deactivated by coke formation. In many researches, Ni is impregnated on different supports, Al₂O₃, ZrO₂, CeO₂ or mixed oxides [3-5]. In general, shapes of catalyst are powder and pellet. Powder catalyst gives high activity but it also gives high pressure drop in reactor. So, pellet catalyst is developed to improve pressure drop but packed bed of catalyst causes high pressure drop like powder catalyst because it is covered by coke after using in reaction. Therefore, an interesting way to reduce pressure drop in reactor is structured catalyst. Open-cell ceramic foam is chosen for this work because of a number of benefits: reducing pressure drop in a reactor, enhancing heat transfer, and good gas permeability [6].

This research studies performance of structured catalyst (Ni/ceramic foam) for hydrogen production in SR reaction at reaction temperature 600°C under atmospheric pressure. Effect of different foam material (Al_2O_3 and ZrO_2) and different pore density (10, 20 and 30 PPI) on glycerol conversion, H_2 yield and carbon deposition are also investigated.

1.2 Objective

To improve and develop nickel catalyst in new ways, form of structured catalyst, for hydrogen production from steam reforming of glycerol.

1.3 Scope of research

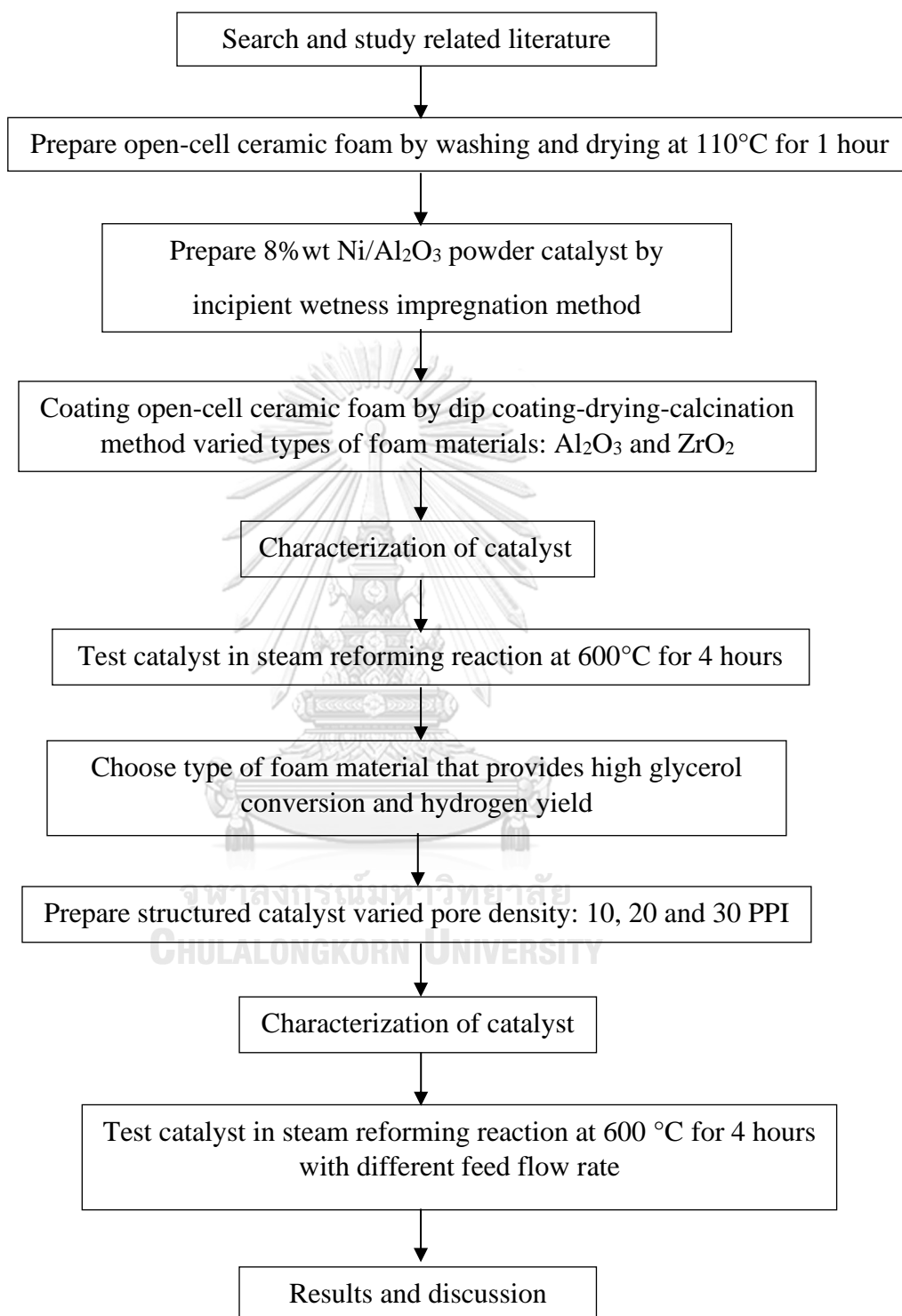
- 1.3.1 Prepare powder of nickel supported on alumina catalyst by incipient wetness impregnation method.
- 1.3.2 Coating open-cell ceramic foam by dip coating-drying-calcination method varied types of foam material (Al_2O_3 and ZrO_2) and pore density of foam (10, 20 and 30 PPI)
- 1.3.3 Investigates performance of structured catalyst (Ni/ceramic foam) for hydrogen production in SR reaction according to below conditions
 - Structured catalyst is reduced by using 100 ml/min of 50% v/v H_2/N_2 at 750°C with heating rate 10°C/min for 1 hour before testing in reaction.
 - Feed molar ratio of glycerol:water is fixed at 1:9.
 - Mixture of glycerol and water is pumped to vaporizing zone to vaporize liquid into gas phase.
 - Test structured catalyst in fixed-bed stainless steel reactor with 15 mm diameter and 500 mm length at reaction temperature 600°C for 4 hours with continuous flow of 50 ml/min N_2 carrier gas.
 - Gas products; H_2 , CO , CH_4 and CO_2 , were measured by gas chromatography with a TCD (Shimadzu, GC-2014) with Porapak-Q and Active carbon packed column.
- 1.3.4 Characterize catalyst by various techniques to observe physical and chemical properties of fresh and spent catalyst.
 - Using temperature-programmed reduction (H_2 -TPR) to observe reducibility of catalyst.
 - N_2 adsorption-desorption for measuring surface area of uncoated and coated ceramic foam.
 - Scanning Electron Microscopy/Energy Dispersive X-ray Spectrometer (SEM/EDX) is used for observing morphology of uncoated foam,

elemental distribution, thickness of coating layer on foam and surface of coated foam.

- Thermogravimetry analysis (TGA) is used to determine carbon deposition of spent catalyst.
- X-ray diffraction (XRD) is used to examine phase and crystalline of foam and nickel catalyst.
- Temperature-programmed oxidation (TPO) is used for observing the type of carbon formation on catalyst surface.



1.4 Research methodology



CHAPTER II THEORY AND LITERATURE REVIEWS

This chapter includes all of information of theories and literature reviews that related with this research.

2.1 Hydrogen

Hydrogen is a colorless, odorless, nonmetallic, tasteless, highly flammable diatomic gas with the molecular formula H_2 . It has a role as an antioxidant, an electron donor, a fuel, a human metabolite and a member of food packaging gas [7]. Hydrogen is mostly used in many industrials. In the chemical industry, it is used to make ammonia for agricultural fertilizer and it is also used to remove sulfur from fuels during the oil-refining process. Moreover, hydrogen-powered fuel cells are 'pollution-free' sources of energy and are now used in some buses and cars [8]. Properties of hydrogen [9] is shown in Table 1

Table 1 Properties of hydrogen

Physical and chemical properties	Data
Molecular weight	1.008 g/mol
Melting point	-259.14 °C
Boiling point	-252.87 °C
Density	0.08988 g/L

2.2 Glycerol

Pure glycerol appears as colorless, odorless and sweet viscous liquid. It can be miscible with water infinitely. Mainly, glycerol is by-product from biodiesel production reaction, transesterification [10], as presented in Figure 1

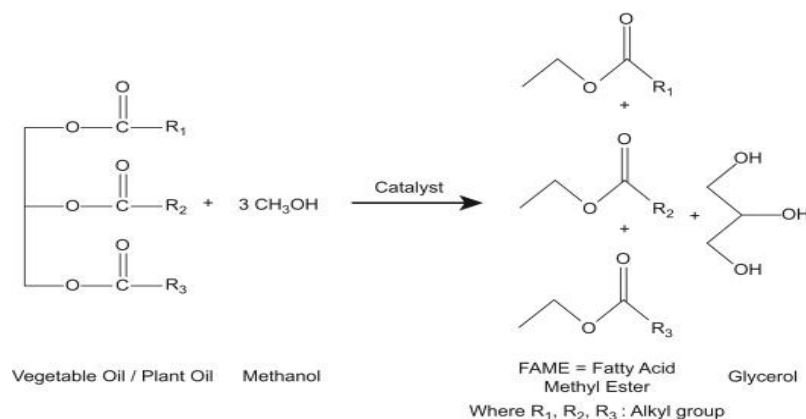


Figure 1 Transesterification

Glycerol has physical and chemical properties [11] as shown in Table 2

Table 2 Physical and chemical properties of glycerol

Physical and chemical properties	Data
Form	Viscous liquid
Molecular weight	92.09 g/mol
Refractive index	1.474
Melting point	20°C
Boiling point	290°C
Density	1.25 g/mL
Specific gravity	1.265
Odor	Odorless

Properties of glycerol make it useful for many applications. Mostly, glycerol's use is for personal care products such as cosmetics, shampoos, soaps, lotions, mouthwash, and toothpaste [11]. Not only pharmaceutical products, glycerol can be converted to valuable chemicals by many ways. One of valuable chemical that can be produced from glycerol is hydrogen gas.

2.3 Glycerol steam reforming reaction

In chemical industry, steam reforming is a promising reaction for hydrogen production from glycerol. In this reaction, glycerol reacts with water in gas phase with

the presence of catalyst. Gas products from this reaction are hydrogen, carbon monoxide, carbon dioxide and methane. Overall reaction is shown in Eq (1).



There are side reactions occurred as presented in Eq (2) to Eq (12)



Normally, steam reforming process is studied in the range of temperature from 525 to 725°C and under atmospheric pressure to obtain high hydrogen gas production [1].

2.4 Catalyst for SR reaction

Steam reforming is an endothermic reaction which has to use catalyst to increase reaction rate, gas product and selectivity. Mainly, configuration of catalyst are metal or active site and support. There are a lot of types of metal and support that are used for improving and developing catalyst.

2.4.1 Metal

2.4.1.1 Nickel

Nickel is a chemical element with the symbol Ni and atomic number 28. Powder of pure nickel has high reactive surface area, shows good chemical activity. Nickel-based catalysts are the mostly used in reforming reactions because of C–C bond rupture capability [12]. Properties of nickel [13] are presented in Table 3.

Table 3 Properties of nickel

Properties	Data
Atomic weight	58.6934 g/mol
Color	Silvery-white metal
Conductivity	Good conductor of heat and electricity
Melting Point	1,455°C
Boiling Point	2,913°C
Density	8.90 g/cm ³

2.4.2 Support

Mostly, high surface area and porous are properties of good support. Support materials such as Al₂O₃, SiO₂, ZrO₂ and zeolites are used in many researches. Support has rather influence to property of catalyst. It directly affects to catalyst, for example, metal dispersion, morphology, metal–support interactions and stability of catalyst which leads to good or bad catalytic performance [14]. Al₂O₃ and ZrO₂ are focused in this research.

2.4.2.1 Alumina

Alumina, also called aluminum oxide with the formula Al₂O₃, a white or nearly colourless crystalline substance. It is a porous and granular substance that is suitable used as a substrate for catalysts [15]. Alumina has high heat resistance, thermal conductivity, strength and high hardness. Other properties of alumina [16] are shown in Table 4

Table 4 Properties of alumina

Properties	Data
Density	3.9 g/mL
Melting point	2015°C
Thermal conductivity	40 W/mK at 20°C
Specific heat at 100 C	930 J/kg K

2.4.2.2 Zirconia

Zirconia is found in three crystal phases at different temperatures. Grain size enables the material to have very smooth surfaces. Zirconia has excellent resistance to chemicals and corrosion. Properties of zirconia are high fracture toughness, high density, good frictional behavior, high temperature capability up to 2,400°C and low thermal conductivity [17]. Due to the high temperature resistance, it is chosen to study as support of catalyst in high temperature reaction. Properties are presented in Table 5. [18]

Table 5 Properties of zirconia

Properties	Data
Chemical formula	ZrO ₂
Molar mass	123.218 g/mol
Appearance	white powder
Density	5.68 g/cm ³
Melting point	2,715 °C
Boiling point	4,300 °C

2.5 Structure catalyst

Shapes of catalyst has effect on properties of catalyst and catalytic performance. Powder and pellet are common shapes in many researches. It provides high surface area and catalytic efficiency but it also has disadvantage in a part of pressure drop. Comparison of catalyst shapes in case of pressure drop can be ranked as following; monolith < rings < pellets < extrudates < powder. So, structured catalyst is a new way to decrease pressure drop in reactor. There are two types of structured support shown as following.

2.5.1 Monolith

Monoliths contains thousands of parallel channels or holes, which are defined by many thin walls as shown in Figure 2. Many small holes have a much larger surface area than one large hole. It offers better properties than powder and pellet shape such as low pressure drop, good mass transfer, good mechanical strength, and high thermal stability [19]. Channels of monolith can be square, hexagonal, round, or other shapes which affects to heat transfer property [20] as shown in Fig.2. Many kinds of materials of monoliths are nickel, alloys, aluminum, AISI (American Iron and Steel Institute) 304 Austenitic stainless steel and ceramics.

