รายงานการวิจัยฉบับสมบูรณ์

ปฏิกิริยาดีออกซิจีเนชันของกลีเซอรอลเป็นแอลกอฮอล์ที่มีคาร์บอน 3 อะตอม
Deoxygenation of Glycerol to C3 Alcohols

นางสาวณัฐธิดา นุ่มวงศ์

ได้รับทุนสนับสนุนงานวิจัยจากงบประมาณเงินรายได้ ประจำปีงบประมาณ พ.ศ. 2558
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ชื่อโครงการ (ภาษาไทย) ปฏิกิริยาดีออกซิจีเนชันของกลีเซอรอลเป็นแอลกอฮอล์ที่มีคาร์บอน 3 อะตอม
แหล่งเงิน งบประมาณเงินรายได้
ประจำปีงบประมาณ 2558 จำนวนเงินที่ได้รับการสนับสนุน 50,000 บาท
ระยะเวลาทำการวิจัย 1 ปี ตั้งแต่ 1 ตุลาคม 2557 ถึง 30 กันยายน 2558
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บทคัดย่อ

กลีเซอรอลเป็นผลผลิตพลอยได้จากกระบวนการผลิตไบโอดีเซลที่มีมูลค่าทางเศรษฐกิจต่ำ การเปลี่ยนกลีเซอรอลเป็นผลิตภัณฑ์ปิโตรเคมีที่มีมูลค่าสูงขึ้นจึงมีความน่าสนใจ งานวิจัยนี้ได้ศึกษาปฏิกิริยาดีออกซิจีเนชันของกลีเซอรอลเป็น 1-โพรพานอลโดยใช้ระบบเบดต่อเนื่อง (sequential bed system) โดยในเบดบนใช้ซีโอไลต์ H-ZSM-5 (อัตราส่วน Si/Al = 12.5) เป็นตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาดีไฮเดรชันของกลีเซอรอล และได้อะโครลีนเป็นผลิตภัณฑ์หลัก (80%) และไฮดรอกซีอะซิโตนเป็นผลิตภัณฑ์รอง (15.1%) ส่วนในเบดล่างใช้นิกเกิล 20 % โดยน้ำหนักบนตัวรองรับซิลิกา (Ni/SiO_2) เป็นตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาไฮโดรจีเนชันของอะโครลีน โดยมีโพรไพนอลดีไฮด์เป็นสารมัธยันต์ และเกิดปฏิกิริยาไฮโดรจีเนชันต่อเป็น 1-โพรพานอล นอกจากนั้นแล้วยังได้กรดโพรพาโนอิกจากปฏิกิริยาการขจัดน้ำด้วย ซึ่งได้พบว่าช่วงอุณหภูมิ 120–200°C ซึ่งเป็นอุณหภูมิที่เหมาะสมสำหรับปฏิกิริยาไฮโดรจีเนชันของอะโครลีน

คำสำคัญ : กลีเซอรอล, โพรพานอล, ดีออกซีจีเนชัน, Ni/SiO_2

Research Title: Deoxygenation of Glycerol to Higher Alcohols

Researcher: Natthida Numwong

Faculty: Science **Department:** Chemistry

ABSTRACT

Glycerol is a low-value by-product from biodiesel process. The conversion of glycerol to more valuable products is interested. In this research, the deoxygenation of glycerol to 1-propanol in sequential bed system was studied. In the upper bed, H-ZSM-5 (Si/Al ratio 12.5) was used as a catalyst for dehydration of glycerol. Acrolein is a major product (80% yield) while hydroxyacetone is minor product (15.1% yield). In the lower bed, 20 wt.% Ni on SiO_2 supports (Ni/SiO_2) is used for the hydrogenation reaction of acrolein. It was found that the propionaldehyde is an intermediate to the desired product, 1-propanol via hydrogenation and a minor product, propanoic acid from water reduction. The reaction temperature in the range of 120–200°C is suitable for promoting the acrolein hydrogenation.

Keywords: glycerol, propanol, deoxygenation, Ni/SiO_2

กิตติกรรมประกาศ

โครงการวิจัยนี้สามารถสำเร็จลุล่วงได้เป็นอย่างดี โดยได้รับทุนสนับสนุนการวิจัยจากสถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง งบประมาณเงินรายได้ ประจำปีงบประมาณ พ.ศ. 2558 และด้วยความกรุณาจาก รองศาสตราจารย์ ดร. ตะวัน สุขน้อย ที่ให้คำปรึกษาตลอดจนอนุเคราะห์อุปกรณ์ เครื่องมือวิเคราะห์และเตาปฏิกิรณ์ตลอดการทำวิจัย

ณัฐธิดา นุ่มวงศ์

สารบัญ

สารบัญ (ต่อ)

สารบัญตาราง

ตารางที่ **หน้า**

สารบัญภาพ

Chapter 1

Introduction

1.1 Motivation

Nowadays, the demand of petroleum fuel and energy usage increases steadily due to an expansion of economy while the source of fossil fuel falls steadily. Alternative energy is required to replace petroleum fuel. One of the examples is biodiesel produced from renewable sources such as palm oil. Biodiesel production process via transesterification reaction produces glycerol, which is a valuable by-product. Glycerol is widely used as a raw material to augment value of chemical compounds such as 1,2-propanediol, acrolein, and hydroxyacetone. Glycerol has three hydroxyl groups. In order to extend the use of glycerol, the hydroxyl groups should be removed [1]. Dehydration of glycerol over acid catalysts produces acrolein and various by-products. Acrolein is an unsaturated aldehyde, making it a suitable substrate for converting into other high value chemical compounds such as 1-propanol.

Glycerol can be converted to 1-propanol via dehydration-hydrogenation. Dehydration yields acrolein as a main product, followed by hydrogenation to 1-propanol, in which propionaldehyde is an intermediate. Acidic catalysts, such as alumina or zeolite, can be used for dehydrating glycerol to acrolein [2,3]. Among the acid catalysts, H-ZSM-5 is possessed high surface area as well as acidity and acid strength. The hydrogenation of acrolein formed can be promoted by active metal catalysts such as palladium, silver, nickel, or platinum over an inert support, such as silica and activated carbon [4]. Nickel is typically used as a catalyst for hydrogenation because it is common and relatively cheaper than palladium and platinum. However, acrolein is highly reactive that can be converted to other products during dehydration process and also difficult to handle during storage. Accordingly, a conversion of acrolein to more stable product will be occurred immediately after its formation. In addition, acrolein facilitate high selectivity to alcohols via hydrogenation of the C=C bond. This hydrogenation reaction can be take place in the gas-phase over transitions metal catalysts such as platinum, palladium, and nickel. This leads to the formation of propionaldehyde and consequently 1-propanol.

In this study, the conversion of glycerol to 1-propanol was investigated in a continuous fixed-bed reactor using sequential bed system. Acid H-ZSM-5 catalyst was used in the upper bed; while supported nickel catalysts were used in the lower bed. From the previous study [2], the reaction conditions in the first catalytic bed were fixed at 300°C, 1 atm, and contact time of 1.7 mmol/h. The effect of contact time and reaction temperature in the lower catalytic bed on the activity and selectivity towards 1-propanol was investigated.

1.2 Objectives

1) To produce 1-propanol from glycerol using sequential bed system (H-ZSM-5 and supported Ni catalysts)

2) To understand the effect of reaction temperature and contact time on the activity and selectivity of the catalyst in the second bed.

3) To understand the mechanism during the conversion of glycerol to 1-propanol

1.3 Scope of study

The scopes of this project are as follows:

1) Preparation of the hydrogenation bed by wetness impregnation: 20 wt.% nickel on silica (Ni/SiO_2).

2) Study on reaction temperature in a range of 100–200°C with contact time between 15–177 g.h/mol that affect catalytic activity and selectivity in a continuous fixed-bed system.

3) Analysis of liquid products by Gas Chromatography with Flame Ionization Detector (GC-FID).

