

Production of γ -Valerolactone (GVL) from one-pot cascade transformation of furfural
over Pt/zeolite-based catalysts



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การผลิตแกมมา-แวลูโรแลคโตนผ่านปฏิกิริยาแบบต่อเนื่องของเฟอร์พูลในเครื่องปฏิกรณ์เดียวโดย
ใช้ตัวเร่งปฏิกิริยาซีโอไลต์



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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เฟอร์ฟูรัลในเครื่องปฏิกรณ์เดียวโดยใช้ตัวเร่งปฏิกิริยาซีโอไลต์. (Production of γ -
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แกมมา-แวลอโรแลคโตนเป็นสารเคมีสีเขียวที่หมุนเวียนได้และเป็นมิตรต่อสิ่งแวดล้อม
ซึ่งสามารถใช้เป็นสารเติมแต่งเชื้อเพลิง ตัวทำละลายอินทรีย์ในอุตสาหกรรมอาหาร และตัวกลาง
ทางเภสัชกรรม การผลิตแกมมา-แวลอโรแลคโตนโดยตรงจากเฟอร์ฟูรัลในเครื่องปฏิกรณ์เดียว
เป็นที่ต้องการอย่างมาก เพื่อลดการใช้ตัวทำละลาย จำนวนหน่วยการผลิต และต้นทุนการผลิต
ปฏิกิริยาแบบต่อเนื่องดำเนินการในเครื่องปฏิกรณ์เดียว โดยใช้แอลกอฮอล์แบบทุติยภูมิเป็นตัวให้
ไฮโดรเจนร่วมกับตัวเร่งปฏิกิริยาที่เป็นกรด หรือที่เรียกปฏิกิริยานี้ว่า ปฏิกิริยาเมียร์ไวน์-พอนน์
ดอร์ฟ-เวอร์ลีย์ ซึ่งใช้ 2-โพรพานอล เป็นตัวให้ไฮโดรเจนกับเฟอร์ฟูรัล ทำการศึกษาผลของซี
โอไลต์ชนิดต่างๆ ได้แก่ HY ที่มีอัตราส่วน Si/Al 15, 100 และ 500 H-ZSM-5 และ H-Beta
นอกจากนี้ ยังศึกษาผลของโลหะแพลทินัม, ผลของอุณหภูมิ, แก๊ส, และความดันในการทำปฏิกิริยา
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อุณหภูมิ, เทคนิคการดูดซับไพรีดีนในอินฟราเรดสเปกโตรสโกปี, กล้องจุลทรรศน์แบบส่องกราด,
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แบบกะ ภายใต้ความดันบรรยากาศไนโตรเจนที่อุณหภูมิ 120 °C และเวลาในการทำปฏิกิริยา 5
ชั่วโมง ตัวซีโอไลต์ HY-15 ให้ผลผลิตสูงสุดของแกมมา-แวลอโรแลคโตนที่ 46.2% ประสิทธิภาพ
ของตัวเร่งปฏิกิริยาที่ดีกว่าตัวอื่นนั้นมาจากขนาดรูพรุนที่มีขนาดใหญ่ อัตราส่วน บรอนสเตด ต่อ ลิว
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γ -valerolactone (GVL) is a green renewable resource, which can be used as fuel additives, organic solvent in food industries, pharmaceutical intermediates. The direct production of GVL from furfural in a one-pot transformation is highly desirable in order to minimize the use of solvents, the number of unit operations, and the production cost. The cascade reaction was carried out in a single reactor, using a secondary alcohol as the hydrogen donor with acid catalysts (so-called Meerwein-Ponndorf-Verley reaction). In this work, the transfer hydrogenation of furfural with 2-propanal as a hydrogen donor was investigated on various zeolites including of HY with Si/Al ratios 15, 100, and 500, H-ZSM-5, and H-Beta. Moreover, the effect of Pt metal as a promoter, effect of temperature, gas and pressure condition were also studied. The characteristics and catalyst properties were analyzed by XRD, N_2 -physisorption, NH_3 -TPD, Pyridine-IR, SEM and ICP. The reaction was normally carried out in a batch reactor under nitrogen atmosphere at 120 °C and 5 h reaction time. The HY-15 zeolite presented the highest yield of GVL at 46.2%. Their superior catalytic performances were attributed to the large pore size, high Bronsted to Lewis ratio, and high total acidity. Over HY zeolites, furfuryl ether could be converted to isopropyl levulinate rather than angelica lactone, which was found on H-ZSM-5 via a non-preferred reaction pathway.

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CHAPTER I INTRODUCTION

1.1 Introduction

The world energy consumption has relied on fossil fuel as the main resource of energy. The current increasing in energy consumption causes environmental problems including water pollution, air pollution, the greenhouse effect leading to global warming and energy shortages because of decreasing in fossil resources [1]. All of these problems affect human life. To solve the current environmental and the global energy problems, new greener renewable resources have been developed to use as a replacement of fossil fuel [2]. Among the various energy resources, biomass energy is an interesting clean renewable energy. Thailand has the advantages of abundant biomass resources such as sugarcane bagasse, corn cob, rice straw, rice husk which are the most plentiful agricultural waste from agro-industry.

The biomass resource of hemicellulose sugar is mainly composed of cellulose, hemicellulose, and lignin. Hydrolysis and dehydration of hemicellulose sugar with acid catalysts produce furfural (FAL) [3]. FAL is used as alternative to levulinic acid to produce value-added biomass-based compounds such as γ -valerolactone (GVL) [4]. GVL is a common lactone that can be used as fuel additives, green organic solvent in food industries, pharmaceutical intermediates, nylon intermediates and other industries [5].

The direct production of GVL from FAL in a one-pot transformation is highly desirable in order to minimize the use of solvents and reduce chemical wastes, the number of unit operations and the process cost [6]. There are multiple step reaction involved in production of GVL from FAL including of Meerwein–Ponndorf–Verley (MPV), reduction of FAL, hydrolysis, ring-opening and lactonization to GVL [7].

All of the cascade reaction can be carried out in a single reactor, using secondary alcohol as the hydrogen donor (to avoid high pressure hydrogen gas) under a nitrogen atmosphere and can be catalyzed by metal catalyst supported on acid zeolites [8]. The catalysts must contain a suitable ratio of Brønsted acid to Lewis acid and can catalyze transfer hydrogenation (TH) in MPV reduction of FAL and acid hydrolysis reactions [7].

Therefore, this research aims to study MPV reduction of furfural over different zeolite catalyst including HY zeolites with Si/Al ratio 15-500, H-ZSM-5 and H-Beta and to analyze the role of Pt promoter on zeolite-based catalysts.

1.2 Objectives

To study MPV reduction of furfural over different zeolite catalysts. The effects of zeolite structure and acidity, role of Pt promoter on zeolite catalyst, and the effect of temperature and pressure on the reaction were focused.

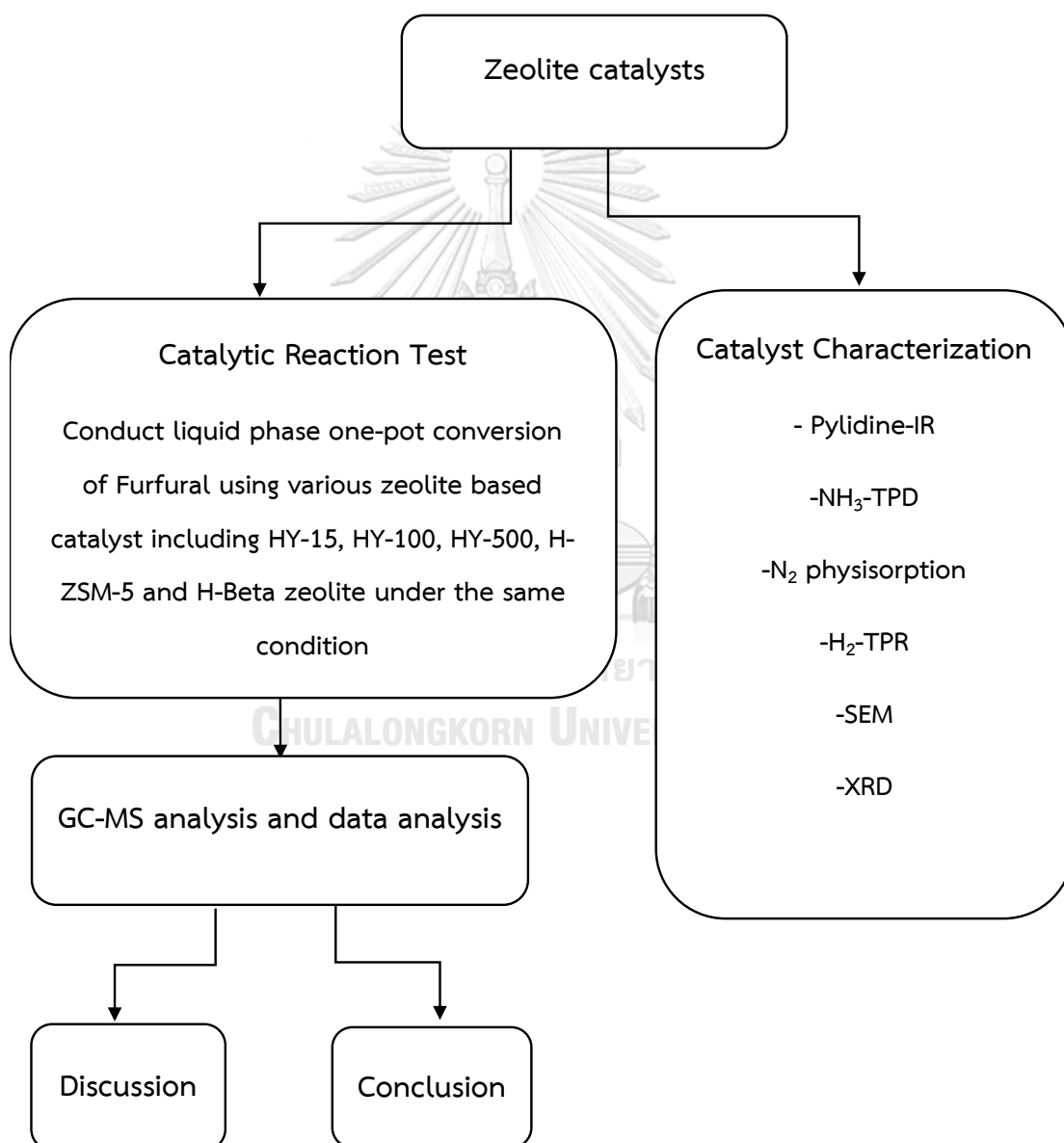
1.3 Scope of the research

- 1.3.1 The reaction was conducted under reaction conditions; 0.2 g catalyst, 0.5 mmol furfural, 13 ml isopropanol, temperature 120 °C, 800 rpm, reaction time 5 h and using zeolites including HY-15, HY-100, HY-500, H-ZSM-5 and H-Beta zeolite as the catalysts. In case of HY-15, the reaction was conducted under various conditions in order to investigate the effect of temperature and pressure.
- 1.3.2 The 1% Pt metal supported on zeolites including HY-15, HY-500, H-ZSM-5 were prepared by incipient wetness impregnation method and used in one pot-transformation of furfural under the same conditions as 1.3.1
- 1.3.3 All the bifunctional catalysts were characterized by various methods including X-ray diffraction (XRD), hydrogen temperature program (H₂ -TPR), nitrogen-physisorption, ammonia temperature program desorption (NH₃ -TPD), pyridine-IR spectroscopy, scanning electron microscope (SEM)

1.4 Research Methodology

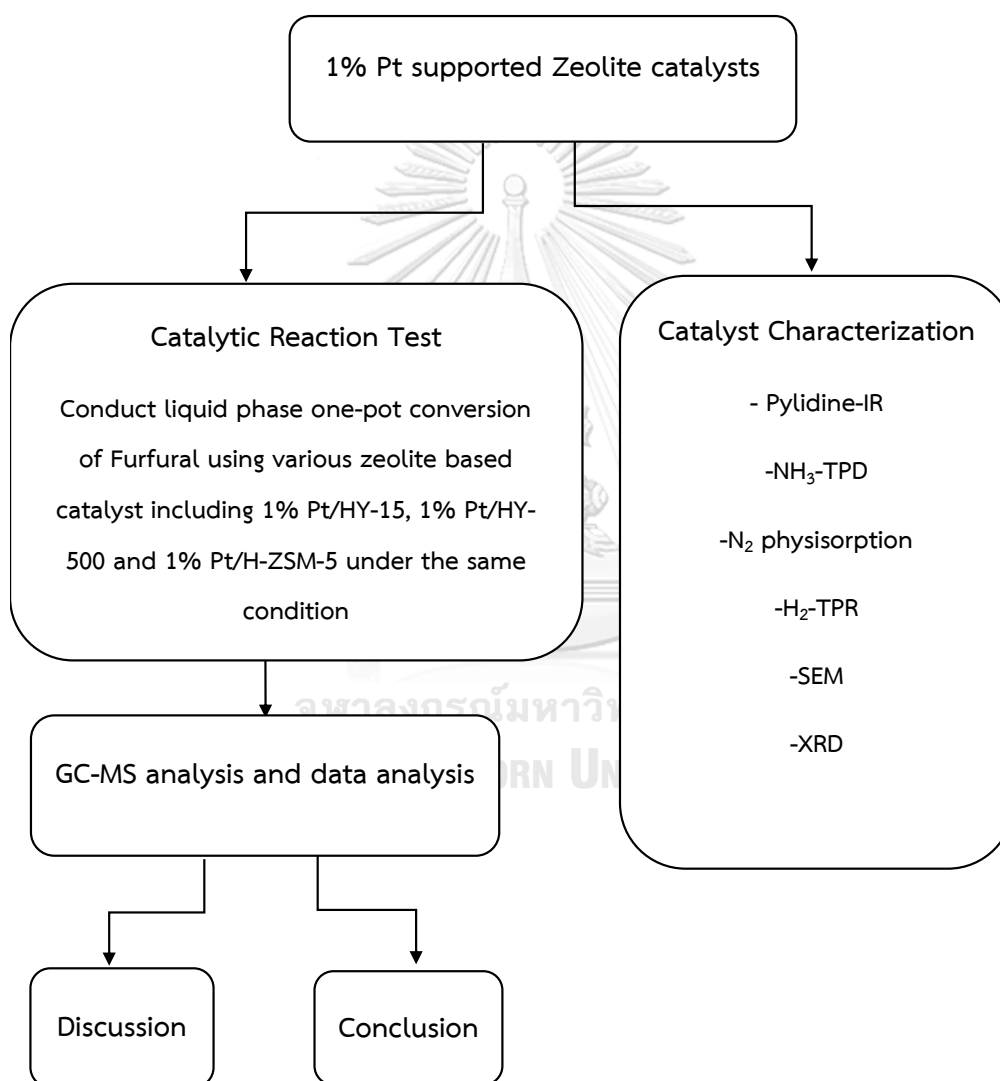
Part I Study the effect of zeolite structure and acidity

Various zeolite catalysts were tested for furfural conversion under the same reaction conditions; 0.5 mmol (42 μ L) of FAL, 10 g (13ml of isopropanal), 0.2 g of catalyst, 120°C, 1 bar of N₂ and stired at 800 rpm for 5 h.