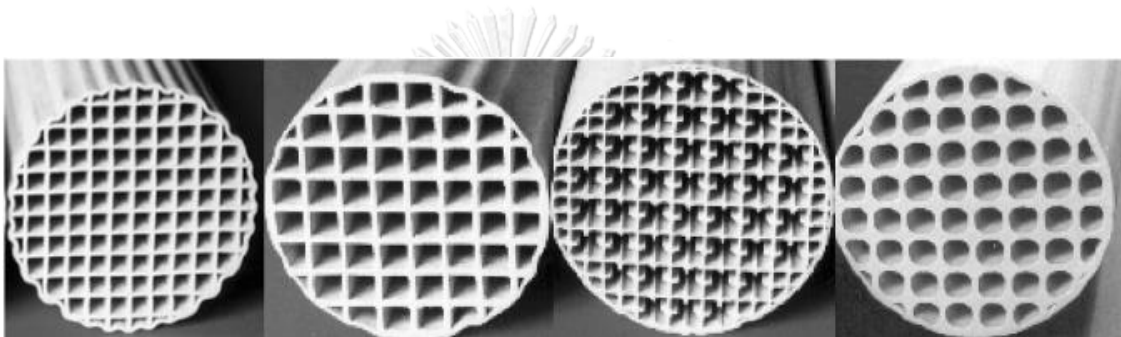


Figure 2 Monolith appearance

2.5.2 Foam

Foam can be divided in two types: Closed-cell foam and open-cell foam. Closed-cell foam is no interconnectivity but open-cell foam has open faces with fluid flow possible [21] as shown in Figure 3

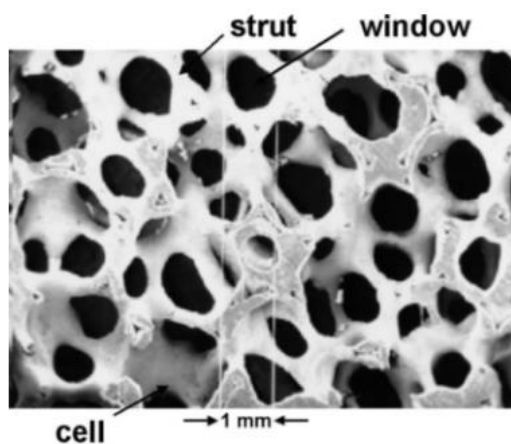


Figure 3 Open-cell foam

Open-cell foam appearance is sponge with pore density from 10-100 PPI (pores per inch). Materials of foam are ceramic foam and metal foam. Ceramic foam is synthesized from immersing polyurethane in aqueous slurry of ceramic: maybe Al_2O_3 or ZrO_2 . Shapes of foam can be cylindrical, ring, rod or other configuration. Properties of ceramic foam are low BET surface area (Approximately $1\text{-}2\text{ m}^2/\text{g}$), good gas permeability etc. Problem of low surface area can be solved by adding high surface area washcoat such as γ -alumina. Main distinctive point of ceramic foam is low pressure drop when using as support of catalyst [21].

2.6 Literature reviews

Catalysts with different metals and supports are tested in SR reaction. Moreover, there are conditions of reaction which is investigated. Many researches study different factors that maybe affect to catalytic performance.

2.6.1 Effect of metal

K. N. Papageridis et al. (2016) [22] studied of Ni, Co, Cu supported on γ -alumina catalysts for hydrogen production via the glycerol steam reforming reaction. All catalysts were prepared by incipient wetness impregnation technique and calcined at $800\text{ }^\circ\text{C}$ for 5 hours. 8%wt loading of metal was used in this research. From results, Ni/ Al_2O_3 provided highest H_2 yield at 3.4 moles and glycerol conversion at 78.5% because Ni/ Al_2O_3 had capacity to promote C-C rupture compared with CO and Cu.

C. K. Cheng et al. (2010) [23] studied Co/ Al_2O_3 catalyst in glycerol steam reforming. 15% wt loading of Co on Al_2O_3 was prepared by wet impregnation method. Salt precursor was $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Catalyst was calcined at $600\text{ }^\circ\text{C}$ for 4 hours. 0.25 g fresh catalyst was tested in stainless-steel fixed bed reactor (10 mm diameter) at atmospheric pressure and reaction temperature between $450\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$. The results showed that Co/ Al_2O_3 catalyst surface contained both weak and strong acid sites. Glycerol conversion of between 30 and 65% was obtained.

2.6.2 Effect of support

R.L. Manfro et al. (2013) [24] studied steam reforming of glycerol by using Ni-based catalyst supported on different types of support, Al_2O_3 , CeO_2 and ZrO_2 . All catalysts were prepared by wet impregnation method with 20%wt of NiO loading. Catalysts were calcined at $500\text{ }^\circ\text{C}$ for 3 hours under air flow and tested at reaction

temperature 500°C with gas hourly space velocity 50,000 h⁻¹. Results showed that Ni/Al₂O₃ provided highest BET surface area and small crystalline size. Highest H₂ selectivity and least coke formation were obtained by using Ni/ZrO₂. This research concluded Ni/ZrO₂ was the best catalyst.

N.H. Zamzuri et al. (2017) [25] investigated steam reforming of glycerol for hydrogen production. Catalysts were nickel supported on various supports. Al₂O₃, La₂O₃, ZrO₂, SiO₂, and MgO were studied as different supports. Using wet impregnation method for synthesizing 10%wt Ni-based catalysts. All catalysts were tested at 650°C for 5 hours with feed molar ratio glycerol to water at 1:6. This results presented that Ni/Al₂O₃ was the best catalyst with high surface area (123.4 m²/g) and high Ni dispersion which produced H₂ selectivity at 71.8%.

N.D. Charissiou et al. (2019) [26] studied the influence of SiO₂ doping Ni/ZrO₂ catalyst. Catalyst was prepared by wet impregnation method and calcined at 800°C for 4 hours. 8%wt Ni loading was fixed for this study. For Ni/ZrO₂, glycerol conversion was 75% at 400°C and 90% at 600-750°C and coke formation was 0.51 g_{coke}/g_{cat}. Moreover, Ni/ZrO₂ could be improved by doping SiO₂. More hydrogen production and less coke formation were obtained when catalyst was doped.

2.6.3 Condition for SR reaction

S. Adhikari et al. (2007) [27] studied thermodynamics of glycerol steam reforming reaction. Effect of several process variables, such as system pressure, temperature, and ratio of reactants on yield of the hydrogen depends were investigated. Two pressure was varied at 1 and 5 atm. Molar ratio of water to glycerol was varied at 1:1, 3:1 6:1 and 9:1. Reaction temperature was varied from 600-900 K. Results showed that optimal conditions that provided highest yield of hydrogen were temperature > 900 K, atmospheric pressure, and a molar ratio of water to glycerol of 9:1.

2.6.4 Structured catalyst

P. Ciambelli et al. (2010) [28] studied different types of supports. 400 cpsi ceramic honeycomb monolith and 65 PPI alumina open-cell foam were chosen to be carrier of Ni in methane autothermal reforming. Catalysts were prepared by dip coating supports into slurry of CeO₂-Al₂O₃ and Ni(CH₃COO)₂·4H₂O and calcined at 1000°C for 1 hour. The results showed that foam catalyst gave higher activity because of random porous network. Foam catalyst improved gas temperature profile in reactor and had higher surface to volume ratio than ceramic monolith.

S. Danaci et al. (2016) [29] investigated CO₂ methanation over Ni/Al₂O₃ coated structured catalysts. Stainless steel support was coated with slurry of Ni/Al₂O₃. Effect of coating suspension composition on properties of coating was reported. Different amount of PVA added into slurry was 1, 3 and 5%. Results showed 3% of PVA in slurry provided the best adhesive coating and gave more homogeneous coating. In the contrary, 1% and 5% of PVA provided cracks on surface and non-homogeneous.

S. Adhikari (2007) [30] studied various metal on ceramic foam monoliths contain 8% silica which has surface area around 1 m²/g with void fraction 0.8; Ni, Rh, Pt, Pd, Ir and Ru. Moreover, CeO₂ was doped to exhibit coke deposition. Dip coating was method for preparing catalysts. After dip coating, catalysts were calcined at 700°C for 5 hours in air. Catalyst loading was measured by weighing bare monolith and coated monolith. In this study, Ni/Al₂O₃ was the best catalyst with highest conversion 82% at 700, 800 and 900°C. Glycerin conversion at 900 °C was in order; Ni>Ir>Pd>Rh>Pt>Ru. Moreover, effect of glycerin to water ratio (3:1, 6:1 and 9:1) was investigated. Results showed that conversion increased with increasing ratio. 9:1 glycerin to water provided highest conversion at 90% by catalyst Ni/Al₂O₃ and H₂ selectivity at 80%.

CHAPTER III EXPERIMENT

This chapter is all about experiments in this research which consists of five parts : materials and chemicals, preparation of powder catalyst, preparation of slurry for coating, preparation of structured catalyst, characterization of catalyst and performance of structured catalyst in steam reforming reaction.

3.1 Materials and chemicals

- 3.1.1 Alumina (γ -Al₂O₃, Sigma Aldrich)
- 3.1.2 Nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O, Sigma Aldrich)
- 3.1.3 Polyvinyl alcohol 99+% hydrolyzed (-CH₂CHOH-, Sigma Aldrich)
- 3.1.4 Acetic acid (CH₃COOH, Sigma Aldrich)
- 3.1.5 Glycerol (C₃H₈O₃, >99.5%, Sigma Aldrich)
- 3.1.6 Alumina foam (Al₂O₃, Pingxiang Zhongtai Environmental Chemical Packing Co., Ltd. China)
- 3.1.7 Zirconia foam (ZrO₂, Pingxiang Zhongtai Environmental Chemical Packing Co., Ltd. China)
- 3.1.8 Nitrogen gas (N₂, 99.999% purity, Linde)
- 3.1.9 Hydrogen gas (H₂, 99.999% purity, Linde)
- 3.1.10 Air zero (99.999%, Linde)
- 3.1.11 Deionized water

3.2 Preparation of powder catalyst

8%wt Ni/Al₂O₃ powder catalyst was prepared by incipient wetness impregnation method. Ni(NO₃)₂.6H₂O was dissolved in deionized water and impregnated on γ -Al₂O₃ powder. The impregnated γ -Al₂O₃ was dried at 110°C for 24 hours and calcined in flow of air at 800°C for 4 hours under atmospheric pressure.

3.3 Preparation of coating slurry

Polyvinyl alcohol (PVA) was added into deionized water and kept stirring overnight. Then, powder of Ni/Al₂O₃ catalyst was added along with acetic acid and also kept stirring overnight.

3.4 Preparation of structured catalyst

Two types of open-cell ceramic foam (Al_2O_3 and ZrO_2) was washed before coating with deionized water and dried at 110°C for 1 hour. After that, ceramic foam was submerged into coating slurry for 30 seconds and blown to remove excess slurry. Then, coated ceramic foam was dried at 110°C for 1 hour and calcined at 550°C for 2 hours. Structured catalysts were obtained.

3.5 Characterization of catalyst

- Temperature-programmed reduction (H_2 -TPR) using Micromeritics chemisorp 2750 Pulse Chemisorption System was used to observe reducibility of catalyst. 0.05 grams of catalyst was put into quartz tube and heated to 300°C in flow of N_2 gas for removing moisture. After that, 10% H_2/Ar
- N_2 adsorption-desorption with Micromeritics ASAP 2020 was used for measuring surface area, pore volume and pore size of uncoated ceramic foam. Samples were degassed before the test under vacuum at 200°C for 12 hours. The Brunauer–Emmett–Teller (BET) method is used for the calculation of surface area. Pore diameter and pore volume of the catalysts were determined by Barret-Joyner-Halenda (BJH) method.
- Scanning Electron Microscopy/Energy Dispersive X-ray Spectrometer (SEM/EDX) is used for observing morphology of uncoated foam, elemental distribution, thickness of coating layer on foam and surface of coated foam. Samples were analyzed by JEOL JSM-35 the SEM model is S3400N and Link Isis Series 300 program Apollo model x.
- Thermogravimetry analysis (TGA) is used to determine carbon deposition of spent catalyst using thermogravimetric analysis with differential scanning calorimeter (TGA/DSC, SDT Q600 Diamond Thermogravimetric and Differential Analyzer, TA Instruments). Temperature of perating condition is the range between room temperature to 1000°C with heating rate of $10^\circ\text{C}/\text{min}$ in $100\text{ ml}/\text{min}$ of air.
- X-ray diffraction (XRD) (X-ray diffractometer SIEMENS D5000) is used to examine phase and crystalline of foam and nickel catalyst using $\text{Cu-K}\alpha$ radiation between 20° and 80° with a step size of 0.06° and a scan speed is 0.5 s per step.

3.6 Performance of structured catalyst in SR reaction

3.6.1 Reaction step

Structured catalyst is packed in 15 mm diameter and 500 mm length stainless steel fixed-bed reactor. For measuring the bed temperature, type-K thermocouple was equipped in the middle of furnace. Catalyst is reduced by using 100 ml/min of mixture gas, H₂ and N₂ (50%v/v), at 750 °C with heating rate 10 °C/min for 1 hour. After reducing catalyst, a reactor is cooled down to reaction temperature 600 °C and purged with nitrogen gas for 1 hour. Then, mixture of glycerol and water at fixed molar ratio 1:9 is fed into vaporizing zone by HPLC pump. Feed gas is carried to reaction zone by N₂ carrier gas. There is condenser in the out of reactor to condense liquid products. Reaction time for testing catalyst is 4 hours. Gas products; H₂, CO, CH₄ and CO₂, were measured by gas chromatography with a TCD (Shimadzu, GC-2014) with Porapak-Q and Active carbon packed column. Scheme is shown in Figure 4.

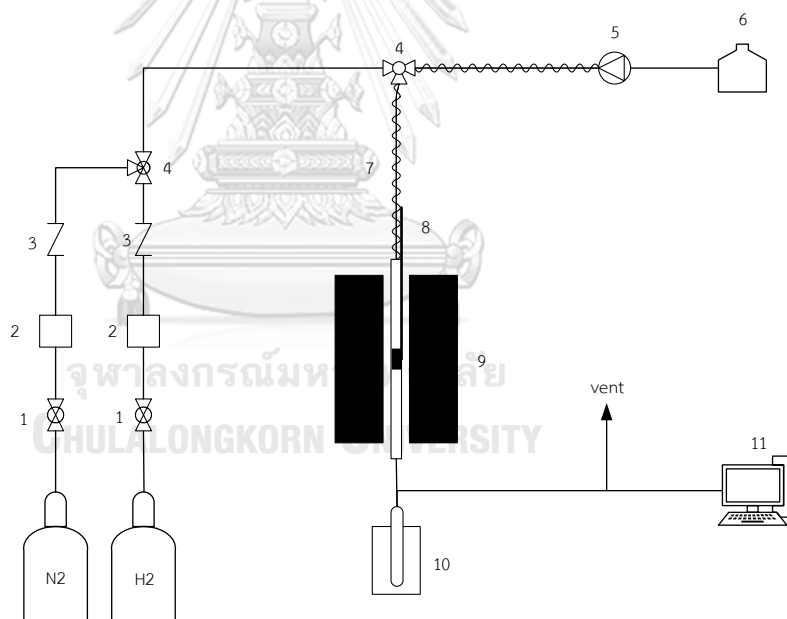


Figure 4 Schematic of reaction

- | | |
|--------------------------------------|---|
| Number 1: Ball valve | Number 7: Vaporizing zone (heating cable) |
| Number 2: Mass flow | Number 8: Type-K thermocouple |
| Number 3: Check valve | Number 9: Reaction zone (Furnace) |
| Number 4: Three-way valve | Number 10: Cold trap |
| Number 5: HPLC pump | Number 11: Gas chromatography |
| Number 6: Glycerol and water mixture | |

3.6.2 Gas chromatography information

Table 6 Gas chromatography information

Gas chromatography	Shimadzu GC-2014	
Detector	TCD	TCD
Column	Active carbon	Porapak Q
- material	Stainless steel	Stainless steel
- length (m)	2	2
- Inner diameter (mm)	3	3
Column temperature (°C)	50	50
Injection temperature (°C)	150	150
Detector temperature (°C)	150	150
Current (mA)	70	70
Analyzed gas	H ₂ , CH ₄ , CO	CO ₂
Carrier gas	Nitrogen (99.999%)	Nitrogen (99.999%)
Carrier gas flow rate (ml/min)	30	30

3.6.3 Calculation of glycerol conversion, H₂ yield and product distribution

Glycerol conversion, product distributions and H₂ yield were measured and calculated using equations below;

$$\% \text{ Glycerol conversion} = \frac{[\text{CO}_2]_{\text{out}} + [\text{CO}]_{\text{out}} + [\text{CH}_4]_{\text{out}}}{3[\text{C}_3\text{H}_8\text{O}_3]_{\text{feed}}} \times 100$$

$[\text{CO}_2]_{\text{out}}$, $[\text{CO}]_{\text{out}}$, $[\text{CH}_4]_{\text{out}}$ and $[\text{C}_3\text{H}_8\text{O}_3]_{\text{feed}}$ are molar flow rate of CO₂, CO, CH₄ and C₃H₈O₃ in mole/min, respectively. Molar flow rate of glycerol and all gases were obtained by substitute area from GC to calibration curve and multiply by flow of gas product (ml/min)

$$\% \text{ Product distributions of } i = \frac{\text{Molar flow rate of } i}{\text{Molar flow rate of all gas species}} \times 100$$

i is H₂, CO, CO₂ and CH₄ gas produced.

$$\text{H}_2 \text{ yield} = \frac{[\text{H}_2]_{\text{produced}}}{[\text{C}_3\text{H}_8\text{O}_3]_{\text{feed}}}$$

$[\text{H}_2]_{\text{produced}}$ is molar flow rate of H₂ produced in mole/min.