1.4 Expected results

It is expected that a new technology for producing 1-propanol from glycerol will be obtained and developed with higher efficiency.

Chapter 2

Theory and Literature Reviews

2.1 Glycerol

Glycerol is a chemical, which has a multitude of uses in pharmaceutical, cosmetic, and food industries. Glycerol produced from oleochemical or biodiesel plant is usually in a crude form that contains various impurities such as oily, alkali, soap components, and a salt or diols, depending on the processes and the type of materials processed [1,5]. Crude glycerol is a low value product as its low purity limits its application as feedstock in industries. Glycerol is an organic compound with the chemical formula of $C_3H_8O_3$. It is synonymous to glycerin, propane-1,2,3-triol, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol, and glycyl alcohol. Glycerol is a low toxicity alcohol that consists of three-carbon chains with a hydroxyl group attached to each carbon (Figure 2.1) that is virtually nontoxic to both human and environment.

Figure 2.1 Structure of glycerol

Glycerol can be generated from transesterification of fat and oils in biodiesel plant. Transesterification is a chemical reaction whereby fat and oils (triglycerides) react with alcohol such as methanol in the presence of a catalyst to produce fatty acid methyl esters with glycerol as a byproduct, as presented in Figure 2.2.

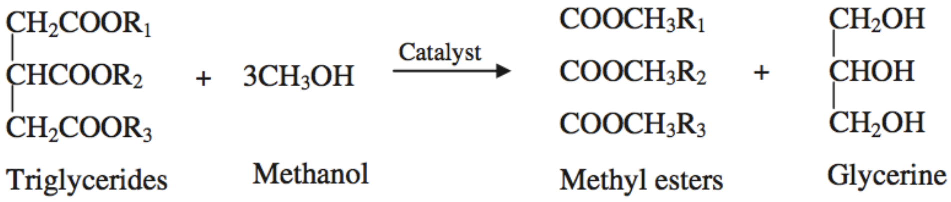


Figure 2.2 Transesterification reaction

2.2 Dehydration of glycerol

Dehydration reaction usually proceeds in aqueous media with continuous extraction. Strong acids such as ion-exchange resins and zeolites have been used as catalysts for this reaction. Zeolites are selective catalysts because side reactions and C-C cleavage are less important [6]. Moreover, they are regenerated easily and can be operated at high temperature. Moredenite has excellence characteristic due to shape selectivity and low mesoporosity. Heterogeneous niobium catalysts (niobic acid, H_3PO_4 treated niobic acid and niobium phosphate) have recently been found to be selective catalysts for dehydration of polyols [6].

According to glycerol is an inevitable by-product of that biodiesel production and the demand for glycerol is not increasing at the same rate as the need for biodiesel. Consequently, the use of glycerol as a starting material becomes economically and environmentally feasible. The study on conversion of low value glycerol to high value chemicals is interesting [7]. One attractive process is the conversion of glycerol to 1-propanol. In this process, glycerol is converted to 1-propanol via dehydration to acrolein followed by hydrogenation to propionaldehyde and 1-propanol, respectively (Figure 2.3).

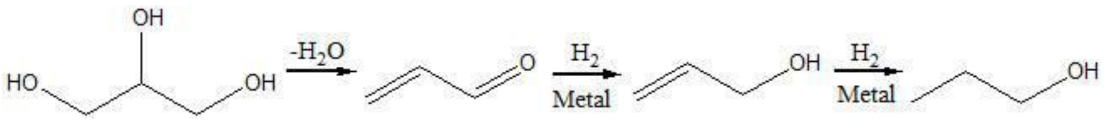


Figure 2.3 Pathway of glycerol to 1-propanol

Glycerol is mainly dehydrated at the secondary hydroxyl. As a result, an intermediate called 3-hydroxypropionaldehyde (3-HPA) would be formed and subsequently dehydrated to acrolein as major product. (Figure 2.4) This is because protonation of a secondary hydroxyl is more favorable over the Brönsted acid sites in the zeolite [8].

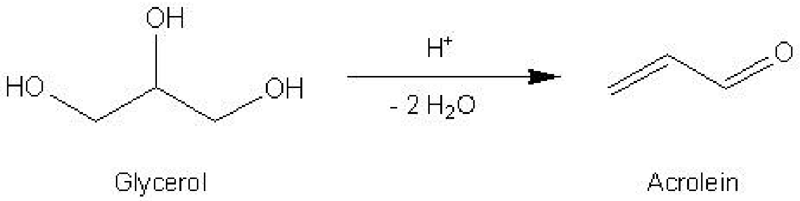


Figure 2.4 Acid-induced dehydration of glycerol to acrolein

Application of various types of catalysts in dehydration of glycerol to acrolein has been reported recently including phosphates and pyrophosphates, mixed metal oxides, heteropoly acids, and zeolites. Mixed oxides, phosphates and pyrophosphates catalysts are wildely used in dehydration reaction to acrolein. In fact, this group of catalysts has many parameters for evaluation and investigation during the optimization of catalytic activity [6]. Suprun *et al*. [9] demonstrated different activity in the catalytic dehydration of glycerol in the gas-phase carried out at 280°C with the presence of Al_2O_3 and TiO_2 supports modified by impregnation with PO_4^- ions and SAPO-11 and SAPO-34 samples as catalysts. The result showed that 72% acrolein selectivity was obtained from SAPO-34 catalyst and the lowest 37% acrolein selectivity was obtained from TiO_2–PO_4 catalyst. They were reported that the mesoporous Al_2O_3–PO_4 and TiO_2–PO_4 catalysts with large pores exhibited high activity but limited selectivity towards acrolein. On the other hand, SAPO-11 and SAPO-34 catalysts with small micropores were less active but more selective. The small pores of SAPO catalysts favor an external surface reaction rather than a reaction inside the channels. Thus, lowering activity and accelerating deactivation. Al_2O_3–PO_4 and TiO_2–PO_4 catalysts possess much larger pores; therefore, the whole surface was available for the reaction for a much longer period of time.

One approach to obtain better acrolein from glycerol is to use supported inorganic acids such as heteropoly acids (HPAs) and phosphorous acid as catalysts. HPAs can be used as acid and oxidation catalysts in both solid and liquid states. HPAs are highly stable against humidity and air, low toxicity, highly soluble in polar solvents (water, acetones, and lower alcohols), produce less quantities of residues than mineral acids and less corrosive [1]. Tsukuda *et al*. [3] studied the production acrolein from glycerol using HPA catalysts. This reaction takes place under atmospheric pressure at 275-325°C in the liquid-phase. The conversion is reached up to 100% and 74.1% acrolein selectivity. The high catalytic activity of this catalyst is due to the strong Brönsted acid sites of the HPA.

Moreover, the activity of zeolite in liquid-phase dehydration of glycerol was also studied by Oliveira *et al*. [8] the reaction was carried out at 250°C, and 70 bar over different large pore molecular sieve including H-Y, H-β, mordenite, SBA-15, and ZSM-23. The activity had almost the same order of the acidity: H-Y > H-β > H-Mor > SBA-15 > ZSM-23. The lower the Si/Al ratio, the higher the activity: A large pore molecular sieves, H-Y showed high performance with 99.5% acrolein selectivity and 89.0% conversion while SBA-15 possessed weak acidity was decreased acrolein selectivity to 84.0% with low conversion at 40.6%. They were reported that large pore zeolites possessing mild or strong acidic sites, as in the case of H-Y and H-β, were highly active for the production of acrolein. However, in the case of leached of the acidic sites led to deactivation. The small microporous mordernite and ZSM-23 had weak to strong acidic sites, but the one-dimensional structure of the channels contributed to the deactivation of the solids by coking. A mesoporous SBA-15 had a mild acidity was able to convert glycerol into acrolein with high selectivity also showed the significant deactivation through poisoning of the acidic sites and blocking by heavy glycerol derivatives.