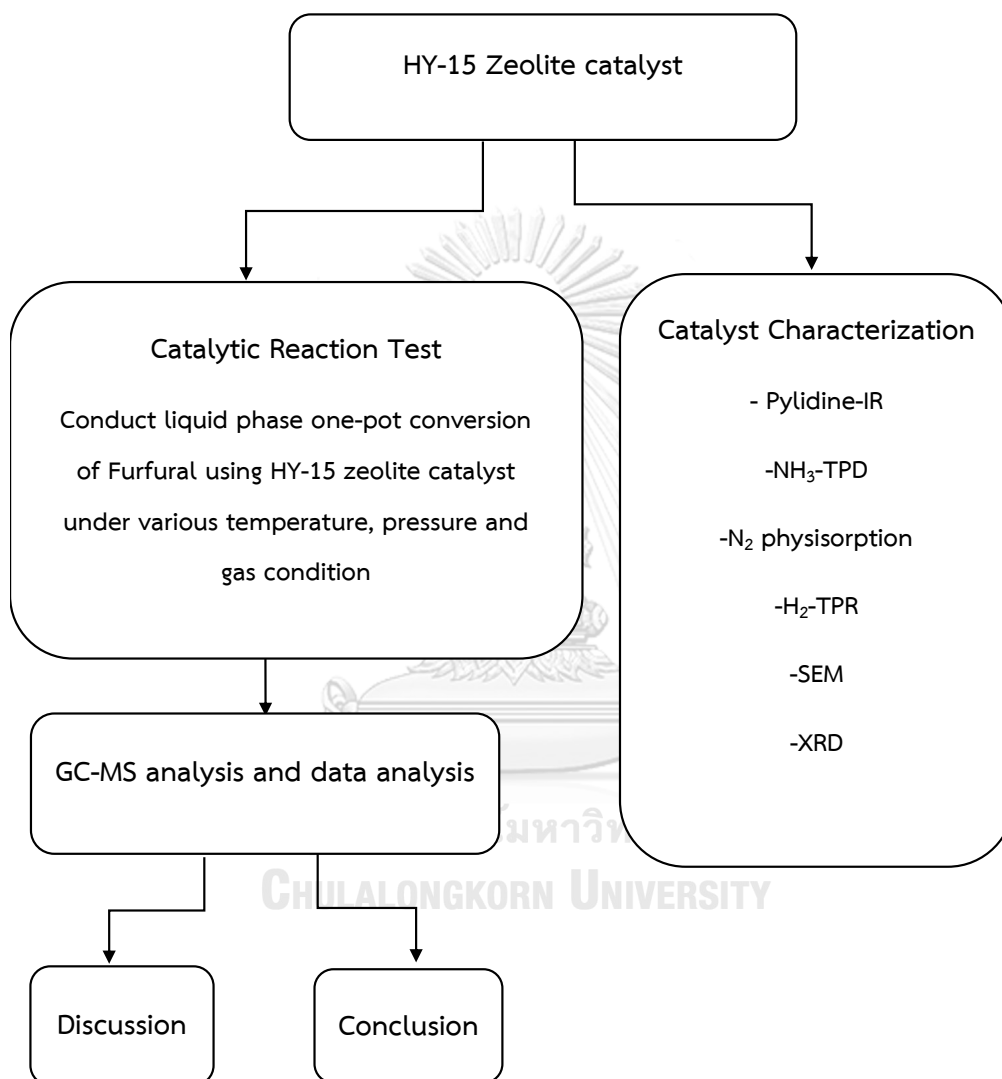
Part II Study the effect of Pt promoter

The platinum promoted zeolite catalysts were tested for furfural conversion under the same conditions; 0.5 mmol (42 μ L) of FAL, 10 g (13ml of isopropanol), 0.2 g of catalyst (reduced under H_2 gas 25 mL/min at 500 $^{\circ}C$ for 2 hr), 120 $^{\circ}C$, 1 bar of N_2 and stirred at 800 rpm for 5 h.



Part III Study the effect of temperature, pressure and gas conditions

The HY-15 zeolite catalyst was tested for furfural conversion under the various condition. studying the effect of temperature, pressure and gas (H_2) conditions.



CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Hydrogenation reaction of furfural

Furfural (FAL) is being used as versatile biobased C5 platform molecules. It is produced from hemicellulose-derived xylose or from other pentose rich polysaccharides. In commercial scale, FAL is produced by hydrolysis and dehydration of hemicellulose sugar with acid catalysts [3].

The use of FAL as green solvents is not desirable because of its higher toxicity level compare to standard petrochemical solvents [9]. On the contrary, it is commonly used as a bio-based raw material for production of further oxidation, hydrogenation or other process. There are various chemicals, which can be directly or indirectly produced from FAL as shown in Figure 1.

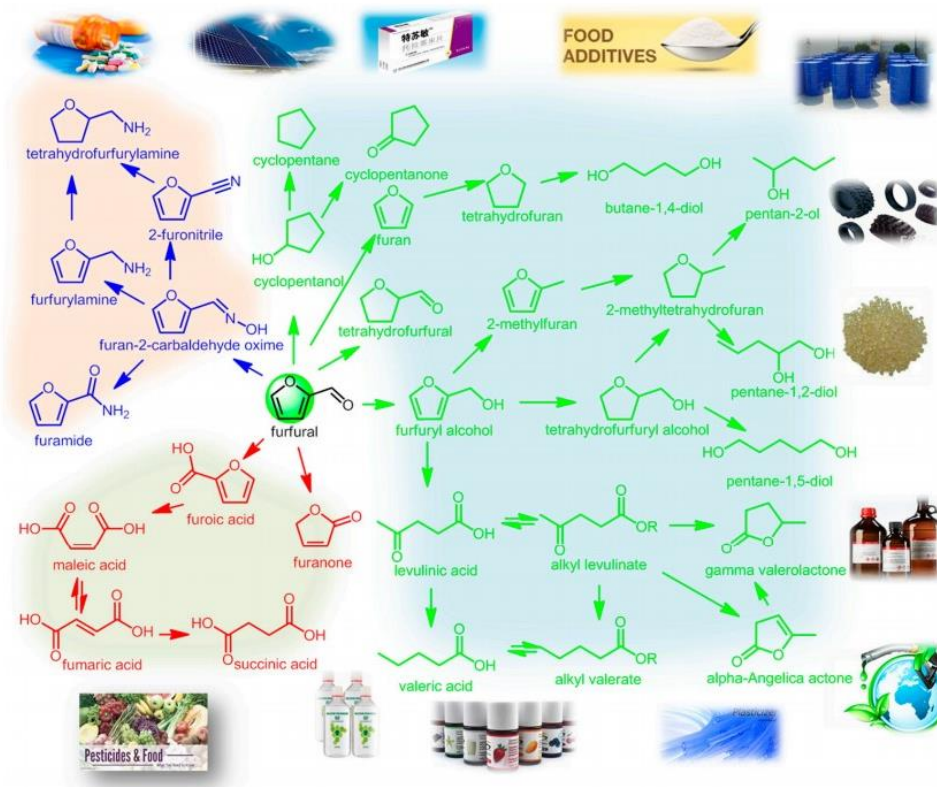


Figure 1 Product of furfural using various process [10]

For example, tetrahydrofurfuryl alcohol (THFA) is used as a green solvent in the pharmaceutical industry and 2-methylfuran (MF) is used as an alternative fuel additive with great combustion performance and high Research Octane Number (RON = 103) [10]. At present, furfuryl alcohol (FAL), tetrahydrofuran (THF), maleic anhydride (MA), 2-methyltetrahydrofuran (MTHF) and pentane-1,5-diol (1,5-PeOL) are the main furan-derivatives produced on a commercial scale [9].

Recent advances in hydrogenation of furfural to furan-derivatives is mainly focused on catalytic processes using different types of metal based catalysts, such as non-noble metal (Cu, Ni, Co, etc.), and noble metal (Pd, Pt, Ru, etc.) [10] under hydrogen pressure (carried out in the presence of molecular H₂) which is required high pressure condition [9]. In order to avoid high pressure, the reduction of FAL should be conducted by using alternative sources of hydrogen via catalytic transfer hydrogenation (CTH) process [11]. In the absence of molecule H₂, the direct hydrogen transfer from the donor molecule of hydrogen source to the acceptor on the catalyst surface leading to the formation of a six-membered transition state which is known as the Meerwein-Ponndorf-Verley reduction (MPV) [9].

2.2 Meerwein-Ponndorf-Verley reduction of furfural (MPV-reduction)

The Meerwein Ponndorf Verley reduction (MPV) is a conventional mechanism, which is used for reducing carbonyl groups into carbinols via hydrogen transfer using an alcohol as hydrogen source. In MPV reduction, the sacrificing alcohol is transformed into a ketone, whereas the starting carbonyl group, either a terminal (aldehyde) or secondary (ketone) group, is reduced into an alcohol because of the net transfer of a hydrogen molecule [12]. For MPV reduction of furfural, the reaction occurs on Lewis acid sites of catalyst, which is reported that can promote hydrogen transfer from secondary alcohols to carbonyl groups through a six-membered ring intermediate [13] as shown in Figure 2.

Even though homogenous Lewis catalysts present high yield, it has been reported that the catalytic activity is sensitive to moisture. There are also a problem with separation, purification and regeneration. Normally, solid heterogeneous catalysts are more preferable because they can be easily recovered. In recent studies, metal oxides such as Al_2O_3 , ZrO_2 or MgO [13] have presented great catalytic activity in MPV reduction of furfural due to their high density of Lewis acid sites.

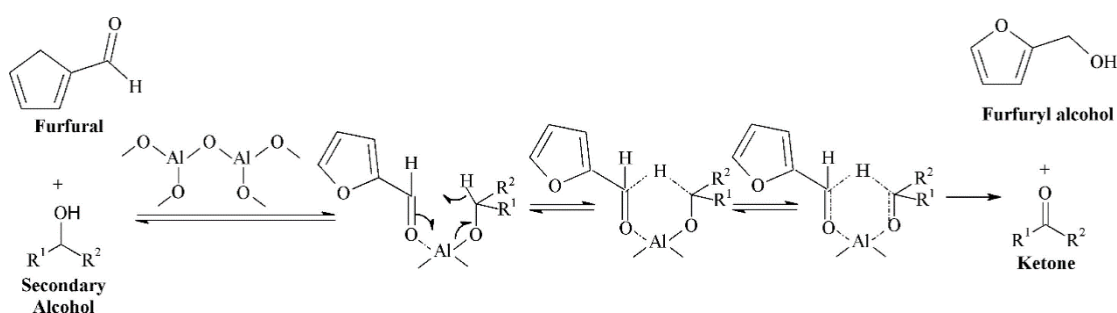


Figure 2 Mechanism of the MPV reduction of furfural and secondary alcohol to furfuryl alcohol and ketone ^[14]

Zeolites or mesoporous silica modified with heteroatoms to generate Lewis acidity has also been used in MPV reduction of FAL. Moreover, the FAL conversion via MPV reduction leads to furfuryl alcohol which can react with the secondary alcohol to produce furfuryl ethers. And furfuryl ethers can lead to the formation of other products, such as levulinic acid or γ -valerolactone which is high value-added product, due to the coexistence of Lewis and Brönsted acid sites on catalysts [14].

2.3 One-pot transformation of furfural via multistep reaction

Because of the low price and accessibility, FAL is used as alternatives to levulinic acid to produce a value-added biomass-based compound [4], γ -valerolactone (GVL), which is used in various industries.

The conventional process of the conversion of FAL to GVL is composed of many reaction steps as shown in Figure 3. Firstly, the hydrogenation of furfural into furfuryl alcohol (FA). After that, FA is converted to furfuryl ether (FE) which is catalyzed by acid catalyst. Then, the Brønsted acids site catalyze the alcoholysis of FA and FE leading to ring-opening and forming of levulinates (PL). Afterwards, most of PLs are catalyzed by Lewis acid to produce the 4-hydroxypentanoates (4-HPs) and a minor of furanone (MF) via reduction of PLs. In the last step, both of 4-HPs and MF undergo lactonization to form GVL [15].

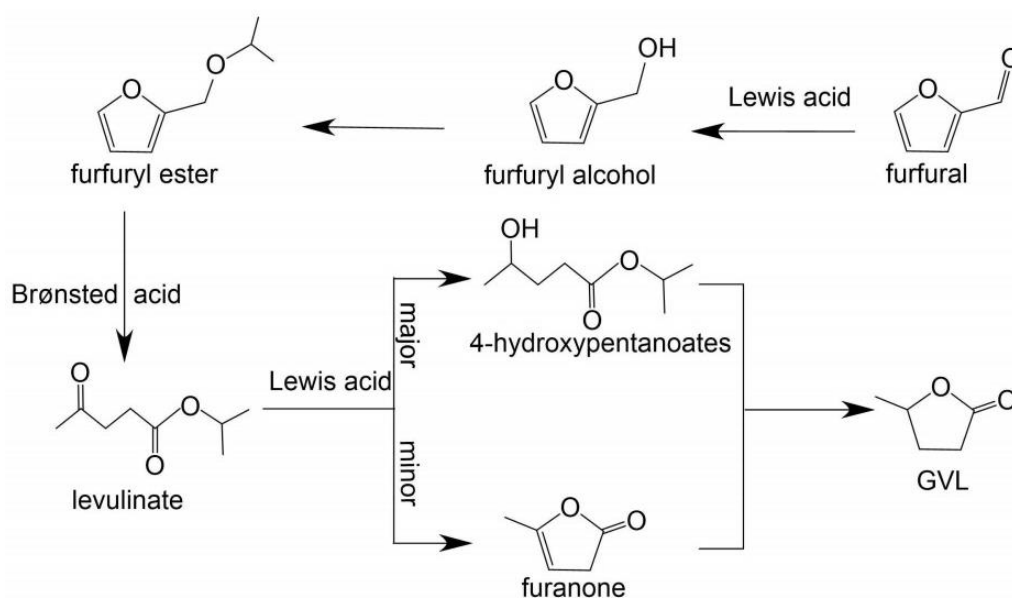


Figure 3 Basic process for the one-pot conversion of FAL to GVL^[15]

Despite, the Hydrogenation in the first step and the reduction of PLs of the cascade reaction can be carried out using gaseous hydrogen under high pressure and catalyzed by precious metal catalysts [16]. These two steps can also be conducted by MPV reduction using an alcohol serves as the hydrogen donor in combination with a Lewis acid catalyst [17].

MPV reduction is more beneficial compared to conventional hydrogenation because it can be carried out at ambient pressure. For catalyst system, inexpensive metal oxides can also be used as Lewis acid catalysts. In the third step, conversion of FA and FE to PL requires Brønsted acid catalysts such as zeolites [18].

In conclusion, Both Lewis as well as Brønsted acid catalysts are required in a catalyst system for the transformation of FAL to GVL. All of these cascade reactions can be conducted in a single reactor and one catalyst system, which is called one-pot transformation of FAL.

2.4 Properties of zeolite support and Platinum

Zeolites are microporous, aluminosilicate minerals which are very stable and durable. They can resist under high experimental conditions because of high melting and boiling points. Zeolites are also resisting to high pressure, organic and inorganic solvents. They are used as catalysts in the industrial including petroleum refineries and petrochemical [19].

For these reasons, zeolites with their well-defined microporous geometry, tunable acidity, high surface area [6] and high intrinsic Lewis acid activity of single-atomic Sn or Zr sites are suitable catalysts for one-pot transformation of FAL [20]. The three-dimensional structure of the zeolites framework is shown in Figure 4.

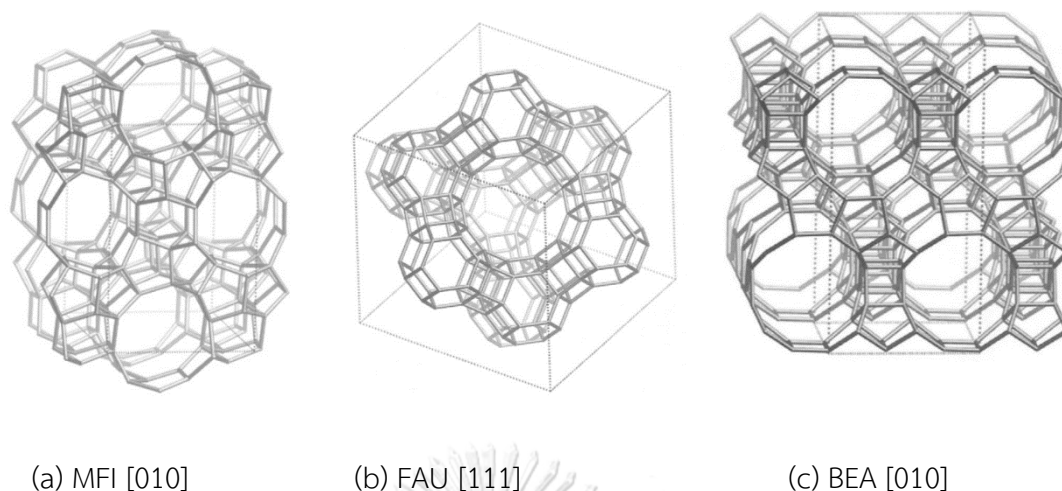


Figure 4 zeolites framework (a) H-ZSM-5^[21], (b) HY^[22] and (c) H-Beta^[23]

Platinum (Pt) is a chemical element with atomic number 78. It is a highly unreactive, precious transition metal. It has 6 isotopes including ¹⁹⁰Pt, ¹⁹²Pt, ¹⁹⁴Pt, ¹⁹⁵Pt, ¹⁹⁶Pt, and ¹⁹⁸Pt^[14] [24]. Physical properties of platinum are shown in Table 1.