From all experiments in this study, glycerol conversion value was especially converting glycerol to gaseous products. Normally, it had liquid product from glycerol steam reforming but this study only focused on gaseous product. Therefore, value of glycerol conversion was less than actual value from reaction.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter includes 4 main parts of results and discussion including effect of ceramic foam materials, effect of pore density (PPI), effect of feed flow rate and characterization of spent catalysts.

4.1 Effect of foam materials on catalyst properties and catalytic activity in glycerol steam reforming

X-ray diffraction (XRD) was used to observe crystalline phase of uncoated and coated foam. Results were presented in Figure 5 and 6. Figure 5 showed phase of catalyst on Al_2O_3 foam. For uncoated Al_2O_3 foam, peaks of α -alumina were observed [31]. α -alumina was stable phase compared to other phases. Peaks of NiO were presented at 2θ : 38.2° and 47° on coated foam. From Figure 6, ZrO_2 foam was monoclinic phase, peaks of NiO and γ -alumina were observed at 2θ : 44.5° and 66.9° , respectively. Therefore, XRD patterns confirmed that powder catalyst was coated on both types of ceramic foam.

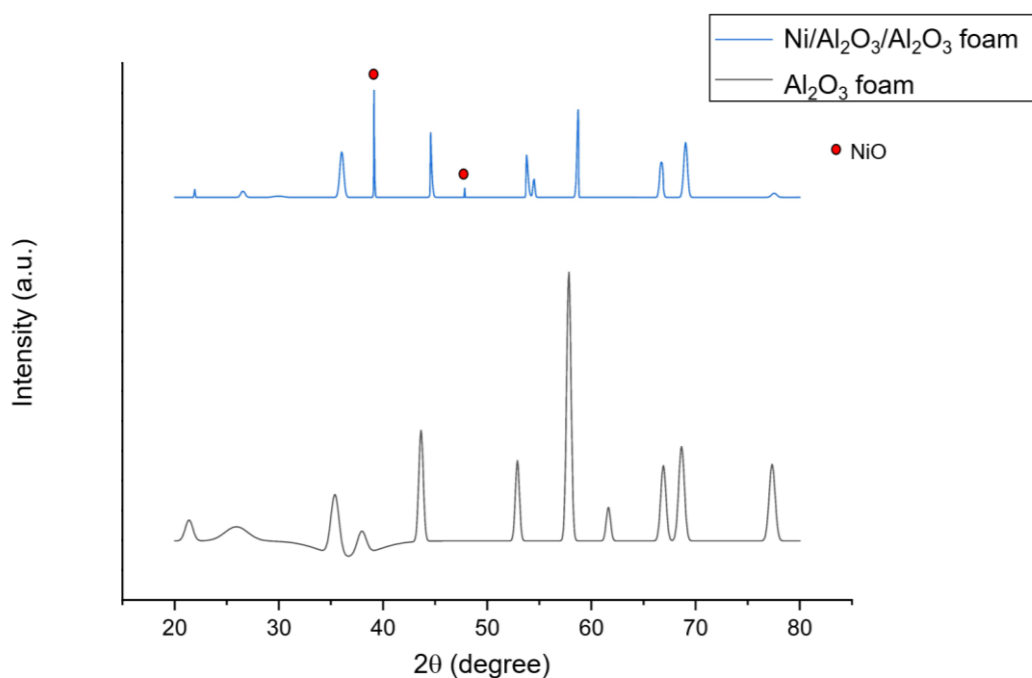


Figure 5 XRD patterns of uncoated and coated Al_2O_3 foam

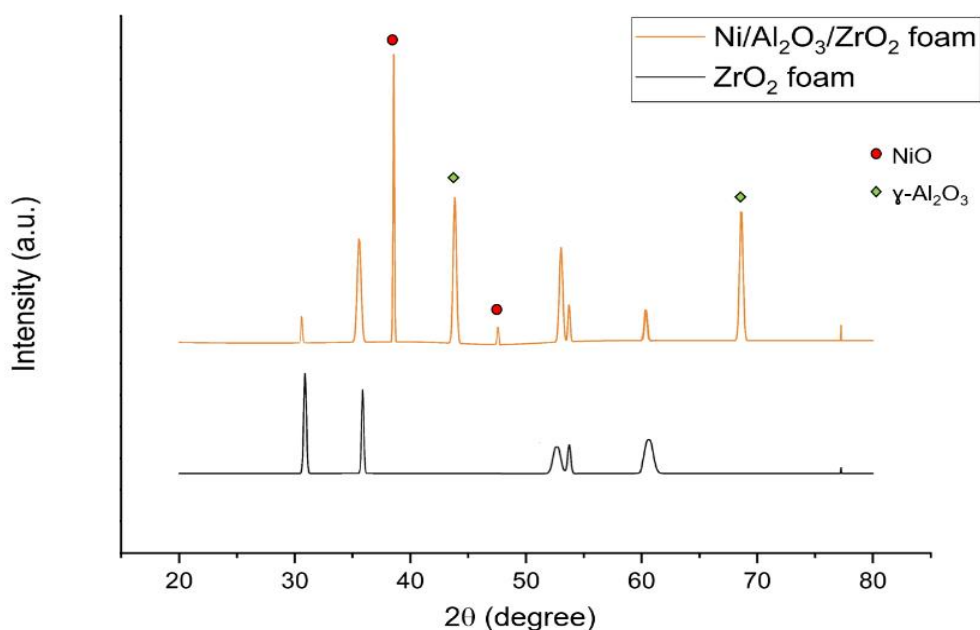


Figure 6 XRD patterns of uncoated and coated ZrO₂ foam

Surface area of uncoated and coated foam were analyzed by using N₂ adsorption and desorption. BET surface area results were presented in Table 7. Both bare Al₂O₃ and ZrO₂ foam had similar surface area around 1 m²/g. Surface area was low because ceramic foam was type of support which was not porous material. Nickel could not be adhered directly on ceramic foam so it had to impregnate nickel on high surface area support before coating.

Table 7 Specific surface area of uncoated ceramic foam

Type of foam	Specific surface area (m ² /g)
Al ₂ O ₃ foam	1.23
ZrO ₂ foam	1.57

After one time coating on ceramic foam, it found that surface area was increased from bare foam as shown in Table 8. Coated ZrO₂ provided the lowest surface area after coating because of the poorest dispersion and adherence of catalyst. Coated Al₂O₃ foam with 10, 20 and 30 PPI showed nearly similar surface area around

6-7 m²/g that was higher than coated ZrO₂ because of better dispersion and adhesion.

Table 8 Specific surface area of coated ceramic foam

Type of coated ceramic foam	Specific surface area (m ² /g)
ZrO ₂ foam	3.85
Al ₂ O ₃ foam (10 PPI)	6.83
Al ₂ O ₃ foam (20 PPI)	7.67
Al ₂ O ₃ foam (30 PPI)	7.89

Morphology of uncoated ceramic foams observed by using scanning electron microscopy (SEM) were presented in Figure 7. There were less roughness and surface area to be support for metal loading according to BET results.

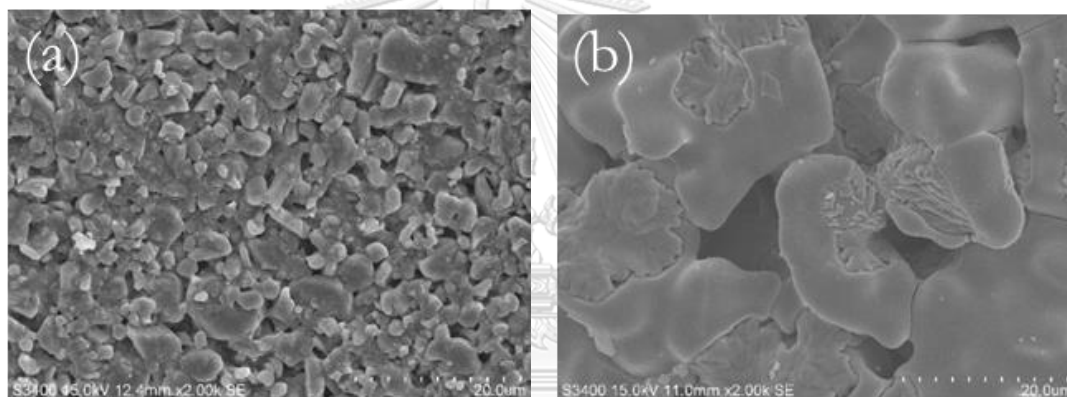
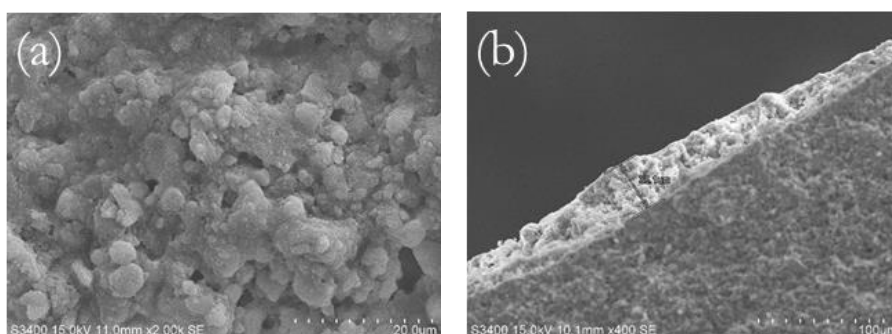


Figure 7 SEM images of uncoated (a) Al₂O₃ foam (b) ZrO₂ foam

After coating, catalyst surface and coating thickness on Al₂O₃ and ZrO₂ foam were also evaluated by SEM as shown in Figure 8. Catalyst coating thickness on Al₂O₃ foam was 38.1 μm and 38.6 μm on ZrO₂ foam. It was nearly similar on both foam but it has a little peel-off on ZrO₂ foam as shown in Figure 9.



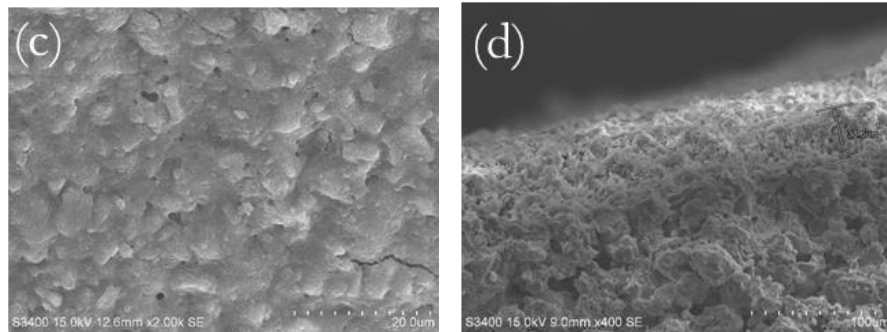


Figure 8 SEM images of surface of catalyst and thickness of coating on ceramic foam (a,b) Al_2O_3 foam (c,d) ZrO_2 foam

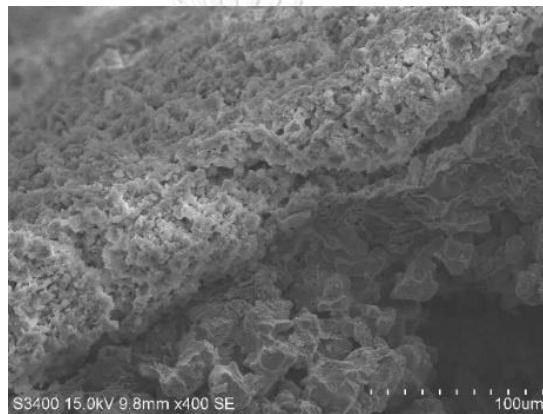
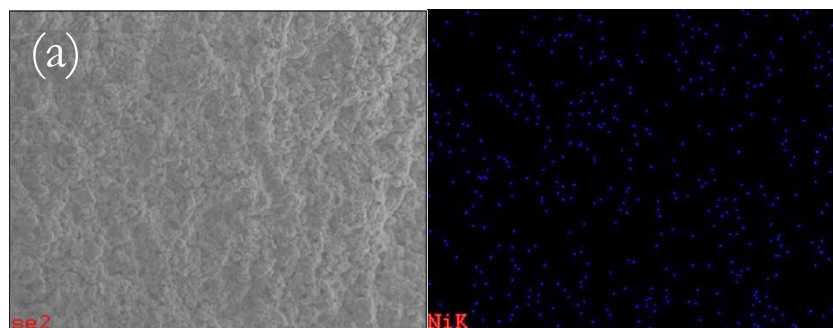


Figure 9 Peel-off of catalyst on ZrO_2 foam

Catalyst dispersion was observed by SEM/EDX technique as presented in Figure 10. From EDX results, catalyst dispersion was quite difficult to see difference between two types of foam.