In addition, Witsuthammakul also shows that the used of H-ZSM-5 zeolites in glycerol dehydration at 330–360°C, the conversion can reached to 100% with an acrolein selectivity of more than 70% [2]. Therefore, H-ZSM-5 zeolite is one of the promising catalysts in glycerol dehydration

2.3 Hydrogenation of acrolein to 1-propanol

The gas phase hydrogenation of acrolein is also an option for the industrial production of alcohols. The use of typical hydrogenation catalysts like Pt, Pd, or Ni supported on non-reducible oxides leads mainly to the saturated aldehyde as shown in the reaction in Figure 2.5, which is understandable since thermodynamics and kinetics favor the hydrogenation of the C=C bond.

Figure 2.5 Reaction pathway of acrolein hydrogenation

2.4 Hydrogenation catalysts [10]

Heterogeneous transition metal catalysts for hydrogenation are usually employed in the states of metal, oxides, or sulfides that are either unsupported or supported. The physical form of a catalyst suitable for a particular hydrogenation is determined primarily by the type of reactors, such as fixed-bed, fluidized-bed, or batch reactor. For industrial purpose, unsupported catalysts are seldom employed since supported catalysts have many advantages over unsupported catalysts. In general, use of a support allows the active component to have a larger exposed surface area, which is particularly important in those cases where a high temperature is required to activate the active component. At that temperature, it tends to lose its high activity during the activation process, such as in the reduction of nickel oxides with hydrogen, or where the active component is very expensive as are the cases with platinum group metals. The effect of an additive or impurity appears to be more sensitive for unsupported than supported catalysts. This is also in line with the observations that supported catalysts are usually more resistant to poisons than are unsupported catalysts. Supported catalysts may be prepared by a variety of methods, depending on the nature of active components as well as the characteristics of carriers. An active component may be incorporated with a carrier in various ways, such as, by decomposition, impregnation, precipitation, coprecipitation, adsorption, or ion exchange. Both low- and high-surface-area materials are employed as carriers. Some characteristics of commonly used supporting materials are summarized in Table 2.1

Table 2.1 Characteristics of commonly used carriers

Carrier	Specific Surface Area ($m^2 .g^{-1}$)	Pore Volumn ($ml . g^{-1}$)	Average Pore Diameter (nm)
α-Al_2O_3	0.1-5	-	500-2,000
Activated Al_2O_3	100-350	0.4	4-9
SiO_2-Al_2O_3	200-600	0.5-0.7	3-15
SiO_2	400-800	0.4-0.8	2-8
Zeolite	400-900	0.08-0.2	0.3-0.8
Activated carbon	800-1200	0.2-2.0	1-4

Chapter 3

Experimental

3.1 Chemical reagents

1. Nickel(II) nitrate hexahydrate, 99%, CARLO ERBA
2. NH_4-ZSM-5 (Si/Al = 12.5), Zeochem
4. Silica, 99.0% on dry, CARLO ERBA
5. Glycerol, 99.5%, CARLO ERBA
6. N-butanol, 99.5%, CARLO ERBA
7. Distilled water

3.2 Apparatus and instruments

1. Catalytic testing rig
2. Gas chromatograph (VARIAN CP-3800)
3. Laboratory glassware
4. Laboratory plasticware
5. Oven
6. Sieve
7. Syringe (10 mL)
8. Syringe pump
9. Mass flow controller
10. Cooling water
11. Tube furnace with a programmable temperature controller

3.3 Catalyst Preparation and modification

3.3.1 Preparation of H-ZSM-5

A powder of NH_4-ZSM-5 was calcined in the tube furnace with programmable temperature controller at 500°C for 5 h to make a proton form; H-ZSM-5 with Si/Al ratio of 12.5. H-ZSM-5 was used as a catalyst for the upper catalytic bed for dehydration reaction.

3.3.2 Preparation of 20 wt.% Ni supported on silica (Ni/SiO_2)

Before impregnation, SiO_2 support was dried at 80°C in an oven for 24 hour in order to remove moisture and impurity. The 2 M Ni precursor solution was prepared by dissolving 9.9 g of $Ni(NO_3)_2•6H_2O$ in 17 mL of water. After that, 8 g of support was impregnated with the Ni precursor solution in plastic beaker. The mixture was gradually dried in an oven at 100°C to remove excess water till support almost dry. Then, it was calcined in a tube furnace at 500°C for 5 h to obtain NiO, reduced at 450°C for 3 hour to Ni metal form.

3.4 Catalytic activity testing

3.4.1. Dehydration of glycerol to acrolein

The H-ZSM-5 Zeolite pellets was packed into the glass reactor (8 mm of inside diameter) and covered by glass wool. The glass beads were loaded under the H-ZSM-5 zeolite bed to facilitate feed flow dispersion.

The catalytic testing rig is shown in Figure 3.1. The reactor was positioned at the center of a vertical tube furnace. The gas flows will be controlled by mass flow controllers and checked by bubble flow meter. The catalyst was activated by heating at 2°C/min to 500°C and held at that temperature for 5 h under the steam of air zero (60 mL/min). After that, the reactor was cooled down to the reaction temperature (300°C). To start the reaction, glycerol solution (10 wt.%) was fed into the reactor by syringe pump at 1.7 mmol/h. The reaction was operated for 6 h on steam and collected hourly.

3.4.2 Subsequent hydrogenation of glycerol dehydrated products

The zeolite H-ZSM-5 and the supported Ni catalysts were sequentially packed in double-bed reactor. Each bed was screened by glass wool. The glass rod was inserted under the lower bed. The glass beads were introduced as flow dispersing between the zeolite H-ZSM-5 and supported Ni catalyst bed.

The double bed tubular down flow reactor was placed within a vertical tube furnace as explained previously. Hydrogen flow rate was controlled by a mass flow controller. The catalyst was reduced at 10°C/min to 450_{o}C and held at that temperature for 3 h under hydrogen flow rate of 100 ml/min. Then, the reactor was cooled to the reaction temperature prior for testing. After that, the catalyst was purged by hydrogen for half an hour under 100 mL/min. 10 wt.% glycerol solution was fed into the reactor by syringe pump with the flowrate of 1.7 mmol/h. The reaction was operated for 6 h on stream. The product effluents were condensed in cooled-trap by coolant and collected hourly. The descriptions of the reaction set-up are summarized in Table 3.1.

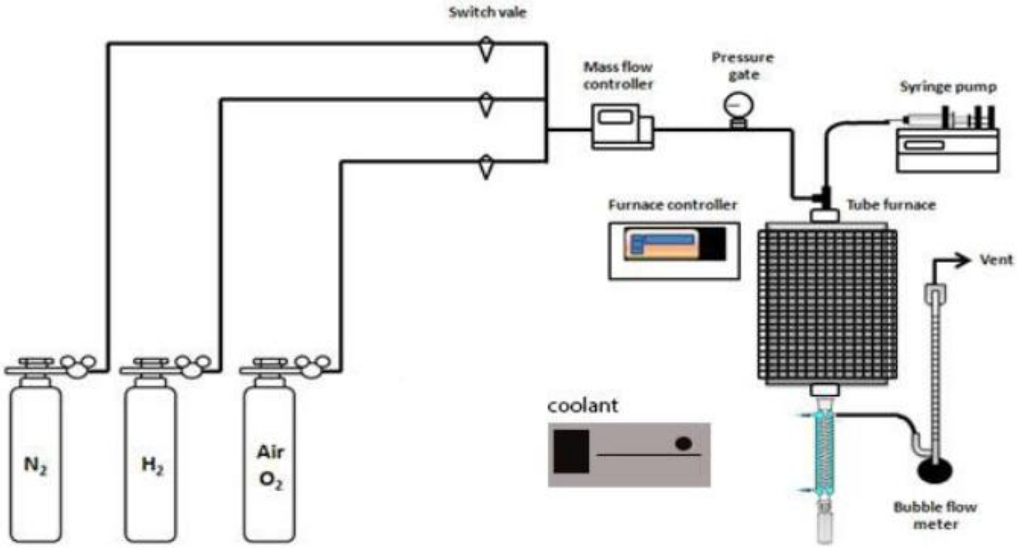


Figure 3.1 Catalytic testing rig

Table 3.1 Description of the reactor set up and the reaction conditions

Parameters	Value
Reactor inside diameter (mm)	6
Reactor outside diameter (mm)	8
Total flow (mL/min)	100
Bed length (cm)	25
Catalyst weight (g)	0.3
Contact time: W/F (g.h/mol)	15, 29, 59, and 177
Catalyst activation (before reaction)	Heating rate: 2°C/min Heat treatment: 500°C hold for 5 hours Gas: air zero (60 mL/min)
Carrier gas	H_2
Reaction temperature	100-200°C
Total reaction pressure	Atmospheric pressure

