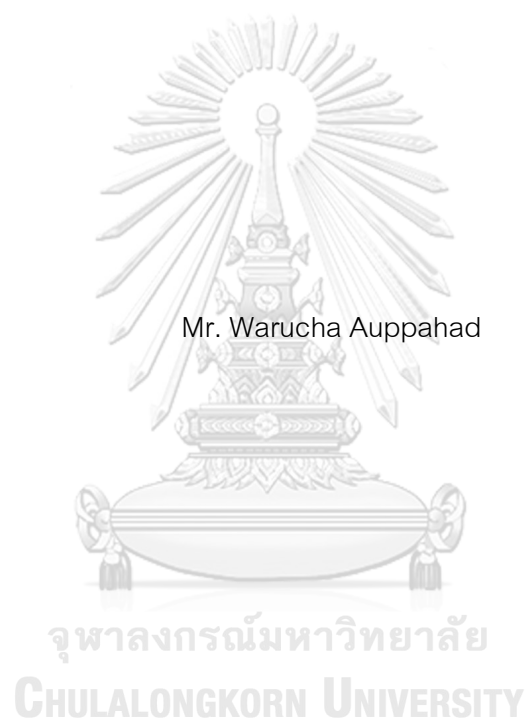One-Pot Conversion of Furfural to g-Valerolactone over Co- and Pt-doped ZSM-5
catalysts

Mr. Warucha Auppahad

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

FACULTY OF ENGINEERING

Chulalongkorn University

Academic Year 2019

การเปลี่ยนเฟอร์ฟิวรัลเป็นแกมมาแวลเลอโรแลคโทนในขั้นตอนเดียวบนตัวเร่งปฏิกิริยา ZSM-5 ที่มี
การเติมโคบอลต์และแพลทินัม

นายวรุชา อุปฮาด

Thesis Title	One-Pot Conversion of Furfural to g-Valerolactone over Co- and Pt-doped ZSM-5 catalysts
By	Mr. Warucha Auppahad
Field of Study	Chemical Engineering
Thesis Advisor	Professor JOONGJAI PANPRANOT, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

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วรุชา อุปฮาด : การเปลี่ยนเฟอร์ฟิวรัลเป็นแกมมาแวลเลอโรแลคโทนในขั้นตอนเดียว
บนตัวเร่งปฏิกิริยา ZSM-5 ที่มีการเติมโคบอลต์และแพลทินัม. (One-Pot
Conversion of Furfural to g-Valerolactone over Co- and Pt-doped ZSM-5
catalysts) อ.ที่ปรึกษาหลัก : ศ. ดร.จูงใจ ปั้นประณต

แกมมาแวลเลอโรแลคโทนเป็นหนึ่งสารประกอบชีวมวลที่มีประโยชน์ที่สามารถ
สังเคราะห์ได้จากหลายกระบวนการที่แตกต่างกันจากเฮมิเซลูโลส การเปลี่ยนเฟอร์ฟิวรัลที่มา
จากเฮมิเซลูโลสไปเป็นแกมมาแวลเลอโรแลคโทน โดยปกติใช้ตัวเร่งปฏิกิริยาเป็นโลหะบนตัว
รองรับตัวเร่งปฏิกิริยา ในงานวิจัยนี้ใช้ตัวเร่งปฏิกิริยาเป็น ZSM-5 ที่มีการเติมโคบอลต์และ
แพลทินัมที่มีปริมาณโคบอลต์ 0-10 โดยน้ำหนัก และ ปริมาณแพลทินัม 0.5-2 โดยน้ำหนัก
เตรียมตัวเร่งปฏิกิริยาโดยวิธีเคลือบฝัง ทำปฏิกิริยาที่อุณหภูมิ 120 องสาเซลเซียส ความดัน
บรรยากาศ และ เวลาทำปฏิกิริยา 5 ชั่วโมง ตรวจสอบผลิตภัณฑ์ด้วยเครื่องแก๊สโครมาโต
กราฟ และแก๊สโครมาโตกราฟ – แมสสเปกโทรเมตรี พบผลิตภัณฑ์หลัก คือ แกมมาแวลเลอ
โรแลคโทน, กรดเลวูลินิค, ไอโซโพรพิล เลวูลิเนต, แองเจลลิกาแลคโทน เมื่อเปรียบเทียบตัวเร่ง
ปฏิกิริยา ZSM-5 ที่ไม่ได้เติมโลหะและที่มีการปรับปรุงด้วยการเติมโลหะ พบว่าเมื่อใส่โลหะลงไป
ทำให้ร้อยละผลได้ของแกมมาแวลเลอโรแลคโทนสูงขึ้นทั้งโคบอลต์และแพลทินัมโดยตัวเร่ง
ปฏิกิริยา 1%Pt/ZSM-5 ให้ร้อยละผลได้ของแกมมาแวลเลอโรแลคโทนสูงที่สุดที่ 85.4% ที่
ภาวะการทดลองดังกล่าว จากการตรวจสอบคุณลักษณะของตัวเร่งปฏิกิริยาด้วยเทคนิค N_2-
physisorption, XRD, TPR, NH_3-TPD and Pyridine-IR spectra พบว่าประสิทธิภาพของตัวเร่ง
ปฏิกิริยามีความสัมพันธ์กับคุณสมบัติทางเคมีและกายภาพของตัวเร่งปฏิกิริยาเช่น ปริมาณและ
ชนิดของตำแหน่งกรดที่ว่องไว

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต
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การศึกษา		....

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KEYWORD: Furfural, **γ**-Valerolactone (GVL), ZSM-5

Warucha Auppahad : One-Pot Conversion of Furfural to g-Valerolactone over Co- and Pt-doped ZSM-5 catalysts. Advisor: Prof. JOONGJAI PANPRANOT, Ph.D.

γ-Valerolactone (GVL) is one of the useful biomass compounds produced via different reaction pathways from hemicellulose. Typically, GVL is produced by conversion of furfural using supported metal catalysts. In this study, Co- and Pt-doped /ZSM-5 catalysts with Co loadings (0-10 wt%) and Pt loadings (0.5-2 wt%) were prepared by impregnation method and employed in the one-pot conversion of furfural to GVL. The reactions were carried out in a 100 cm^3 batch stainless steel reactor at 120 $^\circ$C atmospheric pressure for 5 h. The products were analysed by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS). The major products were GVL, levullinic acid (LA), isopropyllevullinate (IPL), and angelica lactones (AL). Compared to the non-modified H-ZSM-5, Co- and Pt-doped /ZSM-5 produced much higher yield of GVL with 1%Pt/ZSM-5 showed the highest yield at 85.4% under the conditions used. The catalysts were characterized by N_2-adsorption, XRD, TPR, NH_3-TPD and Pyridine-IR spectroscopy. The catalyst performances were correlated to the physicochemical properties of the catalysts such as the amount and type of acid sites.

Field of Study:	Chemical Engineering	Student's Signature
		....
Academic	2019	Advisor's Signature
Year:		....

ACKNOWLEDGEMENTS

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Introduction

Reducing the use of fossil fuels and reducing environmental problems through alternative energy. Lignocellulosic biomass is considered as an alternative feedstock to produce sustainable energy because of the abundance and neutralization of carbon[1]. Usually, lignocellulose biomass consists of cellulose, hemicellulose, and lignin. Xylose, derived from hemicellulose It can be converted to furfural through dehydration process with acid catalyst[2]. Recently, the conversion of furfural to higher valuable chemicals such as γ-valerolactone (GVL), levullinic acid (LA), isopropyl levulinate (IPL), angelica lactones (AL), and levullinate ester (LE) receives considerable attention[3, 4]. Currently, the production of GVL from furfural has been achieved by acid catalyzed reaction using ZSM-5 zeolite, HY zeolite, ZrO_2, and also by catalytic transfer hydrogenation[5].

Shanhui Zhu et al.[6] Shanhui Zhu et al.[6] reported the formation of GVL from reactant and alcohol solvent (IPA) using the combination of Au / ZrO2 with ZSM-5, GVL yield 80.4% was operating by 12.7 ml of reactant, 0.2 g catalyst of Au/ZrO_2 mixed 0.2 g of ZSM-5 zeolite[7]. the studied Zr-Al beta zeolite acid site catalyst for the effect of hydrogen donor for optimized reaction conditions showed GVL selective productivity 0.61 and 70% selectivity of GVL and a productivity of 0.88 $g_{GVL} \cdot g_{CAT}^{-1}$. In this work, one-pot conversion of furfural into higher-value chemicals was investigated using Co and Pt-doped ZSM-5 catalysts under mild reaction conditions.

1.2 Objectives of the Research

To study the characteristics and catalytic performances of Co- and Pt-doped ZSM-5 catalysts in one-pot conversion of furfural to γ-valerolactone.

1.3 Scope of the Research

1.3.1 Preparation of Co dropped ZSM-5 support catalyst by incipient wetness impregnation (IWI) with various cobalt content 1, 5, 10 wt% support after that calcination 500°C under atmospheres for 6 h.

1.3.2 Pt /ZSM-5 catalysts was prepared by incipient wetness impregnation with Pt content 1 wt% support and calcination at 500°C under atmospheres for 6 hours.

1.3.3 The reduction conditions were H_2 flow (50cm^3/min) under 500°C, 120 min.

1.3.4 The activity was tested in the one-pot conversion of furfural to GVL in a batch autoclave reactor at 120°C and 1 bars nitrogen for 5 h using 2-propanol as a solvent.

1.3.5 Characterization of the prepared catalysts by various method including

      1.3.5.1 N_2 physisorption

      1.3.5.2 X-ray diffraction (XRD)

      1.3.5.3 NH_3-temperature program desorption (NH_3-TPD)

      1.3.5.4 H_2-temperature programmed reduction (H_2-TRR)

      1.3.5.5 Pyridine-IR spectra

1.4 Research Methodology

Part I: ZSM-5 catalysts were tested for furfural conversion at 100,120 and 140 °C

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                        ┌─────────────────────────┐
                        │   The ZSM-5 catalysts   │
                        └─────────────────────────┘
                                    │
                                    ▼
                  ┌──────────────────────────────────┐
                  │  Calcination in air at 500°C for 6 h │
                  └──────────────────────────────────┘
                                    │
                                    ▼
                        ┌─────────────────────────┐
                        │    Reduction catalyst   │
                        │     at 500°C for 2 h    │
                        └─────────────────────────┘
```

Catalytic reaction study of liquid phase conversion of Furfural to γ-Valerolactone various at temperature 100, 120, and 140.	Catalyst characterizations
	✔ XRD
	✔ N_2-physisorption
	✔ NH_3-TPD
	✔ H_2-TPR
	✔ XPS
	✔ Pyridine-IR

GC analysis and data analysis

Discussion   Conclusion
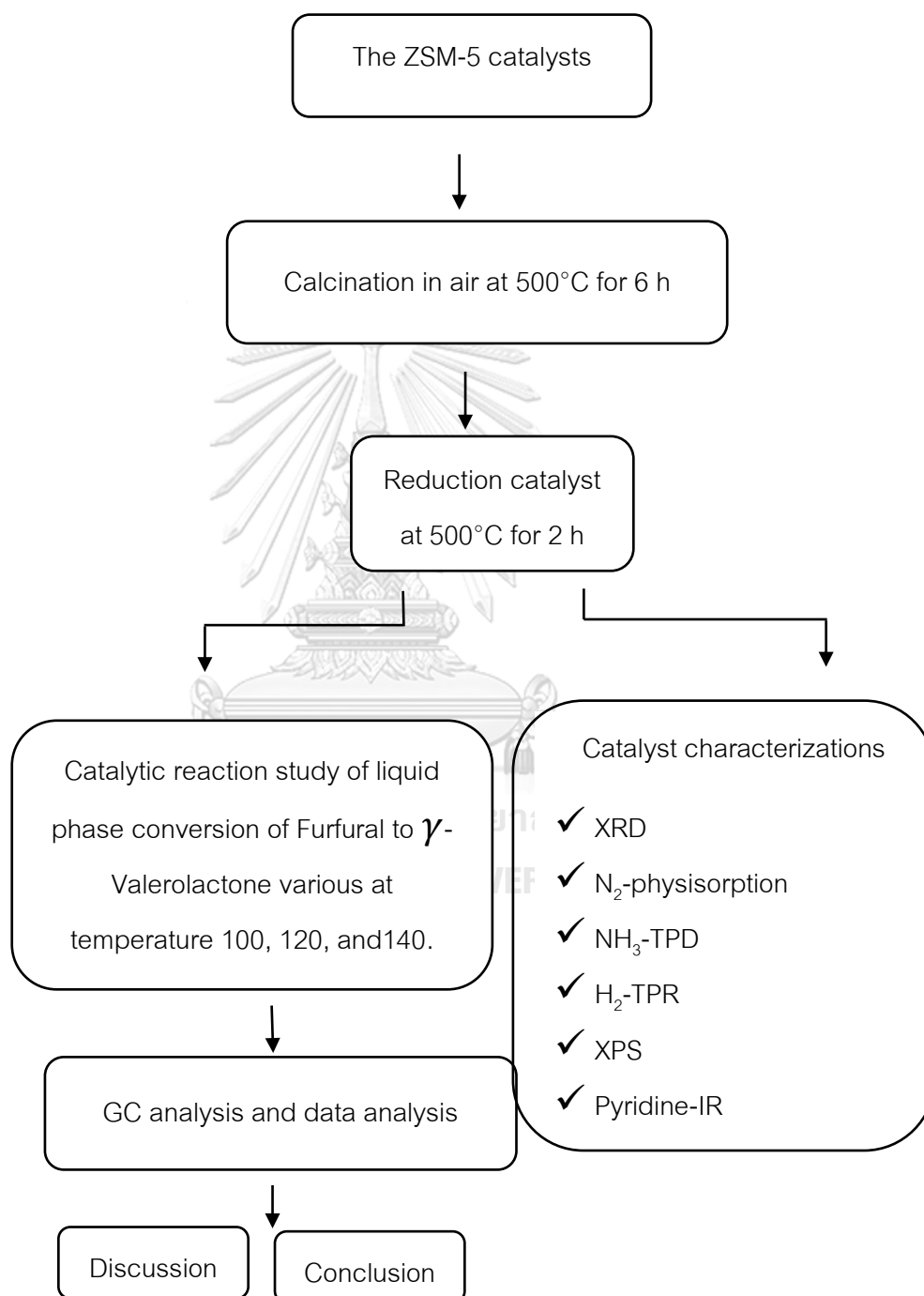
Part II: The catalytic test and cobalt selectivity loaded on ZSM-5 were investigated in furfural conversion to γ- Valerolactone

Preparation of Co add on ZSM-5 catalysts by IWI with various cobalt content 1, 5, 10 wt% support and calcined at 500°C under atmospheres, 360 min.

Calcination in air at 500°C for 6 h

Reduce catalyst at 500°C for 120 min

Catalytic reaction studied liquid phase conversion of Furfural to γ- Valerolactone at 100 °C.

GC analysis and data analysis

Discussions

Conclusion

Catalyst characterizations

✓ XRD

✓ N_2-physisorption

✓ NH_3-TPD

✓ H_2-TPR

✓ XPS

✓ Pyridine-IR

Part III: The catalytic activity and selectivity of Pt loaded on ZSM-5 were investigated in furfural conversion to γ- Valerolactone

Synthesis of Pt /ZSM-5 catalysts by incipient wetness impregnation with Pt content wt% support and calcined 500°C under air atmospheres ,360 min.

↓

Calcination in air at 500°C for 6 h

Reduction catalyst
at 500°C for 2 h

Catalytic reaction study of liquid phase conversion of Furfural to γ- Valerolactone at 100 °C.

Catalyst characterizations

✔ XRD

✔ N_2-physisorption

✔ NH_3-TPD

✔ H_2-TPR

✔ XPS

✔ Pyliline-IR

GC analysis and data analysis

↓

Discussions   Conclusion

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Meerwein-Ponndorf-Verley (MPV) reduction

Meerwein and Schmidt discovered Meerwein–Ponndorf–Verley (MPV) redution, after that Verley found this reaction in 1925. They report that a composition of aluminum ethoxide could reduce aldehydes to their alcohols. The reaction can use ketones for aluminum is opropoxide in isopropanol reported by Ponndorf[8, 9]. Figure 1, shown catalytic cycle connects a six-member ring transition state of Meerwein-Ponndorf-Verley (MPV) reduction. initial, with the aluminum alkoxide 1, carbonyl oxygen is coordinated to achieve the tetra coordinated aluminum intermediate 2. The hydride is transferred to the carbonyl from the alkoxy ligand via a pericyclic mechanism present in Between intermediates 2 and 3. Finally, the new carbonyl dissociates and gives the tricoordinated aluminum species 4 and alcohol from solution displaces the newly reduced carbonyl to regenerate the catalyst[10].
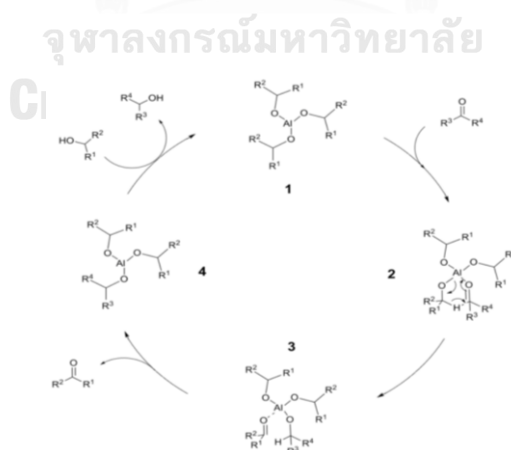
Figure 1 Catalytic cycle of Meerwein–Ponndorf–Verley reduction[8]

2.2 Hydrogenation Reactions

Hydrogenation is a chemical reaction between molecular hydrogen (H_2) by adding pairs of a hydrogen atom to compound (generally unsaturated compound). This process is one of the crucial reactions and widely useful for chemical synthesis of organic compounds in pharmaceuticals, agrochemicals, food industry, and the petrochemical industry[11, 12].

This reaction never happens hydrogen and organic compound lower 480ºC with non-metal but, Pt, Pd, Rh, and Ru are reactive catalysts for lower condition (temperatures and pressure). Hydrogen source and catalyst are important for this reaction generally [13].

2.3 Properties of Platinum

Platinum chemical emblem is Pt with 78 was atomic number and has isotopes 6 symbol thus 190Pt, 192Pt, 194Pt, 195Pt, 196Pt, and 198Pt[14]. Pt using in many industries of Pt for example involuntary, catalytic converters, electronic, glass industries. Pt properties were transition metal, malleable, inestimable, soft[14].

2.4 Properties of Cobalt

Cobalt has symbol was Co and, an atomic number of 27, and cobalt has isotopes as follow 50Co, 56Co, 57Co, 58Co, 59Co, 60Co, and73Co[15]. Cobalt-60 was property radioactive isotope[14]. Co is the main source of gamma-rays used many industries such as cancer treatment, as a tracer, and for radiotherapy.

Table 1 Physical properties of Platinum

Physical properties		
	Platinum	Cobalt
Atomic number	78	27
Atomic weight	195.084	58.9332
Element category	Transition metal	Transition metal
Electron configuration	$[Xe]4f^{14}5d^{9}6s^{1}$	$[Ar]3d^{7}\,4s^{2}$
Melting point	2041.4 K (1768.3ºC,)	1768 K (1495 ºC)
Boiling point	4098 K (3825ºC)	3203 K (2930 ºC)
Density	21.45 g/cm^{3}	8.90 g/cm^{3}

2.5 One-pot conversion of furfural to γ-valerolactone

The reaction for the one-pot conversion of furfural to GVL there is many steps and complex reply pathway in. Step1, the convert furfural toward furfuryl alcohol (FA) into furfuryl ether (FE). This step can be a hydrogenation reaction using a hydrogen donor from isopropyl alcohol (IPA) by dint of Lewis acid from the catalyst. In the second step, the effect of the catalyst present ring-opening of the product by the first step, and the product this step generates with Brønsted acid sites can be achieved levulinic acid (LA) and isopropyl levulinate (IPL) and second for before step 2 was FE can synthesis angelica lactone. In the last step, the main product for this part is 4-hydroxy pentanoate isopropyl ester (4-HPPE) and convert for lactonization selective product GVL from Lewis acid sites.
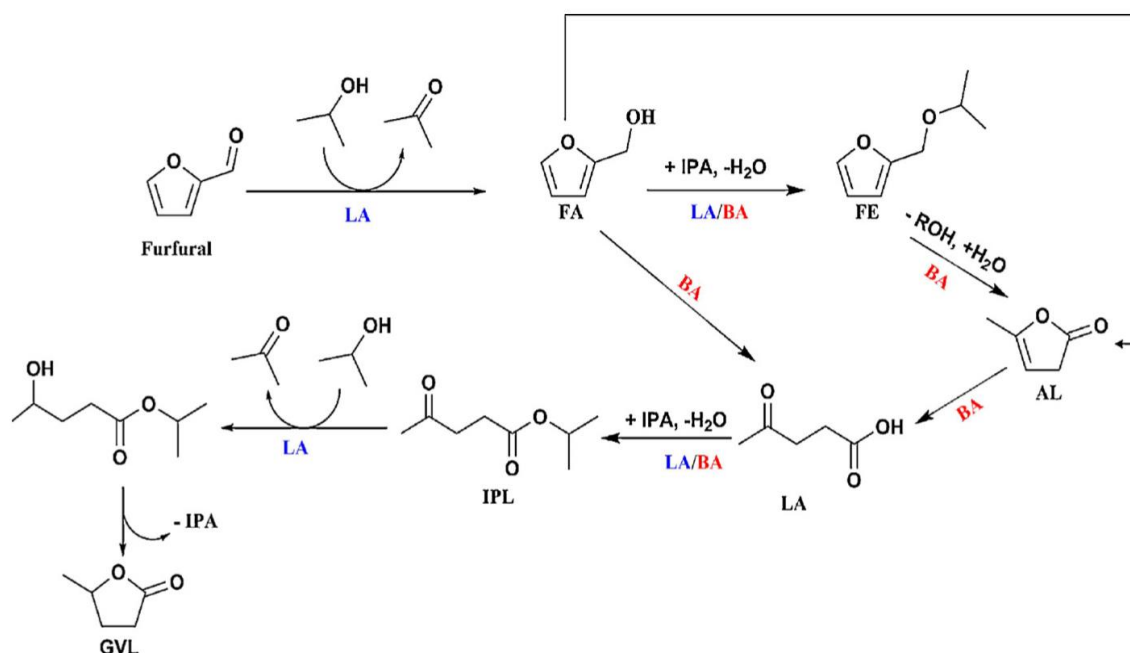
Figure 2 Reaction network for the conversion of furfural to GVL[15].

Table 2 Summary of the research of the furfural hydrogenation on various catalysts under different reaction conditions.

Researcher	Purposes of study	Catalyst and preparation method	Reaction conditions	Results
Jae, J. et al. (2016)	Studied Suitable conditions reaction from furfural into main product γ-valerolactone using Sn-Al-Beta zeolite catalysts.	Sn-Al-Beta catalysts	4–10gcat L^{-1} 0.11 M of furfural, in 20 ml very solvent solution, T=120-180 °C, t=24h, under N$_2$	Sn-Al-Beta 7 showed the highest yield of GVL up to 60% was obtained at 180 °C in 2-butanol after 24 h under N$_2$,
Zhu, S. et al. (2016)	Studied property of Au/ZrO2 mixed ZSM-	Au/ZrO$_2$, Au/CeO$_2$, Au/C,	0.2 g of catalyst, 0.5	Au/ZrO$_2$+ZSM-5 showed the

	5 zeolite for conversion hemicellulose or furfural to the main production of γ-valerolactone.	and ZSM-5 were prepared by modified Hummer's method, ultrasound-assisted deposition, hydrothermal method, ion-exchange method, Incipient wet Impregnation method	mM furfural, 10 g of 2-propanol, T=120 °C, P_{N2}=0.1MPa T= 24 h	highest yield of GVL up to 80.4% was obtained at 120 °C under 0.1 MPa.
Song, S. et al. (2017)	Studied reaction for the product from biomass on qualification Meso-Zr-Al-Beta zeolite.	Meso-Zr-Al-Beta(100-77),	0.12 g of catalyst, 0.05 M furfural, 10 ml of 2-propanol, T=120 °C, P_{N2}=0.1MPa T=24 h	Meso-Zr-Al-Beta(100-77), showed the highest yield of GVL up to 95% Could be achieved after reaction for 24 h at 120 °C
Zhahg, H. et al (2019)	Studied the Zr and Al on zeolite catalysts for the formation c-valerolactone from	Zr-HY-15-20, Zr-HY-6-20, Zr-HY-6-10, Zr-HY-2.6-20, Zr-HY-2.6-10,	0.10 g catalyst, 1mmol furfural, 5	Zr-HY-15-20 and Al-HY-6 showed the highest yield of

	furfural.	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, Beta and HY zeolites were synthesized using a post-synthesis strategy,	mL 2-pentanol, at T= 120°C, T=5 h under N_2.	GVL up to 85% after only 5h at 120°C under N_2
Winopto, H.P. et al. (2019)	Studied characteristic of catalyst Zr-Beta zeolite affect reaction transformation conversion of furfural to γ-valerolactone.	H-Al-Beta, Si-Beta, Zr-Beta, HPW/Si-Beta, HPW/Zr-Beta, HSiW/Si-Beta, HSiW/Zr-Beta were prepared solid-state ion-exchange (SSIE) method	0.11 M furfural, 20 mL 2-pentanol, at T= 160°C, T=24 h under N_2.	HPW/Zr-Beta showed the highest yield of GVL up to 68% after only 24h at 160°C under N_2
Li, W. et al. (2019)	Studied reaction one-pot conversion of furfural to major product γ-	Pristine DUT-67(Hf), DUT-67(Hf)-0.01, DUT-67(Hf)-0.03,	0.3 g catalysts, 0.05mol/L furfural in	sulfated DUT-67(Hf)-0.06 showed the highest yield of

	valerolactone test by Hf-based metal zeolte catalysts .	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, DUT-67(Hf)-0.06	25mL isopropyl alcohol, T=180 °C, P_{N2}=0.6 MPa, t= 20 h.	GVL up to 84.9% at 180°C after 20 h.
Rao B.S. et al. (2019)	Studied zirconia add supported on β-zeolite activity test by the biomass (furfural) to high value (γ-valerolactone)	Zeolite, T-zeolite, Zr-T-zeolite, Ti-T-zeolite, Nb-T-zeolite were prepared impregnation method.	(2.5–11.5g cat./L). 0.196 g furfural in 20 mL of 2-propanol T=130-210°C,N_2	Zr-T-zeolite showed the highest yield of GVL up to 90% at 170°C after 10 h.
Hong Je Cho et.al. (2020)	Studied molecular of Pt and acid of zeolite one-pot conversion to GVL.	Pt/H-ZSM-5 Pt@H-ZSM-5	= 24; furfural/Pt (mol mol^{-1}), 140 °C, 600 psi	Pt@H-ZSM-5 showed the highest yield of VA/EV up to 86% at 140 °C after 24 h.
Audemar M et. al. (2015)	Studied Cobalt drop SBA-15 supported properties affect for Hydrogenation of Furfural to Furfuryl Alcohol .	Cobalt/SBA-15 Prepared The SBA-15 support was synthesized according to the procedure method and Co	Inatypical experiment FAL (1 g) was added to ethanol (9 g), and Co/SBA-15	Cobalt/SBA-15 showed the highest yield of furfuryl alcohol up to 80%.

		Prepared by mpregnation method.	(5 wt%) was added to the solution Under 2MPa H_2 at 150 °C 1.5 h.	
Long X et. Al. (2015)	Co base on Al2O3 support catalyst activity test levulinic acid hydrogenation to γ-valerolactone.	1Co/Al_2O_3 2Co/Al_2O_3 3Co/Al_2O_3 4Co/Al_2O_3 5Co/Al_2O_3 catalysts were prepared by a constant pH co-precipitation method.	Catalyst to FAL ratio = 1:1, FAL or LA (0.2 mmol) Reaction 170 °C, N_2 pressure = 2 MPa, Reaction time = 5 h, 2-propanol volume = 5.0 mL.	LA conversion and >99% GVL selectivity, and would be useful in a large scale biorefinery
Gong W et. Al. (2018)	studied affect property catalyst for conversion furfural and levulinic acid over supported copper catalyst.	10.4%Cu/AC, 17.1%Cu/AC, 22.9%Cu/AC catalysts were prepared by a facile ultrasound-assisted impregnation	Catalyst to FAL ratio = 1:1, FAL or LA (0.2 mmol) Reaction 170 °C, N_2 pressure = 2	

		method	MPa, Reaction time = 5 h, 2-propanol volume = 5.0 mL.	

Jae, J. et al. (2016)[16] studied Sn-Al-Beta zeolites for γ-valerolactone production from furfural by a single-step with suitable acid properties. A Sn-Al-Beta zeolite acid property , which has Lewis acid and Brønsted acid were made by a post-synthesis method and applied to a one-pot conversion of reactant to the main selective product (GVL). Sn-Al-Beta 7 indicate promote 60% yield of major product GVL   because concentration of Brønsted acidity more than of Sn sites. The main production of GVL is by temperature changes at 160-180 and hydrogen donors are solvents of isopropanol or 2-butanol after 1 day.

Zhu, S. et al. (2016)[6] studied the Au/ZrO2 combo ZSM-5 for the furfural activity to γ-valerolactone. The reactants of this reaction are hemicellulose and furfural, and the main product is GVL. It process form with secondary alcohol(IPA) combine catalyst (Au/ZrO2 and ZSM-5). Interaction between Au metal and ZrO2 strong, with well-dispersion of Au nanoparticles, and ZSM-5 showed high quantities of medium-strength acid sites and intersecting channels, which worked synergistically to enhance the activity. Au/ZrO2 Catalyst coupled with ZSM-5 showed improve yield of main production GVL up to 80.4% for reaction time 30 h. The mixed of Au/ZrO2 and ZSM-5 system can be the change hemicellulose into GVL through a two-step process shown overall yield of GVL at 61.5%.

Song, S. et al. (2017)[17] studied catalyst property of mesopore structure catalyst is Zr-Al-Beta for cascade reaction in biomass valorization. Zr-Al-Beta catalyst has both acid site Brønsted and Lewis acid. The proposed physical property good for diffusion of furfural and major products. Meso-Zr-Al-beta(100–77) indicates GVL yield of 95% under 120°C , 24 h. The proper of Brønsted acid sites, Lewis acid sites, and mesopores are important to the success of the multi-functional single zeolite catalyst.

Zhahg, H. et al (2019)[18] use Zr-HY and Al-HY as zeolite catalysts to study the formation of furfural to γ-valerolactone for a one-pot cascade reaction. Zr-HY and Al-HY were used as Lewis and Brønsted acid sites, respectively. This catalyst has the effect of converting a single-furfural to GVL. Furfural and levulinate ester using 2-pentanol as a hydrogen donor for MPV reduction reaction over Zr-HY zeolites. HY-zeolites was purported to the larger pore size and stronger Lewis acidic sites than Zr-Beta catalyst. The excellent activity at 120°C was indicated with an 85% yield of GVL over Zr-HY-15-20 and Al-HY-6 with 2:1 wt ratio after only 5h for the one-pot cascade reaction.

Winopto, H.P. et al.(2019)[1] studied the active catalyst for the one-pot transformation of furfural to γ-valerolactone with hetero polyacid supported on Zr-Beta zeolite.The heteropoly acid (HPA) on Zr-Beta zeolite was prepared by a post-synthesis technique, that consists of the dealumination of Al-Beta, incorporation of Zr into the framework of beta zeolite undergo solid-state ion-exchange and impregnation of the HPA. The one-pot conversion of furfural was tested by HPA/Zr-Beta catalysts to GVL production, they showed higher GVL yields up to compared to Zr-Beta zeolite by the reason of the increased rate of hydrolytic ring-opening reaction encouraged by the BrØnsted acid sites, while the Lewis acid sites promoted the transfer hydrogenation of furfural and levulinic acid(LA) by the intact framework Zr sites in the catalyst. The HPA/Zr-Beta toward the production of GVL 2-3 times greater than Zr-Beta owing to the enhanced hydrolytic ring-opening of the furans stimulated by BrØnsted acidity that was

added in the one-pot cascade conversion of furfural. HPA/ Zr-Beta showed performance for GVL production (〜70mol%) owing to its high thermal stability and stronger BrØnsted acidity. Moreover, its activity far surpasses that of the conventional Sn-Al-Beta zeolite at 160c after 24 h.

Li, W. et al. (2019)[15] studied the bifunctional catalysts, Hf-based metal-organic frameworks, was tested in the one-pot conversion of furfural to γ-valerolactone. They have been successful in producing a novel bifunctional catalyst from heterogeneous catalysts with properties of Brønsted and Lewis acid sites. DUT-67 (Hf) has a mechanism to introduce the Brønsted acid site, which is a modification of zirconium molecule decoration with sulfuric acid in water. The sulfated DUT-67 (Hf) -0.06 property as Lewis acid and Brønsted acid resulting in a 100% furfural conversion and an 84.9% yield of GVL at 180 ° C after 20h. It was confirmed that DUT-67 (Hf) was effective in tandem cascade reactions to produced GVL.

Rao B.S. et al. (2019)[5] studied β-zeolite supported that the existence of zirconia heteropoly tungstate for one-pot selective to γ-valerolactone. Metal oxide and acid series Tungstophosphoric (TPA) is supported by the z-zeolite catalyst prepared by the impregnation method. It has been prepared and evaluated for changing the furfural (FA) selection to important product (GVL) using the hydrogen transfer method. The Bronsted acid from TPA and Lewis acid was essential in the production of by-product and main product. The Zr-T-zeolite showed a 100% furfural conversion including 90% GVL yield after 170 ° C, 10 h.

Hong Je Cho et.al.(2020)[19] studied Pt Nanoparticles(NPs) and acid zeolite for Selective Multistep Tandem Catalysis. Pt@H-ZSM-5 prepared by the PDDA-assisted method for encapsulated Pt NPs. The special sitting of the Al existing of mesopores zeolite that encapsulates Pt metal explains the ion of PDDA and zeolite. This catalyst was active with the multistep tandem conversion of furfural to 86% yield of VA/EV.

Audemar M et. al. (2015)[20] studied cobalt supported SBA-15 catalyst for selective furfural hydrogenation into furfuryl alcohol. The Co/SBA-15 show selective furfuryl alcohol (FOL) from hydrogenated furfural (FAL).The importance of operating conditions such as temperature, pressure and reaction time was considered. The reaction conditions at 150 °C under 2.0 MPa of Hydrogen pressure and 5 wt%Co catalyst loading. It found that 1.5 h of reaction time shows 92% furfural conversion, while increased reaction time to 2 h shown conversion up to 100%.The effect of H2 shown conversion of FAL after 2 h indicated around 81% and selectivity 95% of furfuryl alcohol.

Summary

From the literature review, catalyst used for the conversion of furfural to γ-valerolactone, a cascade reaction requires both Brønsted and Lewis acid sites. Small size platinum metal has advantages of high surface area, stability, and good recyclability, which promotes selectivity to γ -valerolactone from furfural. Cobalt was selected as the non-noble metal that has a positive effect on the selection of valerolactone so that the promotional effect of noble and non-noble metals in the furfural to GVL reaction can be compared. Acidic support is required and ZSM-5 is chosen as an alternative good acidic support for in this reaction.

CHAPTER III

MATERIALS AND METHODS

3.1 Catalyst preparation

3.1.1 Preparation of ZSM-5 supported Co catalyst.

The metal (Pt and Co) supported on H-ZSM-5 were synthesis by incipient wetness impregnation method (IWI). Precursor of metal Pt is Platinum acetylacetonate and cobalt(II) acetate dissolved sovent and dropped on H-ZSM-5 next, precursor were dried in 30 °C for 6 h and dried 110°C 12 houre after that catalysts were calcined in 500°C for 360 min.

Figure 3 Catalyst preparation by incipient wetness impregnation method

Table 3 Chemicals used for catalyst preparation (incipient impregnation method)

Chemicals	Formula	Suppliers
Platinum (II)acetyl-acetonate 99.99%	$Pt(C_5H_7O_2)_2$	Aldrich
Cobalt(ll) Acetate 99.99%	$Co(CH_3COO)_2$	Aldrich
H-ZSM-5 zeolite	H-ZSM-5	Riogen
Xylene 99.8%	C_8H_{10}	Merck
Methanol 98%	CH_3OH	Aldrich

3.2 Catalyst Characterization

3.2.1 X-ray diffraction (XRD)

Equipment for XRD pattern were run by SIEMENS D5000 X-ray diffractometer (Bruker D8 Advance) by Cu Kα irradiation in the 2θ range betwixt 20°-80°. It determine XRD pattern and verage crystallite size .

3.2.2 N_2-physisorption

This apparatus estimate physical properties catalysts such as BET surface area pore size distribution using N^2 physisorption technique on a Micromeritics ASAP 2020 automated system.

3.2.3 Hydrogen Temperature-programmed reduction (H_2-TPR)

The H_2-TPR testing were operatfor reducibility and reduction temperature of catalysts on a Micromeritics Chemisorb 2750 with Chemi Soft TPX software. The catalyst was placed in a U-tube reactor. First, pretreated with an N2 flow (25 cm3/min, 1h, 250ºC). scond, a gas 10%H2/Ar was flow through the U-tube to the sample with a temperature ramp from 30 ºC to 700 ºC rate 10 ºC/min.

3.2.4 NH$_3$ temperature program desorption (NH$_3$-TPD)

Measurements sume total acidity of catalyst by NH$_3$-TPD. Pretreated of catalyst flow at 25 ml/min for Heat at 300 °C,1 h to remove humidity. Next, The TCD signal density was determine from 30 °C to 650 °C for calculated the quantity of desorbed NH$_3$.

3.4 Catalytic performance

Performance of catalysts for one-pot conversion of furfural into γ-valerolactone reaction test with autoclave 100 mL stainless steel reactor (JASCO, Tokyo, Japan) 120 ° C atmospheric for 300 min. Firstly, before using of catalyst have must reduced under H2 (25 mL / min) 500 ° C for 2 hours. Next step, catalyst using 0.2 g, .5 mmol of furfural and 12.7 ml of 2-propanol into an autoclave reactor . The reactor was heated to 120°C and then purged with N2 to remove the air three times After purging, the reactor was pressurized with 1bar of N2 and the reaction was operated at 120°C, 1 bar of N2 for 5 h with a stirring speed of 600 rpm. After stopping the reaction with cooled to down to 20ºC with ice water and carefully depressurized. The quantification of by-product and main-product detect by GC-FID and GC-MS.

Table 4 Chemicals used in the liquid-phase one-pot conversion of furfural into γ-valerolactone.

Chemicals	Formula	Suppliers
Furfural 99%	$C_5H_4O_2$	Aldrich
Furfuryl alcohol 99%	$C_5H_6O_2$	Aldrich
Angelica actone	$C_5H_6O_2$	Aldrich
Levulinic acid	$C_5H_8O_3$	Aldrich
γ-valerolactone	$C_5H_8O_2$	Aldrich
2-propanol	C_3H_8O	Aldrich

Table 5 Gas-Chromatography operating conditions

Gas chromatography (Shimadzu GC-2014)	Conditions
Detector	FID
Packed column	Rtx®5
Carrier gas	Helium (99.99 vol%)
Make-up gas	Air (99.9 vol%)
Column temperature	110 ºC
Injector temperature	260 ºC
Detector temperature	260 ºC
Time analysis	41.80 min

Table 6 Gas-chromatography-mass spectroscopy (GC-MS) operating conditions

Gas chromatography (Shimadzu GC-2014)	Conditions
Detector	FID
Packed column	DB-5
Carrier gas	Helium (99.99 vol%)
Make-up gas	Air (99.9 vol%)
Column temperature	110 °C
Injector temperature	260 °C
Detector temperature	260 °C
Time analysis	41.80 min
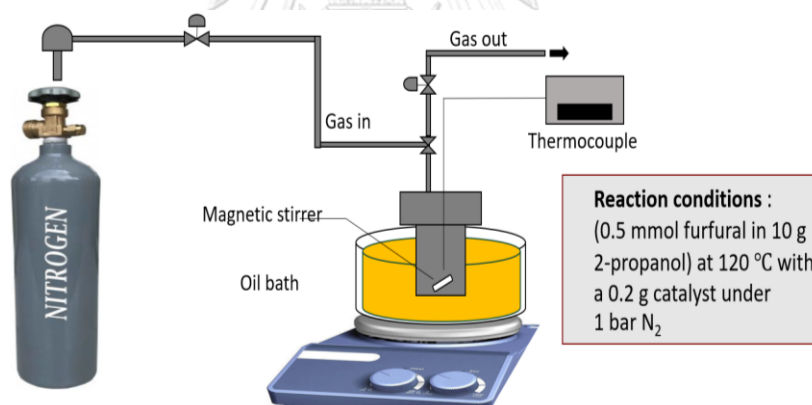
Figure 4 Schematic of the liquid-phase hydrogenation of furfural

CHAPTER IV
RESULTS AND DISCUSSION

This part explains the characteristics and catalytic properties of Co- and Pt-doped ZSM-5. The metal was impregnated on zeolite support catalysts. In the first part, the influence of temperature on the physicochemical and catalytic characteristics of ZSM-5 in the liquid-phase one-pot conversion of furfural to γ -valerolactone is explained in section 4.1. Secondly, the effect of Co-doped ZSM-5 catalysts for liquid phase one-pot conversion of furfural to γ -valerolactone is revealed in section 4.2. And in the final part section 4.3, the effect of Pt-doped ZSM-5 in the liquid phase one-pot conversion of furfural to γ -valerolactone is discussed. The catalyst samples were identified by X-ray diffraction (XRD), N_2 - physisorption, temperature-programmed reduction (H_2 -TPR), Pyridine-IR spectra, NH3-temperature program desorption (NH_3-TPD).

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Part I. The effect of temperature on the physicochemical and properties of ZSM-5 catalyst in liquid phase furfural to γ-valerolactone.

4.1 The performances of ZSM-5 catalyst at several operating temperatures for one-pot conversion of furfural to γ-valerolactone.

Table 7 Reaction results of ZSM-5 with different temperatures

ZSM-5	Conversion	selectivity				yields
		GVL	LA	AL	IPL	GVL
100 °C	51.1	25.3	64.1	6.3	4.3	19.0
120 °C	66.7	53.1	4.0	20.3	22.6	35.4
140 °C	75.1	77.0	4.6	3.2	3.5	39.3

ZSM-5 catalysts were tested in furfural conversion at 100,120, and 140°C. The conversion of furfural at 110 and 120 ° C were 51.1% and 66.7% with 19.0% and 35.4% GVL yield, respectively. The increased reaction temperature to 140 ° C resulted in the conversion to 75.1% with a yield of 53.3% GVL. The yield of the main product (GVL) increased with increasing reaction temperature. Jungho and partners presented a similar result, with the increase in reaction temperature causing the furfural conversion and the yield of GVL to be improved.[21] However, the elevation of temperature to more than 200 °C a drop in main product GVL yield can be observed. The formation of humin by-products led to a decrease in the yield of GVL at relatively high temperature. According to Rao et al [20] a decrease in GVL yield was observed at reaction temperature 200 °C because of the formation of humin by-products In our study, a   moderate

reaction temperature at 120 °C, which showed higher amounts of minor products (Al, IPL). It was decided for further investigation on the effect of catalyst modification by adding Pt or Co in order to convert furfural.

Part II. the effect of Co-doped ZSM-5 catalysts for liquid phase one-pot conversion of furfural into γ-valerolactone.

4.2 The characterization of Co/ZSM-5 catalysts.

      4.2.1 X-ray diffraction (XRD)

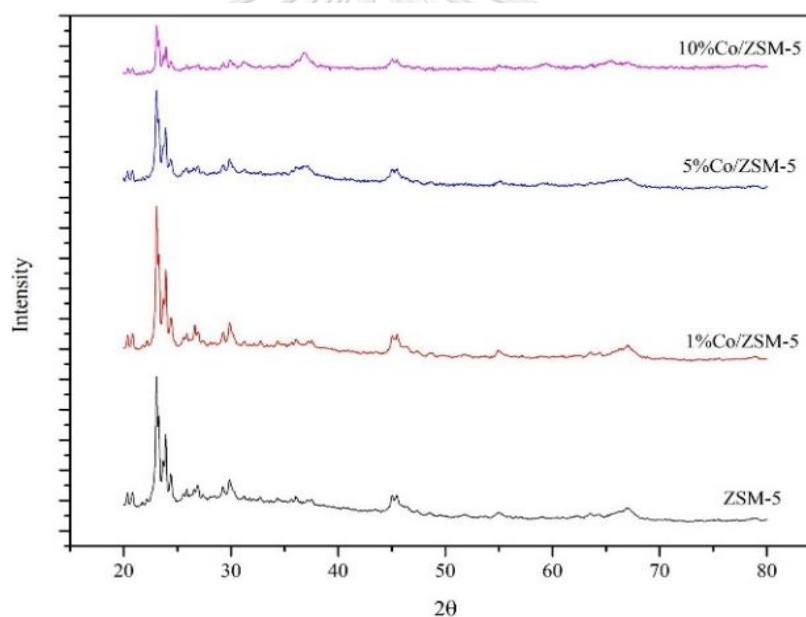**Figure 5** The patterns of the ZSM-5, (1-10) %Co/ZSM-5

      The XRD of catalysts samples were collected in the 2θ range 20°-80° with a scanning speed 0.5 sec/step using a Siemens D500 diffractometer using nickel-filtered Cu K$_\alpha$ radiation. The Scherrer's equation and α-alumina are the external standards for calculation of crystallite size of catalysts. The XRD diffraction of the ZSM-5 and Co/ZSM-

5 zeolite catalysts with phase compositions and average crystallite sizes is shown in Figure 5. The peak of the crystalline phase of ZSM-5 were detected at 2θ =23.1° (major), 23.5° and 23.8°[22]. After Co loading, the patterns showed the disintegration of ZSM-5 structure with the appearance of new angle at 2θ = 21.0˚, 31.8˚, 36.0˚, 38.6˚ and 47.8˚ which were imposing to Co_3O_4. The other peaks at 2θ = 29.3, 42.4˚ and 56.7˚ were the characteristic of cobalt silicate (Co_2SiO_4)[23].

4.2.2 The H_2 -temperature programmed reduction (H2 -TPR)
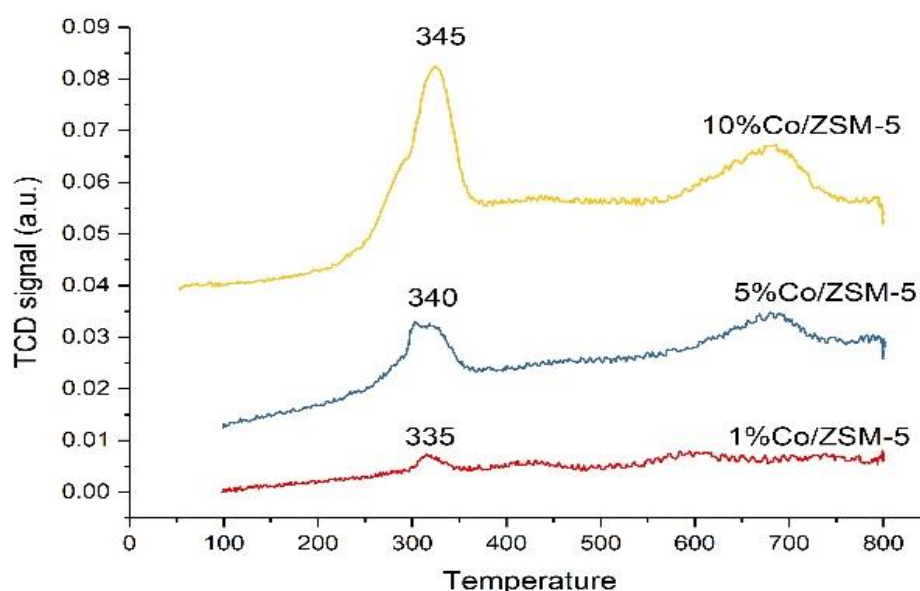
Figure 6 H_2-TPR technique for the (1-10) %Co/ZSM-5

The H_2-Temperature programmed reduction were determined the reduction behavior of Co/ZSM-5 catalyst under the conditions with a temperature ramp to 800 °C from room temperature at heating rate 10°C/min of H_2. The H_2-TPR results also indicated the metal and support interaction on the catalysts. The H_2-TPR profiles of ZSM-5 and Co/ZSM-5 displayed in **Figure 6.** The Co/ZSM-5 catalysts exhibited the two-step reduction of Co_3O_4 to CoO and CoO to metallic cobalt at around 340 °C[24].

4.2.3 N_2 Physisorption

The BET surface area, pore volume and pore diameter of catalyst samples were determined by the N_2 physisorption technique using a Micrometrics ASAP 2020 instrument and the results are shown in **Table 8**. In a number of investigations on Co/ZSM-5 prepared by incipient wetness impregnation, the surface area and pore volume decreased with increasing Co loading. The decrease in BET surface area may occur due to blocking of certain zeolite pores by cobalt.

Table 8 BET surface area, average pore diameter and average pore volume of the catalysts.

Catalysts	BET surface areas(m^2/g)	Average pore size diameter[a] (nm)	Average pore volume[a] (cm^3/g)
ZSM-5	292.0	52.3	0.262
1%Co/ZSM-5	227.0	49.8	0.267
5%Co/ZSM-5	217.0	52.2	0.261
10%Co/ZSM-5	207.0	47.6	0.232

4.2.4 NH_3 temperature program desorption (NH_3-TPD)

The overall acidity of the catalysts was probed by temperature-program desorption of NH_3, the results are shown in **Table 9**. It was found that increasing Co loading led to an increase in total acidity and weak acid but strong acid decreased. Zhu et al. report the similar results that the Co species insertion, the slightly decreasing of strong acid density while the weak acid sites more than ZSM-5. [25]

Table 9 Acidity from NH_3 temperature program desorption (NH_3-TPD)

Catalysts	Total acidity[a] (µmol/g)	Weak	Strong	B/L ratio[b]
ZSM-5	1442.3	858.2	584.1	4.09
1%Co/ZSM-5	1373.2	1107.2	266.0	1.40
5%Co/ZSM-5	1300.7	937.6	363.1	0.90
10%Co/ZSM-5	1463.2	1017.8	445.4	0.93

[a] Determined by NH_3-TPD technique

[b] Determined from pyridine -IR spectra

4.2.5 Pyridine -IR spectra

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. Higher Lewis acid strength correlates with increasing Co loading. The B/L ratio for ZSM-5 was 4.09 while Co loading had a ratio B/L decreasing, indicating different characteristics of the acidic properties. In summary, it can be inferred from pyridine IR studies that ZSM-5 has Brønsted acid more than Lewis acid when Co loaded has the intensity of Brønsted acid decreased or show a Lewis acid higher non-metal.

4.2.6 The catalytic activity of Co/ZSM-5 catalysts with various Co loadings.

Table 10 Reaction results of the Co doped ZSM-5 catalysts with various wt.% of Co .

Catalysts	Conversion	selectivity				yields
		GVL	LA	AL	IPL	GVL
1%Co/ZSM-5	68.0	86.0	3.7	5.7	4.6	58.5
5%Co/ZSM-5	53.4	59.3	22.8	13.9	4.0	31.7
10%Co/ZSM-5	44.6	53.8	27.1	15.7	3.5	24.0

Reaction (0.5 mmol furfural in 10 g methanol) at 120ºC under 1 bars N_2 with a 0.2 g catalyst for 5 h.

The catalytic activity and selectivity of Co (1, 5, 10 wt%) loaded on ZSM-5 were investigated in furfural conversion at 120°C, 1 bar of N_2, and 5 h reaction time. Typically, ZSM-5 contains large amount of Brønsted acid. Co loading on ZSM-5 showed an increase in Lewis acid site and weak acid site. The combination of Lewis acid and Brønsted acid is required for one-pot conversion of furfural to GVL. Co/ZSM-5 with an appropriate qualification can help conversion of the intermediate products (AL, La, and IPL) to GVL. Both furfural conversion, as well as GVL selectivity were markedly increased on the 1%Co/ZSM-5 catalyst, comparing to non-modified ZSM-5. The 1%Co/ZSM-5 catalyst presents the highest conversion and GVL selectivity at 68.0% and 86.0%, respectively. Further increase of Co loading to 10 wt%, both conversion, and selectivity of GVL dropped, due probably to the decrease in BET surface area for high Co loading. The high BET surface area of ZSM-5 may accommodate the diffusion of furfural and GVL. From the catalyst characterization catalysts, week acidic was found to favor the formation of GVL [25].

Part III. The effect of Pt-doped ZSM-5 catalysts for liquid phase one-pot conversion of furfural to γ-valerolactone.

4.3 The characterization of Pt/ZSM-5 catalysts.

4.3.1 X-ray diffraction (XRD)

The patterns of the ZSM-5 and Pt/ZSM-5 catalysts with phase compositions and average crystallite sizes are presented in **Figure 7**. The characteristic peaks of crystalline phase of ZSM-5 are shown at 2θ =23.1° (major), 23.5° and 23.8°. Compared to the H-ZSM-5, the Pt/ZSM-5 exhibited similar diffraction patterns of ZSM-5 but the lower intensity for Pt/ZSM-5. There was no difference in the crystalline patterns of ZSM-5 after Pt was added.
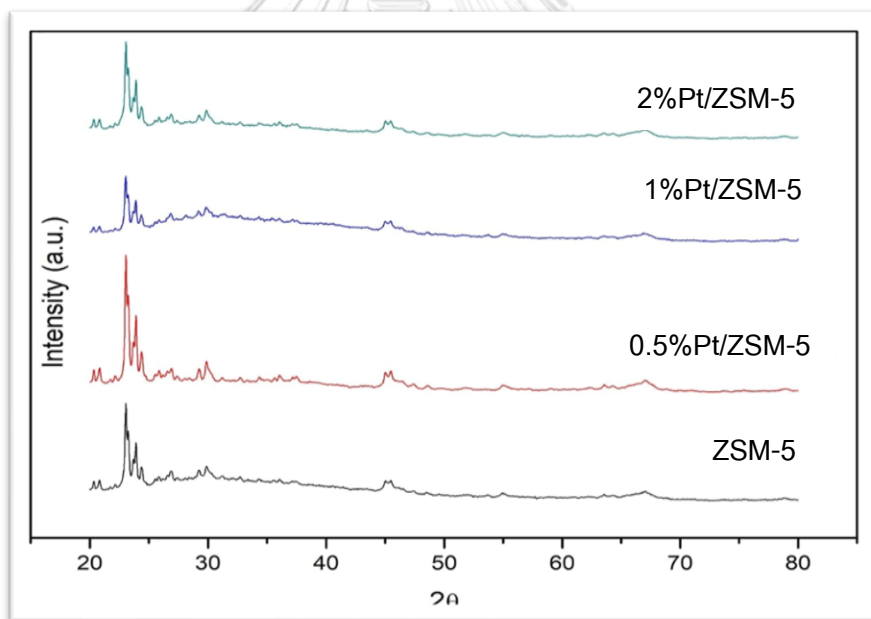

Figure 7 The XRD patterns of the ZSM-5, (1-10) %Co/ZSM-5.

4.3.2 N_2 Physisorption

Table 11 BET surface areas, average pore diameter and pore volume of Pt/ZSM-5

Catalysts	BET surface areas(m^2/g)	Average pore size diameter[a] (nm)	Average pore volume[a] (cm^3/g)
ZSM-5	292.0	52.3	0.27
0.5%Pt/ZSM-5	328.0	41.3	0.339
1%Pt/ZSM-5	320.0	53.4	0.285
2%Pt/ZSM-5	259.0	40.6	0.264

The BET surface area, pore-volume, and pore diameter of catalyst samples were measured by the N_2 physisorption technique with a Micro metrics ASAP 2020 instrument and the results indicated in **Table 11**. The surface area and pore volume of Pt/ZSM-5 catalysts prepared IW-method did not change much with increasing Pt loading. However, some zeolite pores may contain platinum.

4.3.3 NH_3 temperature program desorption (NH_3-TPD)

The overall acidity of the catalyst was probed by NH_3 temperature program desorption (NH_3-TPD) and the results are shown in **Table 12**. It was found that increasing Pt loading led to an increase in total acidity and weak acid while strong acid decreased.

4.3.4 Pyridine -IR spectra

Brønsted and Lewis acidic sites of the catalysts by FT-IR measurement using pyridine. Table 12. summarizes ratio (B/L) of Brønsted to Lewis acids of Pt/ZSM-5 catalysts. When Pt metal was incorporated into the ZSM-5 the B/L ratio of the Pt/ZSM-5 has Lewis acidic sites markedly increased compared to parent ZSM-5.For the B/L ratio appropriate will promote GVL , which shows that Brønsted and Lewis acid sites in close proximity have a synergistic effect in catalyzing this cascade reaction.

Table 12 Acidity from NH_3 temperature program desorption (NH_3-TPD)

Catalysts	Total acidity[a] (μmol/g)	Weak	Strong	B/L ratio[b]
ZSM-5	1442.3	858.2	584.1	4.09
0.5%Pt/ZSM-5	838.17	747.8	90.4	1.04
1%Pt/ZSM-5	1072.7	910.6	162.1	2.56
2%Pt/ZSM-5	1020.67	784.5	236.2	1.45

[a] Determined by NH_3-TPD technique

[b] Determined from FT-IR spectroscopic after desorbing pyridine

4.3.5 The performances of Pt/ZSM-5 catalysts with various Pt loadings.

Table 13 Reaction results of the Pt/ZSM-5 catalysts with various Pt loadings.

Catalysts	Conversion	selectivity				yields
		GVL	LA	AL	IPL	GVL
0.5%Pt/ZSM-5	35.5	59.2	8.7	0	18.7	21.0
1%Pt/ZSM-5	88.8	96.2	0	0	0	85.4
2%Pt/ZSM-5	85.7	82.2	0	0	0	70.2

Reaction (0.5 mmol furfural in 10 g methanol) at 120ºC under 1 bars N_2 with a 0.2 g catalyst for 5 h.

The Pt (0.5, 1, 2 wt%) loaded on ZSM-5 were investigated in furfural conversion at 120°C, 1 bar of N_2, and 5 h reaction time. Both furfural conversion and GVL selectivity were markedly increased on the Pt/ZSM-5 catalyst, comparing to the non-modified ZSM-5. The high BrØnsted acid ZSM-5 catalyst may be necessary for the conversion of FA/FE to AL or LA. The Pt loaded on ZSM-5 indicates an increase in Lewis acid. Pt or Lewis acid site promotes furfural MPV reduction reaction to FA and LA hydrogenation toward GVL.[20, 26] In the one-pot conversion of furfural to GVL a suitable ratio (B/L) on 1%Pt/ZSM-5 catalyst (a B/L ratio 2.56) demonstated the highest conversion and GVL selectivity at 88.8% and 96.2%, respectively. When Pt loading was increased to 2% wt, the BET surface area and BrØnsted acid sites decreased, resulting in lower catalytic activity than 1%Pt loading.

4.3.6 The catalytic performances of Pt/ZSM-5 catalysts with various Pt loadings at longer reaction time.

Table 14 Reaction results of the Pt/ZSM-5 catalysts with various reaction time.

1%Pt/ZSM-5	Conversion	Selectivity				yields
		GVL	LA	AL	IPL	GVL
2 h	46.5	41.2	3.2	0	23.1	19.2
5 h	88.8	96.2	0	0	0	85.4
10 h	95.7	91.7	0	0	0	87.8

Reaction (0.5 mmol furfural in 10 g methanol) at 120ºC under 1 bars N_2 with a 0.2 g catalyst for 5 h.

The reaction affects with time for the furfural conversion, as well as GVL selectivity was investigated. At reaction time of 2 h, furfural conversion (46.5%) was just started towards the selectivity of LA (8.7) and IPL (18.7). After 5 h of reaction, the conversion of reactant was promoted 88.8% with 96.2% yield of GVL. The furfural conversion increased with increasing time and it reached the highest at 10 h of reaction time with 87.8% of GVL yield.
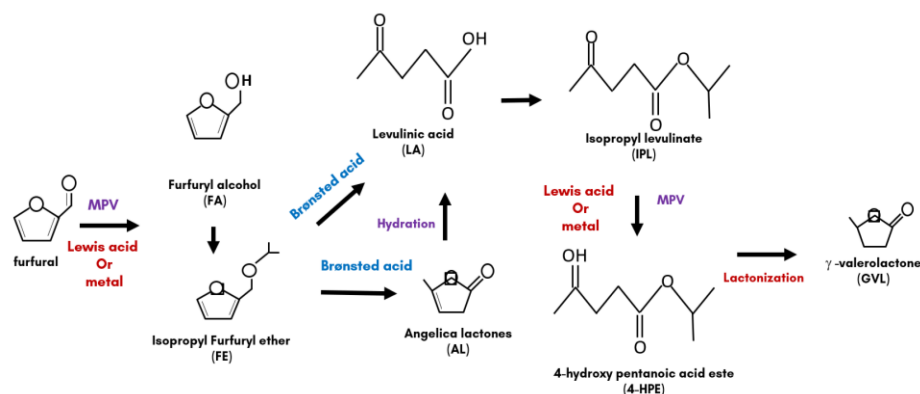
Figure 8 Reaction network for the conversion of furfural to GVL

The one-pot conversion of furfural to γ -valerolactone (GVL) is illustrated in the reaction network proposed in Figure 8. It can be seen that at least three- steps reaction were required to complete the conversion of furfural to GVL, by acid and metal catalyzed reaction (Figure 8.):(1) Lewis acid or metal-catalyzed reaction promoted furfural Meerwein-Ponndorf-Verley (MPV) reduction into furfuryl alcohol (FA). Then, furfuryl alcohol reacts with 2-propanol, which used as a solvent, resulting in furfuryl ether (FE) was form.; (2) Brønsted acid catalyzed hydrolysis and alcoholysis of FA/FE with isopropyl alcohol to LA/IPL or AL; (3) Lewis acid or metal-catalyzed MPV reduction of the Isopropyl levulinate (IPL) to 4-hydroxy pentanoic acid (4-HPE), followed by lactonization to γ -valerolactone (GVL).

CHAPTER V

CONCLUSIONS

5.1 Conclusions

One-pot synthesis of GVL from furfural was studied over H-ZSM-5 and Pt- and Co-modified catalysts. The yield of the main product (GVL) increased with increasing reaction temperature from 100 to 140°C. At a lower reaction temperature of 100 $^{\circ}$C, mostly the reaction reaches the stage of LA formation with small amount of GVL. At the reaction temperature 120 $^{\circ}$C, higher amount of secondary products such as Al, IPL can be converted to GVL especially on the Pt and Co modified H-ZSM-5 catalysts. From the NH$_3$-TPD and the pyridine-IR results, Co- and Pt-loaded on ZSM-5 increased Lewis acid and weak acid which are beneficial for the reaction. Metal-catalyzed pathway facilitated MPV reduction to γ -valerolactone (GVL).1%Pt/ZSM-5 the catalyst presents the highest conversion of 88.8% and GVL selectivity of 96.2% under 120°C, 1 bar of N$_2$, and 5 h reaction time.

5.2 Recommendations

1. The other factors such as H$_2$ pressure, and the weight of catalyst which affects the conversion of furfural to GVL should be further studied.

2. The catalysts may be prepared by other methods in order to obtain different properties of catalysts that affect the conversion of furfural to GVL

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APPENDIX A

CALCULATION FOR CARALYST PREPARATION

For X%Pt/ZSM-5 or X%Co/ZSM-5 catalysts prepared by incipient wetness impregnation method were shown below.

In this work, 1 g of the ZSM-5 supports were used for all preparation and determined based on 100 g of catalysts used.

Reagents: Platinum (II)acetyl-acetonate 99.99%

Cobalt(II) nitrate hexahydrate $(Co(NO_3)_2 \cdot 6H_2O)$, MW = 291.03 g/mol

Xylene 99.8%

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

ZSM-5   100-0.5 = 99.5 g

Platinum or Cobalt   0.5 g

For ZSM-5   1 g

Platinum or Cobalt required   (1 g * 0.5 g)/100 = 0.005 g

ZSM-5   required   1-0.005 = 0.995 g

EXample

Platinum required in precursor $= \dfrac{\text{MW. of Platinum (II)acetyl-acetonate x weight of Platinum required}}{\text{MW. of Platinum}}$

$$= \dfrac{323.29 \times 0.05}{195.078}$$

$$= 0.0101 \text{ g.}$$

APPENDIX B

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye-Scherrer equation

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

From Scherrer equation

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

Where D = Crystallite size, Å

        K = crystallite-shape factor = 0.9

        λ = X-ray wavelength, 1.5418 Å for CuKα

        θ = Observed peak angle, degree

        β = X-ray diffraction broadening, radian

From Warren's formula:

$$\beta = \sqrt{B_m^2 - B_s^2}$$

Where B_M = The measured peak width in radians at half peak height

        B_S = The corresponding width of the standard material

APPENDIX C

CALCULATION FOR CATALYTIC PERFORMANCE

The catalysts performances for the furfural hydrogenation are shown in this below.

$$\%\text{Conversion} = \frac{\text{Mole (in)} - \text{Mole (out)}}{\text{Mole (in)}} \times 100$$

$$\%\text{Selectivity} = \frac{\text{Mole of product}}{\text{Mole of convert reactant}} \times 100$$

$$\%\text{Yield} = \text{conversion} \times \text{selectivity}$$

Example:

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

$$\%\text{Furfuryl alcohol selectivity} = \frac{\text{Mole of furfuryl alcohol}}{\text{Mole of converted furfural}} \times 100$$

$$\%\text{ Furfuryl alcohol Yield} = \text{Furfural conversion} \times \text{Furfuryl alcohol selectivity}$$

The calibration curves of furfural, furfuryl alcohol, and tetrahydrofurfuryl alcohol are shown in Figure C1, Figure C2, and Figure C3, respectively.
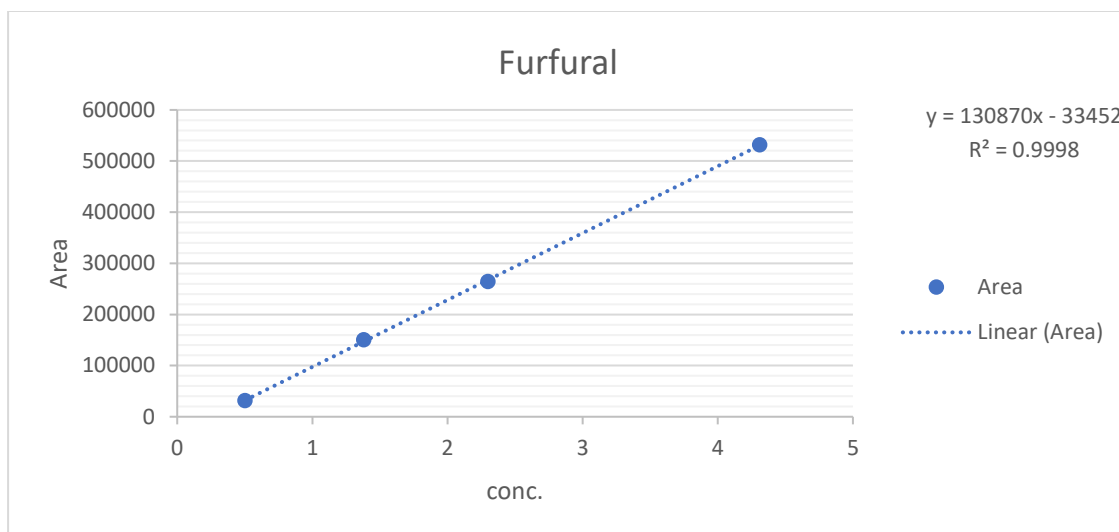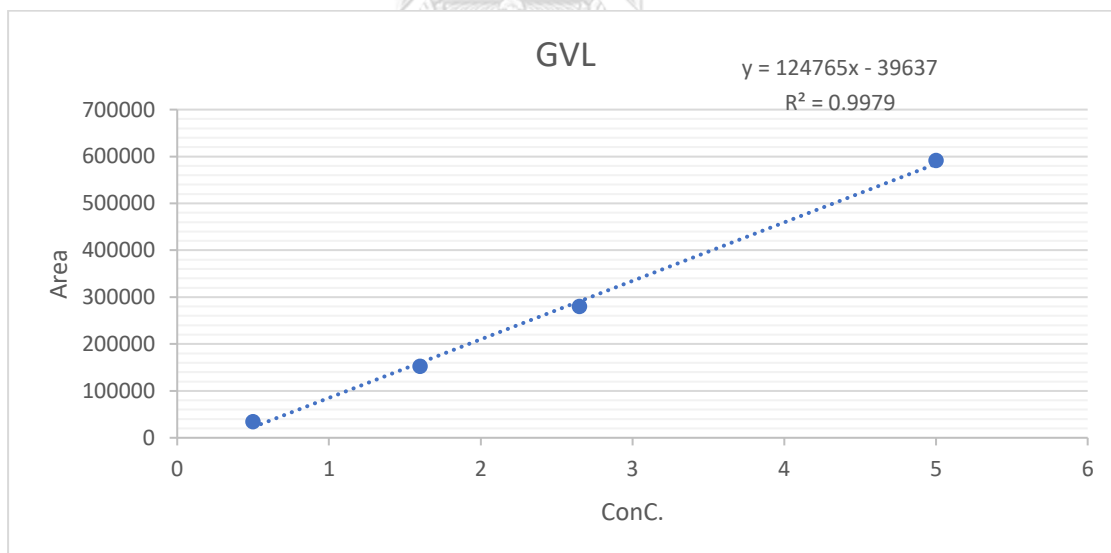

Figure 9 The calibration curve of furfural

Figure 10 The calibration curve of GVL
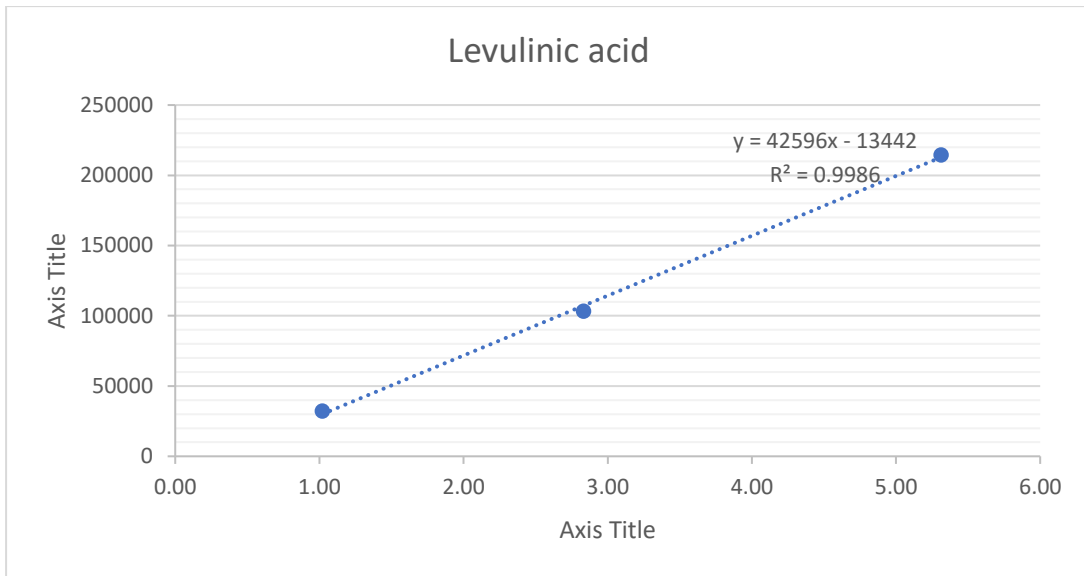
Figure 11 The calibration curve of Levulinic acid
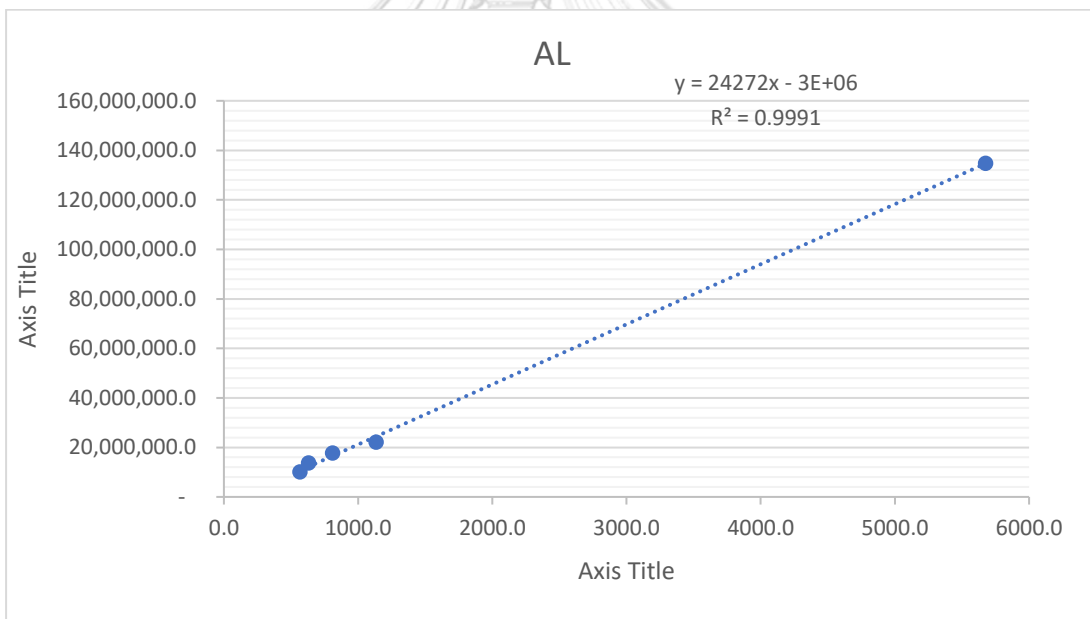

Figure 12 The calibration curve of Levulinic acid AL

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