Table 1 Physical properties of Platinum^[24]

Physical properties	Platinum
Atomic number	78
Atomic weight	195.09
Melting point	1768.3 °C
Boiling point	3825 °C
Density	21.45 g/cm ³
Element category	Transition metal

The Pt metals are considered as active hydrogenation catalysts and most functional groups can be reduced under mild conditions over one or another of these catalysts. Pt metal hydrogenation catalysts are two types including supported and unsupported. Supported platinum metal catalysts have advantages over unsupported catalysts. For example, supported catalysts present greater efficiency in use of the Pt metal by increasing the active metal surface and better resistance to poisoning [25]

2.5 Summary of the research on one-pot transformation of furfural on various zeolite-based catalysts under different reaction conditions

Table 2 Summary of the research of one-pot transformation of furfural on various zeolite-based catalysts

Reference	Catalysts	Reaction Conditions	Objectives	Conclusions
Zhang, Hongwei. et al. (2019) [6]	Zr- zeolite and Al-zeolite at various Si/Al ratio code as Al-HY(or beta)-X Zr-HY(or beta)-X-Y X: Si/Al ratio Y: Si/Al ratio after wet impegnation including of Zr-HY-15-20, ZrHY-6-20, Zr-HY6-10, Zr-HY-2.6-20, Zr-HY-2.6-10, Zr-HY-2.6-5, Zr-Beta-150-150, Zr-Beta-75-75, Zr-Beta-12.5-150, Zr-Beta-12.5-75, Zr-Beta-12.5-12.5, ZrO ₂ , Zr-HY-15-10, Zr-HY-15-5	1mmol furfural ,0.10 g catalyst, 5 mL 2-pentanol, 120°C, 5 h under N ₂ atmosphere	-Studied the effect of Zr and Al on zeolite catalysts for one-pot transformation of furfural -Studied effect of solvent	-The Zr-HY showed much higher activity than Zr-Beta samples which was attributed to a larger pore size and a more hydrophobic nature. -A 2:1 wt ratio of Zr-HY-15-20 and Al-HY-6 was optimum. reaction, with 85% GVL yield after only 5 h at 120 °C.
Rao B.S. et al	Metal oxide modified with tungstophosphoric	0.196 g furfural ,2.5–11.5 g cat/L	-Studied Metal oxide modified with	-The Bronsted acidic TPA was essential for the

<p>(2019) [26]</p>	<p>acid (TPA) support on beta-zeolite including of T-zeolite (beta-zeolite with TPA), Zr-T-zeolite, Ti-T-zeolite, Nb-T-zeolite which were prepared by impregnation method.</p>	<p>solvent, 20 mL of 2-propanol T=130-210°C under N₂ atmosphere</p>	<p>tungstophosphoric acid (TPA) support on beta-zeolite for one-pot transformation of furfural via hydrogen transfer -Studied reaction parameter including of temperature, hydrogen source and catalyst weight.</p>	<p>conversion of FAL/FE to alkyl levulinates. -20%ZrO₂ with 5%TPA on beta-zeolite presented high activity with 90% GVL yield at optimum condition: 2-propanol, 170 °C, 7.5 g cat/L and 10 h.</p>
<p>Winoto, H. P. et al (2019) [8]</p>	<p>Zr support on Beta-zeolite and modified with phosphotungstic acid (HPW) or silicotungstic acid (HSiW) as Brønsted acid sites including of H-Al-Beta, Si-Beta, Zr-Beta, HPW/Si-Beta, HPW/Zr-Beta, HSiW/Si-Beta, HSiW/Zr-Beta</p>	<p>0.11 M furfural, 20 mL of 2-propanol T=120-160°C, 2-48 h under 10 bar N₂</p>	<p>-Studied effect of catalyst anchoring heteropolyacid (HPA) on Zr-Beta zeolite for one-pot conversion of furfural into GVL -Studied effect of the HPW/Zr initial loading amounts on the product</p>	<p>The use of Keggin heteropolyacid (HPA) was resulting in providing Brønsted acid sites over Zr-Beta zeolite which was provided Lewis and Brønsted acid sites in a single zeolite catalyst.</p>

	<p>which were prepared by dealumination of Al-Beta, incorporation of Zr into the beta framework through solid-state ion-exchange and impregnation of the HPA.</p>		<p>distribution.</p>	<p>-HPA/Zr-Beta catalysts was presented higher yields of GVL compared to Zr-Beta due to the increased rate of hydrolytic ring-opening reaction promoted by the Brønsted acid sites.</p>
<p>Lei Ye. et al (2020) [5]</p>	<p>Bifunctional catalyst: Zirconium phosphate (ZrP) support on HZSM-5 zeolite code as HZ-ZrPx-y. x: molar ratio of P to Zr Y: volume of Zirconium precursor ($ZrOCl_2 \cdot 8H_2O$) and also impreg metal oxides on HZSM-5 zeolite</p>	<p>0.1195 M furfural, 0.1-0.2 g catalyst, 20 mL of hydrogen donors T=140-180°C, 12h under 0.5 MPa N_2</p>	<p>- Studied focused on a one-pot value added conversion of FAL to i-PL and GVL using bifunctional catalysts of HZSM-5-supported ZrP prepared by a precipitation method. - Studied the effect of the ratio of Lewis to Brønsted acid and the acid</p>	<p>-HZ-ZrP1-5 and HZ-ZrP1-16 Presented high activity at 93.8% total yield of i-PL and GVL with 0.1 g of catalyst at 180°C for 10 h -Isopropanal given the highest dehydrogenation activity resulting in high FAL conversion and high GVL yield.</p>

			strength of the catalysts by changing the loading amount of ZrP.	
He, Jian et al (2020) [27]	Zr-KIT-5 catalysts with different Si/Zr molar ratios The catalysts are denoted as Zr-KIT-5(x) x = the molar ratio of Si to Zr. including of ZrO ₂ , Zr-KIT-5(5), Zr-KIT-5(10), Zr-KIT-5(25), Zr-KIT-5(40) and Si-KIT-5	1 mmol furfural, 0.1 g catalyst, 5 mL of 2-propanol T =160, 180,200 °C, 2-10 h under N ₂	-Used bifunctional Zr-KIT-5 catalysts with Brønsted and Lewis acidic sites, for hydrogenation-cyclization of levulinates to GVL via catalytic transfer process. with 2-Propanol as H-donor.	-Zr-KIT-5(10) exhibited remarkable catalytic activity, up to 93.8% ethyl levulinate conversion with 91.4% GVL selectivity at 180°C for 6 h and also presented 40.1% yield of GVL for conversion of furfural to GVL in a single pot at 180°C for 6 h
Li, W. et al (2019) [28]	Bifunctional metal-organic frameworks (MOFs) sulfated DUT-67(Hf) by introducing sulfate into	0.3 g catalysts, 0.05 mol/L Furfural, 25mL of isopropyl alcohol,	- Studied reaction onepot conversion of furfural to major product gamma-valerolactone by	- Sulfated DUT-67(Hf)-0.06 exhibits optimal catalytic activity for one-pot conversion of furfural to

	<p>DUT-67(Hf) defined as DUT-67(Hf)-X</p> <p>X=concentrations of sulfuric acid for catalyst treatment including of Pristine DUT67(Hf) (not treated), DUT-67(Hf)-0.01, DUT-67(Hf)-0.03, DUT-67(Hf)-0.05, DUT-67(Hf)-0.06, DUT-67(Hf)-0.07, DUT-67(Hf)-0.09, DUT-67(Hf)-0.1, DUT-67(Hf)-0.2, DUT-67(Hf)-0.4,</p>	<p>T=180 °C, 20 h under 0.6 Mpa N₂</p>	<p>Hf-based metal zeolte catalysts .</p>	<p>GVL about 100% conversion of furfural and a 84.9% yield GVL at 180 °C after 20 h</p>
<p>Wang, Tianlong. et al (2020) [29]</p>	<p>Used chitosan as catalyst support to generate heterogeneous chitosan supported metal complexes denoted as chitosan-M (M = Ru, Pd, Co, Ni)</p>	<p>Condition for One-Pot Conversion of FA to GVL: 3 mol% catalysts (chitosan-M), 8 mg of PPh₃, 200 mg of ZSM-5, 0.5 mmol</p>	<p>-Synthesized a series of chitosan-M (M = Ru, Pd, Co, Ni) and used for both the hydrogenation of FF to FAL and reduction of LA/alkyl levulinate to GVL</p>	<p>-Chitosan-Ru/ PPh₃ system is highly effective for hydrogenation of FF to FAL achieving 99% yield by using HCOOH as hydrogen source</p>

		Furfural, 1.2 mL ethanol alcohol, T=160 °C, 30 h under N ₂	-Used combination of chitosan-Ru/PPh ₃ with ZSM-5 zeolite for one-pot transformation of biomass-derived carbohydrates: FA ,xylose or hemicellulose to GVL	-Combination of chitosan-Ru/PPh ₃ with ZSM-5 achieved 79% yield of GVL from one-pot conversion of FA and for direct conversion of xylose and hemicellulose to GVL: 37% and 30% yield, respectively
Li, X. et al (2020) [30]	A series of delaminated MWW-type Zr-Al-SCM-1 zeolites prepared by a post-synthesized method; partial dealumination of SCM-1 and Zr incorporation based on parent SCM-1 zeolite including H-SCM-1 Zr-Al-SCM-1 (2) Zr-Al-SCM-1 (4) Zr-Al-SCM-1 (6)	0.1 g catalysts, 0.2g Furfural, 10 mL of 2-propanal, T=170 °C, 28 h under N ₂	- Synthesized the Zr-Al-SCM-1 catalyst by partial dealumination of SCM-1 to achieve Lewis acid sites, Brønsted acid sites, a delaminated structure, the incorporation of the Zr species -Determined a suitable B/L acid	The Zr-Al-SCM-1 zeolites exhibited high activity for conversion of furfural into GVL. Zr-Al-SCM-1(4) zeolite presented high selectivity to GVL (47.3%) with 85.4% total carbon balance at 170 °C for 28 h due to its suitable B/L acid

	Zr-SCM-1 (4) Zr-Al-MCM-22 (4) (x)=x% Zr content		ratio on Zr-Al-SCM-1 zeolites for furfural conversion -Studied on the conversion of xylose to GVL over Zr-Al-SCM-1 (4) catalys	ratio around 0.5. Moreover, the Zr-Al-SCM-1(4) also shown high activity for the direct conversion of xylose into GVL up to 36.4% at 170 °C for 48 h.
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Zhang, H. et al. (2019) [6] studied the effect of Zr-HY and Al-HY, which were used as Lewis and Brønsted acid sites, respectively on one-pot transformation of furfural and levulinate ester using 2-pentanol as a hydrogen donor. HY-zeolites presented higher activity than Zr-Beta catalyst due to larger pore size and stronger Lewis acidic sites. The combination catalyst Zr-HY-15-20 and Al-HY-6 with 2:1 wt. ratio presented excellent activity at 85% yield of γ -valerolactone (GVL) after only 5h at 120°C by using 2-pentanol, which was the best choice of alcohol for MPV reduction. Al-HY zeolites were also more effective as Brønsted acid than Al-Beta because they converted furfuryl ether to levulinate ester rather than to beta-angelica lactone. Moreover, the catalyst mixture could be reused for 3 runs without any dramatically drop in activity.

Rao B.S. et al. (2019) [26] studied beta-zeolite supported the metal oxide and tungstophosphoric acid (TPA) for one-pot selective to GVL. The catalysts were prepared by the impregnation method. The catalysts 20%ZrO₂ with 5%TPA on beta-zeolite were presented high activity with 90% GVL yield with 2-propanol as a hydrogen source at 170°C, 10 h, which were optimum hydrogen donor, temperature and time. The high

Lewis acidic was responsible for the outstanding catalytic activity of the catalyst. The Bronsted acid from TPA was also essential in the one-pot transformation of FAL.

Winoto, H.P. et al. (2019) [8] studied the one-pot transformation of furfural to GVL by using catalyst anchoring heteropolyacid (HPA) on Zr-Beta zeolite. Zr-Beta was prepared by impregnation method and used as a Lewis acid catalyst to catalyze the transfer hydrogenation of furfural and levulinic acid/ester using 2-propanol as a hydrogen donor and anchored phosphotungstic acid (HPW) and silicotungstic acid (HSiW) as Bronsted acid sites. The use of HPA for providing Brønsted acid sites over Zr-Beta zeolite is an effective method for creating both isolated Lewis and Brønsted acid sites in a single zeolite catalyst. HPA/Zr-Beta presented higher GVL yields compared to Zr-Beta zeolite. The rate of hydrolytic ring-opening reaction was increased by the Bronsted acid sites while the Lewis acid sites promoted the transfer hydrogenation of furfural and levulinic acid by the intact framework Zr sites in the catalyst. The HPW loaded Zr-Beta showed a high catalytic performance for GVL production at 70% yield under 160 °C, 10 bar N₂ after 24 h because of its high thermal stability and strong Bronsted acidity.

Lei Ye. et al. (2020) [5] studied a one-pot conversion of FAL to i-PL and GVL using bifunctional catalysts of HZSM-5-supported zirconium phosphate (ZrP) prepared by a precipitation method and analyzed the effect of the ratio of Lewis to Brønsted acid and the acid strength of the catalysts by changing the loading amount of ZrP. ZrP mainly provided Lewis acid sites, while the HZSM-5 zeolite had a large amount of Brønsted acid sites. HZ-ZrP series catalysts had higher acid strength than HZSM-5 but it could be used for increasing in the specific surface, pore volume, and pore diameter of catalyst which is beneficial for increasing the adsorbance of the catalyst. The loading of the ZrP active component increased, the GVL yield also improved, indicating that ZrP was beneficial to the furfuryl ether alcoholysis and the lactonization of i-PL. HZ-ZrP1-5 presented high activity at 93.8% total yield of i-PL and GVL with 0.1 g of catalyst at 180°C for 10 h. HZ-ZrP1-16 presented highest GVL production at 64.2% yield of GVL

with 0.2 g of catalyst at 180°C for 14 h. Isopropanol gave the highest dehydrogenation activity and increased the rate of hydrogen transfer reactions resulting in high FAL conversion and high GVL yield.

He, Jian et al. (2020) [27] studied series of dual acidic Zr-KIT-5 catalysts with Brønsted and Lewis acid for catalyzing the transfer hydrogenation-cyclization of biomass-based EL to GVL and one-pot transformation of FAL to GVL. Zr-KIT-5(10) presented up to 93.8% EL conversion with 91.4% GVL selectivity at 180 °C, 6 h with 2-propanol as H-donor. Zr-KIT-5(10) also exhibited a catalytic performance in the direct conversion of biomass-based furfural to GVL 40.1% yield of GVL and 21.2% yield of IPL at 180 °C for 6 h. The large amount of acid sites and surface area, suitable pore volume and pore shape result in better mass diffusion compared to SBA-15 and microporosity were responsible for the outstanding performance of Zr-KIT-5(10). The higher acid amount presented higher conversion and the higher L/B ratio resulted in higher selectivity of GVL.

Li, W. et al. (2019) [28] synthesized sulfated DUT-67(Hf) via a post synthesis method and adjusted the acidity of the catalysts by submersion in different concentrations of aqueous sulfuric acid (for introducing Brønsted acid sites) about 0.01-0.1 mol/L. Sulfated DUT-67(Hf) possessed 0.06 mol/L aqueous sulfuric acid exhibited optimal catalytic activity at 87.1% yield of GVL under the conditions of 180 °C after 24 h. The mechanism of introducing Brønsted acid sites into DUT-67(Hf) was modified by the molecular decoration of the zirconium clusters with aqueous sulfuric acid. The yield of GVL increased slightly using a certain proportion of primary alcohols and secondary alcohols as hydrogen donor.

Wang, Tianlong. et al. (2020) [29] prepared a series of chitosan-M (M = Ru, Pd, Co, Ni) and found that chitosan-Ru/PPh₃ system is highly effective for the hydrogenation of FAL to FA and reduction of LA/alkyl levulinate to GVL, achieving up to 99% product yield by using formic acid as hydrogen source. The zeolite ZSM-5 was presented to

combine with chitosan-M/ PPh_3 system and ethanol was used as hydrogen donor for the one-pot conversion of FF to GVL. The combination of chitosan-Ru/ PPh_3 with ZSM-5 zeolite successfully achieved one-pot transformation of FAL and also xylose and hemicellulose to GVL up to 79%, 37%, or 30% yield, respectively. They studied the effect of the amount of FAL, ZSM-5, chitosan-Ru catalyst, and PPh_3 on one-pot conversion of FA at 160 °C for 30 h. It was shown that the highest yield (79% GVL) were achieved with 3 mol% catalyst loading of chitosan-Ru, 8 mg of PPh_3 , 200 mg of ZSM-5 (Si:Al = 25:1) and 5 equiv FAL.