3.5 Products analysis

Products were quantified by gas chromatograph equipped with flame ionized detector (GC-FID Varaince CP-3800). DB-WAX (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 um) was used as a separating column. The following temperature program; linear velocity is 21.9 cm/sec, 60°C hold for 2 min, then ramp at 8°C/min to 200°C was used for the analysis of liquid hydrocarbon and held at this temperature for 0.5 min by use N_2 as carrier gas. The products were mixed with equal weight of n-butanol as an internal standard. The mixture was injected at 0.1 μL and 200 of split ratio.

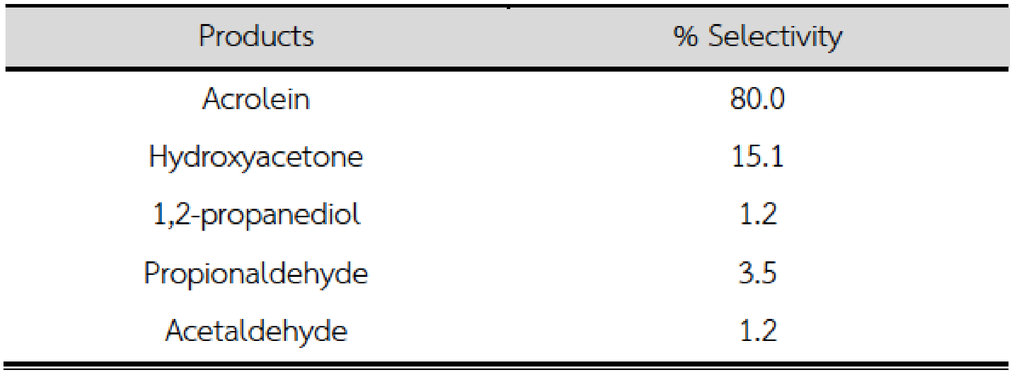
Chapter 4

Results and Discussions

4.1 Dehydration of glycerol to acrolein

Glycerol contains two different hydroxyl groups. The dehydration typically takes place at either secondary or primary hydroxyl group. It is found that the dehydrated product from secondary hydroxyl group is acolein [2]. In a parallel dehydration at primary group, hydroxyacetone and acetaldehyde will be obtained. Acrolein is a major product from dehydration reaction over Bronsted acid catalyst such as zeolite, in which 3-hydroxypropioaldehyde (3-HPA) is an intermediate. Due to stability and storage transportation problems, acrolein should be promptly converted to higher value chemicals after its formations. In this work, subsequently hydrogenation of acrolein to 1-propanol is attempted. The dehydration of glycerol is primarily studied using ZSM-5 zeolite (Si/Al ratio=12.5) as a catalyst at 300°C and ambient pressure. A complete conversion was obtained at contact time of 177 g.h/mol as shown in Table 4.1.

Table 4.1 Products selectivity and conversion of glycerol by dehydration over HZSM-5 (12.5)



Products	% Selectivity
Acrolein	80.0
Hydroxyacetone	15.1
1,2-propanediol	1.2
Propionaldehyde	3.5
Acetaldehyde	1.2

Reaction conditions; temperature: 300°C, feed: 1.575 g/h of glycerol at 10 wt%, ambient pressure, 100 mL/min of hydrogen

From Table 4.1 acrolein is found as a major product (80%) from dehydration at secondary hydroxyl groups, while hydroxyacetone (15.1%) can be generated from dehydration at primary hydroxyl groups [2]. In addition, other products (5.9%) were obtained from decomposition of the feed as shown below in Figure 4.1.

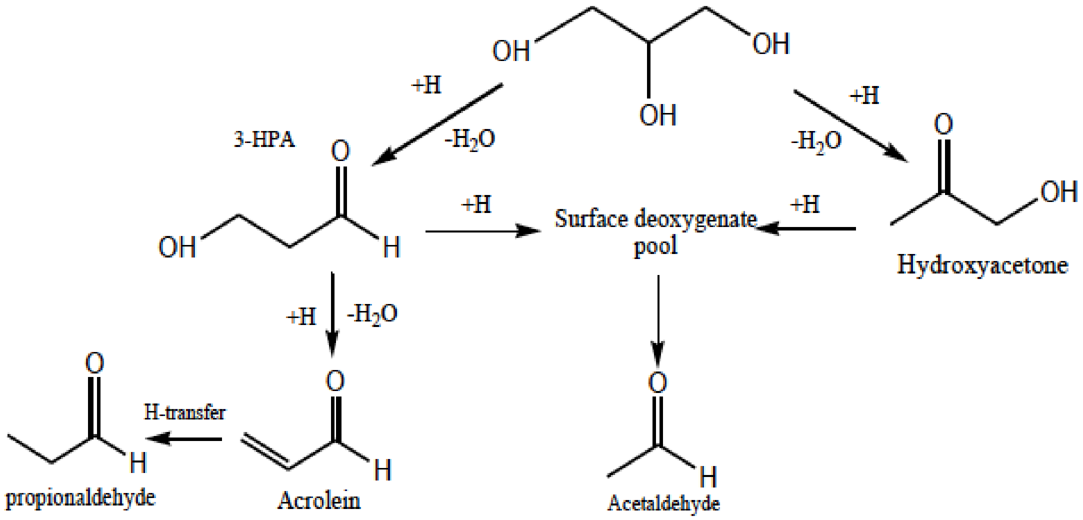


Figure 4.1 Reaction scheme of glycerol dehydration [2]

4.2 Subsequent dehydration-hydrogenation of glycerol to 1-propanol

From the optimum condition for glycerol dehydration obtained in 4.1, a catalytic bed for hydrogenation (Ni/SiO_2) was applied under the upper dehydration bed in the same reactor in order to subsequently convert the dehydrated product to 1-propanol. The hydrogenation of acrolein from glycerol dehydration over Ni supported on SiO_2 catalysts was carried out at 175°C and ambient pressure. It can be seen that a major product from two-bed reaction is 1-propanol. Conversion of acrolein is calculated based on yield of acrolein that obtained from the upper bed (80%). Selectivity of hydrogenated products is based on glycerol conversion. In addition, propionaldehyde, propanoic acid, acetic acid, acetaldehyde and ethanol are observed. The acrolein conversion and selectivity towards 1-propanol, propionaldehyde, propanoic acid, ethanol, and acetic acid is 98.6%, 53.1%, 22.9%, 4.0%, 8.9% and 11.1%, respectively. Considering 1-propanol production, acrolein from dehydration reaction is hydrogenated to propionaldehyde and subsequent hydrogenated to 1-propanol, respectively.

4.2.1 Effect of contact time in second bed

In order to understand the reaction pathway for 1-propanol formation by subsequent hydrogenation of acrolein from glycerol dehydration in the upper bed, Ni/SiO_2 was tested at various contact times as shown in Figure 4.2.