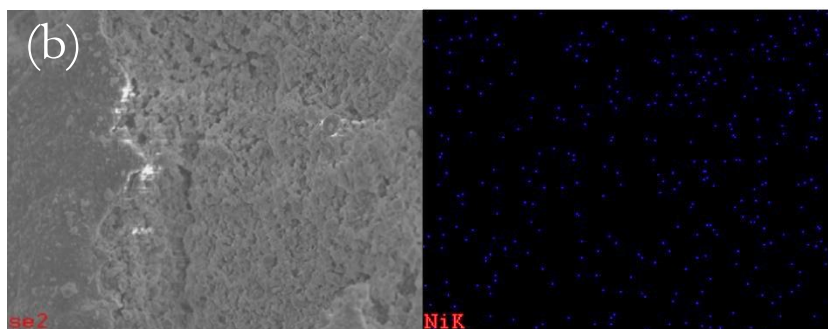


Figure 10 SEM/EDX of catalyst on (a) Al_2O_3 foam and (b) ZrO_2 foam

Reducibility of catalyst was measured by temperature programmed reduction (H_2 -TPR). As shown in Figure 11, reduction temperature was approximately started at 450°C . Result was indicated that NiO was reduced to Ni metal at temperature around 600°C . In the range of temperature between 427 - 627°C , reduction of nickel oxide interacting with support was happened.

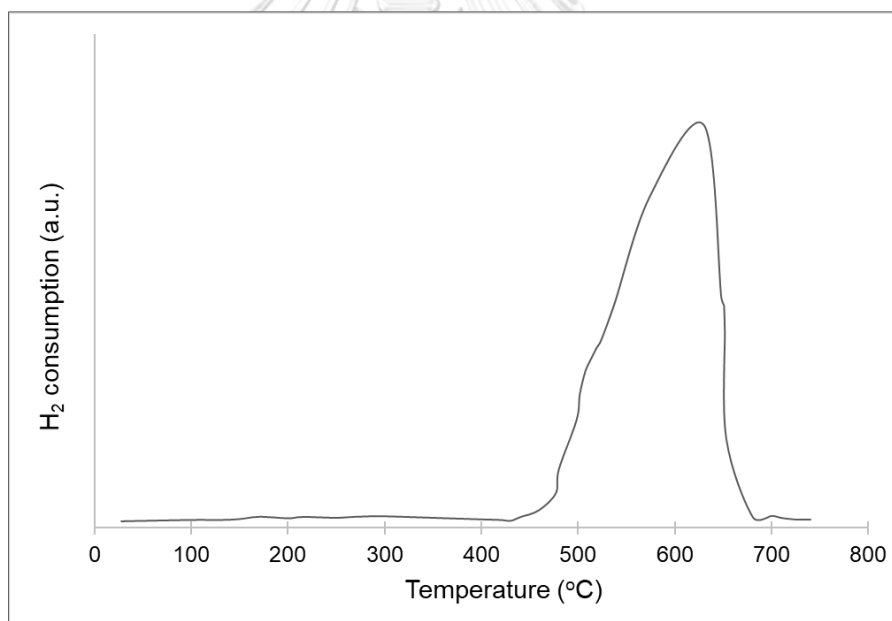


Figure 11 H_2 -TPR profiles of catalyst $\text{Ni}/\text{Al}_2\text{O}_3$

Catalyst on ceramic foam was analyzed by TGA. Normally, PVA decomposition happened at 295°C [32]. From TGA results in Figure 12, there were no peak of decomposition at any temperature. Therefore, it confirmed that there were no PVA contaminated with catalyst on ceramic foams.

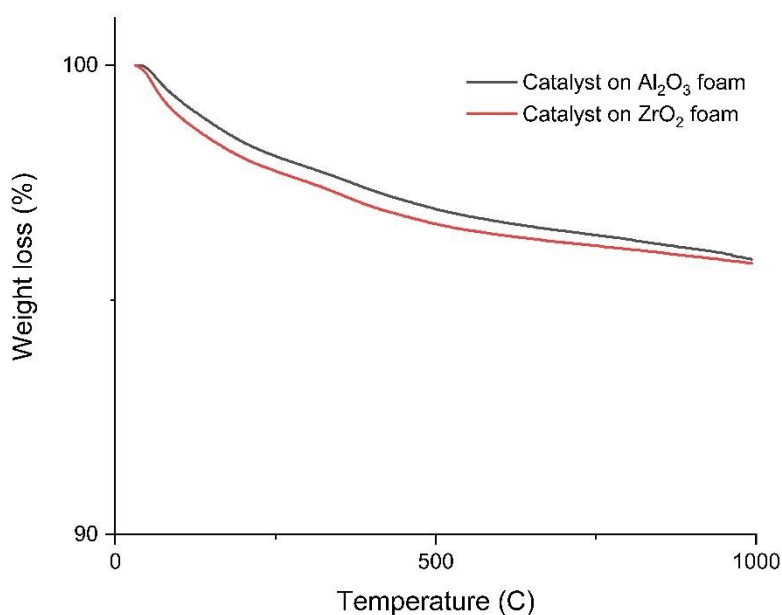


Figure 12 TGA curves of catalyst coating before used on Al₂O₃ foam and ZrO₂ foam

Effect of different ceramic foam materials on catalyst activity was studied. Structured catalyst was tested under atmospheric pressure at 600°C for 4 hours with fixed molar ratio of feed at 1:9 (glycerol:water). Glycerol conversion to gaseous products, hydrogen yield and gas product distribution were measured to compare efficiency between two structured catalysts.

Average conversion with standard deviation of each catalyst was obtained by average conversion throughout 4 hours reaction time and three times testing. Catalyst on Al₂O₃ foam provided higher glycerol conversion at 64.1±0.66% as shown in Figure 13(a) while catalyst on ZrO₂ foam provided only 59.4±1.79% conversion as in Figure 13(b). Since adhesion between catalyst and ZrO₂ foam was not good and catalyst layer peeled off as presented in Figure 9. caused less amount of catalyst and uneven catalyst dispersion on foam.

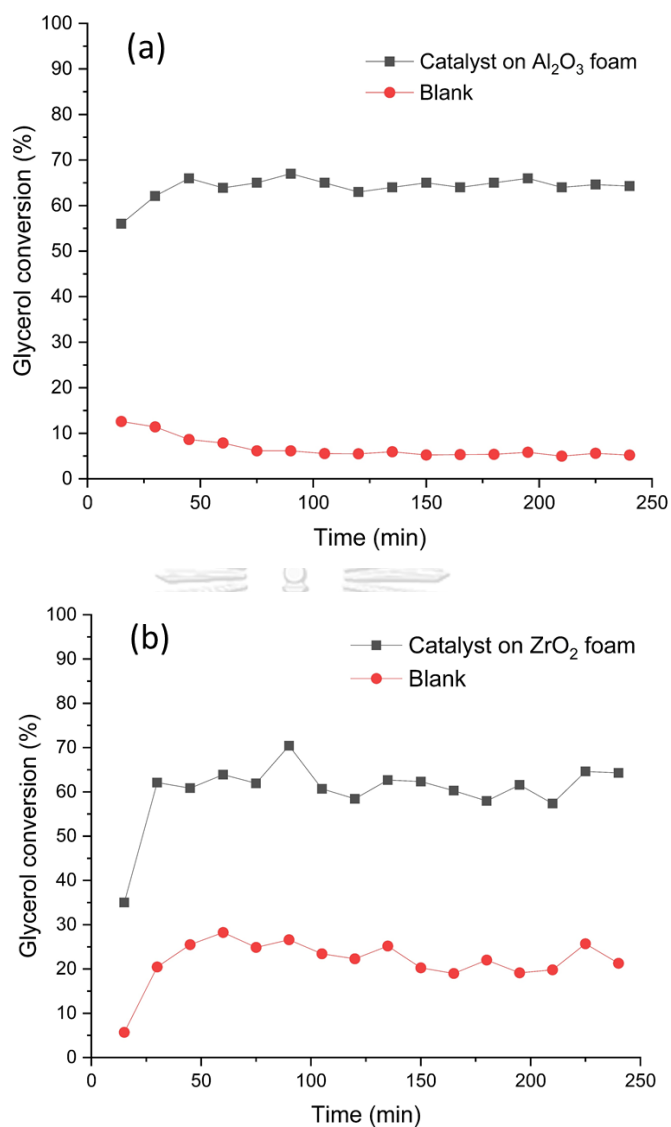


Figure 13 Glycerol conversion of structured catalysts on (a) Al₂O₃ foam and (b) ZrO₂ foam (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed C₃H₈O₃: H₂O is 1: 9, feed flow rate is 0.04 ml/min and GHSV 1,800 h⁻¹)

Moreover, H₂ yield was obtained by calculating throughout 4 hours reaction time and estimate average value. Result of H₂ yield was presented in Figure 14. Higher H₂ yield was happened when using structured catalyst with Al₂O₃ foam at 4.1±0.3 moles/mole of glycerol or approximately 60%.

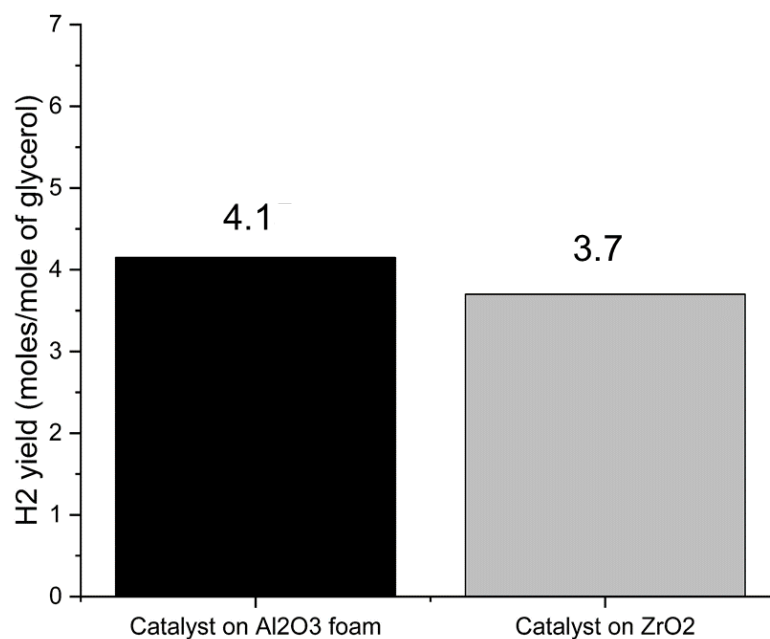


Figure 14 H₂ yield of structured catalysts on two types of foam materials (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed C₃H₈O₃: H₂O is 1: 9, feed flow rate is 0.04 ml/min and GHSV 1,800 h⁻¹)

Gas products from glycerol steam reforming occurred by main and side reaction such as water-gas shift reaction, glycerol decomposition and methanation reaction. Thus, H₂, CO, CO₂ and CH₄ were 4 main gas products. From results in Figure 15, two catalysts with different foam materials provided similar compositions of main gases. H₂ gas was at 70%, CO₂ and CO were 20.5% and 8%, respectively. CH₄ was the lowest amounts at 4.5%. Therefore, different foam materials did not affect gas product distribution.

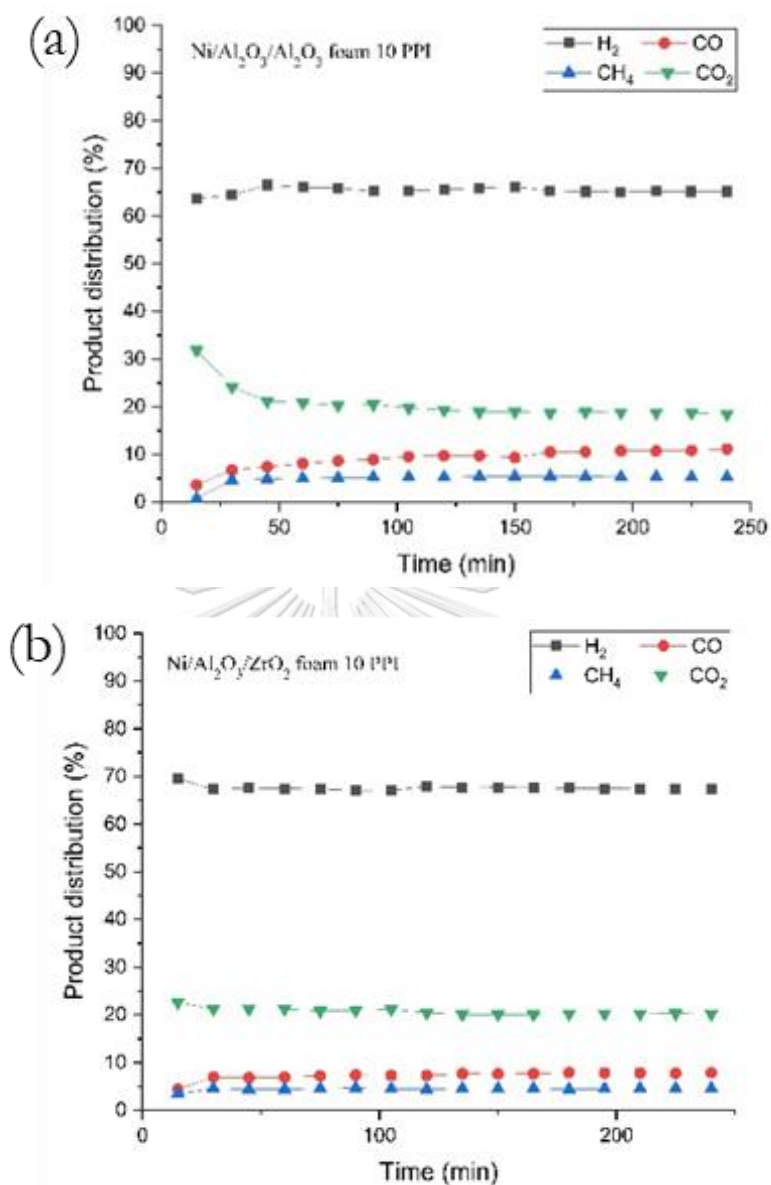
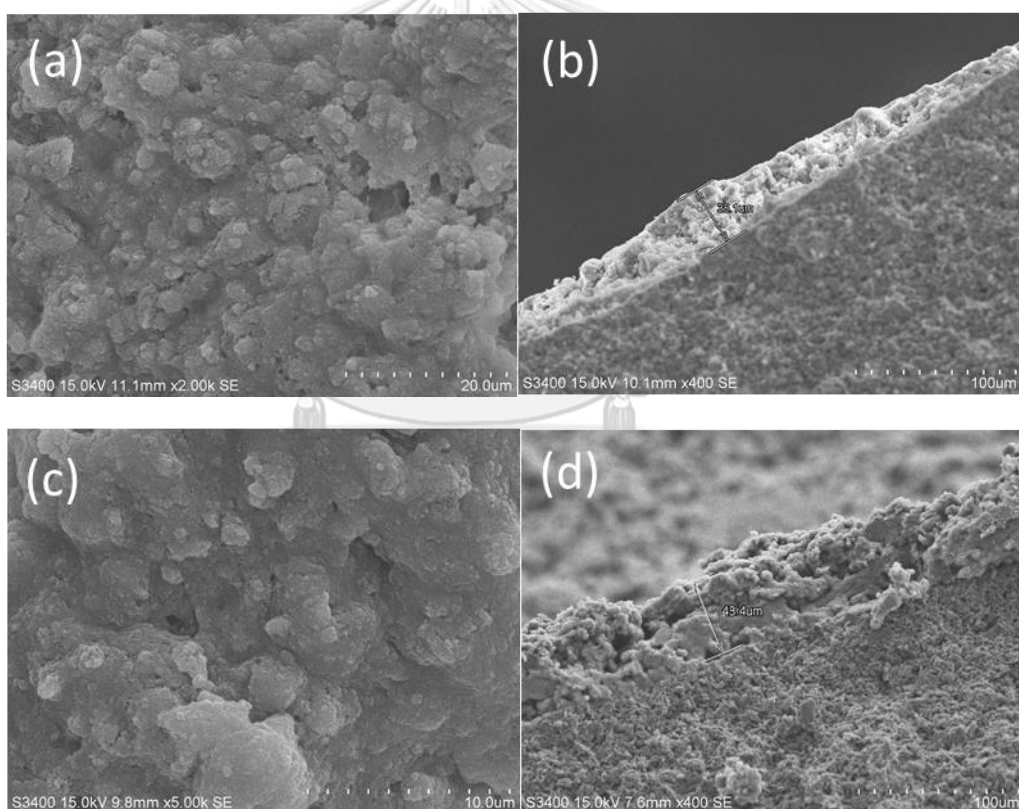