Li, X. et al (2020) [30] prepared and characterized a bifunctional zeolite SCM-1 (Sinopec Composite Material No.1 with a double-layered structure and a nanosheet morphology supported Zr since Zr-based catalysts were the most common use for MPV reduction of biobased furans due to its high catalytic efficiency. The ZrAl-SCM-1 possesses both Lewis acid sites, Brønsted acid sites and a delaminated structure, the incorporation of the Zr species is achieved by partial dealumination of SCM-1. The ZrAl-SCM-1 zeolite exhibits remarkable catalytic performance for the one-pot conversion of xylose to GVL. Especially for Zr-Al-SCM-1(4) at 4% Zr content zeolite treated with 3M $\text{H}_2\text{C}_2\text{O}_4$ exhibited high selectivity to GVL up to 47.3% with 85.4% total carbon yield due to its suitable B/L acid ratio around 0.47, indicating a B/L acid ratio of 0.46 is optimized for this reaction. Moreover, the Zr-Al-SCM-1(4) displays excellent performance for the direct conversion of xylose into GVL up to 36.4% GVL yield is at 170 °C for 48 h. This excellent catalytic performance attributed to its delaminated structure with ultra-large external surface, which could provide better accessibility of active sites and improve the diffusion performance.

In conclusion, The trend of literature was to improve performance of MPV reduction of furfural at ambient pressure and to find optimum secondary alcohol and use inexpensive metal oxides as Lewis acid catalysts. The conversion of furfural and GVL selectivity depended on surface acidity, structure properties of zeolites. The zeolites required both Brønsted and Lewis acid sites in an appropriate ratio.

CHAPTER III

MATERIALS AND METHODS

3.1 Catalyst preparation

3.1.1 Zeolite catalysts

The zeolite catalysts used in the one-pot transformation of furfural are shown in Table 3. Many types of zeolite including, H-ZSM-5 (Si / Al = 19), NH₄ Beta (Si / Al = 27), HY (Si / Al = 15, 100 and 500) were purchased. For H-beta zeolite, the NH₄ Beta zeolite was calcined under the air atmosphere at 350 ° C for 3 h in order to change NH₄- form zeolite to H-form.

Table 3 Zeolite catalysts suppliers

Chemicals	Suppliers
H-ZSM-5	Riogen
HY-15	Sasol
HY-100	Sasol
HY-500	Sasol
NH ₄ Beta	TOSOH

3.1.2 Pt-doped Zeolite

The Pt-doped H-ZSM-5, HY-15, HY-500 were synthesized by incipient wetness impregnation method. Platinum (II) acetylacetonate (Aldrich) 97% as a precursor of Pt metal was dissolved in toluene and added on H-ZSM-5, HY-15, HY-500. After that, the catalysts were dried at 110°C overnight in an oven. Finally, the catalysts were calcined at 500°C for 6 hours under air atmosphere as shown in Figure 5.

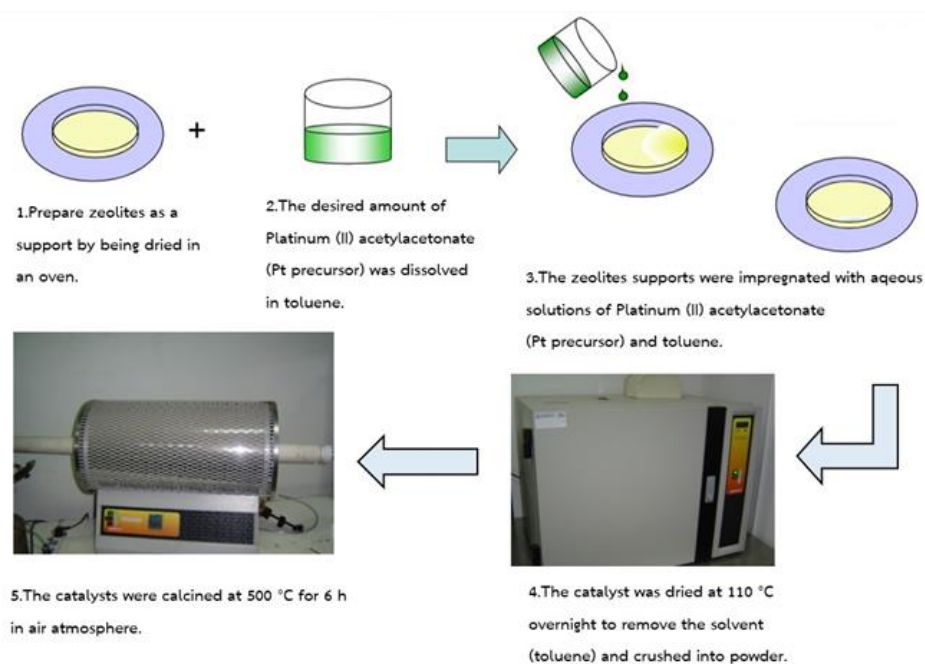


Figure 5 Preparation of Zeolites supported Pt catalyst by incipient wetness impregnation method

3.2 Catalyst characterization

3.2.1 Nitrogen-physorption

The nitrogen-physorption technique on a Micromeritics ASAP 2020 automated system was used for measuring the BET surface area, pore diameter and pore volume which were calculated by BJH method.

3.2.2 Ammonia - temperature program desorption (NH₃ -TPD)

The ammonia - temperature program desorption (NH₃ -TPD) technique was used for measuring the acidity of catalyst by ChemiSoftTPx software in Micromeritics ChemiSorb 2750. A Brief explanation of this technique, starting by pretreated the 0.05 g of catalyst by helium gas flow at 25 ml/min at 300 °C to remove moisture for 1 h and cooldown to 30 °C. After that, the catalyst was exposed to 3 vol.% NH₃/He from 30 °C to 550 °C and the TCD signal density was collected during this heating step for calculated the quantity of desorbed NH₃. The temperature below 280°C is classified as weak acid sites and at temperature above 280°C is classified as strong acid sites.

3.2.3 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns were analyzed by SIEMENS D5000 X-ray diffractometer (Bruker D8 Advance) with Cu K α irradiation from 20° to 80° in the 2θ range at scan speed 0.5 sec/step..

3.2.4 Infrared spectra of coordinated pyridin (Pyridine-IR)

Infrared spectroscopy using pyridine as probe molecule (Pyridine-IR) was used to obtain the Brønsted and Lewis acid site which were represented by B/L ratio. A 0.03 to 0.05 g of catalyst was formed to sheet forming and pretreated at 200°C for 30 minute. After that, the sample was cooled to 50°C and pyridine was adsorbed for 35 minutes and desorbed for 1 h. The spectra were recorded on Bruker EQUINOX 55 at 1, 5, 10, 20 and every 10 minute.

3.2.5 Scanning electron microscope (SEM)

The morphology of the zeolite catalyst is obtained from scanning electron microscopy (SEM)

3.2.6 Hydrogen Temperature-programmed reduction (H₂ -TPR)

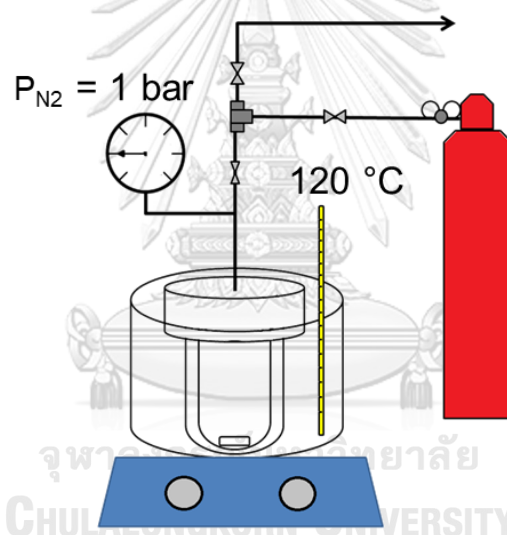
The H₂ -TPR technique was conducted for study the reducibility and reduction temperature of Pt supported zeolite catalysts by ChemiSoftTPx software in Micromeritics ChemiSorb 2750. A Brief explanation of this technique, starting by pretreated the 0.05 g of catalyst by nitrogen gas flow at 25 ml/min at 250 °C to remove moisture for 1 h and cooldown to 30 °C. After that, the catalyst was exposed to 10 vol.% H₂/Ar from 30 °C to 700°C at rate 10 °C/min and the TCD signal density was collected during this heating step.

3.3 Catalytic tests

The one-pot transformation of FAL was conducted in a 100 mL stainless steel autoclave (JASCO, Tokyo, Japan) supplied with a hot plate and magnetic stirrer as shown in Figure 6. The reactant, 0.5 mmol (42 μ L) of FAL, was dissolved in 10 g (13 mL) of isopropanol into the autoclave. All of the chemicals used in the reaction are shown in Table 4.

The catalytic test was started by adding 0.2 g of catalyst into the autoclave (the zeolites supported Pt must be reduced under H_2 gas (25 mL/min) at 500 °C for 2 hr prior use). Then, the autoclave was heated to 120°C (also 140°C and 160°C in Part III) by an oil bath and purged with N_2 three times to remove the air. After purging, the autoclave was pressurized with 1 bar of N_2 (and various pressure in Part III). Finally, the reaction mixture was stirred with a magnetic stirrer at 800 rpm to start the reaction and continued for 5 h.

After 5 h of reaction, the autoclave reactor was immediately cooled down to 10 °C by ice-water to stop reaction and purged the gas from the autoclave. The reaction mixture was centrifuged. The liquid product was analyzed by a Gas chromatograph-mass Spectroscopy (GC-MS) equipped with a DB-5 capillary column which operating condition as shown in Table 4.



Furfural = 0.5 mmol.
Catalyst loading = 0.2 g.
Isopropanol = 10 g.
Stirred rate = 800 rpm
Reaction time = 5 hr.

Figure 6 Schematic of the catalytic test of one-pot transformation of FAL

Table 4 Chemicals in the catalytic test

Chemicals	Suppliers
Furfural 99% (C ₅ H ₄ O ₂)	Sigma-aldrich
Furfuryl alcohol 99% (C ₅ H ₆ O ₂)	Sigma-aldrich
Levulinic acid 98% (C ₅ H ₈ O ₃)	Sigma-aldrich
Propyl levulinate 95% (C ₈ H ₁₄ O ₃)	Sigma-aldrich
Angelica lactone 98% (C ₅ H ₆ O ₂)	Sigma-aldrich
γ -valerolactone (C ₅ H ₈ O ₂)	Sigma-aldrich
2-propanol 99.8% (C ₃ H ₈ O)	Merck

Table 5 Gas-chromatography-mass spectroscopy (GC-MS) operating conditions

Gas chromatography (Shimadzu GC-2014)	Conditions
Detector	FID
Column	DB-5
Carrier gas	Helium (99.99 vol%)
Make-up gas	Air (99.9 vol%)
Injector temperature (°C)	260
Column temperature (°C)	110
Oven temperature (°C)	60
Detector temperature (°C)	260
Time	41.80 min

CHAPTER IV

RESULTS AND DISCUSSION

This chapter IV presents the properties of the zeolite-based catalysts and Pt-impregnated on zeolites and the catalytic performances of the zeolite-based catalysts in one-pot transformation of furfural (FAL) to gamma-valerolactone (GVL). The results and discussion are divided into three parts. For the first part, the study of the effect of zeolite structure and acidity is shown. In the second part, the effect of Pt promoter on zeolites catalyst over catalytic performances is demonstrated. And in the last part, the effect of temperature, pressure, and gas conditions on the catalytic activity is provided. The catalyst samples were characterized by X-ray diffraction (XRD), nitrogen-physorption, scanning electron microscope (SEM), temperature-programmed reduction (H_2 -TPR), pyridine-IR and ammonia temperature program desorption (NH_3 -TPD).

Part I The effect of zeolite structure and acidity

4.1 Characterizations of zeolite catalysts

4.1.1 X-ray diffraction (XRD)

The characteristic diffraction peaks of HY zeolites in the wide angle range of 20.6° – 35.2° 2θ are shown in Figure 7. The XRD patterns of HY zeolites with different Si/Al ratios at 15, 100 and 500 showed diffraction peaks at 2θ degrees 20.6° , 23.1° , 24.0° , 26.1° , 27.4° , 30.1° , 31.2° , 31.8° , 32.9° , 34.6° and 35.2° [31]. Moreover, the peak intensity presented in the order HY-15 > HY-500 > HY-100.

The XRD patterns of H-ZSM-5 zeolite are presented in Figure. 8 The diffraction peaks were detected at $2\theta = 20.3^{\circ}$, 20.8° , 23.0° (main peak), 23.2° , 23.7° , 23.9° , 24.4° , and 29.9° . The diffraction peaks at $2\theta = 21.5^{\circ}$, 22.4° (main peak), 25.3° , and 26.9° peaks were detected for H-beta zeolite. The diffraction peaks at $2\theta = 20.6^{\circ}$, 23.1° , 24.0° (main peak), 26.1° , 27.4° , 30.1° , 31.2° , 31.8° , 32.9° , 34.6° and 35.2° corresponded to the hydrogen form of Y zeolites, HY-500.

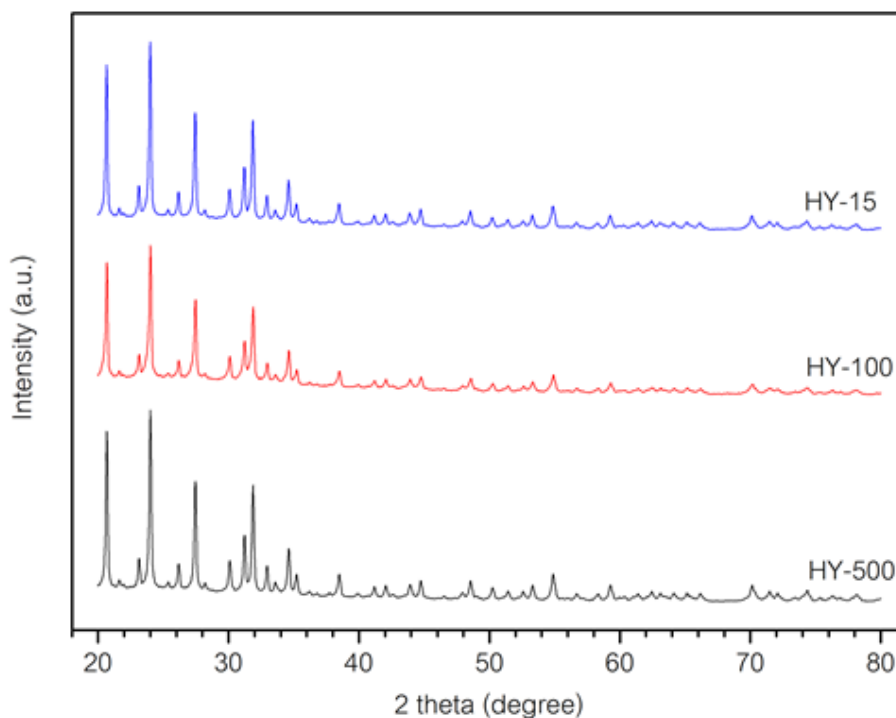


Figure 7 The XRD patterns of HY zeolites

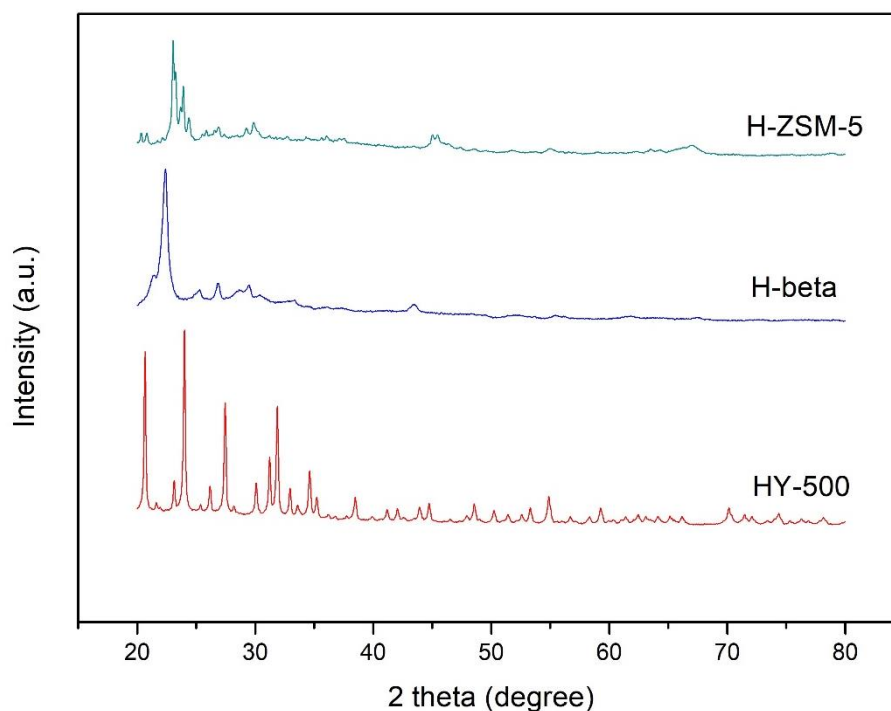


Figure 8 The XRD patterns various zeolites

4.1.2 Scanning electron microscope (SEM)

The SEM images of HY zeolites are shown in Figures 9-14 below. All the catalyst morphology composed of aggregated particles with quite homogenous particle size/shape. The particle size of HY-100 was significantly larger than HY-15 and HY-500 as shown in Figure 10, 9, and 11, respectively. The particle size distributions of the HY zeolites with different Si/Al ratios are shown in Figure 12. It can be seen that HY-100 had the widest range of size distribution than the others. A particle diameter bigger than 800 nm was observed only for the HY zeolite. The average diameter of HY-15 and HY-500 were essentially similar at 350 nm and 390 nm, respectively. The HY-100 had the largest average particle diameter at 550 nm.