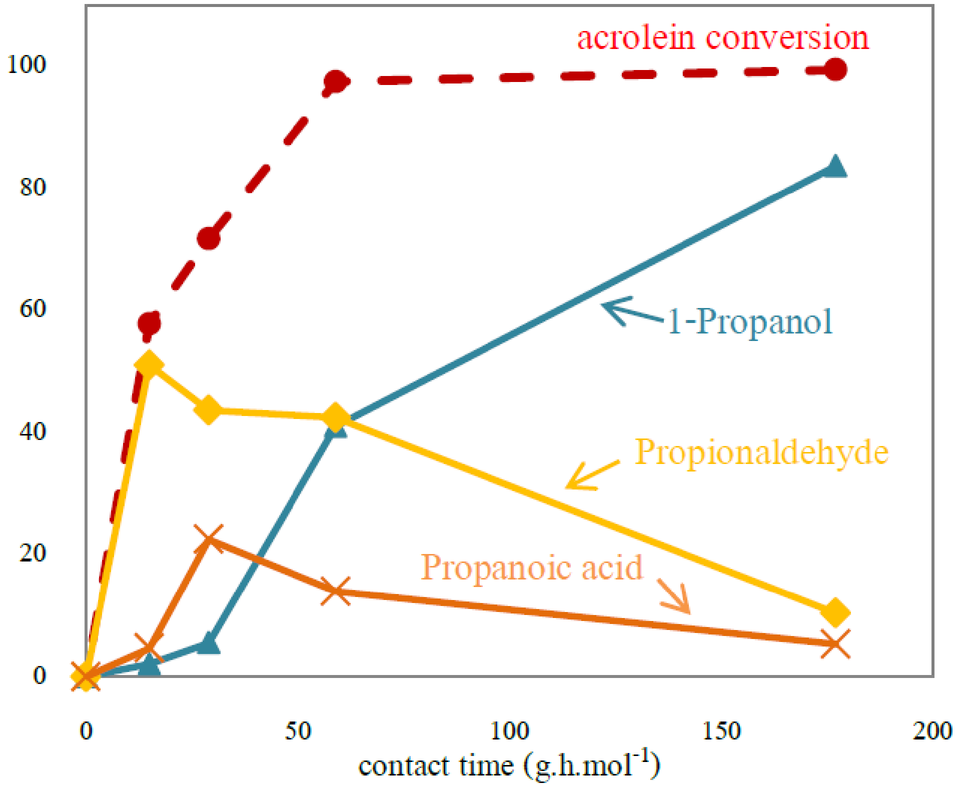


Figure 4.2 The conversion and product yields from subsequent hydrogenation of acrolein from glycerol dehydration as a function of contact time over 20 wt.% Ni/SiO_2 (Reaction condition; 1st bed: temperature: 300°C, contact time: 177 g.h/mol, catalyst: H-ZSM-5 (12.5), 2nd bed: temperature: 175°C, ambient pressure, contact time: 15–177 g.h/mol, feed: 1.575 g/h of glycerol at 10 wt.%, 100 mL/min hydrogen)

It can be seen that acrolein conversion is significantly increased with contact time. As contact time is increased, overall interaction of reactant with active sites of supported Ni catalyst is enhanced. At low contact time, acrolein which is a dehydrated product can be primarily hydrogenated to propionaldehyde over Ni/SiO_2 (Figure 4.2). When contact time is increased, propionaldehyde is decreased while 1-propanol is increasingly observed. It is clear that propionaldehyde will be subsequently hydrogenated to 1-propanol as observed when contact time is increased.

On Ni surface, the C=C bond of acrolein is preferentially adsorbed and hydrogenated to propionaldehyde. This intermediate can be (i) desorbed as products at low contact time or (ii) subsequently hydrogenated at carbonyl groups (C=O) to 1- propanol at high contact time (Figure 4.3).

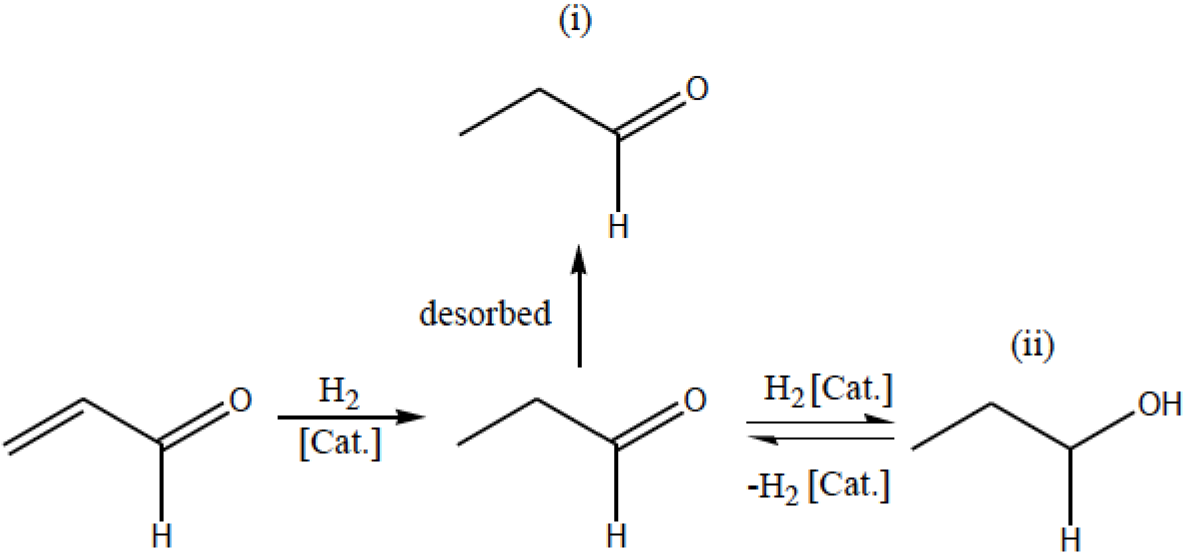


Figure 4.3 The 1-propanol production from glycerol dehydrated product

It is noted that propanoic acid is also found as a minor product being generated in parallel with the hydrogenation reaction at low contact time. It is possible that propanoic acid can be formed by water reduction. As water is largely presence in the reaction stream. Water may react with propionaldehyde on catalyst surface to form 1,1-propanediol, which can be dehydrogenated over Ni surface to propanoic acid as shown in Figure 4.4.

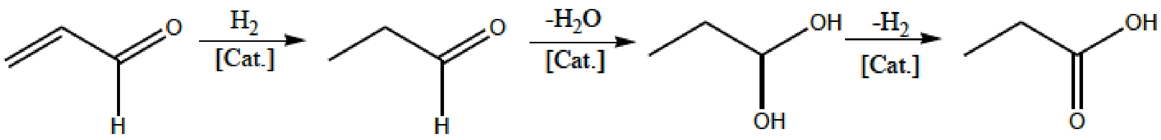


Figure 4.4 The propanoic acid formation

If this is the case, the reaction of propionaldehyde without hydrogen should give more propanoic acid. Hence, 5% propionaldehyde in water is fed over Ni/SiO_2 catalyst under nitrogen. The result is shown in Figure 4.5.