Figure 15 Product distributions obtained during GSR reaction of both structured catalyst on (a) Al₂O₃ foam and (b) ZrO₂ foam (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed C₃H₈O₃: H₂O is 1: 9, feed flow rate is 0.04 ml/min and GHSV 1,800 h⁻¹)

4.2 Effect of pore density of ceramic foam on catalyst properties and catalytic in glycerol steam reforming.

After testing catalyst with different foam materials in glycerol steam reforming, Al_2O_3 foam was better than ZrO_2 foam so it was chosen to be studied effect of pore density varied from 10 to 30 PPI. Catalyst properties was analyzed as follows.

Morphology of bare and coated Al_2O_3 foam with different PPI were observed by using SEM images. Catalyst surface and coating layer thickness of all catalysts were shown in Figure 16 (a)-(f). From all SEM images, dip coating catalyst for 1 time on 10, 20 and 30 PPI Al_2O_3 foam caused nearly similar thickness of coating layer around 38-45 μm .



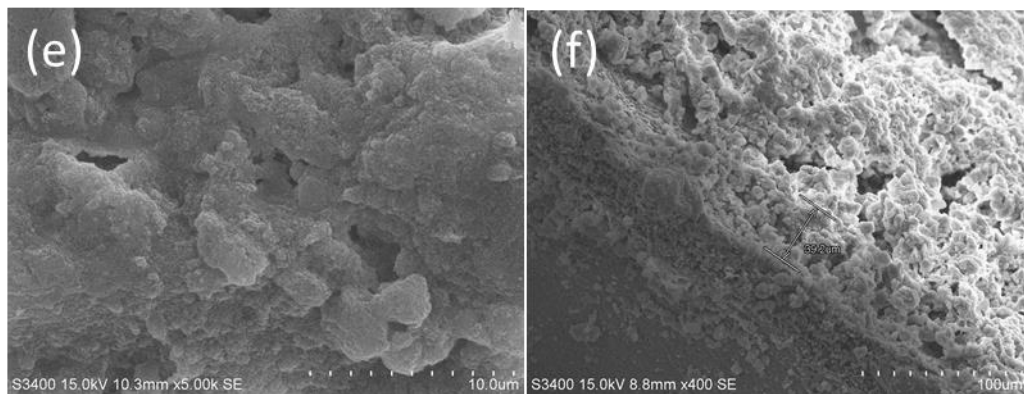
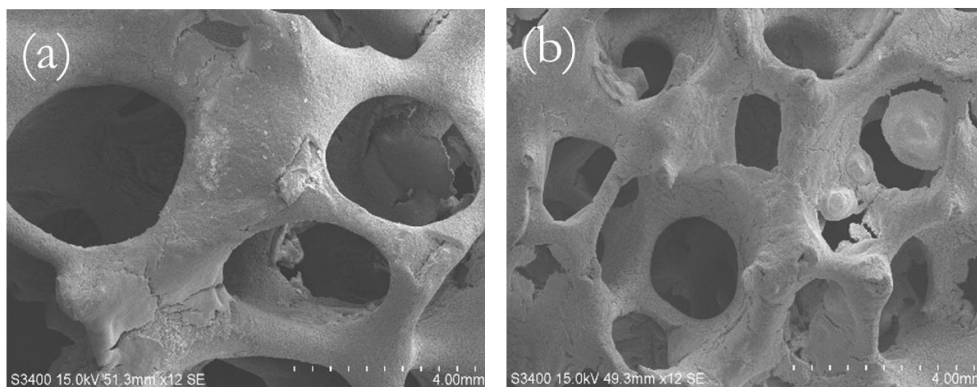


Figure 16 (a) Catalyst surface on 10 PPI foam (b) Coating layer thickness on 10 PPI foam (c) Catalyst surface on 20 PPI foam (d) Coating layer thickness on 20 PPI (e) Catalyst surface on 30 PPI foam (f) Coating layer thickness on 30 PPI

Different pore density caused different size of channels between each struts. Width of channels of 10, 20 and 30 PPI were presented in Table 8. When increasing pore density, it decreased width of channels. Coated Al_2O_3 foam with different pore density was observed by SEM technique. SEM images in Figure 16 showed that 20 and 30 PPI had some pore clogging and it decreased gas permeability.

Table 9 Width of channels between strut of 10, 20 and 30 PPI

Pore density (PPI)	Width of channel (mm)
10	3.56
20	1.71
30	1.26



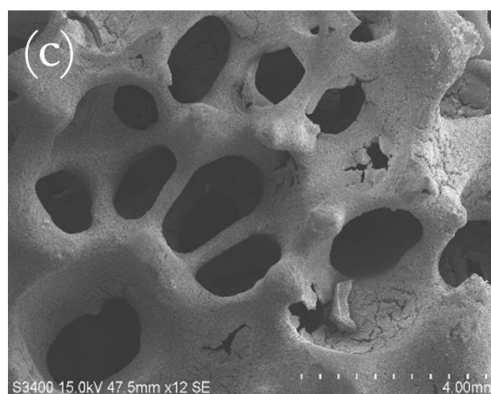


Figure 17 Appearance of different pore density of coated foam (a) 10 PPI (b) 20 PPI and (c) 30 PPI

Catalytic activity was observed in terms of glycerol conversion, H_2 yield and gas product distribution like first section. Glycerol conversion of 3 catalysts were shown in Figure 17. Average conversion with standard deviation of each catalyst was obtained by average conversion throughout 4 hours reaction time and three times testing. From results, the highest pore density structured catalyst, 30 PPI, provided highest conversion at $70.4 \pm 1.04\%$ while 10 and 20 PPI provided average conversion at $67.9 \pm 1.45\%$ and $64.1 \pm 0.66\%$, respectively.

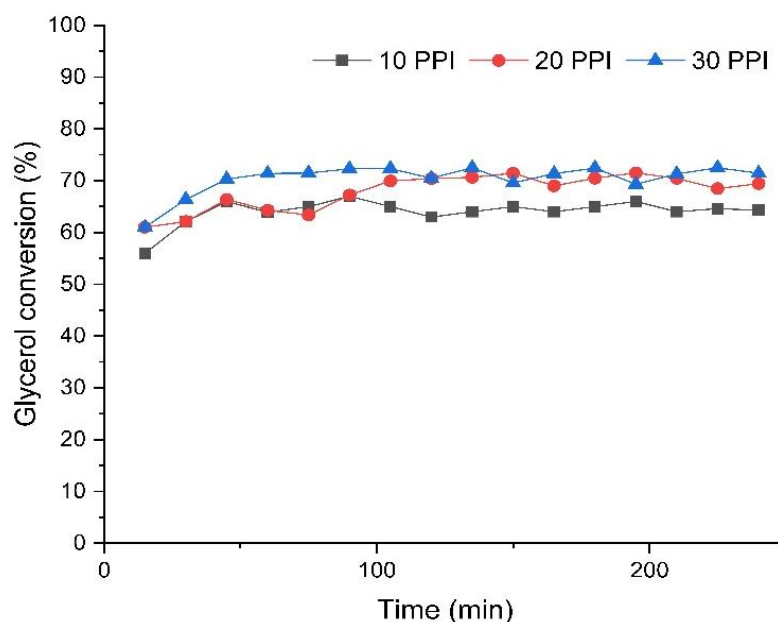


Figure 18 Glycerol conversion of structured catalysts with different pore density (Operating conditions at $600\text{ }^\circ\text{C}$ under atmospheric pressure with molar ratio of feed $C_3H_8O_3$: H_2O is 1: 9, feed flow rate is 0.04 ml/min and GHSV $1,800\text{ h}^{-1}$)

H₂ yield was obtained by calculating throughout 4 hours reaction time and estimate average value. Average H₂ yield was presented in Figure 18. The result showed that H₂ yield had the same trend with glycerol conversion. When pore density was increased, H₂ yield was increased. 30 PPI of structured catalyst provided the highest H₂ yield at 4.6 moles/mole of glycerol or 66% because high pore density caused high area for catalyst coating that increased amount of catalyst on ceramic foam.

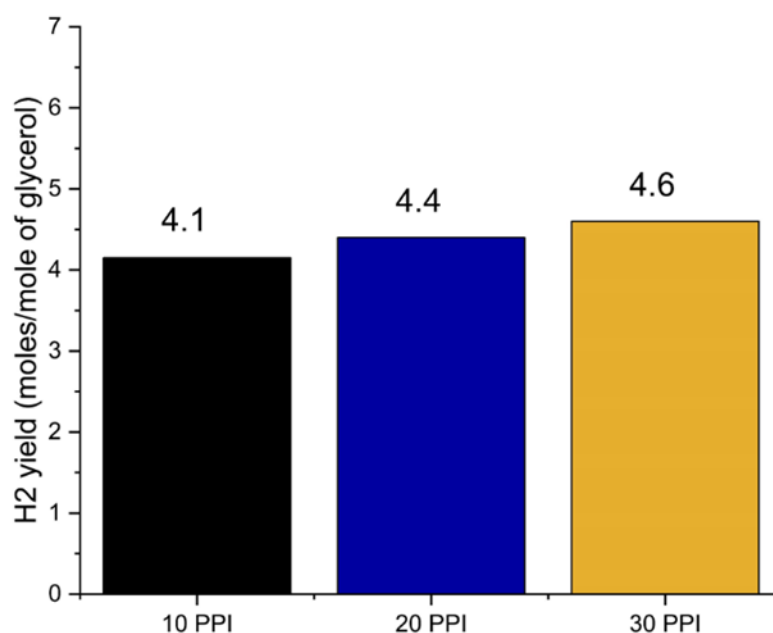


Figure 19 H₂ yield of structured catalysts with different pore density (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed C₃H₈O₃: H₂O is 1: 9, feed flow rate is 0.04 ml/min and GHSV 1,800 h⁻¹)

Main gas product distribution was observed and presented in Figure 19. Results showed that different pore density of ceramic foams did not affect gas product distribution. H₂ gas, desired gas product, was at approximately 70%.

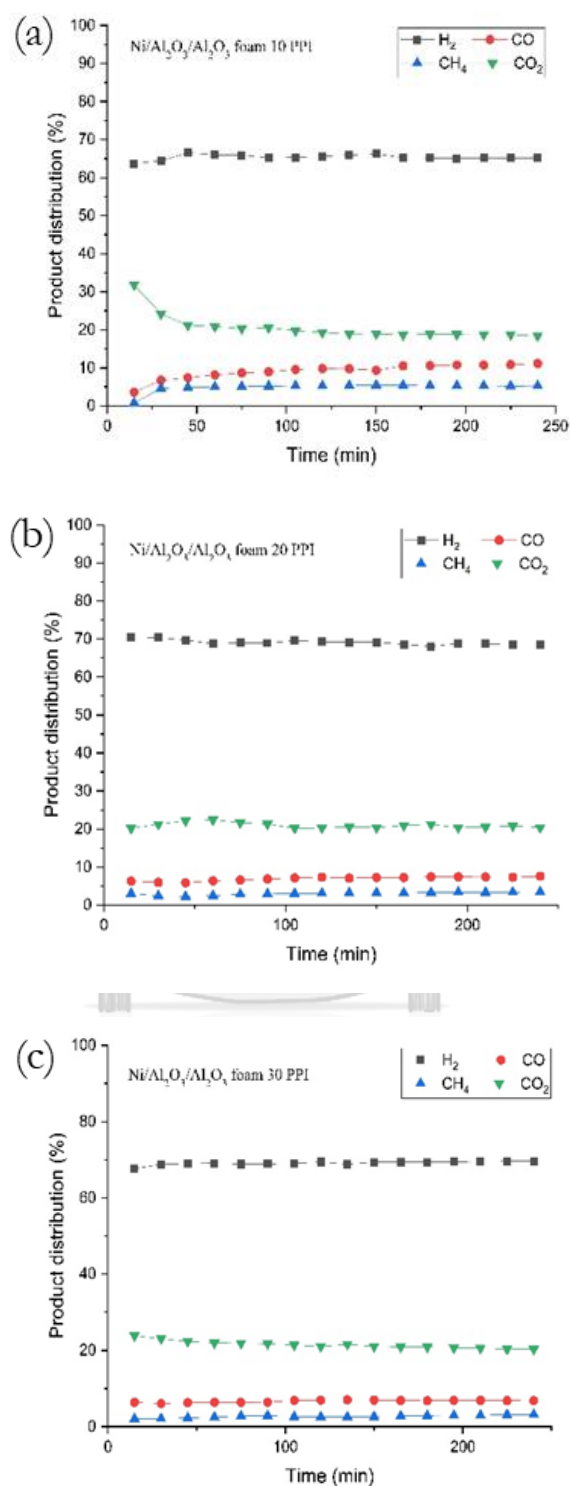


Figure 20 Product distribution obtained during GSR reaction of three structured catalyst with different pore density (a) 10 PPI (b) 20 PPI and (c) 30 PPI (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed $C_3H_8O_3:H_2O$ is 1: 9, feed flow rate is 0.04 ml/min and GHSV 1,800 h⁻¹)

In terms of catalyst shape, comparing structured catalyst with powder catalyst. Powder catalyst showed higher glycerol conversion and H₂ yield at 84.5% and 6 moles/mole of glycerol, respectively [33]. But the highest conversion and H₂ yield of structured catalyst were only 70.4% and 4.6 moles/mole of glycerol. Due to the surface area of powder catalyst was higher than structured catalyst on ceramic foam.