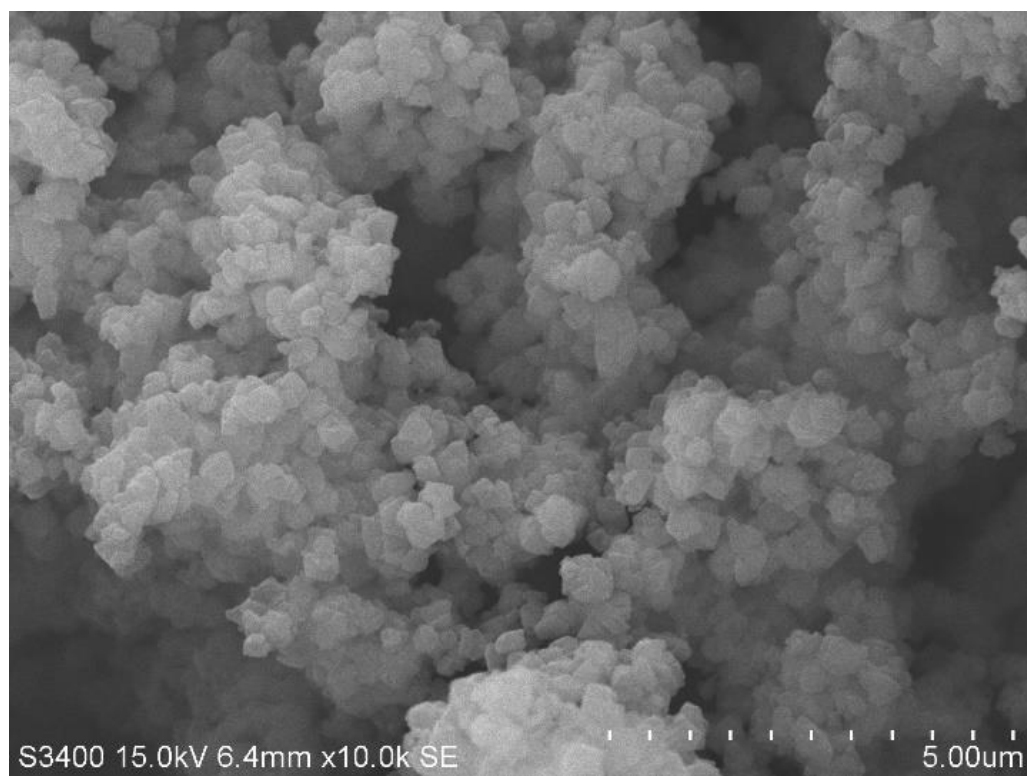


Figure 9 SEM images of the HY zeolite catalyst; HY-15

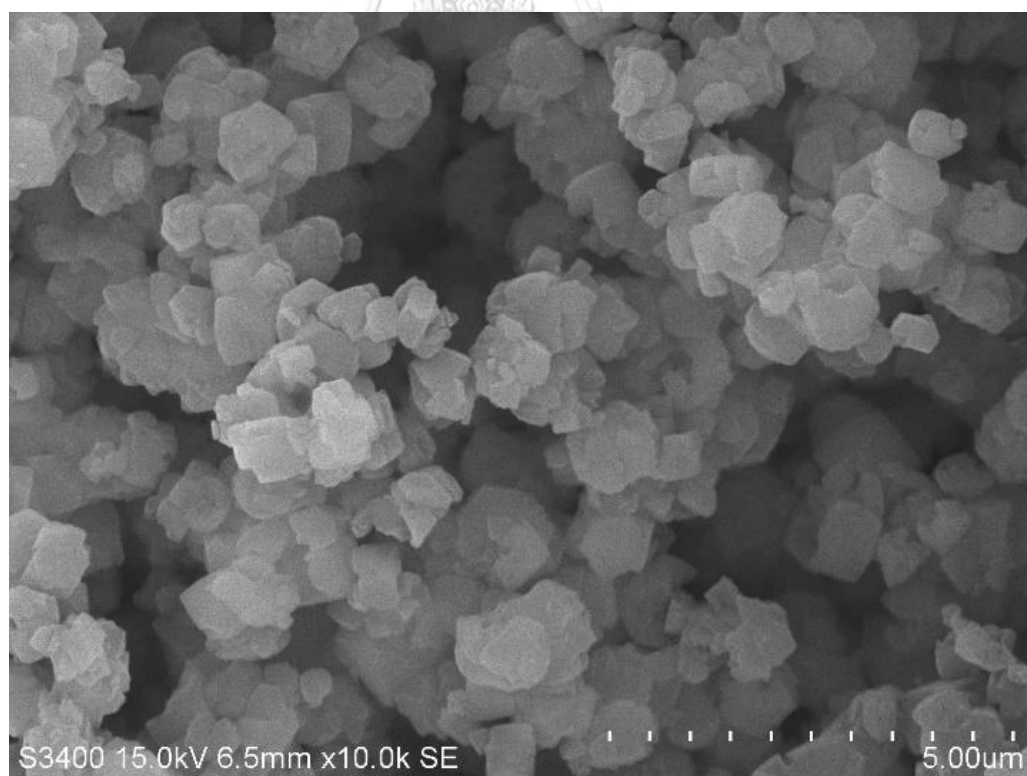


Figure 10 SEM images of the HY zeolite catalyst; HY-100

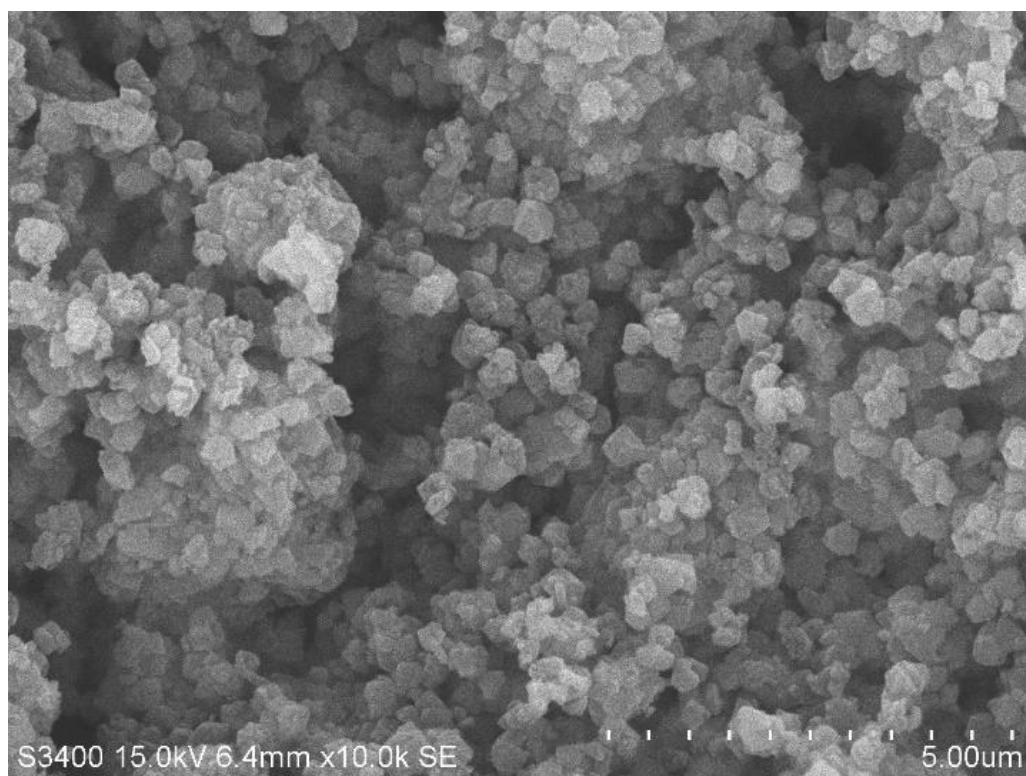


Figure 11 SEM images of the HY zeolite catalyst; HY-500

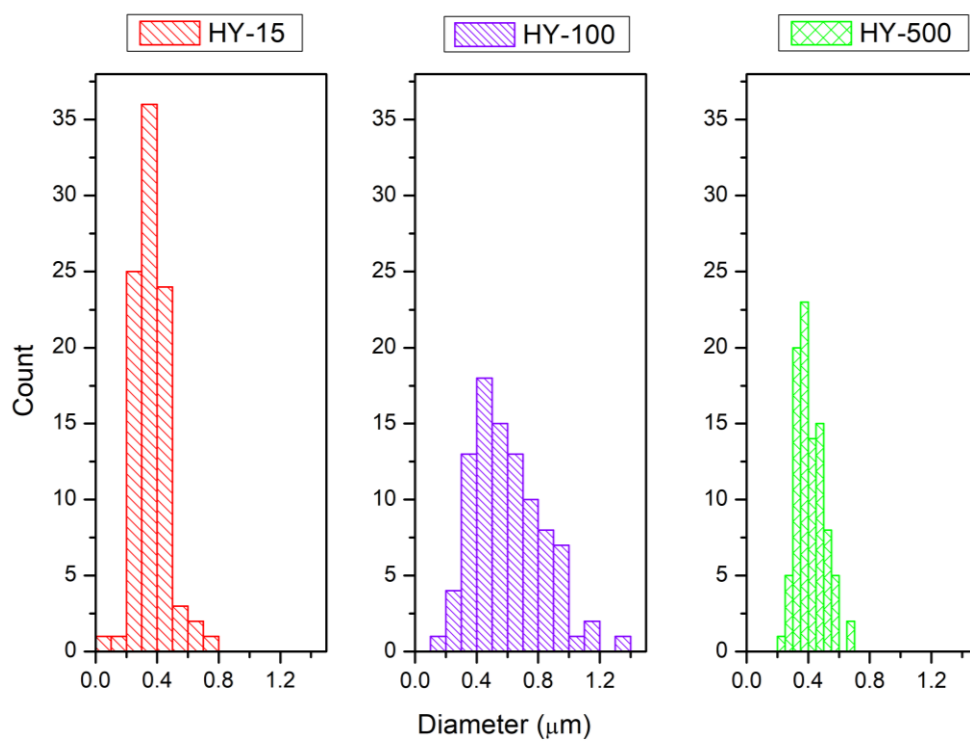


Figure 12 Particle size distribution of HY zeolite catalysts

From the EDX analysis, the Si/Al ratio of HY15, HY100, and HY500 zeolites were 11.4, 109.8, and 449.4, respectively, which were closed to their nominal Si/Ai values.

The morphology of H-ZSM-5 and H-beta zeolite catalysts are shown in Figure 6. The H-ZSM-5 zeolite showed homogenous aggregated particles as shown in Figure 13. The beta zeolite composed of spherical particles with relatively small particle size as shown in Figure 14.

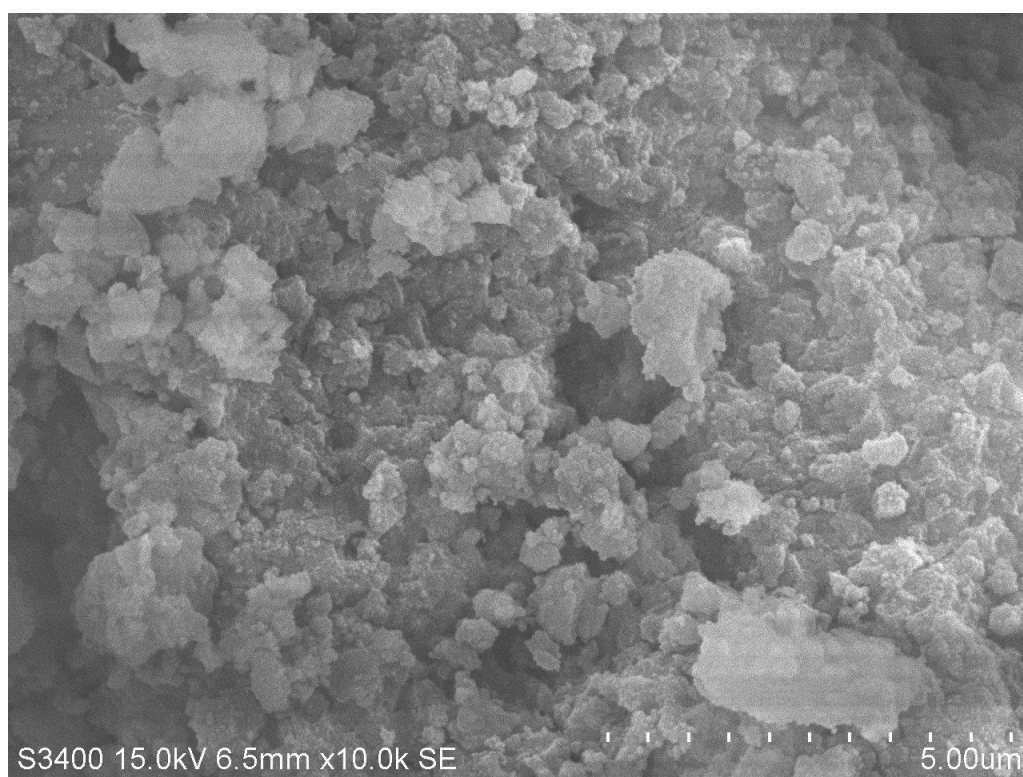


Figure 13 SEM images of the zeolite catalyst; H-ZSM-5

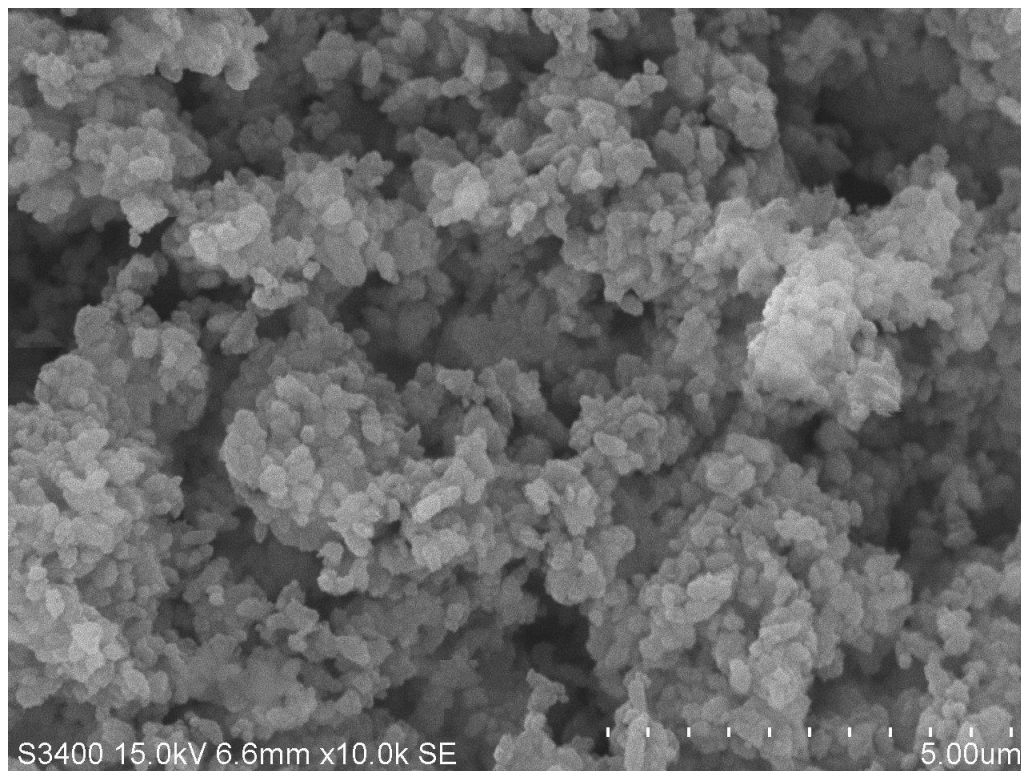


Figure 14 SEM images of the zeolite catalyst; H-beta

4.1.3 Nitrogen physisorption

The BET surface area, pore size, and pore volume of all the catalyst samples are shown in Table 6. The pore size and the pore volume were determined from the Barret-Joyner-Halenda (BJH) desorption method.

The total surface of the HY-zeolite catalyst was increased with increasing Si /Al -ratio. The HY-500 possessed the highest total surface area of 652 m²/g. Nevertheless, the micropore volume, average pore volume, and average pore size did not exhibit any obvious trend with the higher Si / Al ratio. The HY-100 presented the highest average pore volume with the lowest micropore volume and the smallest average pore size as compared to the other HY-zeolite.

By the way, H-ZSM-5 were found to possess the total surface area, micropore volume, average pore volume, average pore size approximately equal to the H-beta zeolite.

Table 6 Physical properties of zeolites catalysts

Zeolite catalyst	Total surface area (m ² /g)	Micropore volume (cm ³ /g)	Pore volume (cm ³ /g)	Pore size (nm)
HY-15	514	0.206	0.171	10.8
HY-100	539	0.191	0.263	6.3
HY-500	652	0.243	0.252	7.9
H-ZSM-5	292	0.052	0.262	5.2
H-beta	293	0.044	0.280	4.7

4.1.4 The acidity of zeolites

The overall acidity of the samples was analyzed by NH₃-TPD. The desorption of NH₃ occurred from 100 to 530°C. The broad desorption peaks could be deconvoluted into three peaks centered at 180, 250 and 350°C, which were attributed to sites of weak, medium, and strong acidity, respectively.

As expected, the total acidity and acid strengths of the HY type zeolite showed an inversion trend to the increasing in Si/Al ratio. The HY-15 presented the highest total acidity amounts and strengths of acids followed by HY-100 and HY-500, respectively.

The H-beta zeolite had the highest amount of acids with the highest weak acid sites at about twice those of the H-ZSM-5 and HY-15. These two zeolites presented similar total acidity and acid strength (both weak acid sites and strong acid sites) as summarized in Table 7.

The Brønsted and Lewis acid sites were obtained from the pyridine-IR techniques and represented by B/L ratio. The acid site distribution of Brønsted (B) and Lewis (L) was identified by pyridine -IR spectra. Absorption bands at 1445–1454, 1576 and 1600–1605 cm⁻¹ indicate the appearance of Lewis acid sites. Absorption bands at 1546 and 1620–1640 cm⁻¹ were associated with pyridine adsorbed on Brønsted acid

sites, while the 1490 cm^{-1} was found for pyridine absorbing both Lewis and Brønsted acid sites.

As shown in Table 7, it was established that the B/L ratio decreased with increasing Si/Al ratio. Moreover, the HY-100 had the lowest B/L ratio at 0.40 whereas those of H-beta and H-ZSM-5 were 0.55 and 0.66, respectively.

Table 7 The acidity of zeolite catalysts

Zeolite catalyst	Si/Al ratio	Total acidity ($\mu\text{mol NH}_3/\text{g}_{\text{cat}}$)	Acid Strength ($\mu\text{mol NH}_3/\text{g}_{\text{cat}}$)		B/L
			Weak acid sites	Strong acid sites	
HY-15	11.4	1294	781	513	1.53
HY-100	109.8	654	245	409	0.40
HY-500	449.4	183	49	134	1.01
H-ZSM-5	19	1442	858	584	0.66
H-beta	14.8	2748	2281	387	0.55

4.2 The catalytic reaction test

The catalytic reaction tests for the one-pot transformation of furfural using various zeolites catalyst and 2-propanol as a hydrogen donor were carried out at $120\text{ }^\circ\text{C}$ for 5 h under 1 bar of N_2 . In order to study the effect of Si/Al ratio, the reaction was conducted by varying the Si/Al ratio of HY-zeolites and the results of the reaction tests are shown in Table 8.

Table 8 The catalytic performances of the HY zeolite catalysts in the one-pot transformation of FAL in isopropanol at 120°C, 5 h

(FAL; furfural, GVL; γ -valerolactone, LA; levulinic acid, IPL; iso-propyl levulinate, FA; furfuryl alcohol, AL; angelica-lactone)

Zeolite catalysts	FAL Conversion (%)	Selectivity (%)					Yield GVL (%)	Carbon Balance (%)
		GVL	LA	IPL	FA	AL		
HY-15	68.71	66.32	10.51	20.12	-	3.81	46.21	96.7
HY-100	76.42	-	83.53	16.47	-	-	-	80.6
HY-500	30.17	61.56	16.75	11.32	10.36	-	19.31	91.9

From the catalytic performances of HY zeolite series, The HY-15 presented the highest yield of GVL (46.21%) and the highest selectivity to GVL (66.32%). The HY-500 presented the lowest conversion of FAL (30.17%) and low yield of GVL. On the contrary, the HY-100 showed the highest conversion of FAL (76.4%) but the reaction was not selective to produce GVL at all due probably to its very low B/L ratio (0.40).

From the reaction test results, the amount of total acid affected the catalytic activity of zeolite catalysts. The HY-500 showed the lowest total acidity and as a consequence resulted in the lowest FAL conversion. In contrast, the HY-15 with the highest acidity showed higher FAL conversion. Regarding the acid type (Lewis and Bronsted acid site), furfural conversion was also found to correlate to the B/L ratio in which the higher B/L ratio resulted in the better catalytic activity.

Table 9 The catalytic performances of the HY-15, H-ZSM-5, H-beta in the one-pot transformation of FAL in isopropanol at 120°C, 5 h

(FAL; furfural, GVL; γ -valerolactone, LA; levulinic acid, IPL; iso-propyl levulinate, FA; furfuryl alcohol, AL; angelica-lactone)

Zeolite catalysts	FAL Conversion (%)	Selectivity (%)					Yield GVL (%)	Carbon Balance (%)
		GVL	LA	IPL	FA	AL		
HY-15	68.71	66.32	10.51	20.12	-	-	46.21	96.7
H-ZSM-5	66.70	53.10	4	22.60	-	20.30	35.42	98.0
H-beta	51.98	28.70	42.13	-	29.17	-	14.91	91.0

From the catalytic performances of zeolite catalysts, the HY-15 presented the highest yield of GVL (46.21%) and the highest selectivity to GVL (66.32%). The H-ZSM-5 presented similar conversion of FAL (66.70%) as HY-15 (68.71%) but it exhibited lower selectivity to GVL. In contrast, the H-beta showed the lowest conversion of FAL (51.98%) and low selectivity to GVL (28.70%)

The three types of zeolite varied largely in terms of their crystalline structures and physical properties. The highest yield of GVL, found in the HY-15, was likely to be attributable to its large pore structure. The HY zeolite possessed a cage structure and large cavity so that the reactant can easily diffuse into the pores of the catalyst [32]. On the contrary, both H-ZSM-5 and H-beta zeolites consisted of a channel structure with smaller pore size than the HY zeolite, which could result in pore diffusion limitation. Therefore, their catalytic activity were lower than HY zeolite catalyst.

Part II The effect of Pt promoter

4.3 Characterizations of Pt on zeolite catalysts

4.3.1 Scanning electron microscope (SEM)

The SEM images of Pt on HY zeolites are shown in Figures below. All the catalyst morphology composed of aggregated particles with quite homogenous particle size/shape. The particle size of Pt/HY-15 was slightly larger than Pt/HY-500 as shown in Figure 15, 16 respectively.

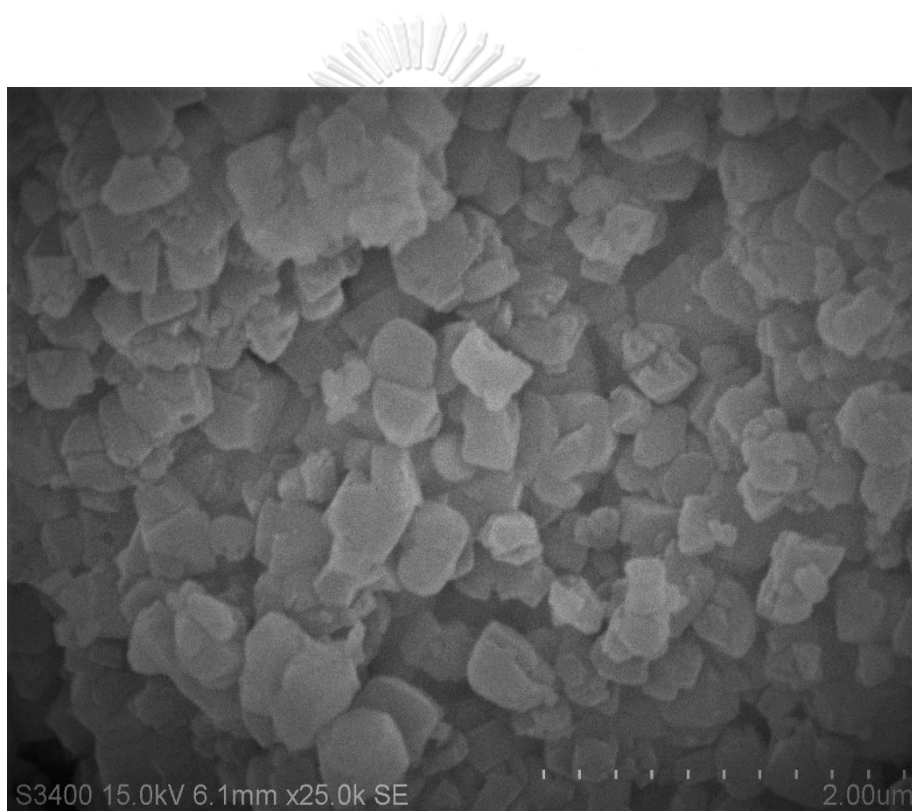


Figure 15 SEM images of the Pt/HY-15 catalyst

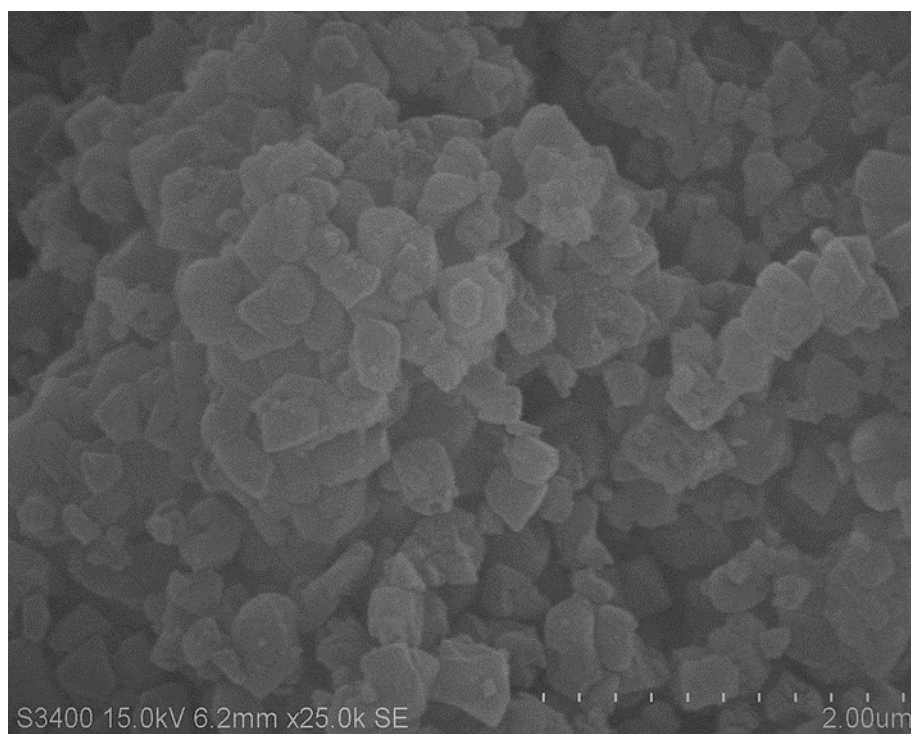


Figure 16 SEM images of the Pt/HY-500 catalyst

4.3.2 Nitrogen physisorption and ICP

The total surface area, micropore volume, and pore size of catalysts were measured by the Nitrogen physisorption technique with a Micro metrics ASAP 2020 instrument and the results showed in Table 10. The surface area and micro pore volume of Pt/HY-15 catalyst prepared by impregnation method were higher compare to pure HY-15 zeolite but pore volume and pore size were approximately the same. For the Pt/HY-500, the total surface area, mesopore volume and pore size did not change much after impregnation of Pt on HY-500. The % Pt content of Pt/HY-500 and Pt/HY-15 tested by ICP method were approximately the same at 1.1-1.2 wt%.

Table 10 Physical properties of Pt on HY zeolites catalysts

Zeolite catalyst	% Pt	Total surface area (m ² /g)	Mesopore ? volume (cm ³ /g)	Pore volume (cm ³ /g)	Pore size (nm)
HY-15	-	514	0.206	0.171	10.8
Pt/HY-15	1.1	586	0.316	0.195	11.2
HY-500	-	652	0.243	0.252	7.9
Pt/HY-500	1.2	639	0.215	0.274	8.5

4.3.3 H₂ temperature-programmed reduction (H₂-TPR)

The H₂ temperature-programmed reduction (H₂-TPR) technique was used to study the reduction behavior of Pt/HY-15 and Pt/HY-500 catalyst. The reduction results of catalysts are shown in Figure 17. The Pt/HY-15 and Pt/HY-500 catalysts prepared by the incipient wetness impregnation method showed one main reduction peak.

The peak with a reduction temperature from 300 to 500 °C (around 400 °C) suggests the existence of a strong interaction between Pt species and the zeolite support [33]. With the decrease of crystallite size (according to the XRD results, HY-500 had smaller crystallite size comparing to HY-15), H₂-TPR were detected in 2 samples, indicating strong interaction between Pt and zeolite surface induced by decreased zeolite crystallite size.

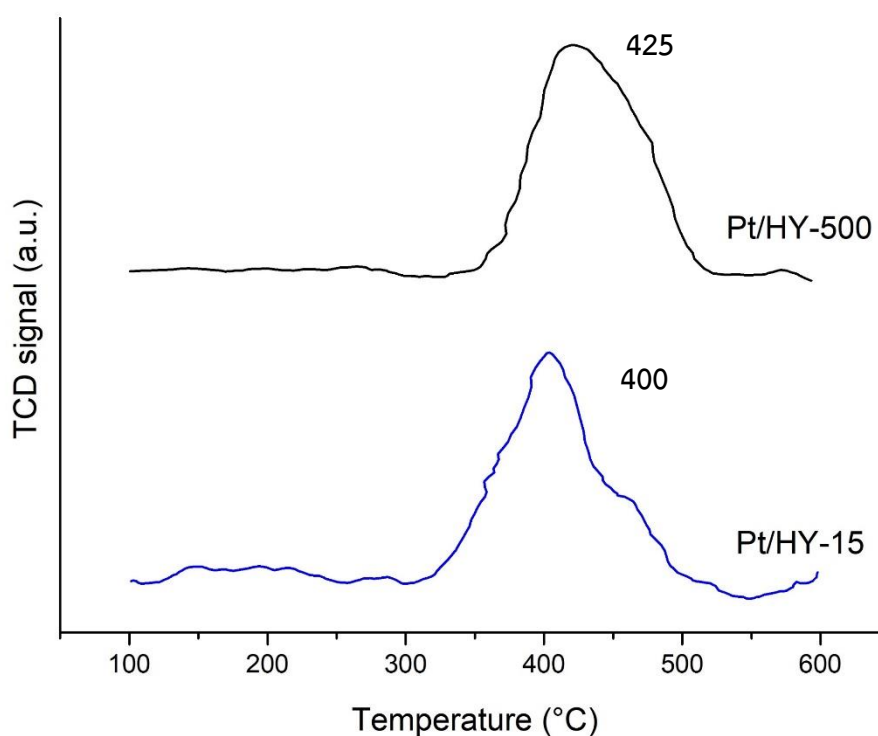


Figure 17 The H_2 -TPR profiles of Pt catalysts on HY zeolites

4.3.4 The acidity of zeolites

The overall acidity of the samples was analyzed by NH_3 -TPD. The desorption of NH_3 occurred from 100 to 530°C. The broad desorption peaks could be deconvoluted into three peaks centered at 180, 250 and 350°C, which were attributed to sites of weak, medium, and strong acidity, respectively. The results are shown in Table 11.

The total acidity and acid strengths of the Pt/HY-15 and Pt/HY-500 was lower compared to HY-15 and HY-500 zeolite, respectively. It was found that Pt loading on zeolite led to a decrease in both weak acid and strong acid sites.

The Brønsted and Lewis acid sites were obtained from pyridine-IR techniques and represented by B/L ratio. The acid site distribution of Brønsted (B) and Lewis (L) was identified by pyridine -IR spectra. Absorption bands at 1445–1454, 1576 and 1600–1605 cm^{-1} indicate the appearance of Lewis acid sites. Absorption bands at 1546 and 1620–1640 cm^{-1} were associated with pyridine adsorbed on Brønsted acid sites, while the 1490 cm^{-1} was found for pyridine absorbing both Lewis and Brønsted acid sites.

As shown in Table 11., After Pt metal was incorporated into the HY-15 and HY-500 zeolite, the B/L ratio of the Pt promoted zeolite catalyst was decreased. The Pt metal also reduced the Brønsted acid site of zeolites due to the loss of electron in zeolites.

Table 11 The acidity of zeolite catalysts

Zeolite catalyst	Total acidity ($\mu\text{mol NH}_3/\text{g}_{\text{cat}}$)	Acid Strength ($\mu\text{mol NH}_3/\text{g}_{\text{cat}}$)		B/L
		Weak acid sites	Strong acid sites	
HY-15	1294	781	513	1.53
Pt/HY-15	856	415	441	0.41
HY-500	183	49	134	1.01
Pt/HY-500	139	45	94	0.58

4.4 The catalytic reaction test

The catalytic reaction tests in the one-pot transformation of furfural using various zeolites catalysts and 2-propanol as a hydrogen donor were carried out at 120 °C for 5 h under 1 bar of N_2 .

Table 12 The catalytic performances of the 1% Pt support on zeolites compare to pure zeolites in the one-pot transformation of FAL in isopropanol at 120°C, 5 h (FAL; furfural, GVL; γ -valerolactone, LA; levulinic acid, IPL; iso-propyl levulinate, FA; furfuryl alcohol, AL; angelica-lactone))

Zeolite catalysts	FAL Conversion (%)	Selectivity (%)					Yield GVL (%)	Carbon Balance (%)
		GVL	LA	IPL	FA	AL		
Pt/HY-15	68.71	66.32	10.51	20.12	-	3.81	46.21	96.71
1% Pt/HY-15	89.40	33.23	-	66.77	-	-	29.71	92.30
Pt/HY-500	30.17	61.56	16.75	11.32	10.36	-	19.31	91.9
1% Pt/HY-500	68.15	40.62	12.47	46.91	-	-	27.68	81.52

The effect of Pt dopant was studied on the HY zeolite with different Si/Al ratios. The catalytic performances of the 1% Pt support on HY zeolites are presented in Table 12. The HY-15 presented the highest yield of GVL (46.21%) and the highest selectivity to GVL (66.32%). Doping 1% Pt on HY-15 resulted in higher conversion of FAL up to 89.4%. However, the selectivity to GVL decreased (33.23%). Similarly, the 1% Pt support on HY-500 also showed the increasing in conversion of FAL (68.15%) with lower selectivity to GVL (40.62%)

The increasing in FAL conversion was due to the fact that Pt-metal sites can catalyzed the hydrogen transfer reaction step and preferred to hydrogenate the aldehyde group of furfural, rather than furan ring. The Pt-metal also reduce the Bronsted acid site of zeolites due to the loss of electron in zeolites. For this reason, the lack of Bronsted site could result in lower selectivity to GVL.

Part III The effect of temperature, pressure, and gas conditions

4.5 The effect of pressure and gas conditions

Table 13 The catalytic performances of the HY-15 in the one-pot transformation of FAL in isopropanol at 120°C, 5 h, various gas condition and pressure

(FAL; furfural, GVL; γ -valerolactone, LA; levulinic acid, IPL; iso-propyl levulinate, FA; furfuryl alcohol, AL; angelica-lactone))

Catalyst	Pressure	Furfural Conversion (%)	Selectivity (%)					Yield GVL	Carbon Balance
			GVL	LA	IPL	FA	AL		
HY-15	1 bar N ₂	68.71	66.32	10.51	20.12	-	3.81	46.21	96.71
	1 bar H ₂	69.97	39.20	-	43.58	17.22	-	27.43	92.11
	5 bar H ₂	79.44	41.92	-	43.47	14.61	-	33.30	95.80
	7 bar H ₂	83.23	29.05	34.38	30.75	5.80	-	24.18	93.05

The gas conditions primarily affected the selectivity of the products. The reaction under hydrogen gas resulted in lower GVL selectivity (39.20%) compared to nitrogen gas (66.32%), the main product was IPL (not GVL), and the conversion of furfural are approximately equal as shown in Table 13. For this reason, the reaction should be conducted under nitrogen gas conditions in order to maximize the yield of GVL.

Although the reaction was carried out under higher pressure of hydrogen gas, the selectivity to GVL was still low comparing to nitrogen gas conditions. The conversion of furfural was higher under the higher pressure of hydrogen (69.97% at 1 bar H₂, 79.44% at 5 bar H₂ and 82.23% at 7 bar H₂). In conclusion, the one pot transformation of furfural to GVL should be conducted under nitrogen gas condition

because the hydrogen atoms from iso-propanol can be used in the reaction and hydrogen gas was not necessary.

4.6 The effect of temperature conditions

Table 14 The catalytic performances of the HY-15 in the one-pot transformation of FAL in isopropanol at 120°C, 140°C and 160°C, 5 h and 1 bar N₂

(FAL; furfural, GVL; γ -valerolactone, LA; levulinic acid, IPL; iso-propyl levulinate, FA; furfuryl alcohol, AL; angelica-lactone))

Catalyst	Temperature	Furfural Conversion (%)	Selectivity (%)					Yield GVL	Carbon Balance
			GVL	LA	IPL	FA	AL		
HY-15	120 °C	68.71	66.32	10.51	20.12	-	3.81	46.21	96.71
	140 °C	75.23	41.35	35.44	-	23.21	-	31.10	91.46
	160 °C	78.54	46.21	45.55	-	8.24	-	36.29	93.56

The effect of temperature on the one pot transformation of furfural was presented in Table 14. HY-15 was tested for conversion of furfural at 120 °C, 140 °C, and 160 °C and the conversion of furfural were 68.71%, 75.23% and 78.54% with 66.32%, 41.35% and 46.21% GVL selectivity, respectively. The distribution of the product was less diversified when the reaction took place at higher temperatures. It is possible that the distribution of the products is influenced by the reaction temperature. However, an increasing in temperature up to 160 °C led to a drop in the main product (GVL) yield. The formation of humin by-products may be occurred which was resulted in lower yield of GVL at high temperature. According to Rao et al [26] a decrease in GVL yield was observed at reaction temperature 200 °C because of the formation of humin as a by-product. In conclusion, the reaction should be carried out under temperature at 120 °C, which showed the highest GVL selectivity.

CHAPTER V

CONCLUSIONS

5.1 Conclusions

One-pot conversion of furfural to GVL was studied over various zeolite catalysts. The physical properties of HY-15 and HY-100 were not much different. The high surface area of the HY-500 catalyst were beneficial to high selectivity to GVL. However, due to their relatively low total acidity, the HY-500 resulted in the lowest conversion of furfural. The cage structure and larger cavity of HY zeolite led to higher activity and GVL selectivity compared to the H-ZSM-5 and H-Beta zeolite. The HY zeolite had weaker acid strength with higher ratio of Brønsted to Lewis acid sites compared to H-Beta zeolite and H-ZSM-5. The HY-15 zeolite with the highest acidity and the highest Bronsted to Lewis ratio presented the highest furfural conversion of 68.71% and GVL selectivity of 66.32% under 120°C, 1 bar of N₂, 5 h reaction time using isopropanol as a hydrogen donor. The reaction should be carried out under nitrogen gas conditions and supply of hydrogen gas was not necessary. The Pt-metal sites can improve the conversion of furfural in a hydrogen transfer reaction but with a trade-off in the selectivity of GVL because of the reducing Bronsted to Lewis ratio.

5.2 Recommendations

1. The other factors such as use of solvents, use of various metal as a promoter, and solvent (H-donor) concentration in the one pot transformation of FAL to GVL should be studied.

2. The stability of the Pt metal on zeolite catalysts prepared by impregnation method and reusability should be investigated.

REFERENCES

1. Ansell, T. and S. Cayzer, *Limits to growth redux: A system dynamics model for assessing energy and climate change constraints to global growth*. Energy Policy, 2018. **120**: p. 514-525.
2. Han, Y., et al., *Lignin-based solid acid catalyst for the conversion of cellulose to levulinic acid using γ -valerolactone as solvent*. Ind. Crops Prod., 2019. **127**: p. 88.
3. Ye, L., et al., *A review about GVL production from lignocellulose: Focusing on the full components utilization*. Ind. Crops Prod., 2020. **144**: p. 112031.
4. Enumula, S.S., et al., *Conversion of furfuryl alcohol to alkyl levulinate fuel additives over Al₂O₃/SBA-15 catalyst*. Sustainable Energy & Fuels, 2017. **1**(3): p. 644-651.
5. Ye, L., et al., *HZ-ZrP Catalysts with Adjustable Ratio of Brønsted and Lewis Acids for the One-Pot Value-Added Conversion of Biomass-Derived Furfural*. ACS Sustainable Chemistry & Engineering, 2020. **8**(19): p. 7403-7413.
6. Zhang, H., et al., *A combo Zr-HY and Al-HY zeolite catalysts for the one-pot cascade transformation of biomass-derived furfural to γ -valerolactone*. Journal of Catalysis, 2019. **375**: p. 56-67.
7. Zhang, T., et al., *One-pot production of γ -valerolactone from furfural using Zr-graphitic carbon nitride/H- β composite*. Int. J. Hydrogen Energy, 2019. **44**(29): p. 14527.
8. Winoto, H.P., et al., *Heteropolyacid supported on Zr-Beta zeolite as an active catalyst for one-pot transformation of furfural to γ -valerolactone*. Appl. Catal., B, 2019. **241**: p. 588.
9. Xu, C., et al., *Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural*. Chemical Society Reviews, 2020. **49**(13): p. 4273-4306.
10. Wang, Y., et al., *Recent advances in catalytic hydrogenation of furfural*. Catalysts, 2019. **9**(10).

11. Espro, C., et al., *Catalytic Transfer Hydrogenolysis as an Effective Tool for the Reductive Upgrading of Cellulose, Hemicellulose, Lignin, and Their Derived Molecules*. *Catalysts*, 2018. **8**: p. 313.
12. Iglesias, J., et al., *Zr-SBA-15 Lewis Acid Catalyst: Activity in Meerwein Ponndorf Verley Reduction*. *Catalysts*, 2015. **5**: p. 1911-1927.
13. López-Asensio, R., et al., *Influence of Structure-modifying Agents in the Synthesis of Zr-doped SBA-15 Silica and Their Use as Catalysts in the Furfural Hydrogenation to Obtain High Value-added Products through the Meerwein-Ponndorf-Verley Reduction*. *International Journal of Molecular Sciences*, 2019. **20**: p. 828.
14. López-Asensio, R., et al., *Selective production of furfuryl alcohol from furfural by catalytic transfer hydrogenation over commercial aluminas*. *Applied Catalysis A: General*, 2018. **556**: p. 1-9.
15. Xu, R., et al., *Falling Leaves Return to Their Roots: A Review on the Preparation of γ -Valerolactone from Lignocellulose and Its Application in the Conversion of Lignocellulose*. *ChemSusChem*, 2020. **13**(24): p. 6461-6476.
16. Yan, Z.-p., L. Lin, and S. Liu, *Synthesis of γ -Valerolactone by Hydrogenation of Biomass-derived Levulinic Acid over Ru/C Catalyst*. *Energy & Fuels*, 2009. **23**(8): p. 3853-3858.
17. Wang, J., et al., *Post-synthesized zirconium-containing Beta zeolite in Meerwein-Ponndorf-Verley reduction: Pros and cons*. *Applied Catalysis A: General*, 2015. **493**: p. 112-120.
18. Lange, J.P., van de Graaf, W. D., & Haan, R. J., *Conversion of furfuryl alcohol into ethyl levulinate using solid acid catalysts*. *ChemSusChem*, 2009. **2**: p. 437-441.
19. Galadima, A. and O. Muraza, *Zeolite catalyst design for the conversion of glucose to furans and other renewable fuels*. *Fuel*, 2019. **258**: p. 115851.
20. Kim, K.D., et al., *Cascade reaction engineering on zirconia-supported mesoporous MFI zeolites with tunable Lewis-Brønsted acid sites: a case of the one-pot conversion of furfural to γ -valerolactone*. *RSC Advances*, 2020. **10**(58): p. 35318-35328.

21. Baerlocher, C., L.B. McCusker, and D.H. Olson, *MFI - Pnma*, in *Atlas of Zeolite Framework Types (Sixth Edition)*, C. Baerlocher, L.B. McCusker, and D.H. Olson, Editors. 2007, Elsevier Science B.V.: Amsterdam. p. 212-213.
22. Baerlocher, C., L.B. McCusker, and D.H. Olson, *FAU - Fd $\bar{3}$ m*, in *Atlas of Zeolite Framework Types (Sixth Edition)*, C. Baerlocher, L.B. McCusker, and D.H. Olson, Editors. 2007, Elsevier Science B.V.: Amsterdam. p. 140-141.
23. Baerlocher, C., L.B. McCusker, and D.H. Olson, *BEA - P4122*, in *Atlas of Zeolite Framework Types (Sixth Edition)*, C. Baerlocher, L.B. McCusker, and D.H. Olson, Editors. 2007, Elsevier Science B.V.: Amsterdam. p. 72-73.
24. *Platinum*. [cited 2008; Available from: <https://www.lookchem.com/Periodic-Table/Platinum/>].
25. Rylander, P.N., *1 - Platinum Metal Catalysts*, in *Catalytic Hydrogenation Over Platinum Metals*, P.N. Rylander, Editor. 1967, Academic Press. p. 3-29.
26. Rao, B.S., et al., *One pot selective conversion of furfural to γ -valerolactone over zirconia containing heteropoly tungstate supported on β -zeolite catalyst*. *Mol. Catal.*, 2019. **466**: p. 52.
27. He, J., et al., *Dual acidic mesoporous KIT silicates enable one-pot production of γ -valerolactone from biomass derivatives via cascade reactions*. *Renewable Energy*, 2020. **146**: p. 359-370.
28. Li, W., et al., *Hf-based metal organic frameworks as bifunctional catalysts for the one-pot conversion of furfural to γ -valerolactone*. *Molecular Catalysis*, 2019. **472**: p. 17-26.
29. Wang, T., J. He, and Y. Zhang, *Production of γ -Valerolactone from One-Pot Transformation of Biomass-Derived Carbohydrates Over Chitosan-Supported Ruthenium Catalyst Combined with Zeolite ZSM-5*. *European Journal of Organic Chemistry*, 2020. **2020**(11): p. 1611-1619.
30. Li, X., et al., *Catalytic production of γ -valerolactone from xylose over delaminated Zr-Al-SCM-1 zeolite via a cascade process*. *Journal of Catalysis*, 2020. **392**: p. 175-185.

31. Rongxin Zhang, Shaojun Xu, Duaa Raja, Nor Binti Khusni, Jinmin Liu, Jiaoyu Zhang, Samer Abdulridha, Huan Xiang, Songshan Jiang, Yanan Guan, Yilai Jiao, Xiaolei Fan, *On the effect of mesoporosity of FAU Y zeolites in the liquid-phase catalysis*, *Microporous and Mesoporous Materials*, 2019. **278**: p. 297-306.



APPENDIX A

CALCULATION FOR CARALYST PREPARATION

Calculation of preparing 1% Pt/HY-15 and 1% Pt/HY-500 catalysts by incipient wetness impregnation method were presented below.

Precursor

Platinum(II) acetylacetonate ($\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$) 99.99%, MW.= 393.29 g/mol

Calculation

Based on 1 g of catalysts used, the composition of catalysts will be as follows:

For preparation of 2 g 1% Pt/HY-15 catalyst

$$\text{Pt required} = 0.02 \text{ g}$$

$$\text{HY-15 required} = 2 - 0.02 = 1.98 \text{ g}$$

Platinum 0.02 g was prepared by using Platinum (II) acetylacetonate 99.99%

=

$$\frac{(\text{MW.of platinum (II) acetylacetonate } 99.99\%)(\text{weight of Pt required})}{\text{MW.of Pt}}$$

$$= \frac{393.29 \frac{\text{g}}{\text{mol}} \times 0.02 \text{ g}}{195.084 \frac{\text{g}}{\text{mol}}}$$

$$= 0.0403 \text{ g}$$

So, Platinum (II) acetyl acetonate 0.0403 g and HY-15 support 1.98 g were required.

APPENDIX B

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size was calculated from the width at half of the height or full width of the diffraction peak of the XRD pattern by the Debye-Scherrer equation.