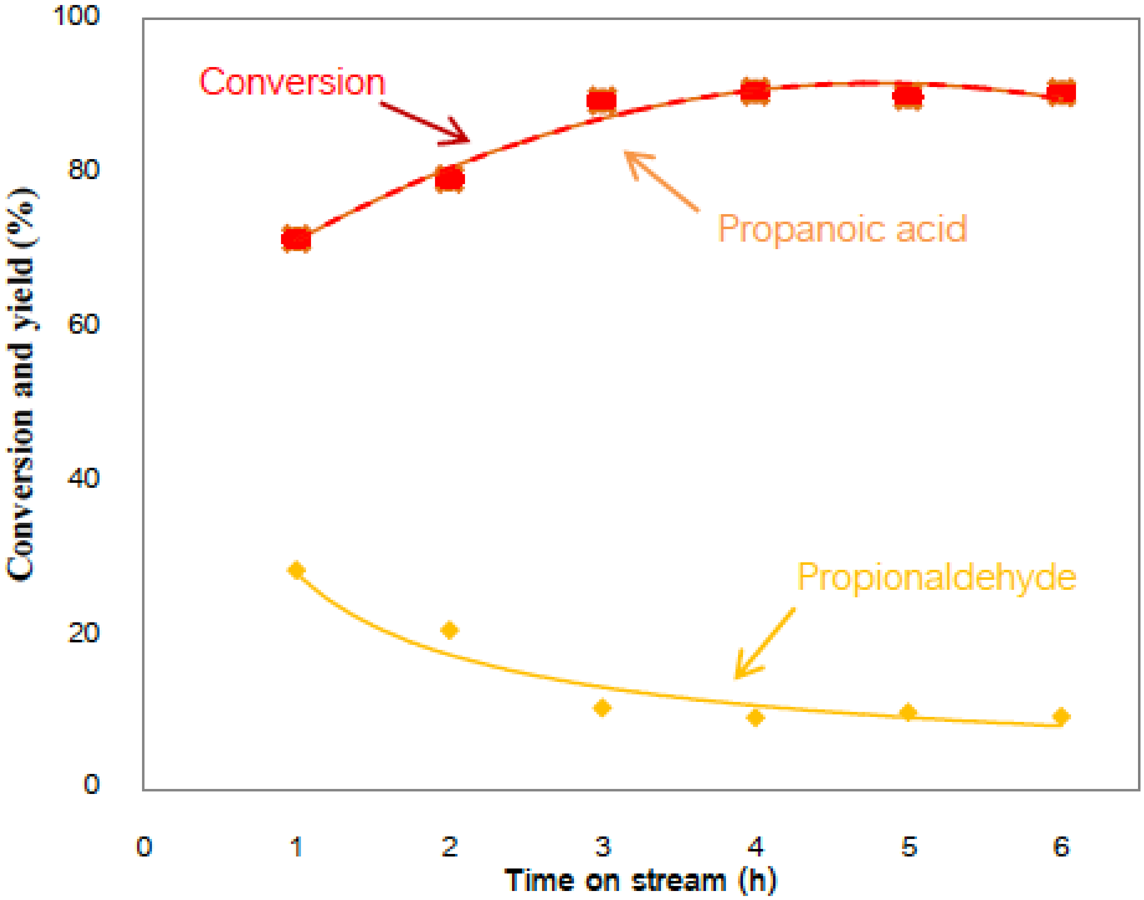


Figure 4.5 Yield of propanoic acid over time on stream of the reaction. (Reaction condition; temperature: 175°C, ambient pressure, contact time: 177 g.h/mol, catalyst: Ni/SiO_2, feed: 1.575 gmol/h of propionaldehyde at 5 wt.% , 100 mL/min nitrogen)

From Figure 4.5, it can be seen that only propanoic acid is produced. Explanation for the observed propanoic acid formation is the reaction of water in the feed with propionaldehyde to form 1,1-propanediol, which is subsequently dehydrogenated over Ni catalyst as discussed (Figure 4.3). Since in the subsequent dehydration-hydrogenation, H_2 is present. Therefore, yield of propanoic acid is relatively less as compared to the reaction in nitrogen.

The overall reaction can be summarized as follows: (i) propionaldehyde is occurred from hydrogenation at C=C of acolein from glycerol dehydration then desorbed as a product, (ii) 1-propanol is produced from subsequently hydrogenation of propionaldehyde at carbonyl group (C=O) and (iii) propanoic acid formation by reaction of water with propionaldehyde and subsequently hydrogenation (Figure 4.6).

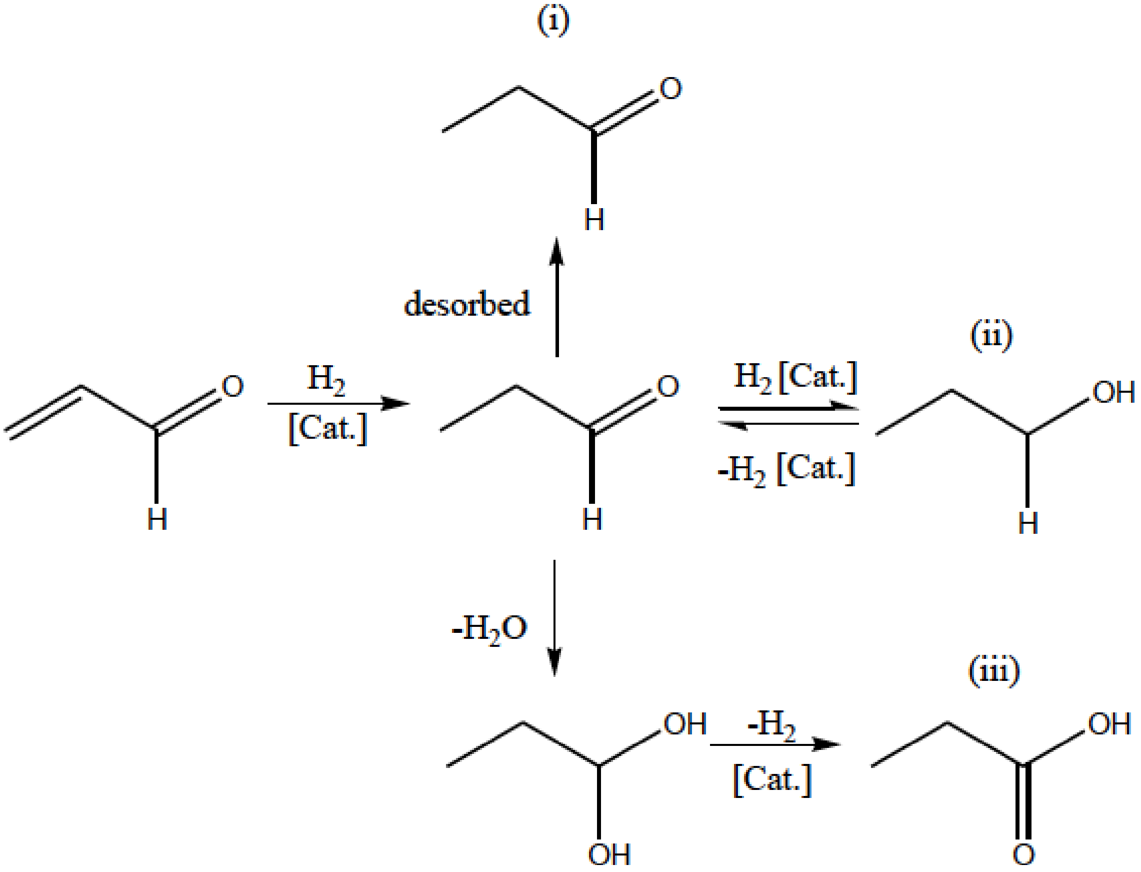


Figure 4.6 The propanoic acid production from water reduction of propionaldehyde

4.2.2 Effect of reaction temperature

Due to hydrogenation reaction is favor at low temperature, the effect of reaction temperature on subsequent hydrogenation of acrolein from glycerol dehydration to 1-propanol is investigated over Ni/SiO_2 as shown in Figure 4.7.

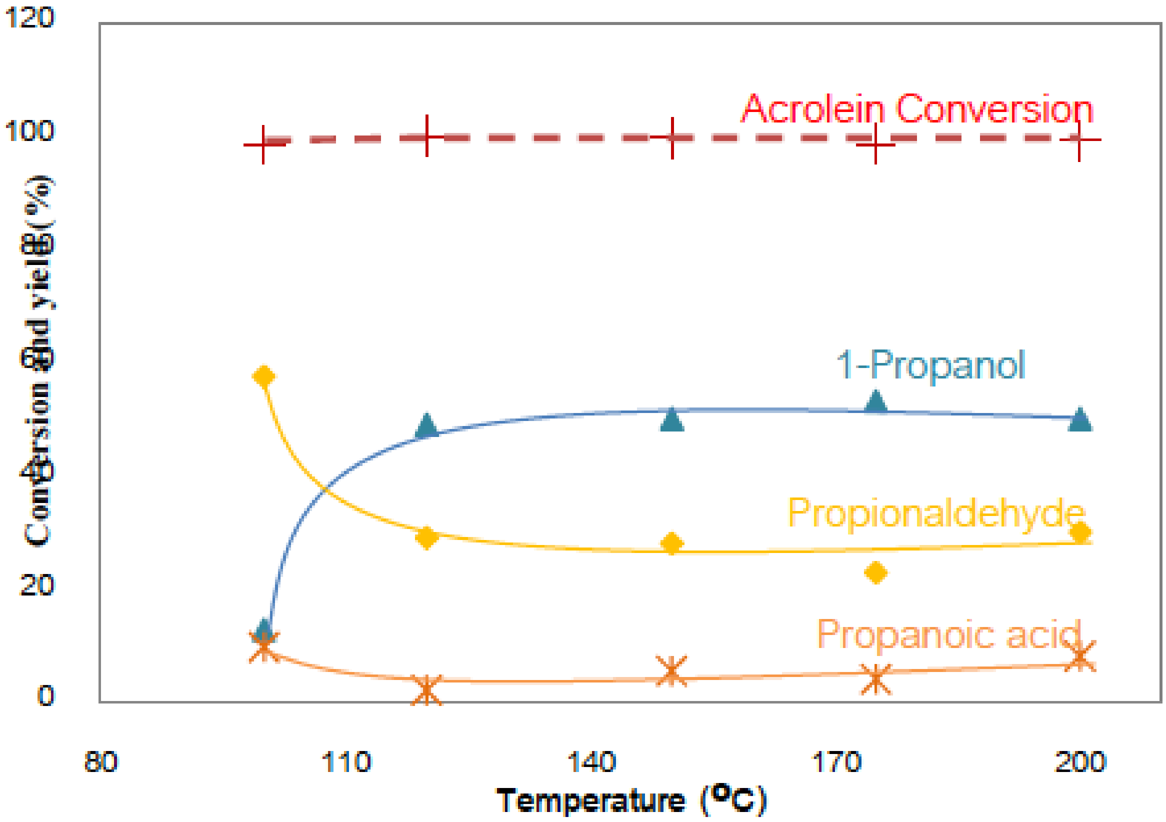


Figure 4.7 The effect of reaction temperature on acrolein conversion as a function of time on stream (Reaction condition; 1st bed: temperature: 300°C, contact time: 177 g.h/mol, catalyst: H-ZSM-5 (12.5), 2nd bed: temperature: 100–200°C, ambient pressure, contact time: 177 g.h/mol, catalyst: Ni/SiO_2, feed: 1.575 g/h of glycerol at 10 wt.%, 100 mL/min hydrogen)

The results show that a complete conversion is obtained at temperatures >120°C. At low temperature (100°C), propionaldehyde is found as a main product. This is because only C=C of acrolein from glycerol dehydration can be readily hydrogenated but the hydrogenation at carbonyl group (C=O) of propionaldehyde requires higher activation energy.

Therefore, low yield of 1-propanol is obtained at 100°C. As the temperature is increased (120–200°C), it is noticed that yield of 1-propanol and propionaldehyde is similar for all temperature tested. This is because 1-propanol produced from propionaldehyde can adsorb on the Ni surface. Hence, dehydrogenation back to propionaldehyde could be expected over large Ni particle. Accordingly, yield of propionaldehyde and 1-propanol is not significantly change at temperature of 120–200°C. The water reduction to produce propanoic acid seems not to be affected by temperature.

However, at the temperature higher than 200°C, it is found that the yields toward hydrogenated products are dramatically decreased, despite the conversion is still complete. This is because at high temperature decarbonylation of acrolein and propionaldehyde to ethylene and carbon monoxides is promoted. These gas products cannot be trapped. Hence, no product can be observed in the liquid collected at temperature >200°C. The overall reaction pathway for the hydrogenation of acrolein from glycerol dehydration is shown in Figure 4.8.

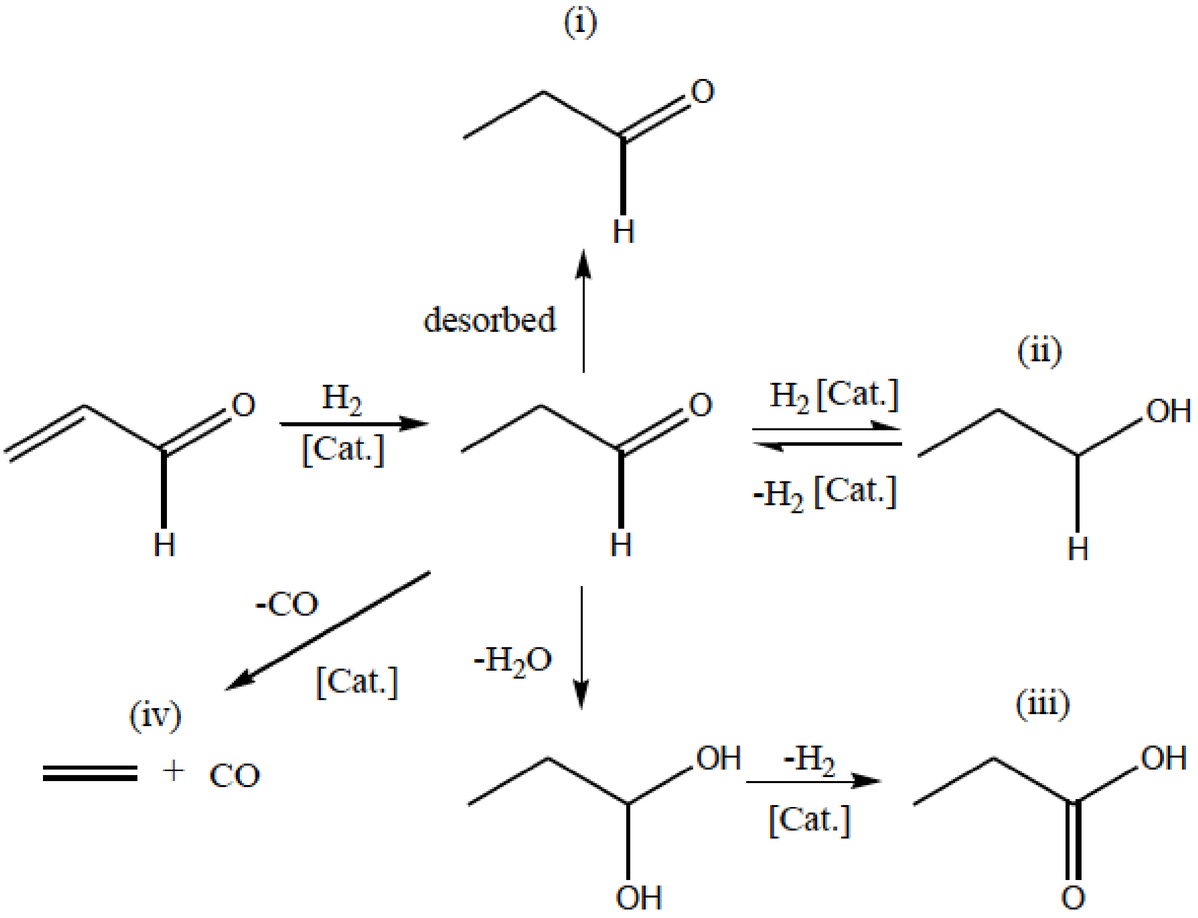


Figure 4.8 The pathway for hydrogenation of acrolein from glycerol dehydration

Chapter 5

Conclusions and Suggestions

5.1 Conclusions

The catalytic deoxygenation of glycerol to 1-propanol was studied using sequential bed system. In the upper bed, H-ZSM-5 (Si/Al=12.5) is used as a catalyst for dehydration of glycerol. Acolein and hydroxyacetone is a major and minor product, respectively. In the lower bed, Ni supported on SiO_2 catalyst (Ni/SiO_2) are used for subsequently hydrogenation of acrolein to 1-propanol. It was found that propionaldehyde is an important intermediate to produce major product, 1-propanol via hydrogenation while propanoic acid is a minor product obtained from water reduction. Interaction between metal and support significantly affects the hydrogenation activity and yield of 1-propanol in the lower catalytic bed. At low temperature (100°C), propionaldehyde is found as a main product because activation energy for C=O hydrogenation is insufficient. As the temperature is increased (120–200°C), it is noticed that yield of 1-propanol and propionaldehyde is similar for all temperature tested, presumably due to the saturated kinetics for hydrogenation-dehydrogenation over large Ni particle. However, at temperature >200°C the decarbonylation of propionaldehyde to ethylene and carbon monoxides is promoted.

5.2 Suggestions for Future Studies

5.2.1) The elimination of silanol group of H-ZSM-5 from glycerol dehydration in the first bed likely increases yield of acrolein that is major product.

5.2.2) Changing feed solvent from water to others is interested to decrease the yield of by-product propanoic acid from water reduction in second bed.

Chapter 6

Research Outcomes

- เผยแพร่ผลงานแบบโปสเตอร์หัวข้อ “Catalytic deoxygenation of glycerol to 1-propanol over zeolite and supported Ni catalyst in sequential bed system” ในสัปดาห์วิทยาศาสตร์ คณะวิทยาสาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง 2558

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ภาคผนวก

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Reaction

Table 1 The yield of glycerol dehydration at contact time = 177 g.h.mol^{-1} (H-ZSM-5 ratio 12.5).

Time on stream (h)	Conversion (%)	Yield (%)				
		Acrolein	Propanal	Hydroxy acetone	1,2-PDO	Acetaldehyde
1	100	85.6	5.7	10.0	1.1	1.4
2	100	86.1	4.5	8.0	1.3	1.3
3	100	74.8	3.1	20.5	1.6	1.5
4	100	78.0	3.3	17.6	1.1	1.1
5	100	81.6	3.5	14.1	0.7	0.7
6	100	77.9	3.1	17.5	1.5	1.5

Table 2 The yield of the glycerol deoxygenation over zeolite H-ZSM-5 and 20 wt.% Ni/SiO_2 at contact time = 177 g.h.mol^{-1}

Time on Steam (h)	Acrolein Conversion (%)	Yield (%)						
		Hydroxy-acetone	1-Propanol	Propional-dehyde	Propano-ic acid	Acetalde-hyde	Ethanol	Acetic acid
1	96.9	100	57.8	8.0	11.6	0	9.4	10.6
2	99.4	90.8	67.0	8.3	4.3	0	8.3	7.7
3	99.4	59.3	59.7	18.0	1.8	0	8.1	3.8
4	98.7	56.9	52.4	24.4	2.0	0	2.8	8.6
5	99.0	43.0	44.1	34.1	1.0	0	6.0	2.6
6	98.0	10.8	33.5	42.2	2.6	0	0	2.2

Reaction condition; 1st bed: temperature: 300°C, contact time: 177 g.h.mol^{-1}, catalyst: H-ZSM-5 (12.5), 2nd bed: temperature: 175°C, ambient pressure, contact time: 177 g.h.mol^{-1}, catalyst: Ni/SiO_2, feed: 1.575 g.h^{-1} of glycerol at 10 wt.%, 100 ml/min hydrogen.

ภาคผนวก ข

สรุปค่าใช้จ่ายการดำเนินงานโครงการวิจัย

รหัสโครงการ/รหัสสัญญา 2558 02050042

แบบรายงานการใช้จ่ายเงินโครงการวิจัย

สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

รายงานฉบับสมบูรณ์ ประจำปีงบประมาณ 2558

☐ แหล่งงบประมาณแผนดิน (แบบปกติ) ☑ แหล่งเงินรายได้

ชื่อโครงการ (ภาษาไทย) ปฏิกิริยาดีออกซิจีเนชันของกลีเซอรอลเป็นแอลกอฮอล์ที่มีคาร์บอน 3 อะตอม

(ภาษาอังกฤษ) Deoxygenation of Glycerol to C3 Alcohols

ชื่อ-สกุลหัวหน้าโครงการวิจัยผู้รับทุน/ผู้วิจัย ดร. ณัฐธิดา นุ่มวงศ์

รายงานในช่วงตั้งแต่วันที่ 1 ตุลาคม 2557 ถึง 30 กันยายน 2558

ระยะเวลาดำเนินการ 1 ปี ตั้งแต่วันที่ 1 ตุลาคม 2557 ถึง 30 กันยายน 2558

ข้อมูลการรายงานค่าใช้จ่ายงบประมาณโครงการวิจัย

1. การเบิกจ่ายงบประมาณ

งวดที่ 1 50,000 บาท 100 % วันที่ได้รับอนุมัติให้เบิกจ่ายเงิน (ป/ด/ว) พฤศจิกายน 2557

2. สรุปงบประมาณค่าใช้จ่ายที่ใช้นับตั้งแต่เริ่มทำการวิจัยถึงปัจจุบัน

หมวดค่าใช้จ่าย	งบประมาณรวมทั้งโครงการ	ค่าใช้จ่าย (บาท)	คงเหลือ (หรือเกิน)
งบบุคลากร :ค่าจ้างชั่วคราว	-	-	-
งบดำเนินงาน			
ค่าตอบแทน	-	-	-
ค่าใช้สอย	14,500.00	14,270.00	230.00
ค่าวัสดุ	35,500.00	35,730.00	-230.00
ค่าสาธารณูปโภค	-	-	-
งบลงทุน: ค่าครุภัณฑ์	-	-	-
รวม	50,000.00	50,000.00	0.00

(ดร.ณัฐธิดา นุ่มวงศ์)

หัวหน้าโครงการวิจัยผู้รับทุน

21 / มี.ค. / 2559

ข้อมูลประวัติคณะผู้วิจัย

ประวัติส่วนตัว

ชื่อ-สกุล	ดร.ณัฐธิดา นุ่มวงศ์
ตำแหน่งปัจจุบัน	อาจารย์ ภาควิชาเคมี คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

ประวัติการศึกษา

ชื่อย่อปริญญา	สาขา	สถาบันที่จบ	ปีที่จบ
วท.บ.	เทคโนโลยีปิโตรเคมี	สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง	2549
ปร.ด.	เทคโนโลยีปิโตรเคมี	วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย	2555

ทุนการศึกษาและทุนวิจัยที่เคยได้รับ

ปี พ.ศ.	ทุนการศึกษาและทุนวิจัย	สถาบันที่ให้
2550	Full Scholarship for Master Student	วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย
2551	ทุนปริญญาเอกจุฬาดุษฎีพิพรรธ์	จุฬาลงกรณ์มหาวิทยาลัย
2556	ทุนนักวิจัยรุ่นเยาว์	สถานเอกอัครราชทูตฝรั่งเศสประจำประเทศไทย
2557	ทุนส่งเสริมนักวิจัย งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
2558	ทุนส่งเสริมนักวิจัย งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
2558	ทุนสนับสนุนทุนวิจัยร่วมกับหน่วยงานภายนอกสถาบัน งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

ผลงานวิจัยระดับนานาชาติ

1. **Numwong N.**, Luengnaruemitchai A., Chollacoop N., and Yoshimura Y., Effect of SiO_2 Pore Size on Partial Hydrogenation of Rapeseed Oil-Derived FAMEs. Applied Catalysis A: General 441–442 (2012) 72– 78

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