Moreover, if comparing cylindrical and sphere catalyst shape with structured catalyst, it showed that structured catalyst with 20 and 30 PPI provided glycerol conversion nearly similar to cylindrical and spherical pellets which was approximately at 68-70% and H₂ yield were 4.4, 4.6, 5.2 and 5.4 moles/mole of glycerol, respectively [33].

After catalysts were tested in glycerol steam reforming reaction, it was found that powder, cylindrical and spherical catalysts had some disadvantages. When testing was over a period of time, catalysts was covered by carbon formation on the top of the catalyst bed caused loss of catalyst surface area. Furthermore, it worsened the flow of gas through the bed which resulted in a high pressure drop. So, structured catalyst was a catalyst shape that was developed to counteract the disadvantages of conventional catalyst. Structured catalyst was open-cell structure. There were wide channels. It was good for gas permeability and no hot or cold spots occurred so reactant could contact all the catalyst surface in the entire bed. In terms of carbon formation, after testing structured catalyst in reaction for the same duration as powder, cylindrical and spherical catalysts, carbon formation also covered catalyst surface but it did not affect the pressure drop in the reactor.

4.3 Effect of feed flow rate on catalytic activity in glycerol steam reforming

Effect of different feed flow rate on catalyst properties and performance were observed in glycerol steam reforming reaction. Feed flow rate was varied at 0.04, 0.2 and 0.4 ml/min. Performance of catalyst was measured in terms of glycerol conversion and hydrogen yield.

4.3.1 Feed flow rate at 0.04 ml/min

Catalysts with different PPI at 10, 20 and 30 PPI were tested in glycerol steam reforming reaction at 600°C for 4 hours using N₂ gas as carrier gas. Feed flow rate 0.04 ml/min could be converted to gas hourly space velocity (GHSV) at 1,800 h⁻¹. Glycerol conversion and H₂ yield were shown in Figure 18 and 19 in part 4.2. From results, glycerol conversion and H₂ yield of 30 PPI catalyst were the highest value at 70.4±1.04 percent and 4.6±0.32 moles/mole of glycerol but it almost similar to 10 and 20 PPI despite the amount of catalyst was greater. Because flow was too slow, amount

of glycerol entering the reactor was low and almost completely converted from the top of the catalyst bed. Therefore, the catalyst in the entire bed was not used.

4.3.2 Feed flow rate at 0.2 ml/min

From using feed flow rate 0.04 ml/min or GHSV 1,800 h⁻¹, it was found that conversion and yield were similar for all three PPI catalysts so feed flow rate had to be increased to speed up the reactant passing through entire catalyst bed. Feed flow rate was increased to 0.2 ml/min or GHSV around 5,580 h⁻¹. Glycerol conversion and H₂ yield were presented in Figure 21 and 22. When GHSV was increased, glycerol conversion and H₂ yield were decreased for all three catalysts because of lower retention time. But when considering 3 catalysts, 10, 20 and 30 PPI, it was found that increasing feed flow rate or GHSV provided the obvious difference of conversion and yield that was affected by the amount of catalyst coated on ceramic foam. 30 PPI catalyst showed the highest conversion and H₂ yield at 30.4±1.15% and 3.1±0.96 moles/mole of glycerol.

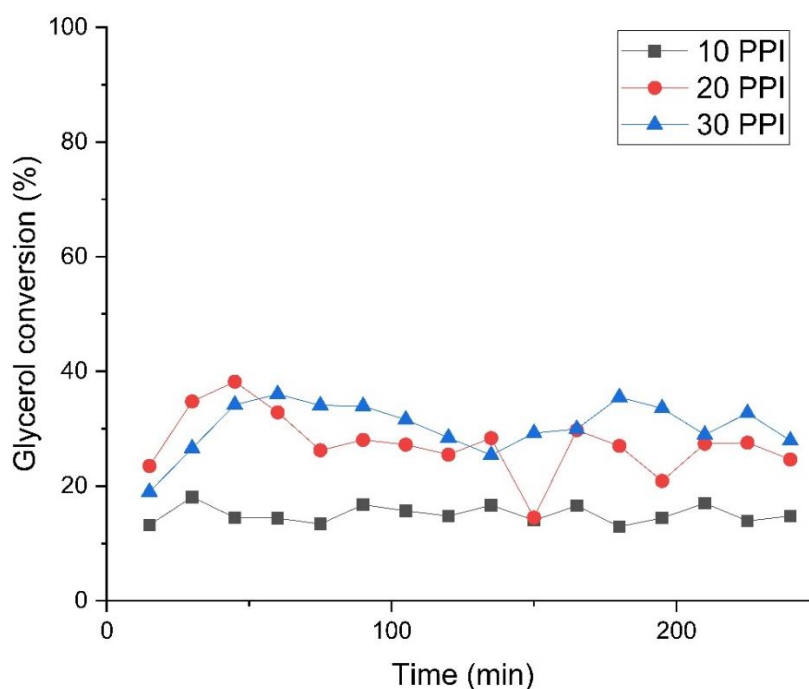


Figure 21 Glycerol conversion of structured catalysts with different pore density (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed C₃H₈O₃: H₂O is 1: 9, feed flow rate is 0.2 ml/min and GHSV is 5,580 h⁻¹)

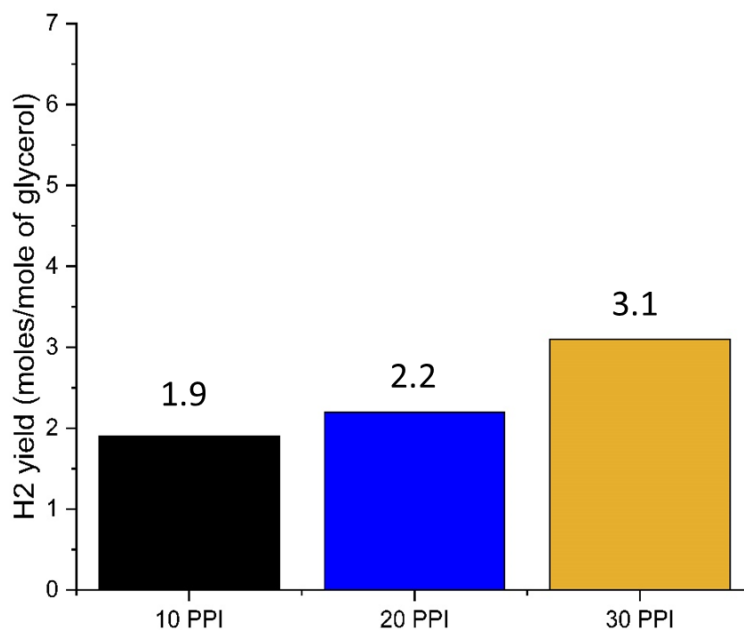


Figure 22 H₂ yield of structured catalysts with different pore density (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed C₃H₈O₃: H₂O is 1: 9, feed flow rate is 0.2 ml/min and GHSV is 5,580 h⁻¹)

4.3.3 Feed flow rate 0.4 ml/min

Feed flow rate 0.4 ml/min could be converted to GHSV around 10,350 h⁻¹. The trend of glycerol conversion and H₂ yield tended to be decreasing, but using GHSV around 10,350 h⁻¹ showed a little glycerol conversion and H₂ yield as shown in Figure 23 and 24. A large quantity of liquid at the exit of reactor including glycerol which was not completely converted and liquid product from side reaction was clearly observed. Because GHSV was high, the flow through the catalyst bed was too fast so catalyst cannot convert in time and vaporizing zone was too short. From results, 30 PPI catalyst showed the highest conversion and H₂ yield at 20±1.45% and 2.3±0.83 moles/mole of glycerol.

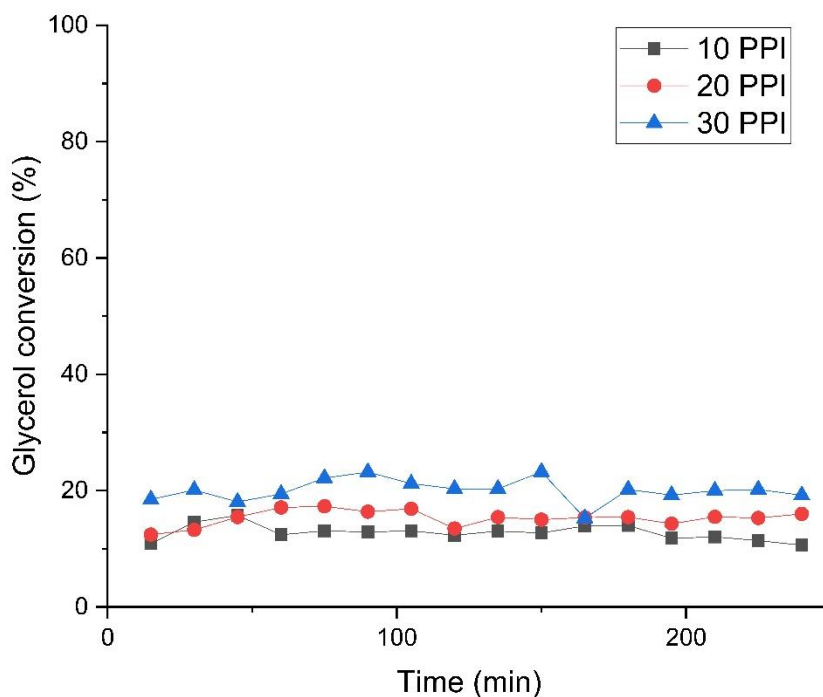


Figure 23 Glycerol conversion of structured catalysts with different pore density (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed $C_3H_8O_3$: H_2O is 1: 9, feed flow rate is 0.4 ml/min and GHSV is 10,350 h^{-1})

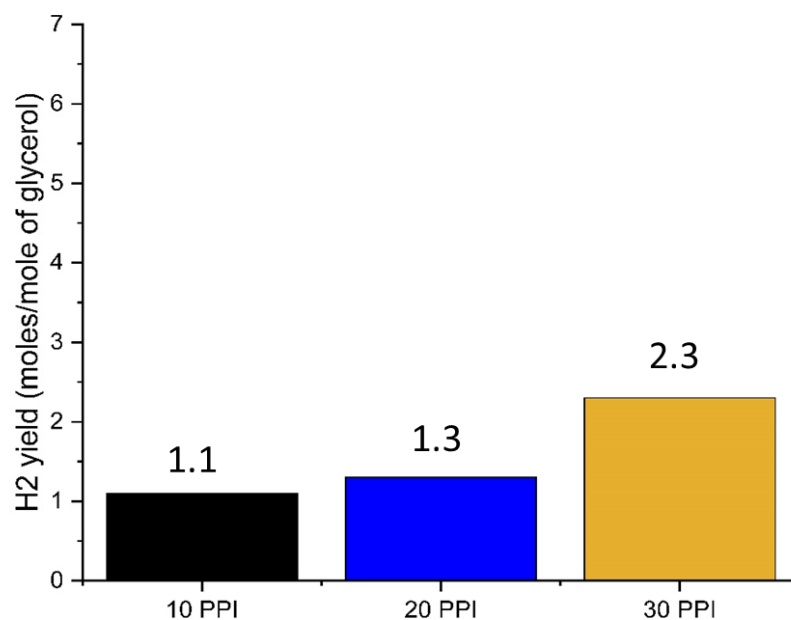
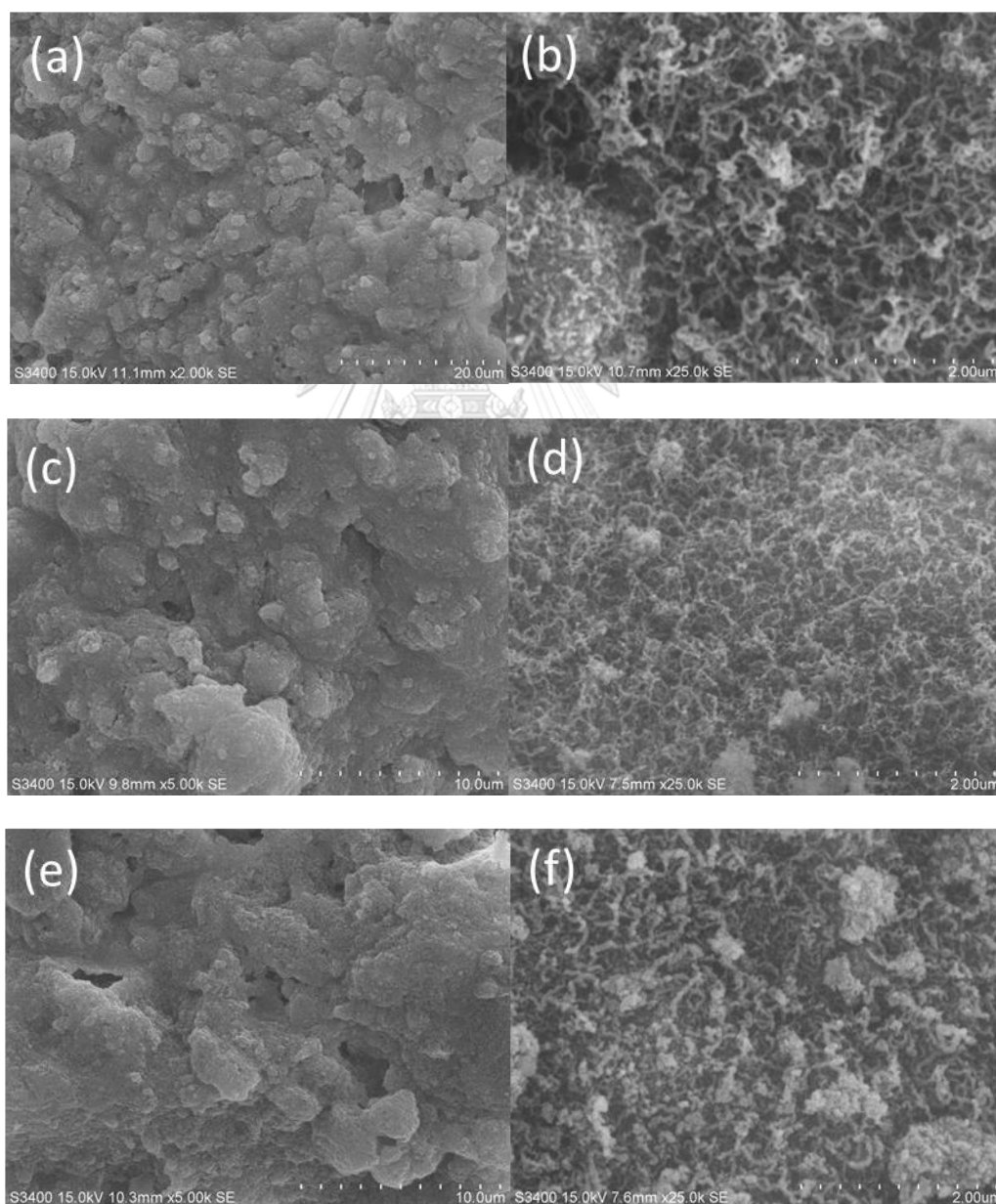


Figure 24 H₂ yield of structured catalysts with different pore density (Operating conditions at 600 °C under atmospheric pressure with molar ratio of feed $C_3H_8O_3$: H_2O is 1: 9, feed flow rate is 0.4 ml/min and GHSV is 10,350 h^{-1})

4.4 Characterization of spent catalysts

After catalyst was tested in glycerol steam reforming at 600 °C for 4 hours, spent catalyst was characterized by various techniques.