Debye-Scherrer equation

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where

D = Crystallite size, Å

k = Crystallite-shape factor = 0.9 for

λ = X-ray wavelength, 1.5418 Å for CuK α

β = X-ray diffraction broadening, radian

θ = Observed peak angle, degree

The X-ray diffraction broadening (β) can be obtained by Warren's formula:

$$\beta = \sqrt{\beta_M^2 - \beta_S^2}$$

Where

β_M = Measured peak width at half of peak height

β_S = Corresponding width of the standard material

APPENDIX C

CALCULATION FOR CATALYTIC PERFORMANCE

The catalytic performances for the one-pot transformation of FAL were shown in terms of FAL conversion, GVL selectivity, and GVL yield.

The catalytic performances for the hydrogenation of furfural (FAL) was shown below.

$$FAL \text{ conversion (\%)} = \frac{\text{Mole of } FAL_{in} - \text{Mole of } FAL_{out}}{\text{Mole of } FAL_{in}} \times 100$$

$$GVL \text{ selectivity (\%)} = \frac{\text{Mole of GVL}}{\text{Mole of } FAL_{in} - \text{Mole of } FAL_{out}} \times 100$$

$$GVL \text{ yield (\%)} = \frac{FAL \text{ conversion (\%)} \times GVL \text{ selectivity (\%)}}{100}$$

The calibration curve of FAL and various products are shown in Figure C.1-C.6.

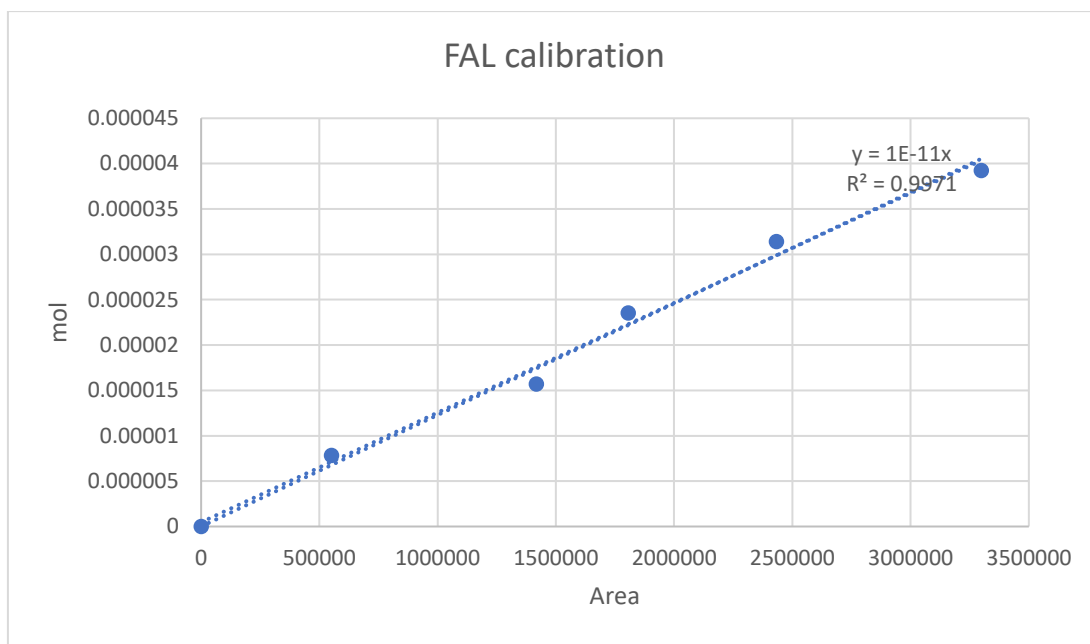


Figure C.1 The calibration curve of furfural

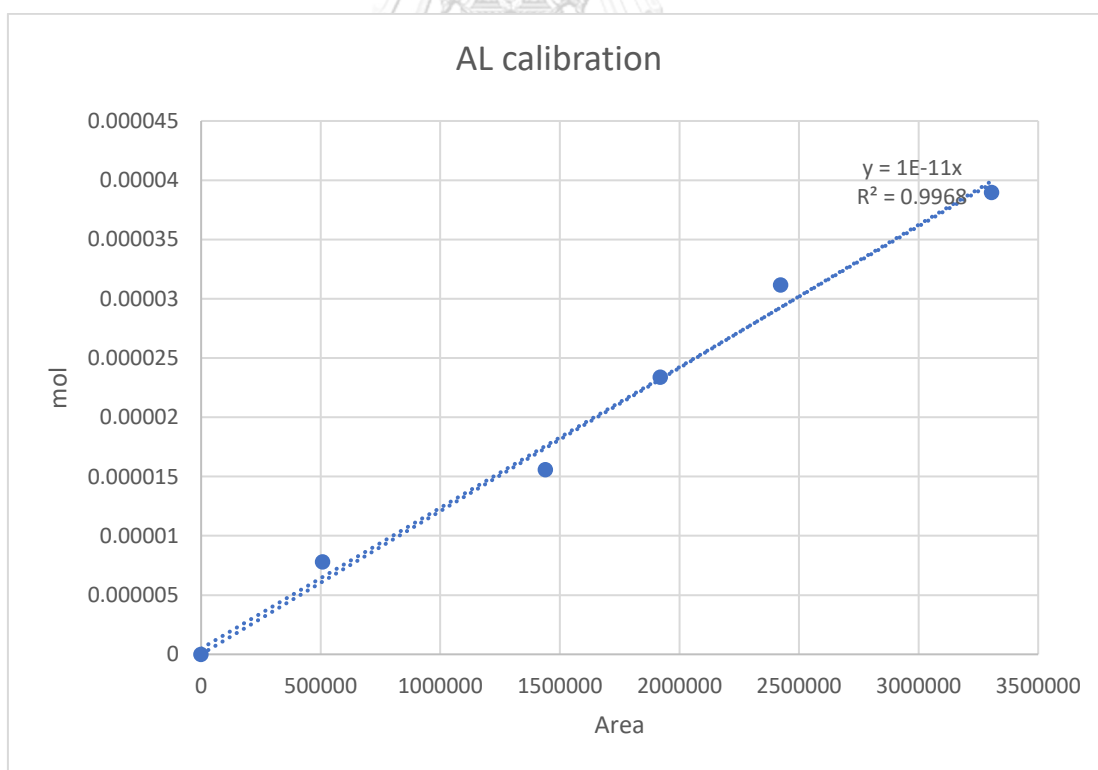


Figure C.2 The calibration curve of angelica lactone

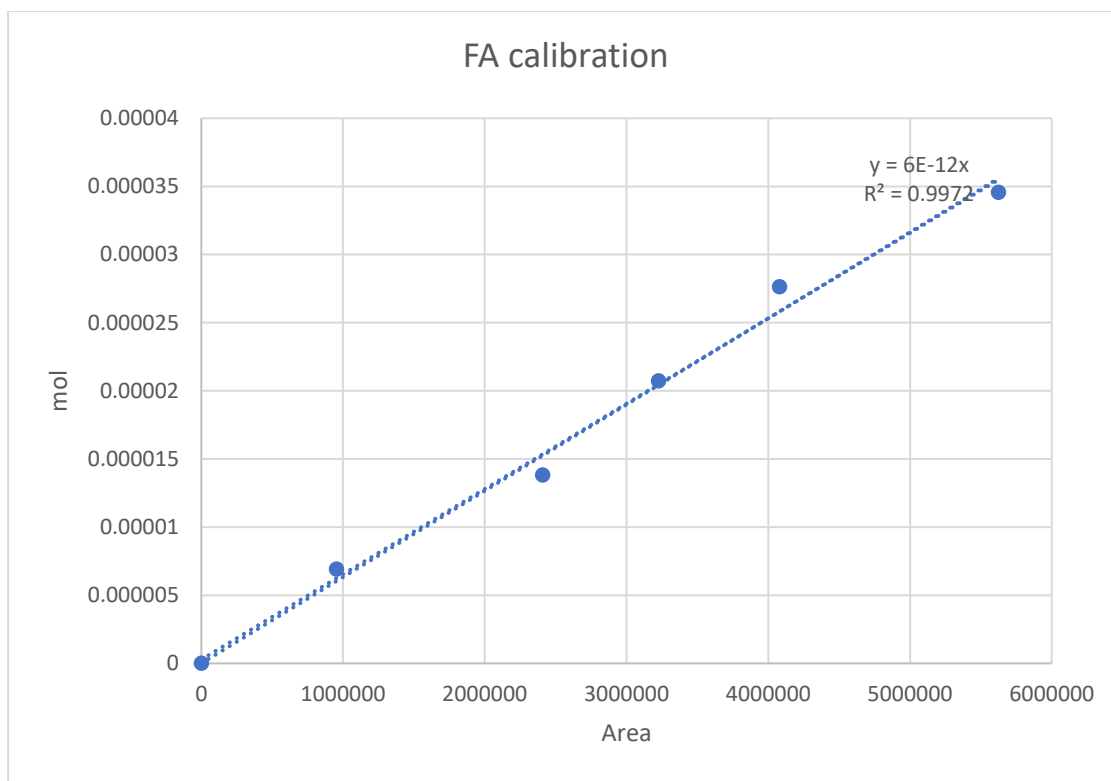


Figure C.3 The calibration curve of furfuryl alcohol

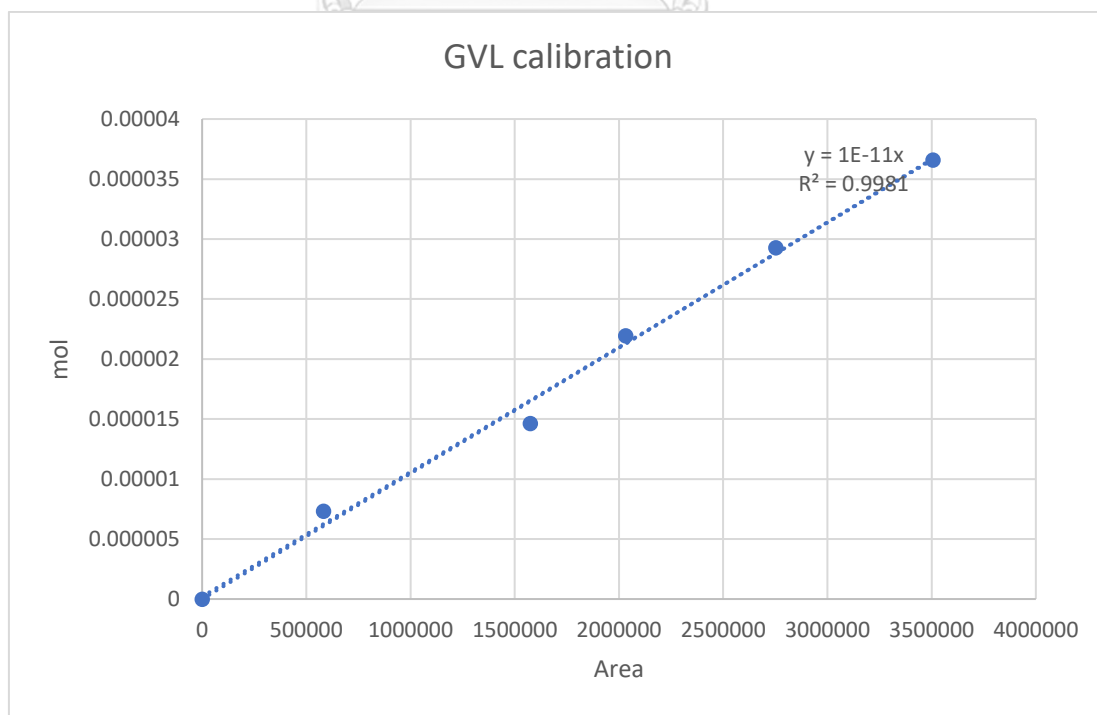


Figure C.4 The calibration curve of gamma-valerolactone

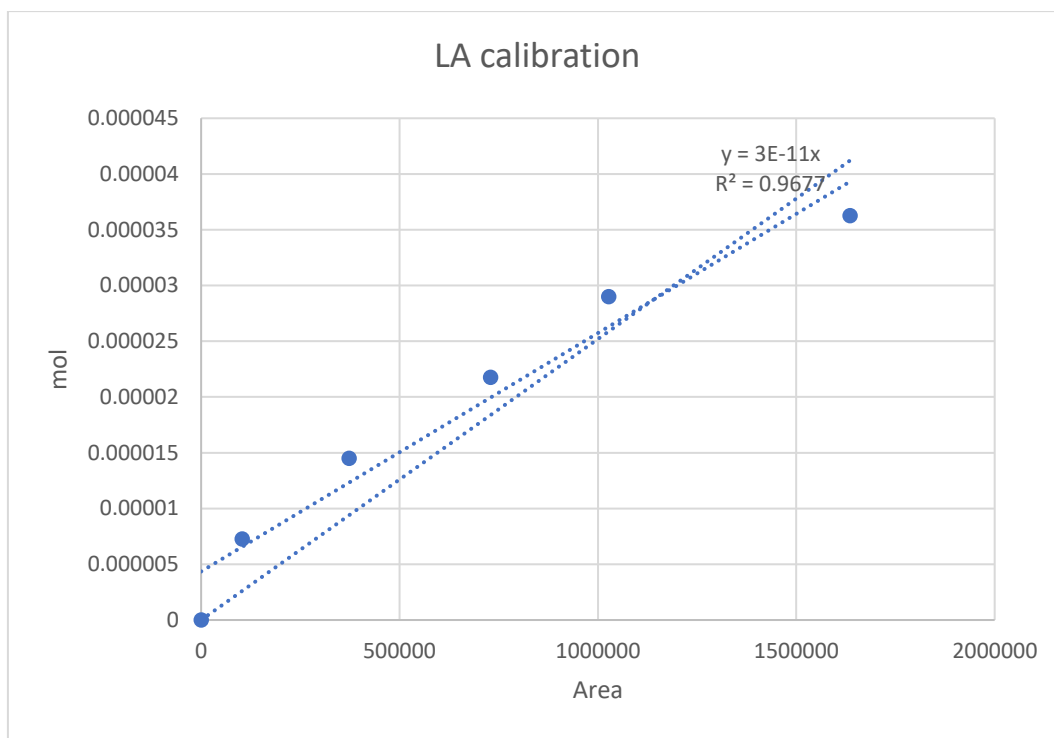


Figure C.5 The calibration curve of levulinic acid

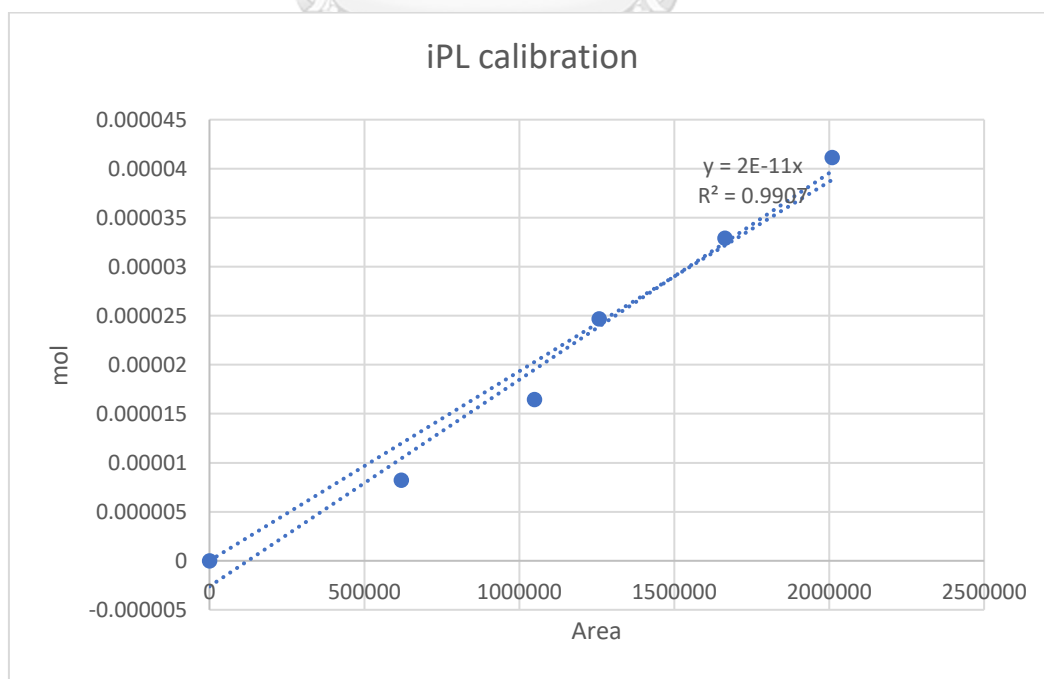


Figure C.6 The calibration curve of iso-propyl levulinate

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