SEM technique was used for observing morphology and surface of all catalyst after tested in reaction. Figure 25 (a)-(h) showed surface of all fresh and used catalyst. There was filamentous coke on catalyst surface.



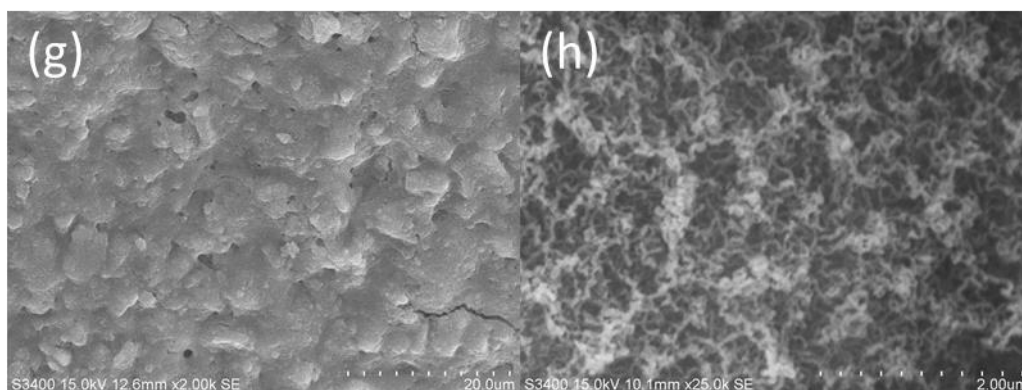


Figure 25 (a) Fresh catalyst on 10 PPI Al₂O₃ foam (b) Used catalyst on 10 PPI Al₂O₃ foam (c) Fresh catalyst on 20 PPI Al₂O₃ foam (d) Used catalyst on 20 PPI Al₂O₃ foam (e) Fresh catalyst on 30 PPI Al₂O₃ foam (f) Used catalyst on 30 PPI Al₂O₃ foam

Amount of carbon deposition was measured and calculated by using TGA. TGA curve was presented in Figure 26. Catalyst on ZrO₂ foam was higher weight loss. It could be explained that catalyst coating on ZrO₂ was uneven, so agglomeration of catalyst was happened which was unstable and caused easily decomposed. Catalyst on different types of ceramic foam provided different amount of carbon. From results in Table 9 that was calculated, catalyst on Al₂O₃ foam provided lower amount of carbon deposition at 12% or 0.119 g_{coke}/g_{catalyst}

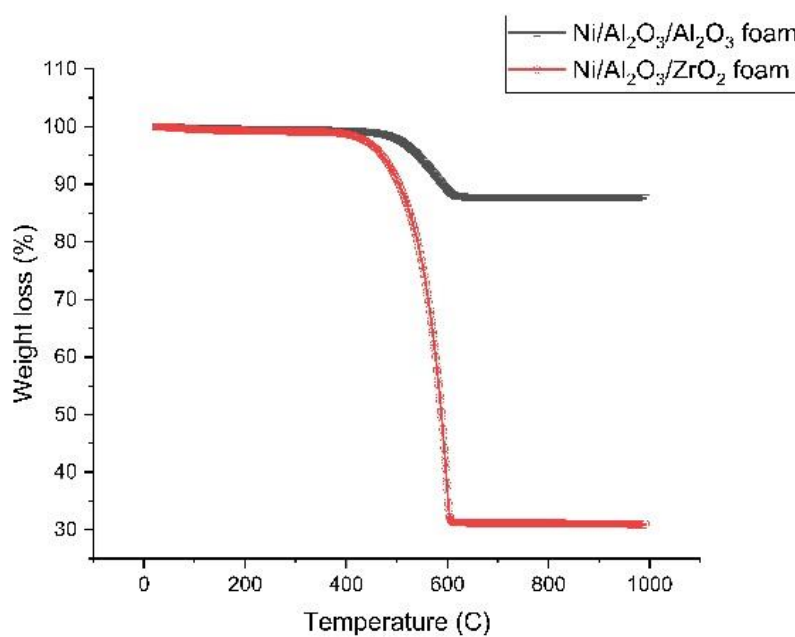


Figure 26 TGA analysis of the spent catalyst

Table 10 Amount of coke deposition on structured catalysts with different type of foam

Type of foam	Weight loss (%)	Amount of coke deposition ($\text{g}_{\text{coke}}/\text{g}_{\text{cat}}$)
Al_2O_3 foam	12	0.119
ZrO_2 foam	69	0.689

Amount of coke that deposited on catalyst surface coating on different pore density (PPI) Al_2O_3 foam were also evaluated by TGA. Weight loss of three catalysts were presented in Figure 27. From TGA curves, 10 PPI showed the lowest weight loss at 12% and 30 PPI was pore density of catalyst that had the highest weight loss at 32%. Calculation of amount of coke on three pore density structured catalysts were shown in Table 10. From results in Table 10, a large quantity of coke 0.329 $\text{g}_{\text{coke}}/\text{g}_{\text{catalyst}}$ was happened when using 30 PPI structured catalyst because 30 PPI had higher amount of catalyst coated on surface of foam.

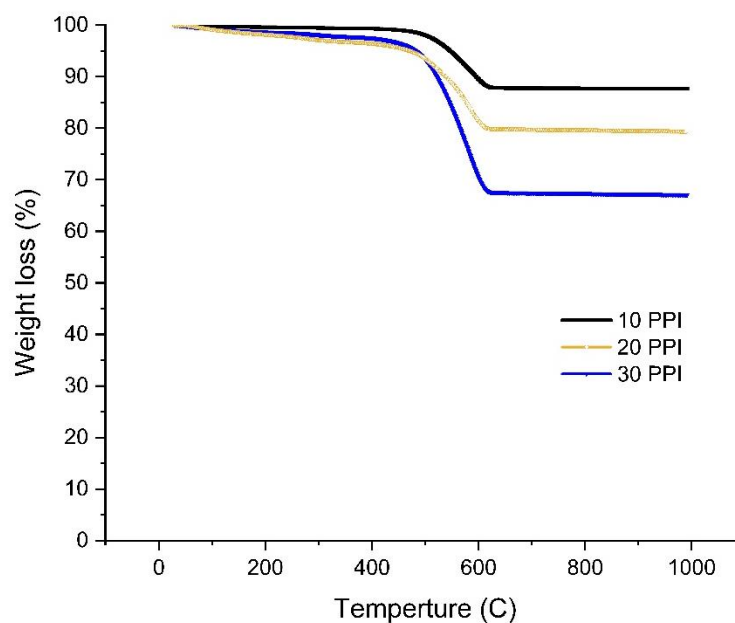


Figure 27 TGA curves of different pore density

Table 11 Amount of coke deposition on structured catalysts with different pore density of foam

Pore density	Weight loss (%)	Amount of coke deposition (g _{coke} /g _{cat})
10 PPI	12	0.119
20 PPI	20	0.207
30 PPI	32	0.329

Temperature programmed oxidation (TPO) was used for observing types of carbon formation on surface of catalyst. The TPO results for two catalysts with different ceramic foams were presented in Figure 28. TPO profiles showed peak at temperature around 500°C which indicate the existence of amorphous coke. Peak at temperature around 600-800°C was decomposition of filamentous carbon according to SEM images in Figure 25.

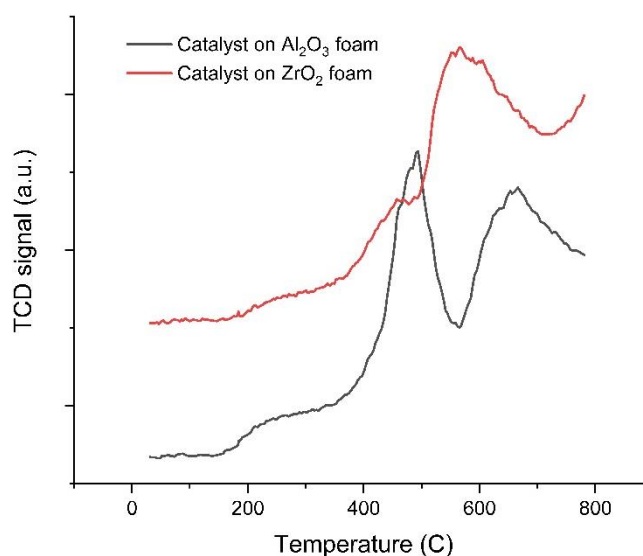


Figure 28 TPO profiles of spent catalyst on Al₂O₃ and ZrO₂ foam

TPO profiles of catalyst with different pore density of foam (10, 20 and 30 PPI) were presented in Figure 29. 10 and 20 PPI provided peaks at similar temperature around 500°C and 600°C which was amorphous and filamentous coke [34]. Moreover, 30 PPI showed peaks at high temperature around 700-800°C which could be explained that it was graphitic carbon species. It was an inert coke which did not easily react with oxygen [35].

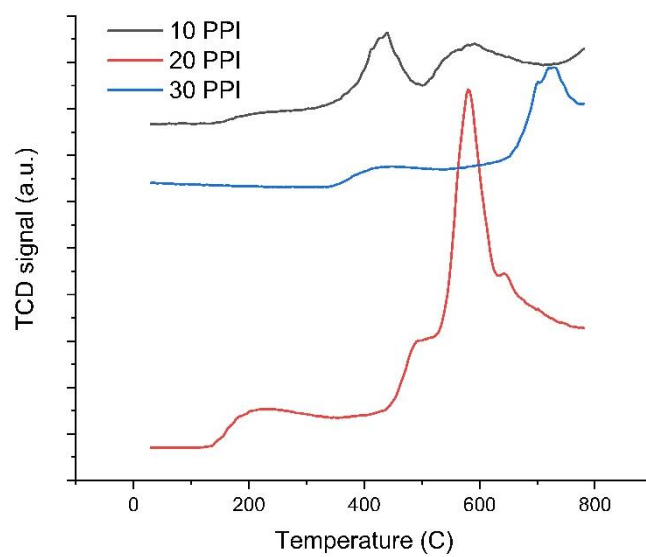


Figure 29 TPO profiles of spent catalyst on different pore density Al₂O₃ foam



CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Nickel catalyst supported on ceramic foam was prepared by dip-coating drying and calcination process. Structured catalysts were employed in glycerol steam reforming at 600°C for 4 hours under atmospheric pressure. Effect of ceramic foam materials, pore density and feed flow rate on catalyst properties and catalytic activity were studied.

The study showed that two ceramic foams had small specific surface area from BET results so γ -alumina was used to increase surface area for Ni coating. Structured catalyst on Al_2O_3 foam showed better catalyst coating than ZrO_2 foam. Catalyst on ZrO_2 foam was little peel-off. Catalytic activity of structured catalyst on Al_2O_3 foam was greater than ZrO_2 foam. The highest pore density 30 PPI Al_2O_3 foam provided the highest activity in reaction at $70.4 \pm 1.04\%$ glycerol conversion and 4.6 ± 0.32 moles H_2 /mole of glycerol. Foam materials and pore density did not affect to product distribution. By varying feed flow rate, low feed flow rate resulted in high conversion and H_2 yield and it almost similar for all three values of pore density because catalyst was not used for entire 2 cm bed length. Higher gas hourly space velocity (GHSV), 5,580 and 10,350 h^{-1} , provided low retention time resulting in lower glycerol conversion and H_2 yield but entire catalyst bed was used. Therefore, it could be seen the effect of catalyst content on different pore density of ceramic foam at high feed flow rate or GHSV. For all catalysts, it should be used at proper feed flow rate and GHSV. Furthermore, all catalyst after testing had filamentous coke deposited on surface and catalyst on 10 PPI Al_2O_3 foam had the lowest carbon deposition at 12% or $0.119 \text{ g}_{\text{coke}}/\text{g}_{\text{catalyst}}$ at low feed flow rate because of low catalyst content.

5.2 Recommendations

From the experimental results, the following recommendations are suggested:

1. In the process of dipping ceramic foam in slurry, the speed of pulling up and down should be controlled.
2. H_2 gas from glycerol steam reforming should be increased purity by using some process.
3. Coating ceramic foam with high pore density should be blown to prevent porous clogging.
4. High surface area support should be used to increase surface area for metal loading on ceramic foam.



APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX A

POWDER CATALYST PREPARATION

Ni/Al₂O₃ powder catalyst with 8%wt Ni loading was prepared by incipient wetness impregnation method. Amount of Ni(NO₃)₂.6H₂O and Al₂O₃ support were calculated as follows;

Total weight of powder catalyst was 5 g.

8% wt Ni of total catalyst = (0.08)(5) = 0.4 g

Al₂O₃ support = 92% of total catalyst = (0.92)(5) = 4.6 g

Using Ni(NO₃)₂.6H₂O precursor with molecular weight 290.79 g/mol while molecular weight of Ni is 58.693 g/mol

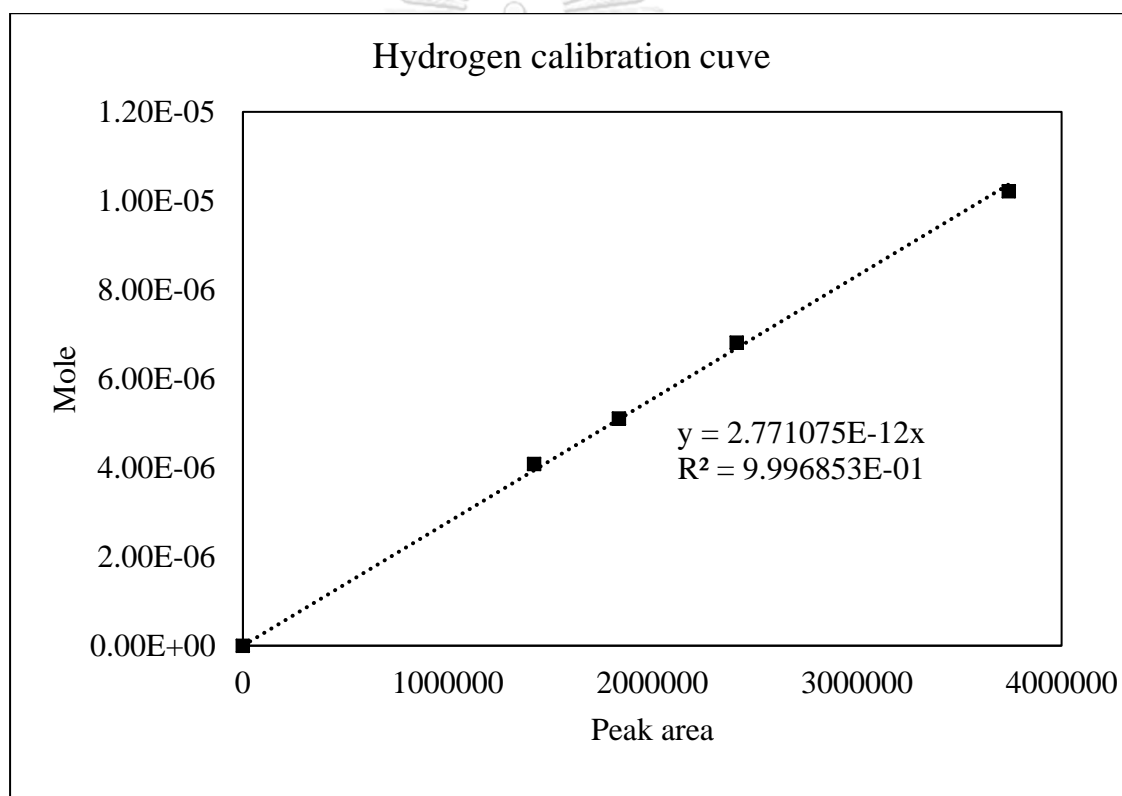
Ni 58.693 g in Ni(NO₃)₂.6H₂O 290.79 g

Ni 0.4 g in Ni(NO₃)₂.6H₂O $\frac{(0.4)(290.79)}{58.693} = 1.9818$ g

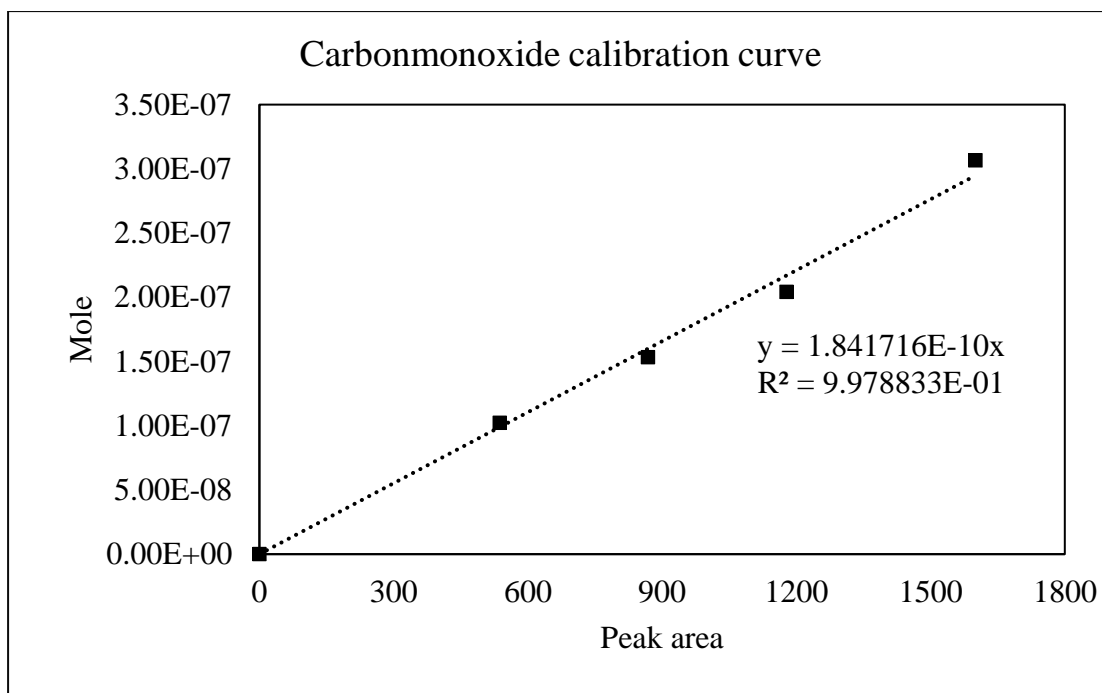
APPENDIX B

CALIBRATION CURVES

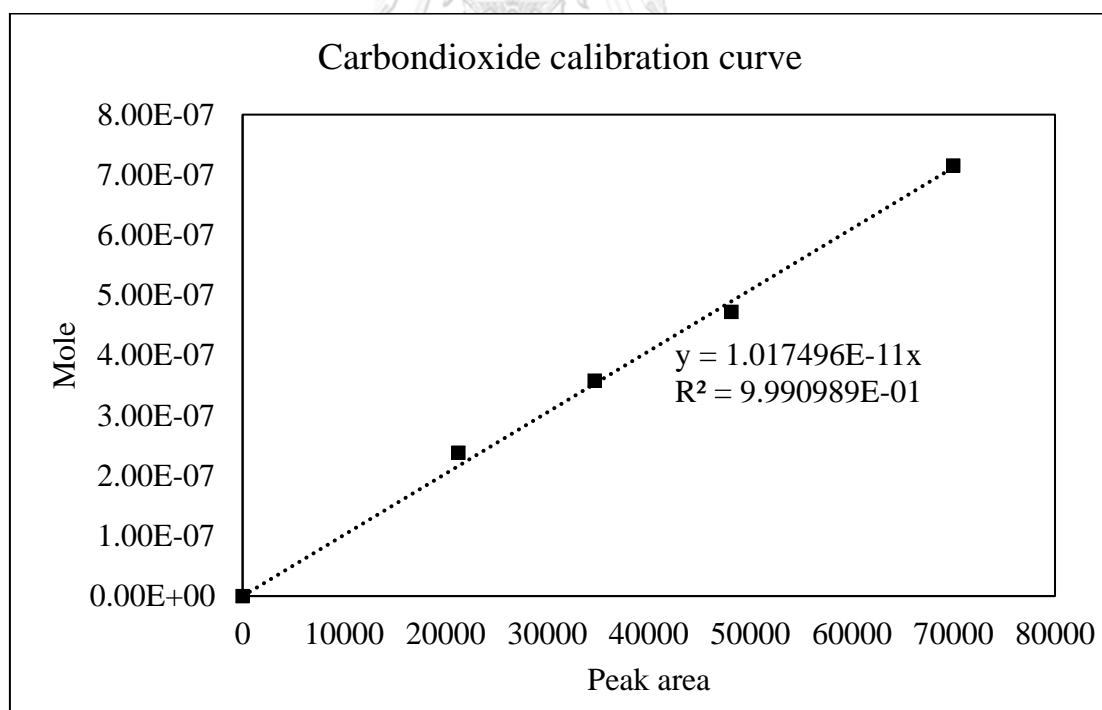
Calibration curves of reactant and gas products; glycerol, H₂, CO, CH₄ and CO₂ were plotted by varying concentration of gas and liquid standard injected to gas chromatography (Shimadzu GC-2014 and Shimadzu GC-8A) and shown in Fig B.1-B.5. Graphs were plotted between mole versus peak area.

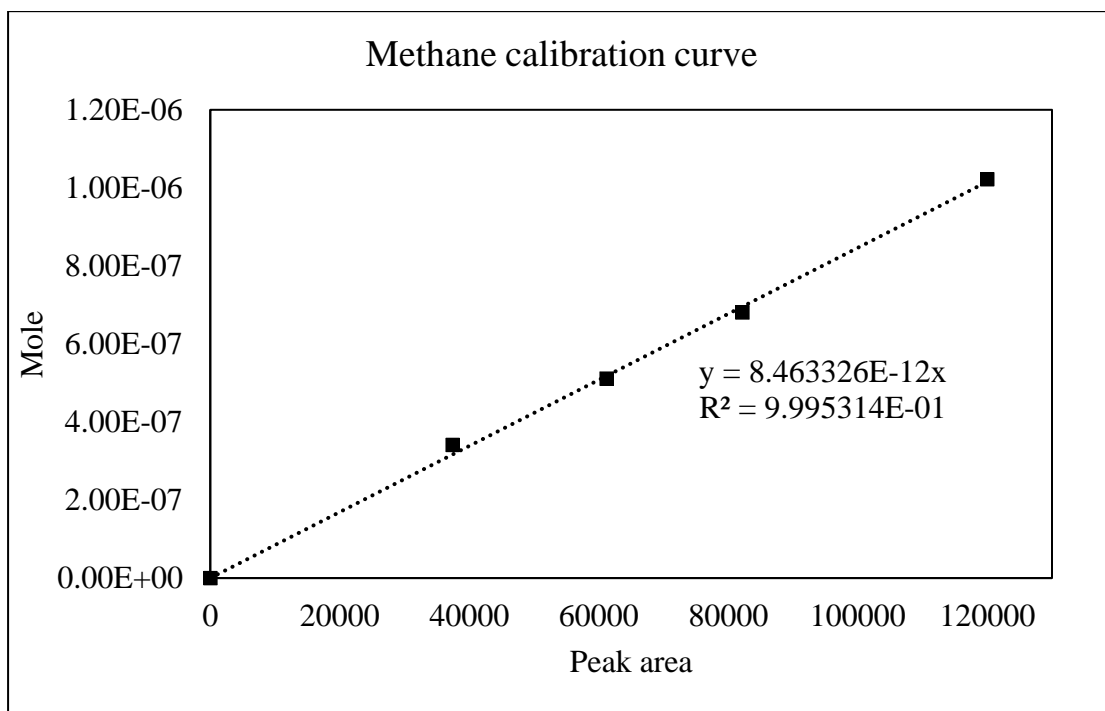
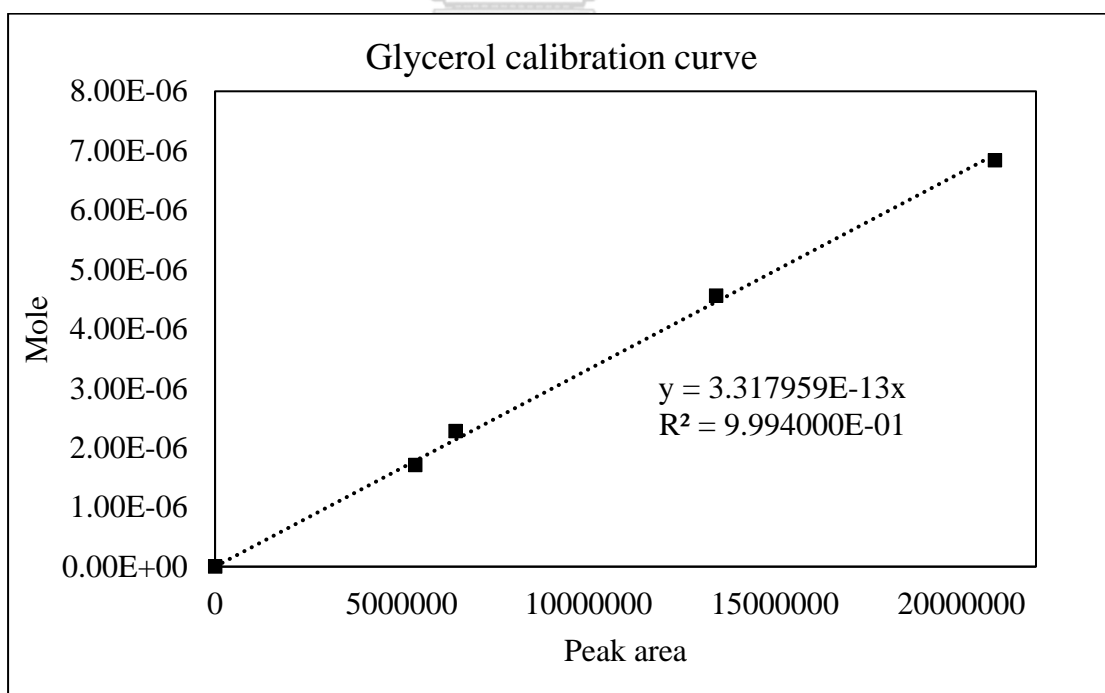


B.1 Calibration curve of H₂



B.2 Calibration curve of CO

B.3 Calibration curve of CO₂

B.4 Calibration curve of CH₄

B.5 Calibration curve of glycerol

APPENDIX C

CATALYST PERFORMANCE

Glycerol conversion, product distributions and H₂ yield were measured and calculated using equations below;

$$\% \text{ Glycerol conversion} = \frac{[\text{CO}_2]_{\text{out}} + [\text{CO}]_{\text{out}} + [\text{CH}_4]_{\text{out}}}{3[\text{C}_3\text{H}_8\text{O}_3]_{\text{feed}}} \times 100$$

[CO₂]_{out}, [CO]_{out}, [CH₄]_{out} and [C₃H₈O₃]_{feed} are molar flow rate of CO₂, CO, CH₄ and C₃H₈O₃ in mole/min, respectively.

$$\% \text{ Product distributions of } i = \frac{\text{Molar flow rate of } i}{\text{Molar flow rate of all gas species}} \times 100$$

i is H₂, CO, CO₂ and CH₄ gas produced.

$$\text{H}_2 \text{ yield} = \frac{[\text{H}_2]_{\text{produced}}}{[\text{C}_3\text{H}_8\text{O}_3]_{\text{feed}}}$$

[H₂]_{produced} is molar flow rate of H₂ produced in mole/min.

APPENDIX D

CARBON DEPOSITION ON CATALYST

Percentage of weight loss results from TGA technique were used for amount of carbon deposition on catalyst surface calculation. Thus, calculation of amount of carbon deposited on catalyst surface was as follows:

$$\begin{array}{lcl} \text{Analysis catalyst weight} & = & 13.1380 \quad \text{mg} \\ \text{Weight loss form TGA} & = & 12\% \end{array}$$

Calculation of coke occurred based on 1 g of catalyst weight

$$\begin{array}{lcl} \text{Amount of coke} & = & \frac{(12)(13.1380) \text{ mg}}{100} = 1.5766 \text{ mg}_{\text{coke}} \\ \text{Total amount of carbon deposited} & = & \frac{(1 \text{ g})(1.5766 \text{ mg})}{(13.1380 \text{ mg})} = 0.119 \text{ g}_{\text{coke}} \end{array}$$

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จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

VITA

NAME Phichamon Sookjitsumran
DATE OF BIRTH 23 January 1996



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY