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Doctoral Dissertation

**Syntheses of Levulinic Acid and γ -Valerolactone
from Biomass-derived Compounds Using
Heterogeneous Catalysts**

PHAM ANH SON

Supervisor: Professor Doctor Kohki Ebitani

School of Materials Science

Japan Advanced Institute of Science and Technology

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Referee-in-chef: **Professor Dr. Kohki Ebitani**
Japan Advanced Institute of Science and Technology

Referee: **Professor Dr. Masayuki Yamaguchi**
Japan Advanced Institute of Science and Technology

Professor Dr. Noriyoshi Matsumi
Japan Advanced Institute of Science and Technology

Associate Professor Dr. Kazuaki Matsumura
Japan Advanced Institute of Science and Technology

Professor Dr. Hisao Yoshida
Kyoto University

Preface

The present dissertation is a collection of the author's studies which have been carried out under the direction of Professor Dr. Kohki Ebitani during 2010-2013 at the School of Materials Science, Japan Advanced Institute of Science and Technology.

The depletion of fossil resource reserves and the degradation of the environment stimulate the search for sustainable and renewable resources. The main purpose of this dissertation is the study on transformation of biomass-derived compounds to levulinic acid using heterogeneous catalysts as well as upgrading of levulinic acid to γ -valerolactone over various supported metal catalysts using formic acid as the hydrogen donor source. Levulinic acid and γ -valerolactone have been identified as platform molecules for the synthesis of various organic chemicals for production of polymers, fuels, additives, organic solvent, *etc.*

The first chapter is a general introduction according to the objective of this research. Chapter 2 presents the utilization of solid acid catalysts for acid-catalyzed syntheses of levulinic acid from carbohydrate-related compounds. In Chapter 3, the preparation of zirconium carbonate as solid base catalyst for glucose-fructose isomerization and one-pot production (in combination with a solid acid catalyst) of levulinic acid will be introduced. Chapter 4 describes the synthesis of γ -valerolactone from catalytic upgrading of levulinic acid or direct transformation of C6-sugars using supported metal catalysts and formic acid as hydrogen donor source. The last chapter, Chapter 5, summarizes the conclusive items of this dissertation.

Pham Anh Son

Ebitani Laboratory,
School of Materials Science,
Japan Advanced Institute of Science and Technology

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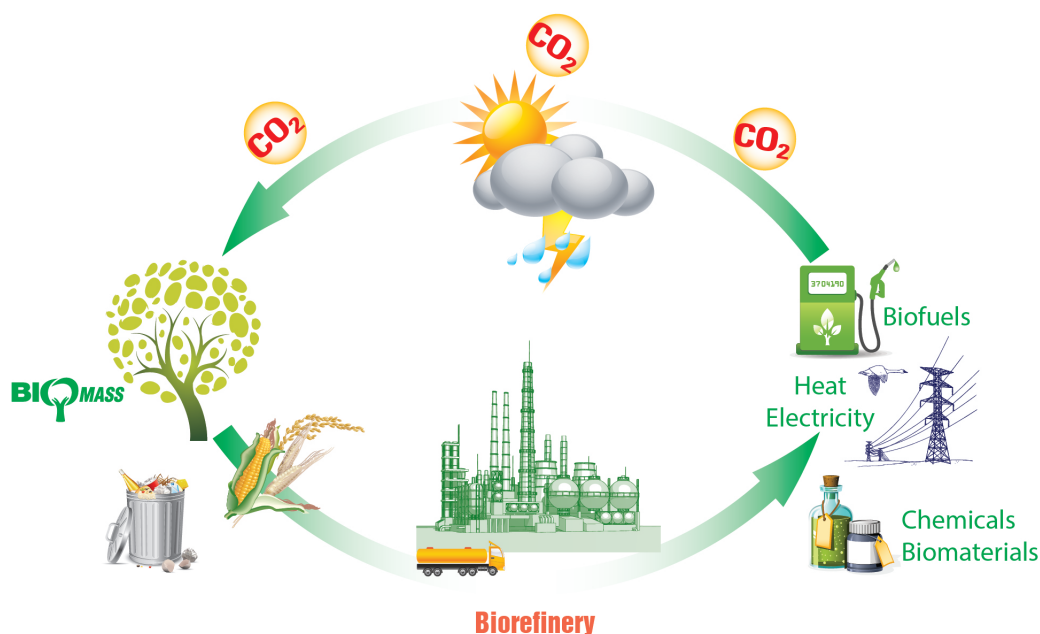
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Chapter 1

General Introduction

Abstract



In this chapter, a general overview of biomass and its transformations into value-added chemicals and fuels will be provided. General introduction about heterogeneous catalyst for catalytic upgrading of biomass-derived compounds is also presented. Subsequently, the production and application of levulinic acid (LA), γ -valerolactone (GVL) and their derivatives are reviewed. It will show that LA and GVL are important and interesting platform chemicals for synthesis of various organic compounds. The objectives and the outline of this thesis is presented at the end of this chapter.

1.1 Biomass: definitions, composition and sources

The term “Biomass” is defined as any renewable organic material derived from living, or recently living organisms (plant, animal and microorganism) such as wood, agricultural crops or residues, animal products or wastes and all microorganic matters [1]. Nature produces about 1.7×10^{11} tonnes biomass each year and 75% of which can be assigned to the class of carbohydrates. But only 3-4% of these compounds are used by human for food or non-food purposes [2]. In the context of biomass for energy, this term is usually used to refer to plant-based material [3].

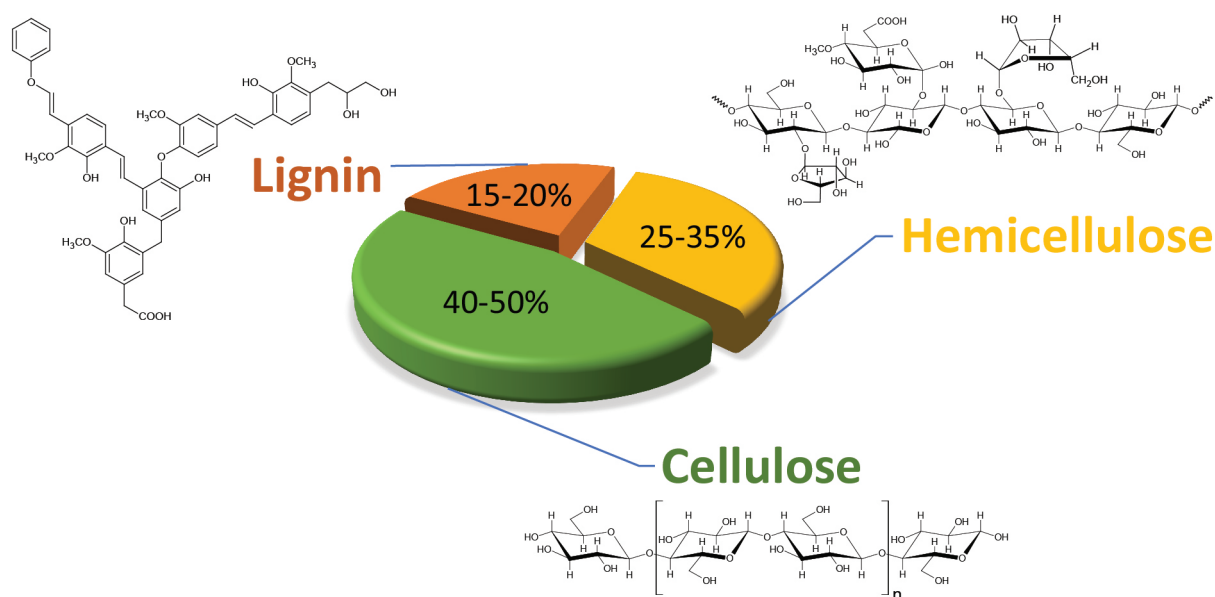


Figure 1.1: Lignocellulose composition: cellulose, hemicellulose and lignin

Plant biomass is generated from a process called photosynthesis in which the energy from the sun converts carbon dioxide and water to carbohydrates and oxygen. The primary products formed are C6-sugars (mainly glucose, mannose and galactose) and C5-sugars (mainly arabinose and xylose) that form cellulose, hemicellulose and lignin. These three components are the main constituents of lignocellulosic materials. The content of each component depends strongly on the source. Generally, lignocellulose consists of 40-50% cellulose, 25-35% hemicellulose and 15-20% lignin (Figure 1.1) [1, 4].

Cellulose, the most abundant biopolymer synthesized by nature, is a linear polymer of glucose linked *via* β -1,4-glycosidic bonds and is usually arranged in microcrystalline structures, which is very difficult to be dissolved or hydrolyzed under natural conditions. The degree of polymerization of cellulose chains is in the range from 500 to 25000. Hemicellulose is a heteropolysaccharide composed of different hexoses, pentoses, and glucuronic acid. Hemicellulose is more soluble than cellulose and is frequently branched with *ca.* 100 to 200 monomers. In this material, the functionalities are not as well protected by the crystalline structure as in cellulose. These make hemicellulose easy to be hydrolyzed by acids, bases or enzymes [5]. The third component, lignin, is a highly irregular and insoluble cross-linked polymer built of substituted phenols. Lignin also has the potential to be converted into fuels and high valuable chemicals, but the complexity of its structure and non-uniformity of its composition makes it more difficult to process than the other fractions. Lignin, together with cellulose and hemicellulose, gives strength to plants [6]. Besides those components, plant is also able to elaborate energy storage products such as lipids, sugars, and starches as well as other products relatively rich in hydrogen and carbon (terpenes) found in essential oils that are components of resins, steroids and rubber [5, 7].

1.2 Biomass for bio-fuel and chemical production

The increasing industrialization and motorization of the world has led to a steep rise for the demand of fossil fuels (petroleum, natural gas and coal) [8]. The world energy consumption by fuel is shown in Figure 1.2. Today, fossil fuels take up 84% of the primary energy consumed in the world and 54% of which is consumed by the transport sector [8]. In addition, almost modern products such as polymers, resins, lubricants, fertilizers, textiles, *etc.* are also derived from fossil fuels.

However, the worldwide supply of fossil fuel is drastically depleting and becoming

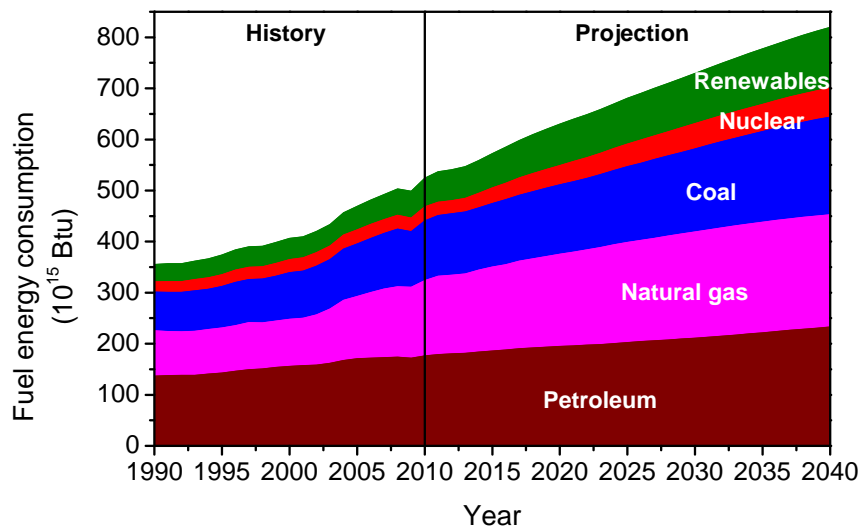
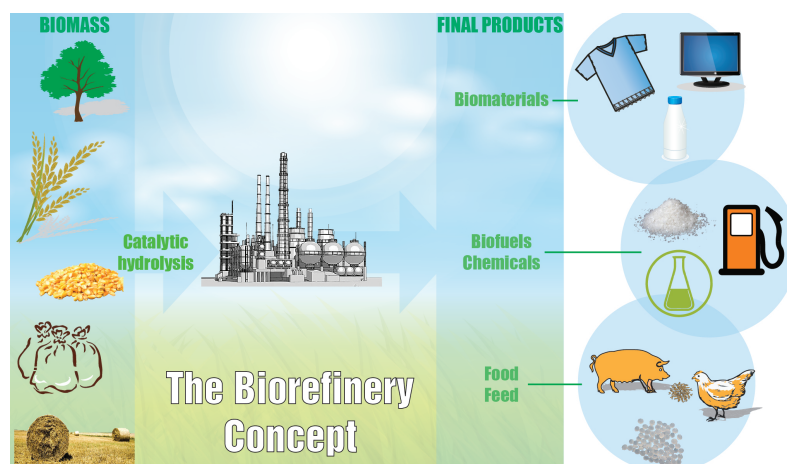


Figure 1.2: World energy consumption by fuel from 1990 to 2040 (taken from [8])

more expensive. Furthermore, the combustion of fossil fuels and its derivatives for the industrial and human activities causes the increase in greenhouse gas levels [9].

Sustainable economic growth requires environment-friendly and renewable resources for the industrial production to replace the fossil carbon resources that are depleting rapidly. Among many energy alternatives (biomass, solar power, wind power, geothermal energy, *etc.*), biomass is a prime candidate for the fossil resource. Biomass is an essentially potential resource for production of biofuels [10–14] as well as many products based on biomass resource [7, 14–17].

The research and development activities of biomass utilization for the production of non-food products in many countries in the world lead to the generation of a novel concept: “Biorefinery” [18]. The biorefin-



ery concept is analogous to today’s petroleum refineries, which produce multiple fuels and products from petroleum.

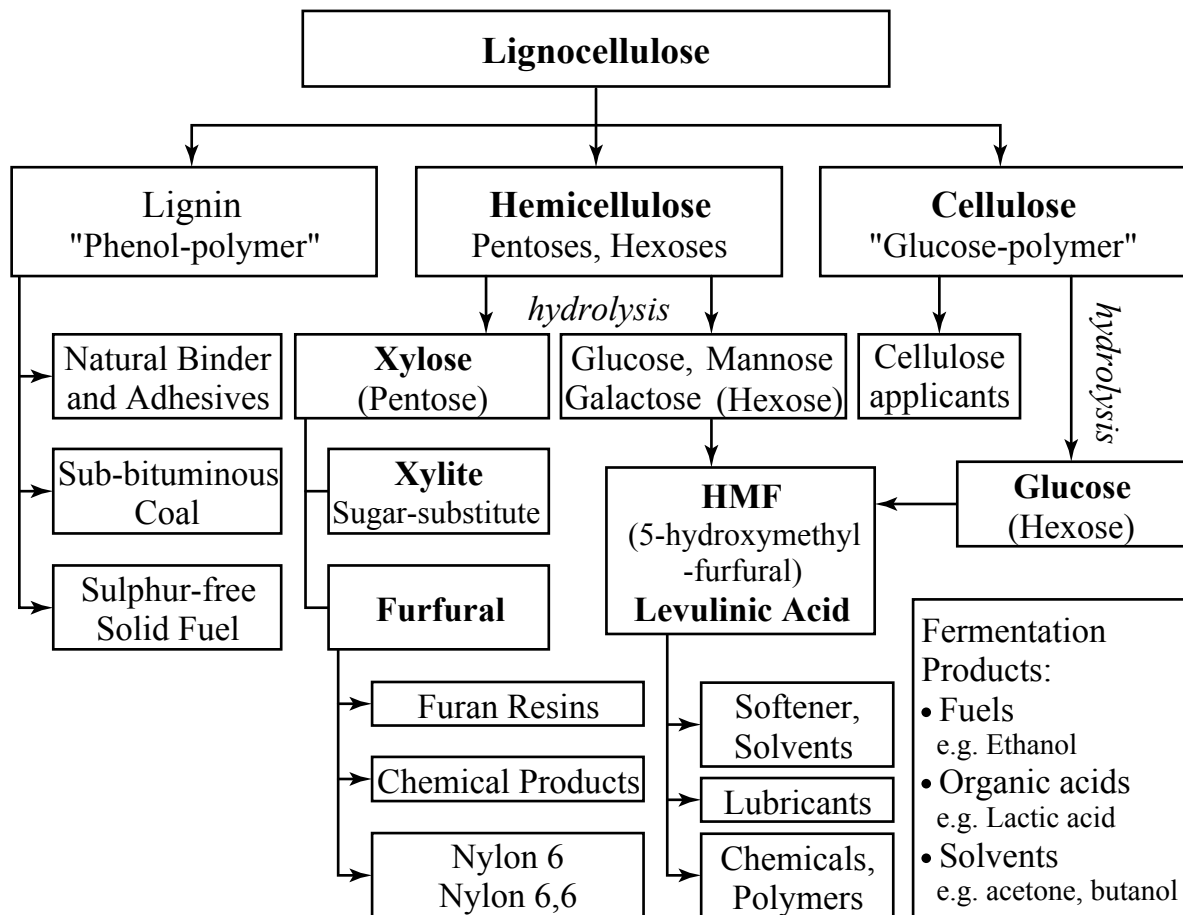


Figure 1.3: An overview of the potential products of a lignocellulose biorefinery (taken from [18])

According to the American National Renewable Energy Laboratory (NREL), a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass [19].

As shown in Section 1.1 (p. 2), biomass term usually refers to plant-based materials whose main component is lignocellulose (a composite of cellulose, hemicellulose and lignin). Lignocellulose is one of the most available and sustainable feedstock for the biorefineries. Unlike starch, hydrolysis of lignocellulose by enzymes is not effectively. Therefore, before enzymatic processes, lignocellulose should be pre-treated by thermal, thermo-mechanical or thermo-chemical step to break up its extremely stable structure. However, lignocellulose are still potential feedstock for large-scale industrial biorefiner-

ies.

An overview of the potential products of a lignocellulose-feedstock-biorefinery is shown in Figure 1.3. In this pathway, furfural, 5-hydroxymethylfurfural and levulinic acid are the most interesting products. They are used as building blocks for producing various bio-fuels and chemicals [20–27].

1.3 Heterogeneous catalyst for biomass transformation

As highlighted above (Section 1.1, p. 2), plant captures about 1% of the incoming solar radiation into biomass [28] and stores this energy in complex compounds such as carbohydrates, lignins, proteins, glycerides and others [29]. However, direct extraction of this resource to obtain fuels or chemicals is not easy. Generally, the reduced formula of carbohydrates is $C_x(H_2O)_y$, in which x and y are almost equal. The O/C mole ratio of such compounds is much higher than that of nature gas, coal or crude oil. Therefore, the direct utilization of biomass for energy is less efficient because the combustion of compounds possessing higher O/C mole ratio liberates less energy [30–32].

Beside O/C mole ratio, H/C ratio is also an important index. Burning the materials having higher H/C mole ratio not only gives more energy, but also decreases the released amount of CO_2 .

Because of above reasons, an efficient strategy to decrease the oxygen content of biomass is necessary. The transformation of biomass to compounds with lower O/C and higher H/C mole ratios can be easily achieved by catalytic processes, such as dehydration, deoxygenation (for reducing O/C mole ratio), hydrogenation (for rising H/C mole ratio), *etc.*

In the chemical industry and the industrial research, catalysts play an extremely important role. Indeed, most chemical processes utilize catalysts and the various catalysts are in constant development to fulfill demands of chemical and fuel production. Gen-

erally, solids, molecules or enzymes can be used as catalysts. The use of homogeneous catalysts has some advantages. Firstly, the excellent dissolubility of homogeneous catalysts make them easily interact with the dispersed solid biomass in the reaction medium. Secondly, these catalysts are very selective and require milder reaction conditions. However, solid catalysts are the preferred option for most processes and dominate the chemical industry (80-85% of catalytic processes in chemical industry use solid catalysts) [5, 33].

The main reason make heterogeneous catalysts to be preferably employed in industry than homogeneous catalysts and enzymes is the easy separation and recovery of catalysts after the reaction. The separation processes occupy more than one half of the total equipments and consume huge amount of energy. Therefore, the utilization of solid catalysts promises to reduce the production cost and energy consumption [34].

The mission of transformation of biomass to liquid fuels are reducing O/C mole ratio and increasing H/C mole ratio as much as possible. This work can be done by three type of reactions: dehydration, hydrogenolysis, and hydrogenation. The hydrogenation and hydrogenolysis are usually catalyzed by acid-base catalysts, while most hydrogenation reaction requires supported-metal catalyst. In the primary step, the hydrolysis of lignocellulose also needs the presence of acid catalyst. This step does not change significantly the O/C and H/C ratios but creates smaller molecules for subsequent transformations that decrease O/C ratio.

In the chemical chemistry, reaction catalyzed by metal oxides and zeolites, respectively, represent *ca.* 30% and 40% of total acid-catalyzed processes [35]. However, zeolites are not suitable for lignocellulose conversion because of the restrain of their narrow pore size (< 2 nm [36]). Thus, the fabrication and application of solid acid catalysts for hydrolysis of lignocellulose, dehydration and hydrogenolysis of its derivatives still attracts many researches.

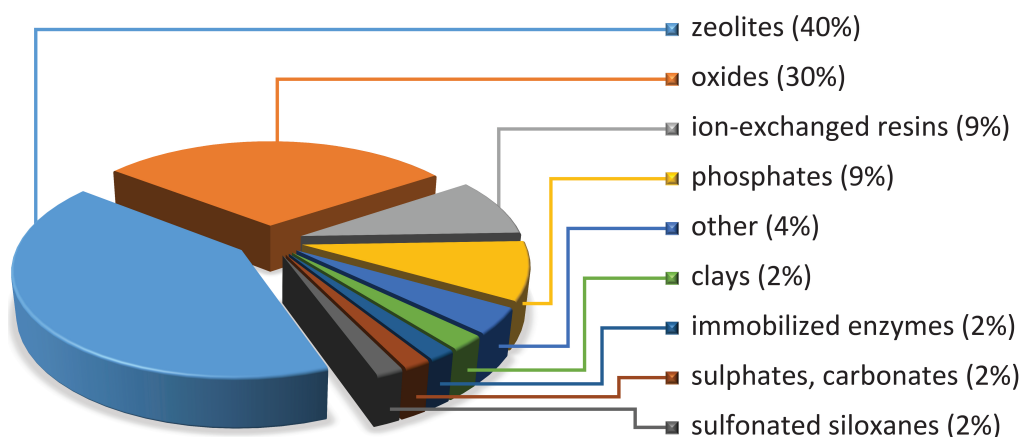


Figure 1.4: Solid acid catalysts used in chemical industry (data was taken from [35])

Metal and supported metal catalysts are also important materials that are employed in a numerous of transformation of biomass-derived compounds, especially, hydrogenation reaction. The challenge in this field is the to find catalysts that can resist against the aggressive reaction media, harsh reaction conditions and poisoning often found in the biomass processing [5, 37]. Metal leaching is another problem that have to be regarded because it not only causes the decrease in lifetime of catalyst, but also contaminates the final products.

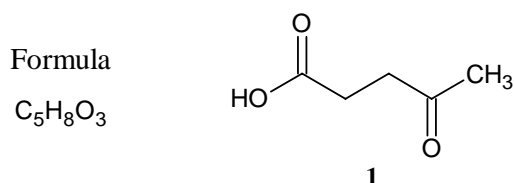
1.4 Introduction to levulinic acid and γ -valerolactone

1.4.1 Introduction to levulinic acid

The researchers of PNNL (Pacific Northwest National Laboratory) and NREL (National Renewable Energy Laboratory) carried out to screen over 300 possible building block chemicals to select a smaller group comprising 30 best substances [38]. Finally, the list was reduced to 12 building block chemicals that can be produced from sugars *via* biological or chemical transformations. The twelve building blocks can be subsequently converted to number of high-value bio-based chemicals or materials. One of these promising top-twelve building blocks is levulinic acid.

Levulinic acid is a low-molecular-weight fatty acid having two important functional

Table 1.1: Physical properties of LA



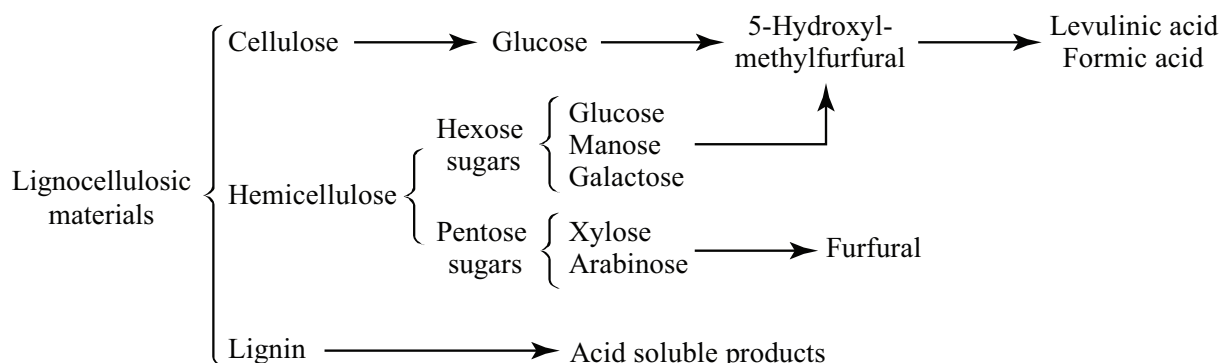
Physical property	Value
Molecular weight	116.11 g mol ⁻¹
p <i>K</i> _a (25 °C)	4.59
Melting point	37 °C
Boiling point	246 °C
Density (25 °C)	1.1447 g mL ⁻¹
Refractive index (25 °C)	1.1441
Surface tension (25 °C)	39.7 dyne cm ⁻¹
Heat of vaporization (150 °C)	0.58 kJ mol ⁻¹
Heat of fusion	79.8 J mol ⁻¹

groups: a ketone carbonyl group (CO) and a carboxyl group (COOH). LA is readily soluble in water, ethanol, diethyl ether, acetone and many other organic solvents. In water, LA is fairly well dissociated, its p*K*_a (25 °C) is 4.59. In other words, the acidity of LA is comparable with that of the majority of lower alkane carboxylic acids. Some selected physical properties of LA [39] are listed in Table 1.1.

1.4.2 Levulinic acid production

LA can be obtained from treatment of 6-carbon sugar carbohydrates (composition of starch or lignocellulose) with acid. The transformation of a lignocellulosic materials to LA is shown in Scheme 1.1.

LA was prepared the first time in 1840s by heating sucrose with HCl at high temperature [40] [Note: the details on the reaction conditions and LA yield are unknown].



Scheme 1.1: Pathway for conversion of lignocellulose into levulinic acid

Although this pathway was discovered long time ago, the degradation of biomass by acids is still the most widely method to prepare LA. Normally, the LA yields do not excess 70 mol% due to the formation of undesired black insoluble-materials known as humins. Another possible by-product of biomass hydrolysis is furfural formed by the decomposition reactions of C5-sugars.

Table 1.2: Literature review of acid-catalyzed production of LA from derived-biomass compounds

Substrate	C_o (wt%)	Catalyst	C_{acid} (wt%)	T (°C)	t (h)	LA yield (mol%) ^a	Ref.
Glucose	32	HCl	20	110	24	21	[41]
Corn starch	29	HCl	6.5	162	1	36	[42]
Fructose	29	HCl	6.5	162	1	35	[42]
Glucose	29	HCl	6.5	162	1	34	[42]
Sucrose	29	HCl	6.5	162	1	41	[42]
Cane sugar	28	HCl	18	100	24	23	[43]
Corn starch	33	HCl	1.8	200	0.5	49	[44]
Sucrose	6	H ₂ SO ₄	9	125	16	42	[45]
Sucrose	6	HCl	97	125	16	60	[45]
Sucrose	6	HBr	9	125	16	70	[45]
Glucose	20	H ₂ SO ₄	4	200	10	54	[46]
Glucose	10	HCl	6	160	0.25	64	[47]
Sucrose	29	Resin-Dowex	6.25	100	24	26	[48]
Fructose	18	HCl	7	100	24	70	[49]

Table 1.2 (continued from previous page)

Substrate	C_o (wt%)	Catalyst	C_{acid} (wt%)	T (°C)	t (h)	LA yield (mol%) ^a	Ref.
Fructose	50	LZY-zeolite	50	140	15	67	[50]
Glucose	12	Metal@clay	3	150	24	19	[51]
Glucose	12	HY-zeolite	3	150	24	9	[52]
Apen wood	10	H ₂ SO ₄	15	250	7	21	[53]
Apen wood	10	HBr	15	250	7	17	[53]
Apen wood	10	HCl	15	250	7	18	[53]
Cellulose	10	H ₂ SO ₄	15	250	7	35	[53]
Cellulose	10	HBr	15	250	7	39	[53]
Cellulose	10	HCl	15	250	7	36	[53]
Cellulose	10	H ₂ SO ₄	3	250	2	35	[54]
Wood	20	H ₂ SO ₄	5	250	4	21	[54]
Sorghum grain	10	H ₂ SO ₄	8	200	0.67	33	[55]
Glucose	2.2	HCl	3	100	0.5	35	[56]
Sucrose	2.2	HCl	3	100	0.5	50	[56]
Extruded starch	25	H ₂ SO ₄	4	200	0.67	47	[57]
Starch	25	H ₂ SO ₄	4	200	0.67	48	[57]
Wheat straw	6.4	H ₂ SO ₄	3.5	210	0.63	27	[58]
Bagasse	4	HCl	4.5	220	0.75	23	[59]
Paddy straw	4	HCl	4.5	220	0.75	24	[59]
Glucose	1	MFI-zeolite	0.8	180	8	36	[60]
Cellulose	2	SPAO ^b	2	165	5	8	[61]
Starch	2	SPAO ^b	2	165	5	31	[61]
Cellulose	6	SAC13+25%NaCl	3	200	120	72	[62]
Glucose	5	SO ₄ ²⁻ /ZrO ₂	2.5	200	3	30	[63]
Cellulose	2.4	HCl	3.3	180	0.83	60	[64]
Glucose	10	ZrP ^c	3	160	4	15	[65]
Glucose	10	Amberlyst 70	3	160	4	28	[65]
Cellulose	2	Nafion SAC-13	6.7	160	16	6	[66]
Cellulose	2	Propylsulfonic	6.7	160	16	53	[66]
Cellulose	2	Tosic	6.7	160	16	55	[66]
Cellulose	2	ZSM-5	6.7	160	16	2	[66]

^a LA yield was calculated base on C6 sugar amount

^b SPAO: Sulfonated Polyarylene oxindole

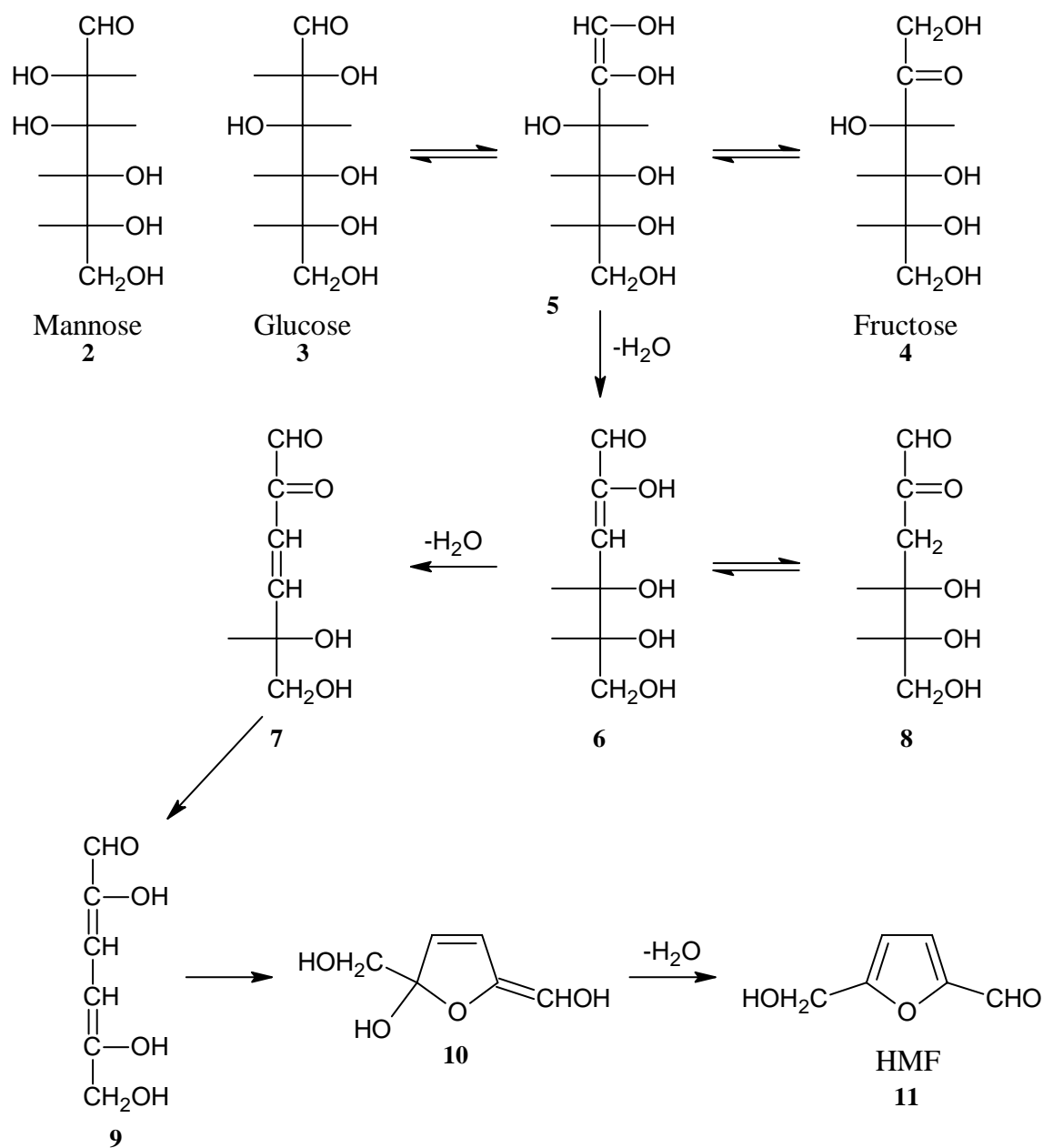
^c ZrP: Zirconium phosphate

The performance of LA production depends on the starting materials, type of catalyst, temperature, pressure as well as concentration of reaction mixture. Usually, mineral acids such HCl and H₂SO₄ are utilized as homogeneous acid catalyst for hydrolysis and dehydration of saccharides to result LA. The production of LA from various starting materials and acid catalysts is shown in Table 1.2.

LA is also synthesis from different types of substances [67]. For instance, LA can be produced by acid-catalyzed hydrolysis of furfuryl alcohol [68–71], hydrolysis of acetyl succinate esters [72], oxidation of ketones [73, 74], carbonylation of ketones over Pd catalyst [75], alkylation of nitroalkanes [76]. However, these methods frequently generate large amount of side products or require expensive starting materials.

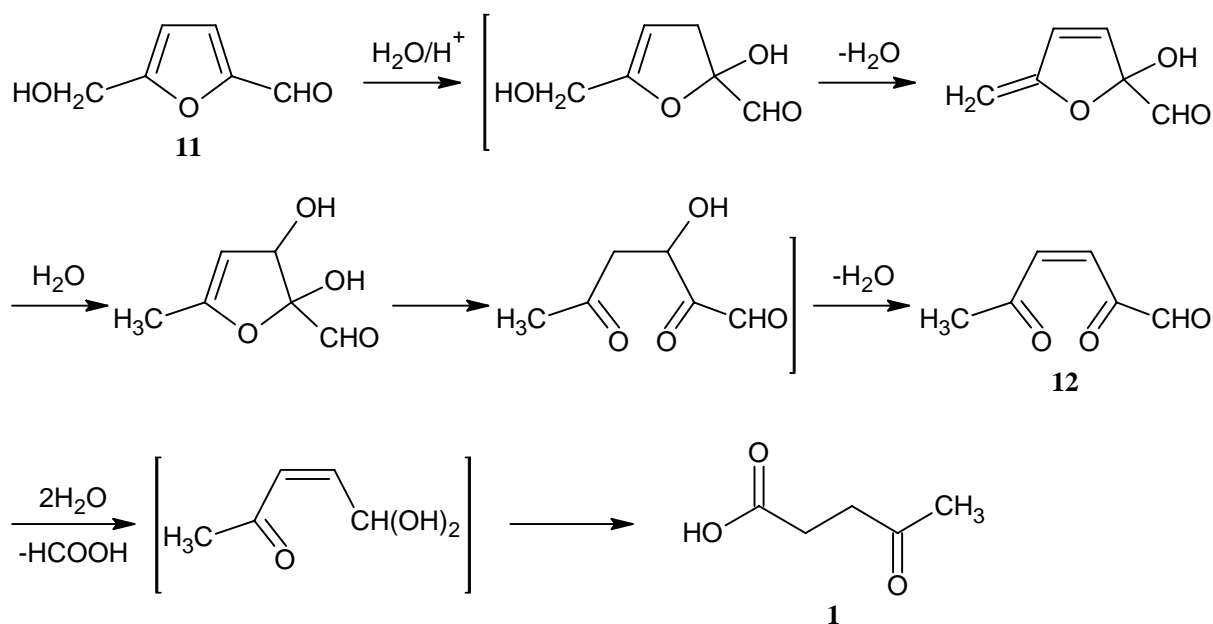
It can be realized that, up to now, most researches have been focused on the utilization of mineral acid (H₂SO₄, HCl, HBr, *etc.*). There have been few studies concerning the utilization of heterogeneous catalysts for upgrading of biomass-derived compounds to LA. The use of solid acid catalysts in these researches usually gave low yield or needed long time to achieve a moderate LA yield. Therefore, the development of one-step acid-catalyzed dehydration of lignocellulosic materials or sugars to LA still attracts many researcher. The aims are increasing the selectivity, reducing the side reactions and developing new solid acid catalysts to replace liquid catalyst or improving existing catalyst based systems.

Concerning with the formation mechanism of LA from biomass (comprise mainly cellulose, hemicellulose or starch), many studies have been reported. Firstly, biomass is undergone the acid-catalyzed process affording sugars (mainly consist of glucose and fructose). Consequently, the transformation of hexose sugars is usually considered as a combination of dehydration process resulting in the formation of 5-hydroxymethylfurfural (HMF) and subsequent hydration of HMF affording LA. The formation of HMF takes place through a series of reactions [77–79].



Scheme 1.2: HMF formation from dehydration of hexose sugars

The enediol compound **5**, that formed from enolization of D-mannose (**2**), D-glucose (**3**) and D-fructose (**4**) in acidic media, is the key intermediate in the formation of HMF (**11**). Dehydration of enediol **5** affords compound **6** that is dehydrated to yield **7**. The later is readily converted into dienediol **9** which results in HMF *via* intermediate cyclic compound **10**. In this reaction, large amount of humin compounds are formed as the undesired products [78].

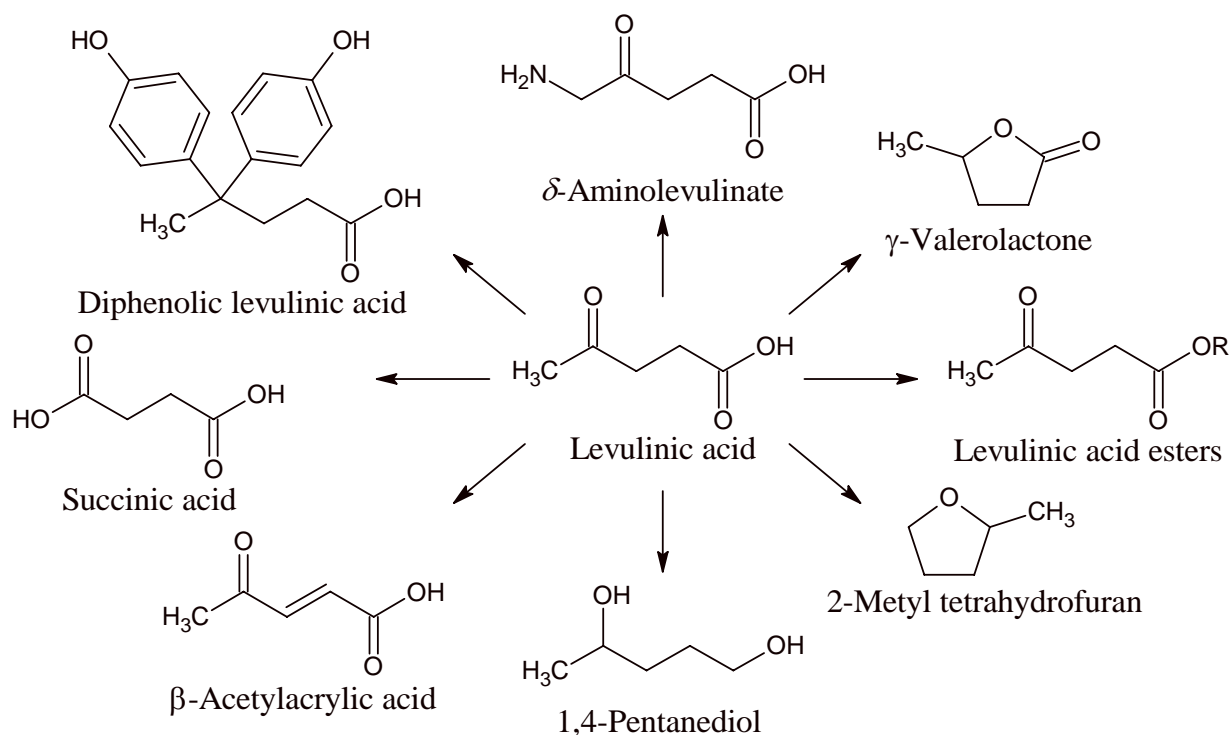


Scheme 1.3: The formation of LA from hydration of HMF

LA is obtained from the hydration of HMF according to the mechanism proposed by Horvat *et al.* [80] that is shown in Scheme 1.3. The conversion of HMF into LA is a result of addition of a molecule of H_2O to the C2-C3 double bond in the furan ring, leading to ring-opening with formation of an unstable tricarbonyl intermediate **12** that decomposes into final products (levulinic acid and formic acid). Humins compounds are also side products in this reaction.

1.4.3 Primary transformation of levulinic acid to derivatives

Possessing highly active functional groups, LA is used as a starting material for preparation of many chemical compounds. LA has been used to produce various heterocyclic compounds, saturated and unsaturated ketones and diketones, organic acid, alcohols, and so on. The applications of LA and its derivatives have been reviewed intensively [7, 38, 39, 67, 81]. Some transformations involving the carboxylic, carbonyl, methyl groups as well as oxidation and reduction reactions are briefly summarized below.



Scheme 1.4: Derivatives of levulinic acid

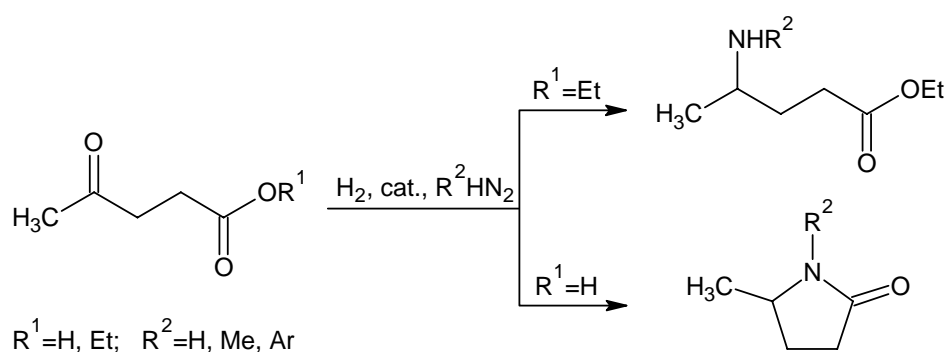
1.4.3.1 Reactions involving the carboxylic group

One of the most reaction concerning with carboxylic group is esterification which yields useful levulinates. The reaction of LA with primary alcohols is a first-order reaction with both of reactants [82] and can even occurs at room temperature [83]. The high yield of levulinate esters are usually obtained when reaction is carried out in the presence of an acid, for example sulfuric acid, polyphosphoric acid, *p*-toluenesulfonic acid or ion-exchanged resin [84, 85].

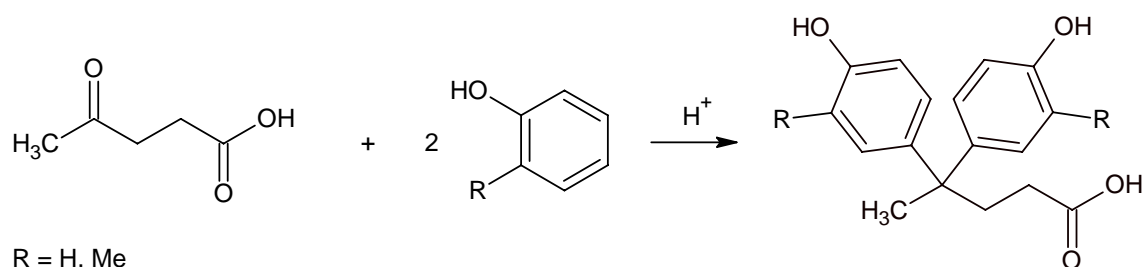
Esters of levulinic acid are important compounds which are used for flavoring, solvents, and plasticizers [86–88]. Moreover, these ketoesters are substrates for a variety of condensation and addition reactions at the ester or keto groups [89]. They are also used as oxygenate additives in fuels and octane [90].

1.4.3.2 Reactions involving the carbonyl group

Many interesting LA derivatives can be obtained by nucleophilic additions to the carbonyl group. The reactions of LA with such nucleophiles are not terminated by their addition to the carbonyl group or formation of the corresponding amide but result in heterocyclization [91, 92].



Scheme 1.5: Reactions of LA with nitrogen-containing nucleophiles

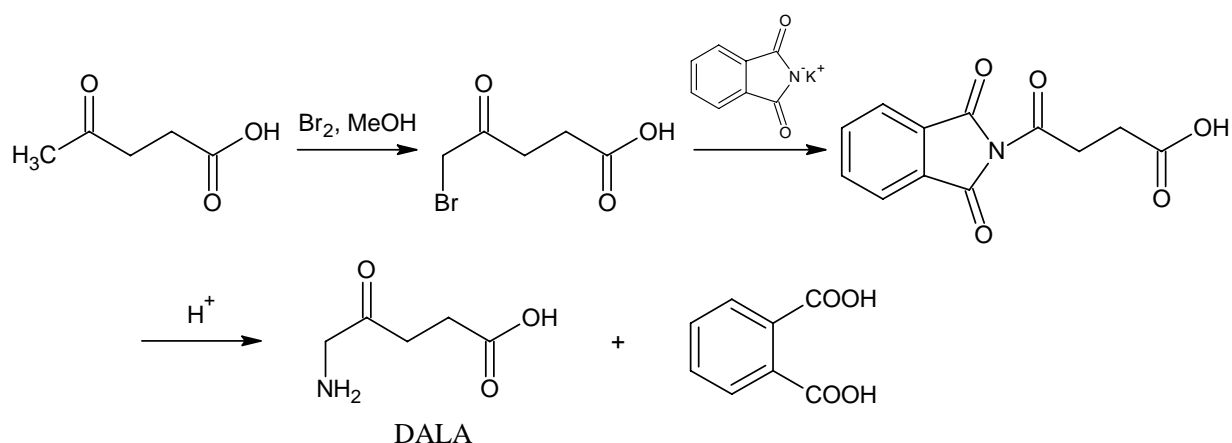


Scheme 1.6: Synthesis of diphenolic acid

Like other aldehydes and ketones, LA can also undergo through an acid-catalysed condensation reaction with aromatic or heterocyclic alcohols to give 4,4-diaryl-substituted valeric acids. A typical example is diphenolic acid that is prepared by reacting one mol of LA with two moles of phenol. Diphenolic acid has found wide application in production of polymers and other materials [93, 94].

1.4.3.3 Reactions involving the methyl group

The methyl group of LA can be easily halogenated using bromide or chloride affording organic halides. For example, 5-bromolevulinic acid (a precursor for δ -aminolevulinic

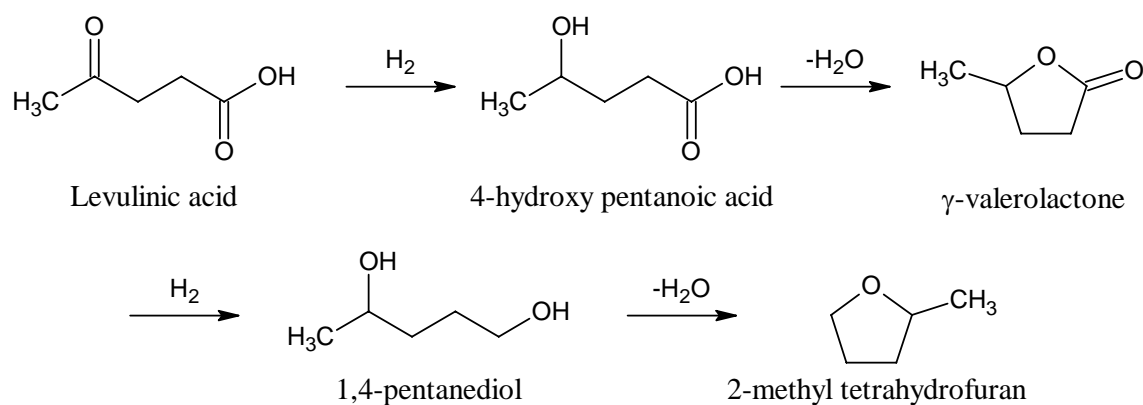


Scheme 1.7: Preparation of δ -aminolevulinic acid

acid (DALA) production) can be obtained by the bromination of LA in methanol [95]. DALA is prepared by reacting 5-bromolevulinic acid with nitrogen-containing nucleophiles, such as sodium azide or potassium phthalimide (Scheme 1.7). Recently, the use of sodium diformylamide as the N-nucleophile to give an intermediate product has been reported [96]. DALA is an active ingredient of a biodegradable herbicide. In the pharmaceutical industry, DALA has also been used in limited quantities as an active component in photodynamic cancer treatment [97].

1.4.3.4 Oxidation and reduction reaction

1 LA can be oxidized to various derivatives using homogeneous or heterogeneous catalysts. The result of oxidation strongly depends on the type of the oxidant. At high temperature (375-390 °C), LA is oxidized using oxygen in the presence of V₂O₅ catalyst to afford 83% yield of succinic acid [98]. Lower temperatures are required to oxidize LA to succinic acid using H₂O₂ as oxidant, SeO₂ as catalyst, and tert-butanol as solvent. However, the yields of succinic acid were considerably lower because of the formation of 2-methylsuccinic as a side-product [99]. Succinic acid (1,4-butanedioic acid) is one of the top 12 value-added chemicals [38]. It is used for fuel additives, solvents, polyesters, tetrahydrofuran, γ -butyrolactone, plasticizer, pharmaceuticals, *etc.* [100–102]



Scheme 1.8: Products formed by hydrogenation of levulinic acid

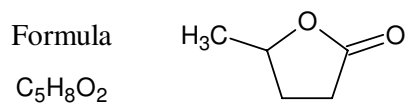
Catalytic hydrogenation of LA results different products depending on the catalyst and reaction conditions. The general pathways of reduction are presented in Scheme 1.8. LA is reduced to 4-hydroxypentanoic acid, which readily dehydrates to γ -valerolactone (GVL). GVL is hydrogenated to 1,4-pentanediol (PDO), which dehydrates to 2-methyl tetrahydrofuran (MTHF). The side products are pentanoic acid and pentanol.

Catalytic production of GVL has been performed by hydrogenation of LA using supported metal catalysts such as Ir complexes, Ru/C, Pt/C, Au/ZrO₂, Ni, CuO-Cr₂O₃, *etc.* [103–105] with molecular hydrogen or formic acid as hydrogen donor source [106, 107]. GVL is known to be useful in industry as a solvent for lacquers, insecticides, adhesives, and it has also found some use in cutting oils and brake fluids as well as fuel additive [108–111]. MTHF is useful as a fuel or fuel additive because it is miscible with gasoline at all proportions and hydrophobic, and it is also useful for making polymer fibers [112].

1.4.4 Introduction to γ -valerolactone

Gamma-valerolactone (GVL) is a five-carbon-cyclic ester with 5 atoms in ring. GVL is a colorless liquid, stable at normal conditions, has a sweet and herbaceous odor that makes it suitable for perfume and food additives. Some important properties of GVL are listed in Table 1.3.

Table 1.3: Main properties of GVL



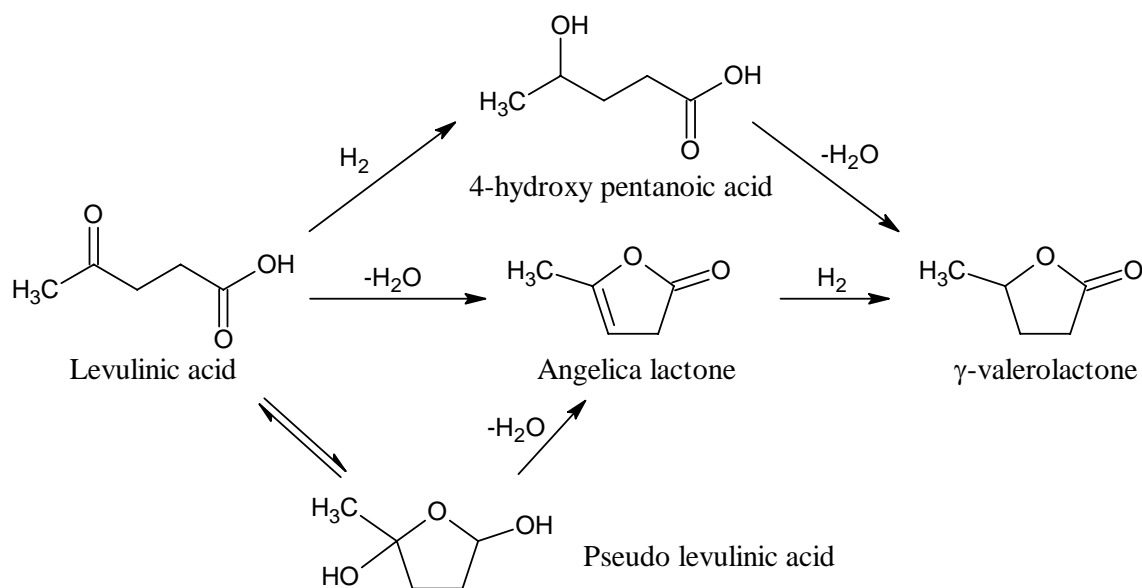
Properties	Value
Molecular weight	100.112 g mol ⁻¹
Boiling point	207-208 °C
Melting point	-31 °C
Density (25 °C)	1.05 g mL ⁻¹
Refractive index (25 °C)	1.432
Solubility in water	100 %
Open cup flash point	96 °C
Vapor pressure (25 °C)	0.65 kPa
Vapor pressure (80 °C)	3.2 kPa
LD ₅₀ , oral for rat	8800 mg kg ⁻¹

GVL has low melting point, high boiling and open cup flash points. Moreover, the low vapor pressure (even at high temperature) makes the flammability risk at normal conditions low. GVL has low toxicity, definitive but acceptable smell that makes it to be easily recognized when leaking or spilling. It does not degrade with time and stable at moderate temperature. These characteristics suggest that GVL has promising application for fuel additives and solvent [108].

1.4.5 Preparation of γ -valerolactone

1.4.5.1 Production of γ -valerolactone from hydrogenation of levulinic acid

Generally, GVL is produced from hydrogenation of LA using metal catalysts and molecular hydrogen or hydrogen donors such as formic acid, secondary alcohols at high temperature and pressure.



Scheme 1.9: Reaction pathway of LA hydrogenation to GVL

One of the methods used in commercial-scale for GVL preparation was hydrogenation of LA in vapor phase. This reaction was done by passing mixtures of LA and H_2 over $\text{CuO}/\text{Cr}_2\text{O}_3$ catalyst at $200\text{ }^\circ\text{C}$ and atmospheric pressure [113]. Precious metal catalysts such as Ru/C , Pd/C and Pt/C have been used for vapor phase reaction [114]. The obtained results revealed that Ru/C had highest activity, enabling quantitative conversion of LA to GVL without significant loss of activity after 10 days. While Pd/C and Pt/C catalysts showed lower activity than Ru/C . The vapor phase method usually gives high yield and is suitable for continuous process. However, this methodology requires huge amount of energy for vaporization of LA and is not suitable for the LA product mixtures obtained from carbohydrate feedstocks.

The hydrogenation of LA to GVL in liquid phase is more common. Supported metal catalysts have extensively investigated. Manzer *et al.* screened the activity of 5wt% Ir, Rh, Pd, Ru, Re and Ni supported on activated carbon [107]. The reactions were performed in 1,4-dioxane at $150\text{ }^\circ\text{C}$ and H_2 pressure of 55 bar. The results showed that Ni, Pt, Re gave low activities, the moderate activity was obtained from catalysts containing Ir, Rh and Pd (30-40 % GVL yield) and Ru/C was the most active catalyst

that gave highest yield of GVL (70 %). The optimized conditions allowed to achieve 95% GVL yield.

The same results was obtained by Liu and co-workers [115]. Palkovits *et al.* studied the effect of supports on the reaction. The results revealed that Ru supported on C gave higher yield of GVL than on the other supports (TiO_2 , SiO_2 , Al_2O_3) [116].

Because of high cost of noble metals, some options have been proposed to improve GVL yield under milder reaction conditions. For instance, the combination of an acid catalyst and Ru catalyst gave higher yield of GVL [117]. Some studies have been focused on the employment of Ru or Ir complexes as homogeneous catalysts aiming to improve turnover frequency of catalysts [104, 118, 119]. Other researchers have been attempted to replace noble metals by base metals to reduce the cost of catalysts. Hengne *et al.* studied the hydrogenation of LA and its ester over Cu-ZrO₂ and Cu-Al₂O₃ nanocomposites in the presence of methanol solvent [103]. While Cu-ZrO₂ can catalyzed the reaction yielding 90% GVL, Cu-Al₂O₃ resulted metal leaching and gave lower yield.

Beside traditional solvents (water and other organic solvents), super critical CO₂ (scCO₂) is considered to use as a potential green solvent for the hydrogenation of LA to GVL. The reaction can be performed in both batch or continuous reactors [120, 121]. However, the reactions usually take place under harsh conditions.

The worldwide H₂ production is reliant on the steam reforming of fossil carbon, a notoriously energetically intensive procedure [105, 122, 123]. Therefore, this hydrogen source is not sustainable and has low environmental benefit. Recently, formic acid (FA) has been focused as an attractive hydrogen source for GVL production. FA is a by-product from acid-catalyzed dehydration of carbohydrates. Theoretically, the mole ratio of LA and FA is 1:1. In practice, however, the amount of formed FA is slightly higher than LA [106]. The utilization of FA allow to avoid costly purification of LA and increase the atom-efficiency.

Table 1.4: An overview of GVL production from hydrogenation of LA or its esters

Catalyst	Reaction condition	Temp. (°C)	LA conv. (%)	GVL yield (%)	Ref.
CuO/Cr ₂ O ₃	Vapor phase, H ₂ (0.1 MPa)	200	100	100	[113]
5wt% Ru/C	Vapor phase, H ₂ (0.1 MPa)	265	100	99	[114]
5wt% Pd/C	Vapor phase, H ₂ (0.1 MPa)	265	100	90	[114]
5wt% Pt/C	Vapor phase, H ₂ (0.1 MPa)	265	100	30	[114]
5wt% Cu/SiO ₂	Vapor phase, H ₂ (1 MPa)	265	100	84	[124]
Raney Ni	Batch reactor, H ₂ (5 MPa)	220	N.A.	94	[125]
Re	Batch reactor, H ₂ (15 MPa)	106	100	71	[126]
5wt% Ir/C	Batch reactor, 1,4-dioxane, H ₂ (5.5 MPa)	150	49	47	[107]
5wt% Rh/C	Batch reactor, 1,4-dioxane, H ₂ (5.5 MPa)	150	30	28	[107]
5wt% Pd/C	Batch reactor, 1,4-dioxane, H ₂ (5.5 MPa)	150	30	27	[107]
5wt% Ru/C	Batch reactor, 1,4-dioxane, H ₂ (5.5 MPa)	150	80	72	[107]
5wt% Pt/C	Batch reactor, 1,4-dioxane, H ₂ (5.5 MPa)	150	13	10	[107]
5wt% Re/C	Batch reactor, 1,4-dioxane, H ₂ (5.5 MPa)	150	7	6	[107]
5wt% Ni/C	Batch reactor, 1,4-dioxane, H ₂ (5.5 MPa)	150	2	1	[107]
5wt% Ru/C	Batch reactor, methanol, H ₂ (1.2 MPa)	130	90	86	[115]
5wt% Pd/C	Batch reactor, methanol, H ₂ (1.2 MPa)	130	17	6	[115]
Raney Ni	Batch reactor, methanol, H ₂ (1.2 MPa)	130	18	5	[115]
5wt% Ru/TiO ₂	Batch reactor, ethanol-water, H ₂ (1.2 MPa)	130	81	71	[116]
5wt% Ru/C	Batch reactor, ethanol-water, H ₂ (1.2 MPa)	130	99	89	[116]
5wt% Ru/Al ₂ O ₃	Batch reactor, ethanol-water, H ₂ (1.2 MPa)	130	94	76	[116]
5wt% Ru/SiO ₂	Batch reactor, ethanol-water, H ₂ (1.2 MPa)	130	98	75	[116]
5wt% Ru/C	Batch reactor, solven-free, H ₂ (1.2 MPa)	190	100	100	[116]
Cu-ZrO ₂	Batch reactor, methanol, H ₂ (3.5 MPa)	200	100	90	[103]
Cu-Al ₂ O ₃	Batch reactor, methanol, H ₂ (3.5 MPa)	200	100	86	[103]
5wt% Ru/C	Batch reactor, water, Amberlyst-70, H ₂ (3 MPa)	70	100	100	[117]
5wt% Ru/Al ₂ O ₃	Batch reactor, scCO ₂ (10.5 MPa) H ₂ (14.5 MPa)	150	99	99	[120]
5wt% Ru/SiO ₂	Reaction setup utilized, scCO ₂ (10 MPa)	200	100	100	[121]
RuSn/C	Reaction stream contains LA, FA in alkyl-phenol	150	98	93	[127]
1mol% Au/ZrO ₂	Batch reactor, water, equimolar of LA and FA	150	99	99	[128]
1mol% Au/ZrO ₂	Batch reactor, water, equimolar of BL and BF	170	98	95	[129]

One of the first studies concerned with the utilization of FA as hydrogen source was conducted by Deng *et al.* [106]. They use the ruthenium complexes as homogeneous catalysts to convert LA and FA in the presence of a base at 150 °C into GVL with high yield (94%). They also observed the rapid increase in pressure in autoclave reactor revealing that FA is decomposed into H₂ and CO₂. Several other catalyst systems have been developed to resist against the deactivation by acid such as RuSn/C [127], RuRe/C [130], Au/ZrO₂, Au/TiO₂ [128, 129], and so on.

1.4.5.2 Production of γ -valerolactone from biomass

For the GVL production, most researches have been used commercial LA or mixture of LA and FA simulating the products that would be obtained from hydrolysis of carbohydrates. Few studies have considered the direct conversion of biomass into GVL. In these researches, mineral acids, such as H₂SO₄ or HCl, have been utilized to hydrolyze carbohydrate materials affording LA that is sequentially hydrogenated to GVL [128, 131–133].

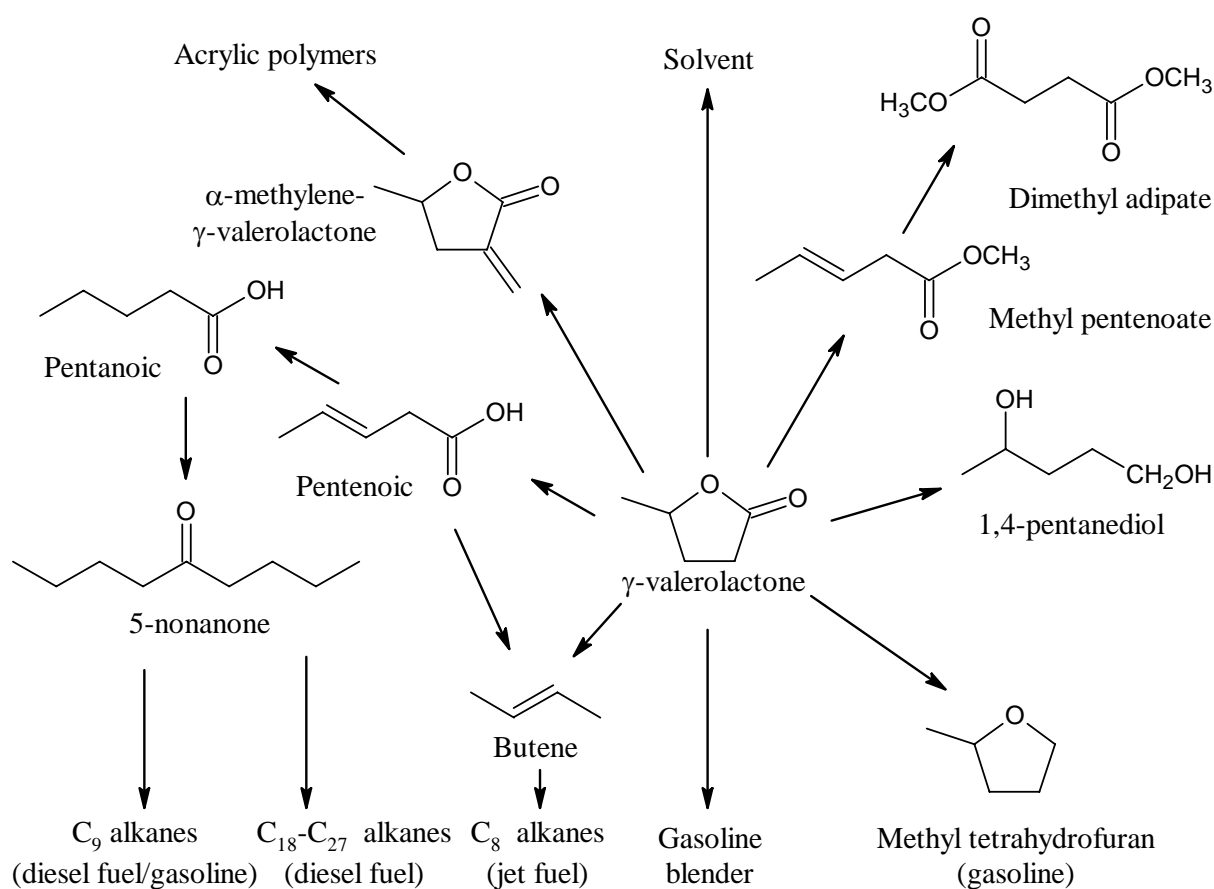
The acid catalyzed hydrolysis of biomass usually generates large amount of insoluble products known as humins. In addition, the impurities and mineral acids present in the feed usually deactivate the hydrogenation catalysts (Ru, Pd, Pt, *etc.*). To improve the acidic resistance of catalyst, some researchers have fabricated supported bimetallic catalysts, such as RuSn/C, RuRe/C [127, 131]. To minimize the effect of mineral acids, Alonso *et al.* proposed extracting LA from the aqueous solution using alkylphenol solvents [127]. This solvent can extract 80% LA, while the aqueous solution phase retained all of H₂SO₄. The extracted LA was hydrogenated to GVL over Ru/C or RuSn/C.

Other studies have been used water-alcohol biphasic solvents. In these systems, formed LA reacts with alcohol to obtain levulinate esters that are easily separated from aqueous solution [70, 134, 135]. The issue with this method is the recovery of the alcohol, which has to be used in excess to achieve adequately high yield of the ester.

Generally, up to now, the production of GVL usually uses hydrogen gas as the reductant for hydrogenation of levulinic acid. There have been few researches focus on the utilization as hydrogen donor source for hydrogenation of biomass-derived compounds to GVL. In addition the recent catalyst systems is not robust and have low reusability. Therefore the research should concentrates on (i) the employment of FA as hydrogen donor source for direct conversion of biomass-derived compounds to GVL; (ii) finding the acid-tolerant catalysts to improve the reusability.

1.4.6 Applications of γ -valerolactone

GVL can be used in a number of application, ranging from direct use as a fuel additive or solvent to diverse upgrading strategies for the production of fuels and chemicals [136] (Scheme 1.10).



Scheme 1.10: Transformation of γ -valerolactone to chemicals and fuels

1.4.6.1 γ -Valerolactone – A “green solvent”

The physical and chemical properties of GVL make it an excellent candidate as a solvent as well as precursor for production other green solvents [137]. Jessop *et al.* recently reported a series of key considerations for screening green solvents [138]. According to these criteria, GVL has advantages compared to other common solvents. GVL is non-toxic and the production of GVL requires fewer steps than other solvents such as trichloromethane, THF, and most ionic liquids. In addition, the intermediate or by-products generated from GVL production are miscible with water which facilitates their biodegradability.

GVL has been used as solvent to produce the high-value-platform molecules: HMF, LA, and GVL from fructose [139]. The system is a significant improvement for GVL production since no separation of the product from the solvent, GVL, is required. There are, however, challenges in terms of catalyst separation as well as LA and HMF purification. The problem of catalyst separation is mitigated by adding an aqueous phase modifier, such as salt or sugars, to create a biphasic system using GVL as the organic layer [140].

Cellulose can be well dissolved in GVL stimulating the utilization of solid acid catalysts [141]. The LA yield can achieve over 60% from cellulose using Amberlyst 70 and no other acid catalysts. GVL is also used as solvent for upgrading HMF to other valuable compounds such as 2,5-dimethylfuran (DMF) [140], 2,5-furandicarboxylic acid (FDCA) [142–144].

1.4.6.2 Utilization of γ -valerolactone and its products as fuels and fuel additives

Like ethanol, GVL can be used directly as a liquid fuel or fuel additive to current petroleum. GVL has similar combustion energy to ethanol (*approx.* -29.7 kJ g^{-1}) but higher energy density. In contrast to the ethanol, GVL is separated easily from water by

distillation because there are no azeotropes. Hováth *et al.* compared mixtures of 90 vol% conventional gasoline with 10 vol% GVL or 10 vol% ethanol [108]. They observed that the mixture with GVL had a lower vapor pressure which improve the combustion at similar octane numbers.

GVL can be converted to 2-methyl tetrahydrofuran (MTHF) which has already been considered as the renewable component of an alternative fuel [81, 145–147]. MTHF can be used alone or may be mixed in any proportions with conventional fuels. The hydrogenation of GVL to MTHF has been performed by using various type of catalyst such copper, Raney nickel, rhenium, platinum oxide, or other homogeneous catalysts [125, 126, 148]. MTHF can be used directly as fuel or fuel additive or further transformed to C₄-C₉ alkanes in the presence of and acid and metal catalyst at high pressure and moderate temperatures [149].

Another important product obtained from hydrogenation of GVL is pentanoic acid [110, 150]. Pentanoic acid is further converted in to valeric esters, 5-nonanone that serve as important substances for production of diesel fuel or gasoline [110, 151].

1.4.6.3 γ -Valerolactone for other chemicals production

GVL is useful starting material for producing monomers to make polymers that are similar to those derived from petroleum.

Manzer *et al.* [107] produced biomass-derived monomers such as α -methylene- γ -valerolactone from GVL. This compound has similar properties to methyl methacrylate, and the incorporation of the lactone structure increased the thermal stability of the polymer.

γ -Hydroxy(amino)amide compounds are produced by ring-opening of the GVL [152]. This reaction was catalyzed by SnCl₂ at 50 °C with GVL and an amine present, for example, 1,2 diaminoethane. This new family of compounds can be used as monomers to produce polymers such as polyethers or polyurethanes. Another product obtained from

ring-opening reaction of GVL is methyl pentenoate. The reaction was carried out in methanol over acid catalysts [109]. The methyl pentenoate was then converted into nylon precursors such as caprolactone, caprolactam, or adipic acid by hydroformylation, hydrocyanation, or hydroxycarbonylation, respectively.

1.5 Research objectives and dissertation outline

1.5.1 Research objectives

The main purpose of this thesis is finding the new heterogeneous catalysts for transformation of biomass-derived compounds to higher valuable compounds that are used as platform molecules for production of fuels or chemicals. Studies of this thesis, therefore, will focus on:

1. Investigation of the utilization of solid acid catalysts for synthesis of levulinic acid from HMF, hexose sugars and other carbohydrates.
2. Preparation of solid base catalysts for isomerization reaction of glucose into fructose and further synthesis of levulinic acid from glucose in combination with solid acid catalyst.
3. Development of highly active and renewable supported metal catalysts for production of γ -valerolactone from biomass-derived compounds.

1.5.2 Outline of Dissertation

Introduction chapter provides a general overview of biomass and its transformations into value-added chemicals and fuels. General introduction about heterogeneous catalyst for catalytic upgrading of biomass-derived compounds is also presented. Subsequently, the production and application of levulinic acid (LA), γ -valerolactone (GVL) and their derivatives are reviewed. It will show that LA and GVL are important and interesting biomass-derived compounds.

In the Chapter 2, the author investigates the utilization of solid acid catalyst for synthesis of levulinic acid in water under mild reaction conditions. The reaction was carried out at different temperatures and amounts of catalysts to find the best reaction conditions. Ion-exchanged resins possessing high the amount of acid site reveal the high activity and recyclability for the dehydration/hydration of biomass-derived compounds to levulinic acid.

Chapter 3 describes of the preparation and characterization of zirconium carbonate as solid base catalyst for isomerization of glucose to fructose. The effect of catalyst drying temperature, isomerization temperature will be studied. The obtained catalyst is assessed its reusability and heterogeneity. Furthermore, zirconium carbonate will be applied for the production of levulinic acid in combination with a solid acid catalyst.

Chapter 4 is the synthesis of γ -valerolactone from catalytic upgrading of levulinic acid or direct transformation of C6-sugars using supported metal catalysts. In this reaction, formic acid is attempted to use as hydrogen donor source for replacing hydrogen gas as the reactant.

Finally, the author summarizes overall conclusions of the present dissertation in Chapter 5. The prospects of these works in this thesis are also mentioned.

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Chapter 2

Synthesis of Levulinic Acid from Biomass-Derived Compounds using Solid Acid Catalysts

Abstract

Levulinic acid (LA) was obtained by hydration/dehydration of 5-hydroxymethylfurfural (HMF) or fructose over solid acid catalysts under mild reaction conditions in water. Solid acid catalyst could convert more than 90% HMF affording *ca.* 80% yield of LA. For transformation of fructose to LA, the reaction was carried out at different temperatures and amounts of catalysts to find the best reaction conditions. Among tested heterogeneous catalysts, Amberlyst-15 gave the highest LA yield (52%) with the lowest HMF yield (below 3%) under optimum conditions. LA was isolated from the mixture after reaction by rotary vacuum evaporator with 47% isolated yield. The recycling experiments showed that Amberlyst-15 exhibited good activity even after 5 runs, though the LA yield gradually decreased from 52 to 30%.

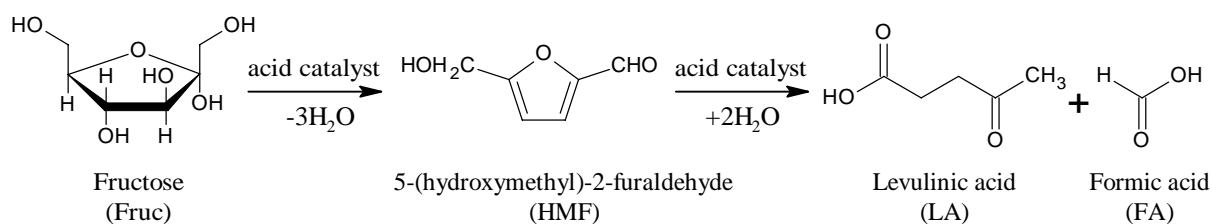
The optimum reaction conditions found with fructose were also applied to other hexose sugars and their dimer or polymer compounds. The reaction took place slowly giving small quantity of product. Higher reaction temperature (*ca.* 150 °C) and longer reaction time (*ca.* 60 h) were needed in order to get a meaningful LA yield.

2.1 Introduction

LA is a low-molecular-weight fatty acid having two important functional groups: a ketone carbonyl group (CO) and a carboxyl group (COOH) [1]. Because of its highly active functional groups, LA is used as a starting material for preparation of many chemical compounds such as 2-methyltetrahydrofuran, acrylic acid, δ -aminolevulinate, diphenolic acid, 1,4-pentanediol, *etc* [2]. The most widely used method to produce LA is the dehydrative treatment of hexose sugars or carbohydrates with acid catalyst (see Section 1.4.2, Chapter 1, p. 9). Traditionally, homogeneous catalysts such as HCl, H₂SO₄ and H₃PO₄ have been used for synthesis of LA [3–8]. The advantages of these homogeneous catalysts are availability, easy to use, short reaction time and high performance (the yield can reach 60-70% based on the hexose content of the carbohydrate [2]). However, the disadvantages include difficult recovery of catalyst and cause of environmental pollutions.

To overcome above disadvantages of homogeneous acid catalysts, heterogeneous catalysts are promising substitution. However, minimal attention has been given to the use of solid acid catalyst for converting hexose sugars as well as carbohydrates into LA. Schraufnagel and Rase used acidic ion-exchange resins for the production of 5-hydroxymethylfurfural (HMF) and LA from sucrose [9]. However the process took a long time to achieve moderate yields. Other studies have been reported under severe reaction conditions as follows: Dehydration of fructose to LA over LZY zeolite [10] and dehydration of glucose by Y zeolite [11, 12] at temperatures between 110-160 °C for 8-15 h gave yields of LA around 40% with a low yield of HMF (*ca.* 4%). ZRP zeolites with different SiO₂/Al₂O₃ ratios converted glucose into LA with 36% yield at 180 °C in an autoclave for 8 h [13]. The use of pillared clay catalysts for dehydration of glucose gave a low LA selectivity (20%) [14] because of a coke formation. Chen *et al.* [15]

prepared solid superacid ($\text{S}_2\text{O}_8^{2-}/\text{ZrO}_2\text{-SiO}_2\text{-Sm}_2\text{O}_3$) for converting rice straw into LA with yield around 23% at high temperature (200 °C) in an autoclave reactor. Sanborn [16] reported synthesis of LA over solid acid catalyst Amberlyst-35 with yield of 41% from fructose and 62% from high-fructose corn syrup at 150 °C in an autoclave reactor for 4.5 and 18 h, respectively.



Scheme 2.1: Synthesis pathway of LA from fructose

In this chapter, I report the synthesis of LA from fructose using Amberlyst-15, an ion-exchange resin with strongly acidic sulfonic groups, under mild reaction conditions in water. The formation of LA from fructose includes two steps (Scheme 2.1): in the first step, fructose is dehydrated to HMF; in the second step, hydration of HMF followed by carbon-carbon cleavage gives one molecule of LA and one molecule of formic acid (FA) [17]. To the best of our knowledge, this is the first study on the synthesis of LA from sugar with high yield (> 50% yield of LA) using solid acid catalyst at low reaction temperature (120 °C).

2.2 Experimental

2.2.1 Materials

The following chemicals were used for the experiments: D-fructose, sulfuric acid (98%), hydrochloric acid (35%) and ethanol (99.5%) were purchased from Kanto Chemical Co., Inc. Commercial LA was supplied from Tokyo Chemical Industry Co., Ltd. Hydroperoxide (30%) was obtained from Wako Pure Chemical Ind., Ltd. Amberlyst-15, Nafion NR50, tri-block co-polymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene

oxide) (P123, (EO)₂₀(PO)₇₀(EO)₂₀, M=5800), tetraethylorthosilicate (98%, TEOS), 3-mercaptopropyl trimethylsilane (95%, MPTMS) were bought from Sigma-Aldrich.

2.2.2 Catalyst preparation

In this work, besides acidic cation-exchange resins, sulfonic acid-functionalized mesoporous silica (SBA-SO₃H) was also utilized. The SBA-SO₃H catalyst was prepared by the reported method [18] with some modifications. Typically, 2 g of P123 was dissolved with 15 mL of water and stirred at 40 °C for 3 h. After that, 35 mL of 2 M HCl was introduced and continued to stir 20 min followed by addition of 4 mL of TEOS 98% into the solution. The mixture was kept under the same conditions for 8 h for pre-hydrolysis before addition of 1 mL of functional group precursor, MPTMS. After 12 h, the mixture was transferred to a teflon-lined steel autoclave and heated at 100 °C for 24 h. The template P123 was removed by reflux at 80°C with 80 mL of ethanol. For oxidation of thiol group (-SH) to sulfonic acid group (-SO₃H), the solid was treated with 80 mL of H₂O₂ 5% at 50 °C for 5 h. Thereafter, the white solid was collected by centrifugation, washed with distilled water and dried at 60 °C for 24 h.

2.2.3 Reaction procedure

Dehydration of HMF

The reactions were carried out in capped glass tubes: 0.2 g (1.67 mmol) of fructose and a certain amount (0.1-0.4 g) of catalyst were added to 3 mL of water and the mixtures were heated at different temperatures (100-140 °C) with stirring (500 rpm) in an oil bath. After the reaction, the reactors were taken out of the oil bath and immersed immediately into cool water to quench the reaction. The mixtures were diluted ten times followed by filtration through 0.2 µm Millex filter unit.

Dehydration of carbohydrate compounds

Carbohydrate compounds used as starting materials in this experiment include: C6-sugars (fructose, glucose, mannose, galactose), disaccharide (sucrose, cellobiose), inulin and cellulose. Typically, 0.3 g starting material and a certain amount (0.1-0.4 g) of catalyst were added to 6 mL of water and the mixtures were heated at different temperatures (100-140 °C) with stirring (500 rpm) in an oil bath. After the reaction, the reactors were taken out of the oil bath and immersed immediately into cool water to quench the reaction. The mixtures were diluted ten times followed by filtration through 0.2 µm Millex filter unit. Yield of products are calculated based on the mole of hexose sugars.

2.2.4 Product analysis method

The reactant and product amounts were determined by a high performance liquid chromatograph (HPLC, Waters Co.) equipped with Aminex HPX-87H column (Bio-Rad Laboratories, Inc.) and a refractive index detector. The conditions for the analysis were set as follows: 10 mM H₂SO₄ aq. eluent at flow rate of 0.5 mL min⁻¹, both of column and detector were operated at 50 °C.

The conversion (Conv.) of reactant, yield and selectivity (Sel.) of product are calculated by following formulas:

$$\text{Conv. (\%)} = \frac{\text{reacted moles of reactant}}{\text{initial moles of reactant}} \quad (2.1)$$

$$\text{Yield (\%)} = \frac{\text{obtained moles of product}}{\text{initial moles of reactant}} \quad (2.2)$$

$$\text{Sel. (\%)} = \frac{\text{obtained moles of product}}{\text{reacted moles of reactant}} \quad (2.3)$$

2.3 Result and discussion

Characterization of catalysts

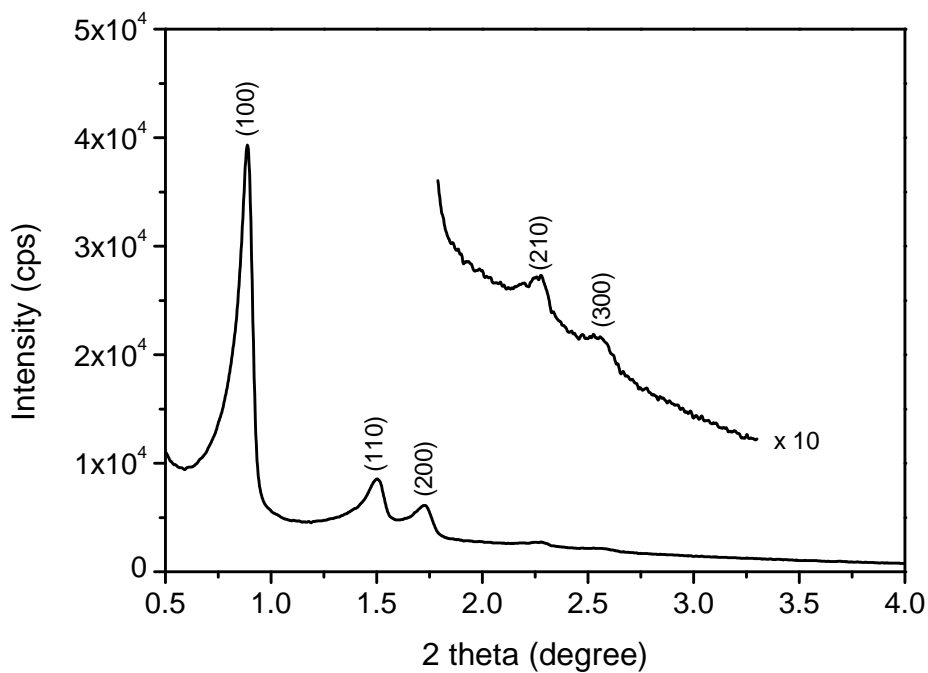


Figure 2.1: Small angle X-ray diffraction pattern of SBA-SO₃H

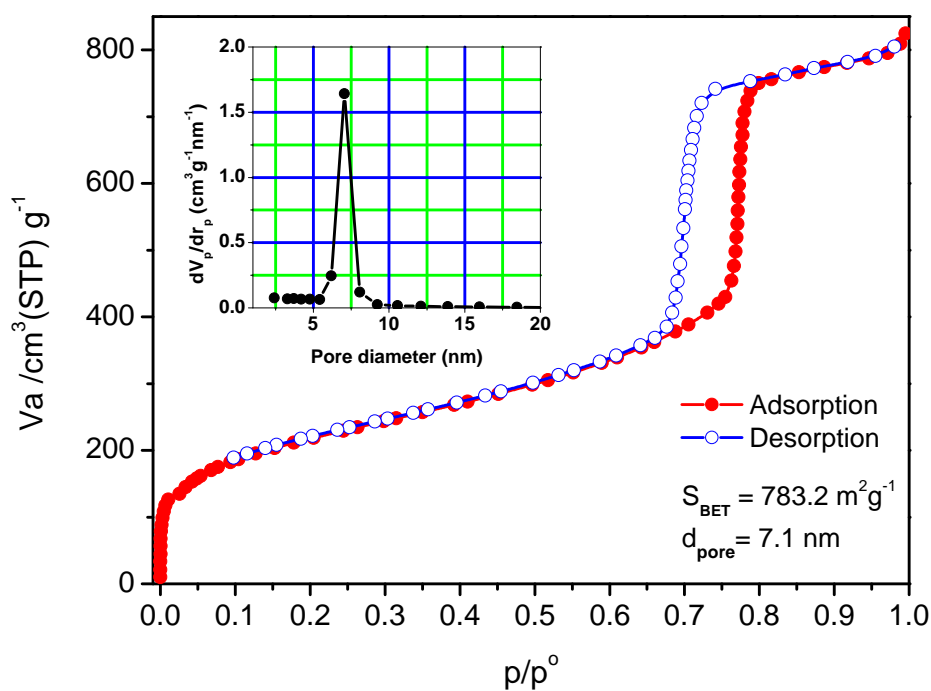


Figure 2.2: Nitrogen adsorption-desorption isotherm and pore size distribution of SBA-SO₃H

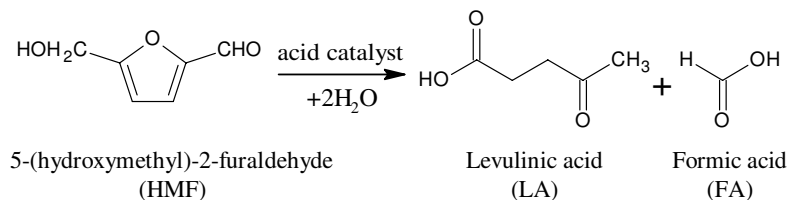
Results of small angle X-ray diffraction and nitrogen adsorption-desorption analysis of synthesized SBA-SO₃H are shown in Fig. 2.1 and 2.2. XRD pattern has a strongest peak at 0.887°, two medium intensity peaks at 1.503°, 1.724° and two other weak peaks at 2.267°, 2.561°. These peaks are correlative with 100, 110, 200, 210 and 300 reflections, respectively, charactering for ordered hexagonal structure of SBA-SO₃H. The isotherm of SBA-SO₃H indicates the type-IV adsorption isotherm associated with the mesoporous material (according to IUPAC nomenclature [19, 20]). On the isotherm, the hysteresis loop appeared in range of relative pressure $P/P_o = 0.675 - 0.800$ revealing the capillary condensation occurred during the analysis. The shape of hysteresis loop shows the H1-type which is a characteristic of a regular array of independent cylindrical pores. Values of pore size and specific area BET are 7.1 nm and 783 m² g⁻¹, respectively.

The exchange capacity (or acid site content), defined as mmol of H⁺ per 1 g of catalyst, was measured by a titration method [21] as following procedure: 0.1 g of solid acid catalyst was added to 10 mL of 2 M NaCl (as an exchange agent) and stirred for 45 min. Thereafter, the solution was titrated with solution of 0.05 M NaOH. The results are shown in Table 2.1.

Table 2.1: Acid capacity of solid acid catalysts

Catalyst	Exchange capacity (mmol H ⁺ g ⁻¹)
Amberlyst-15	4.57
Nafion NR50	0.98
SBA-SO ₃ H	1.49
Sulfated zirconia	1.60
Nafion SAC13	0.17

Hydration of HMF



Scheme 2.2: LA production form acid-catalyzed hydration of HMF

Table 2.2: Conversion of HMF to LA using Nafion-NR50

Entry	Temperature /°C	Time /h	HMF Conv. /%	Yield /%	
				LA	FA
1	80	1	22	1	4
2		3	22	3	7
3		5	25	5	9
4		8	30	8	12
5		12	30	13	18
6		18	39	18	24
7		24	46	22	29
8	100	1	22	4	8
9		3	36	10	15
10		5	38	18	24
11		8	46	27	34
12		12	57	36	43
13		18	69	50	57
14		24	76	64	73
15	120	1	27	11	16
16		3	51	28	33
17		5	69	51	55
18		8	78	57	62
19		12	88	69	78
20		18	94	78	89
21		24	96	78	80

Reaction conditions: HMF (0.2 g), water (3 mL), Nafion-NR50 (0.4 g), 500 rpm.

Firstly, a series of preliminary experiments for the production of LA was carried out with hydration reaction of HMF (Scheme 2.2). Two important factors selected are

temperature and reaction time. At each reaction temperature, the reaction mixture was sampled at 1, 3, 5, 8, 12, 18 and 24 h. Reaction and product contents were determined by HPLC.

The achieved results were shown in Table 2.2, 2.3 and LA yields were illustrated in Fig. 2.3.

Table 2.3: Conversion of HMF to LA using Amberlyst-15.

Entry	Temperature /°C	Time /h	HMF Conv. /%	Yield /%	
				LA	FA
1	80	1	14	2	5
2		3	20	4	8
3		5	24	7	11
4		8	26	10	18
5		12	33	17	21
6		18	42	24	29
7		24	46	31	36
8	100	1	26	6	10
9		3	34	17	21
10		5	41	27	32
11		8	54	38	42
12		12	66	50	54
13		18	80	62	70
14		24	85	69	80
15	120	1	31	19	24
16		3	62	43	48
17		5	78	62	64
18		8	89	71	73
19		12	94	77	82
20		18	96	81	88
21		24	96	80	87

Reaction conditions: HMF (0.2 g), water (3 mL), Amberlyst-15 (0.4 g), 500 rpm.

In both reactions over Nafion-NR50 and Amberlyst-15, the hydration of HMF took place slowly at low temperature (80 and 100 °C), and reactions had not yet completed after 24 h. In contrast, at 120 °C, the reactions occurred fast within 10 h and more slowly after that. Generally, the reaction catalyzed by Amberlyst-15 was slightly faster than promoted by Nafion-NR50. Nafion-NR50 needed at least 18 h to achieve *ca.* 80%

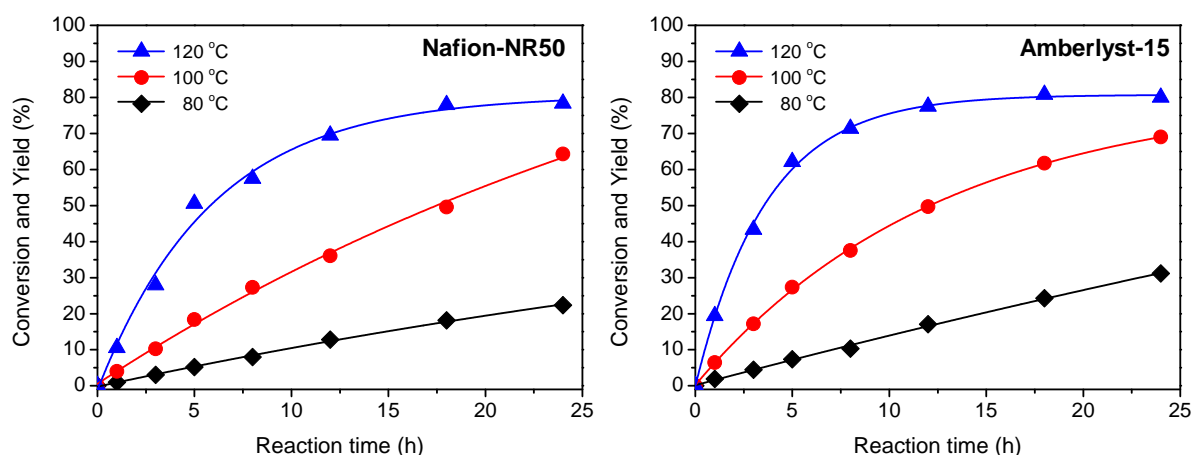


Figure 2.3: Hydration of HMF over Nafion-NR50 and Amberlyst-15 at 80 °C (*diamond*), 100 °C (*circle*) and 120 °C (*triangle*). Reaction conditions: HMF (0.2 g), water (3 mL), catalyst (0.4 g), 500 rpm.

LA yield, while Amberlyst-15 required only 12 h to reach same value of LA yield.

Dehydration of fructose

Figure 2.4 shows a time course of the reaction. The conversion of fructose and yield of LA gradually increased as the reaction progressed, and the LA yield reached the maximum of 52% after 36 h, whereas the HMF yield was 15% and stable at the initial stage of the reaction and then gradually decreased after 8 h of reaction time (the HMF yield was below 3% after 24 h). This suggests that the hydration of HMF to the LA was faster than the dehydration of fructose in the reaction.

The conversion of fructose and yields of products depended on the reaction temperature and amount of catalyst. The results are listed in Table 2.4. According to the stoichiometry of the formation reaction of LA from HMF [17], the yields of FA and LA should be same. However, the yield of FA is always higher than that of LA. Deng [22] explained that after the cleavage of FA, some intermediates (such as 5,5-dihydroxypent-3-en-2-one) were created before the formation of LA as a final product. Other authors [13] proposed that the differences between the yields of LA and FA are concerned with properties of the catalysts such as acidic strength and porous property. Therefore, it is

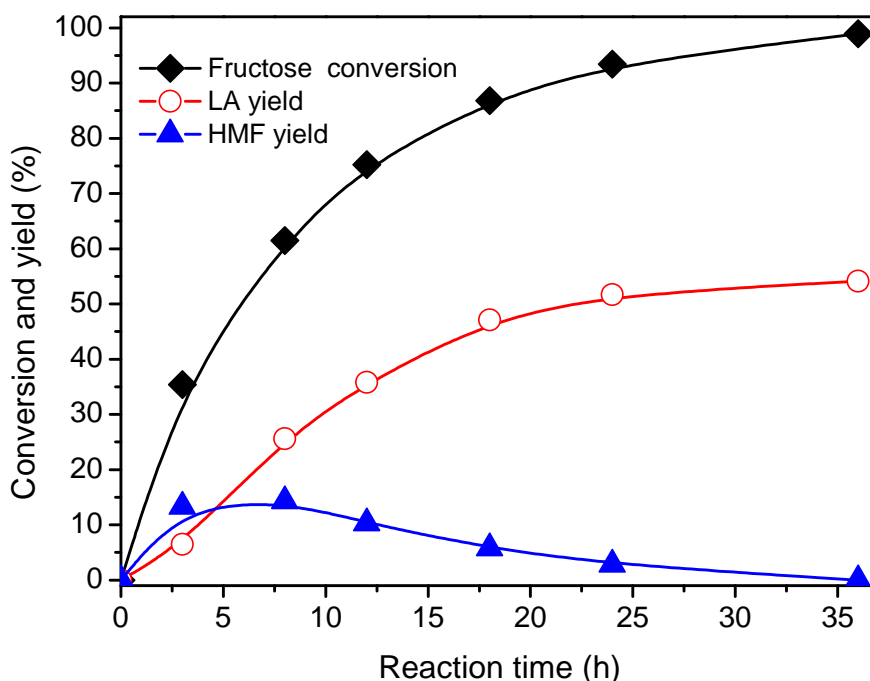


Figure 2.4: Fructose conversion (*diamond*), LA yield (*open circle*) and HMF yield (*triangle*) as a function of reaction time. *Reaction conditions*: fructose (0.3 g, 1.67 mmol), water (6 mL), Amberlyst-15 (0.4 g), 120 °C.

expected that the further decomposition of LA on the acidic sites occurred.

To further investigate the reaction, it was carried out under different conditions. The results are shown in Table 2.4. At 100 °C (entries 1-4), both the yields of LA and HMF slightly increased with an increase of the amount of catalyst. However, the LA yields were quite low. When the temperature increased from 100 to 120 °C, the yield of LA drastically increased. Moreover, when the amount of catalyst increased at 120 °C, the yields of LA increased sharply from 18 to 52% while the yields of HMF decreased from 15 to below 3% (entries 5-8). These results indicated that both the reaction temperature and the amount of acid catalyst enhanced the dehydration of fructose and hydration of HMF. Interestingly, the formation rate of LA increased faster than that of HMF by the amount of acid catalyst. When the temperature was increased to 140 °C (entries 9-10), higher yields of LA with lower yields of HMF were obtained even at shorter reaction time (8 h). However, the catalyst was broken down after the reaction and could not be

Table 2.4: Fructose conversion and yields of products under different conditions using Amberlyst-15.

Entry	Temperature /°C	Amberlyst-15 /g	Fructose Conv./%	Yield /%		
				LA	FA	HMF
1	100	0.1	12	1	5	6
2		0.2	22	4	8	9
3		0.3	28	8	12	9
4		0.4	37	13	17	10
5	120	0.1	57	18	32	15
6		0.2	72	35	41	11
7		0.3	88	47	54	5
8		0.4	93	52	58	3
9 ^a	140	0.3	98	54	59	2
10 ^a		0.4	99	56	60	0

Reaction conditions: fructose (0.3 g, 1.67 mmol), water (6 mL), time (24 h, ^a 8 h).

recovered. It was considered that the use of 0.4 g of Amberlyst-15 at 120 °C (entry 8) gave the best condition for the LA formation.

To confirm the product, the reaction mixture was purified and the isolated product was characterized by NMR. The isolation process was carried out by using a rotary vacuum evaporator. HPLC result showed that the solution after reaction contained only LA (main product), FA (by product) and HMF (side product). Because of the much difference of boiling points between LA and FA, HMF (Table 2.5) [23], LA can be easily isolated by rotary vacuum evaporator. The vacuum evaporation was carried out at 45 °C under reduced pressure of 0.1 bar for 4 h to remove solvent and by products. Finally, obtained LA was completely dried in vacuum at room temperature for 2 days before NMR analyses. The isolated yield of LA was 47%.

The ¹H NMR and ¹³C NMR spectra were recorded by a Bruker Advance 400 spec-

Table 2.5: Physical properties of some chemicals.

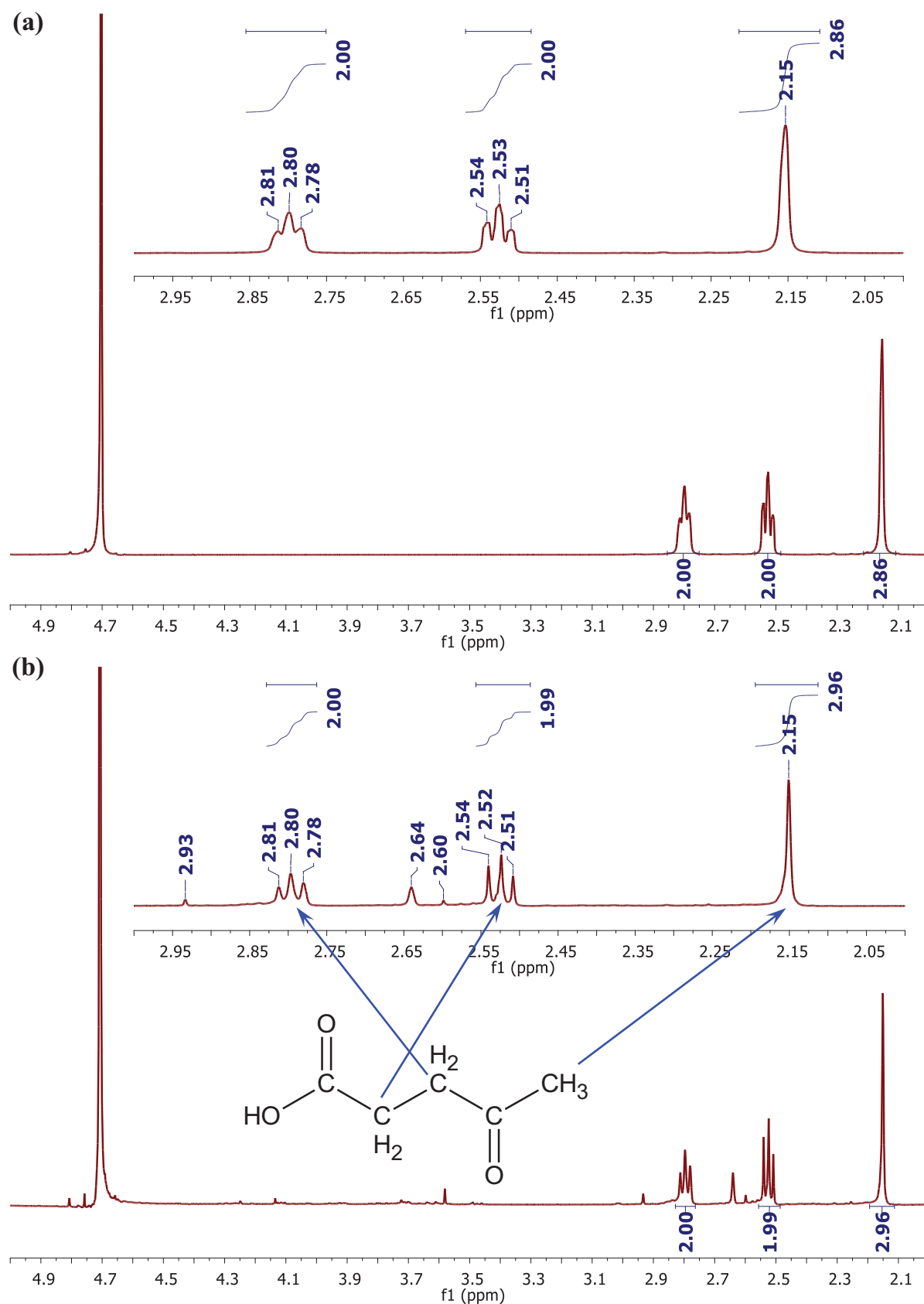
Chemical	Molar weight (g mol ⁻¹)	T_m /°C	T_b /°C
Levulinic acid	116.11	37	246
Fructose	180.6	103	Decomp.
HMF	126.11	32	115
Formic acid	46.03	8.4	100.8

T_m - melting point, T_b - boiling point

trometer using D₂O and TMS as solvent and internal standard, respectively. The spectra of the product well agreed with those of commercial LA (Figures 2.5 and 2.6). In the ¹H NMR spectrum, the peaks with chemical shifts at 2.15, 2.52 and 2.80 ppm were assigned to -CH₃ group, -CH₂- (adjacent to the carboxyl group) and -CH₂- (adjacent to the ketone carbonyl group), respectively. The assignation of carbon atoms in ¹³C NMR spectrum was also listed in Figure 2.6.

For comparison with Amberlyst-15, the Nafion NR50, sulfonic acid functionalized mesoporous silica (SBA-SO₃H), Nafion SAC13 and sulfated zirconia were also attempted for the reaction.

The catalytic activity and exchange capacity of Amberlyst-15 were compared with those of other catalysts. The results are shown in Table 2.6. Without catalyst (entry 9), only small amount of fructose was converted into products, and the LA was not detected. In this experiment, the HPLC chromatograms indicated no other products except for fructose, LA, FA and HMF. Therefore, it was supposed that some residuals such as humins were formed by only heating the fructose in the presence of acid catalyst. The catalytic activity of Amberlyst-15 was as good as H₂SO₄ and much higher than Nafion NR50, synthesized SBA-SO₃H, Nafion SAC13 and sulfated zirconia because of its high exchange capacity (H⁺ = 4.57 mmol g⁻¹). Therefore, Amberlyst-15 is the most potential solid acid catalyst replacing homogeneous catalysts for production of LA.



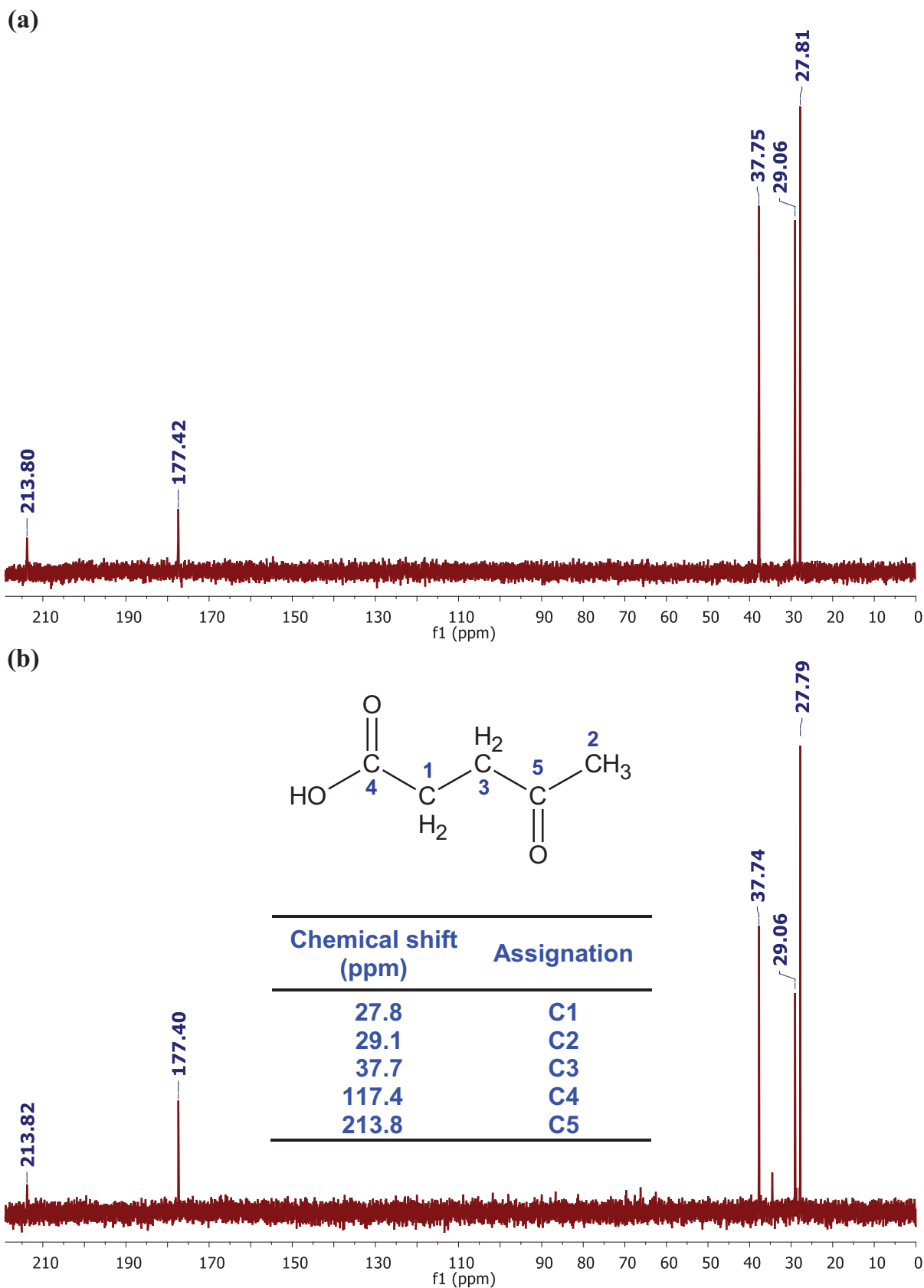


Figure 2.6: ^{13}C NMR spectra of commercial levulinic acid (a) and isolated product (b).

Table 2.6: Comparison of catalytic activity between Amberlyst-15 and other catalysts.

Entry	Catalyst	Exchange capacity (mmol H ⁺ g ⁻¹)	Fructose Conv. /%	Yield /%		
				LA	FA	HMF
1	Amberlyst-15	4.57	93	52	58	3
2 ^a	Amberlyst-15		75	36	41	10
3	Nafion NR50	0.98	78	41	46	6
4	SBA-SO ₃ H	1.49	84	29	35	20
5	Sulfated Zirconia	1.60	89	14	18	13
6	Nafion SAC13	0.17	36	5	7	14
7 ^b	0.1M H ₂ SO ₄	-	99	62	67	3
8 ^a	0.1M H ₂ SO ₄		90	47	51	19
9	Blank	-	24	0	0	4

Reaction conditions: fructose (0.3 g, 1.67 mmol), Amberlyst-15 (0.4 g), water (6 mL), 120 °C, time (24 h, ^a 12 h); ^b 6 mL of 0.1 M H₂SO₄ (equivalent to 1.2 mmol of H⁺).

In the previous studies, the recyclability of solid acid catalysts has not been investigated in detail [9–16]. For the recycle runs, the catalyst was recovered after each reaction and treated as follows to remove residual organic compounds: the reacted catalyst was washed with 5 mL of water three times followed by 5 mL of acetone two times to remove residual organic compounds. Thereafter, the catalyst was washed once by 5 mL of water again and then immersed in 2.5 mL of diluted-sulfuric acid at 45 °C for 4 h. Finally, the catalyst was washed twice with 5 mL of water and dried at 45 °C overnight. Amberlyst-15 showed a good activity for the synthesis of LA even after 5th run (Figure 2.7). However, the LA yield gradually decreased from 52 to 30% during 5 runs. The decrease in the catalytic activity is related to residuals such as humins formed by decomposition of fructose depositing on the surface of catalyst because the color of the catalyst became gradually darker.

To further study the synthesis of LA over Amberlyst-15 catalyst, the effect of fruc-

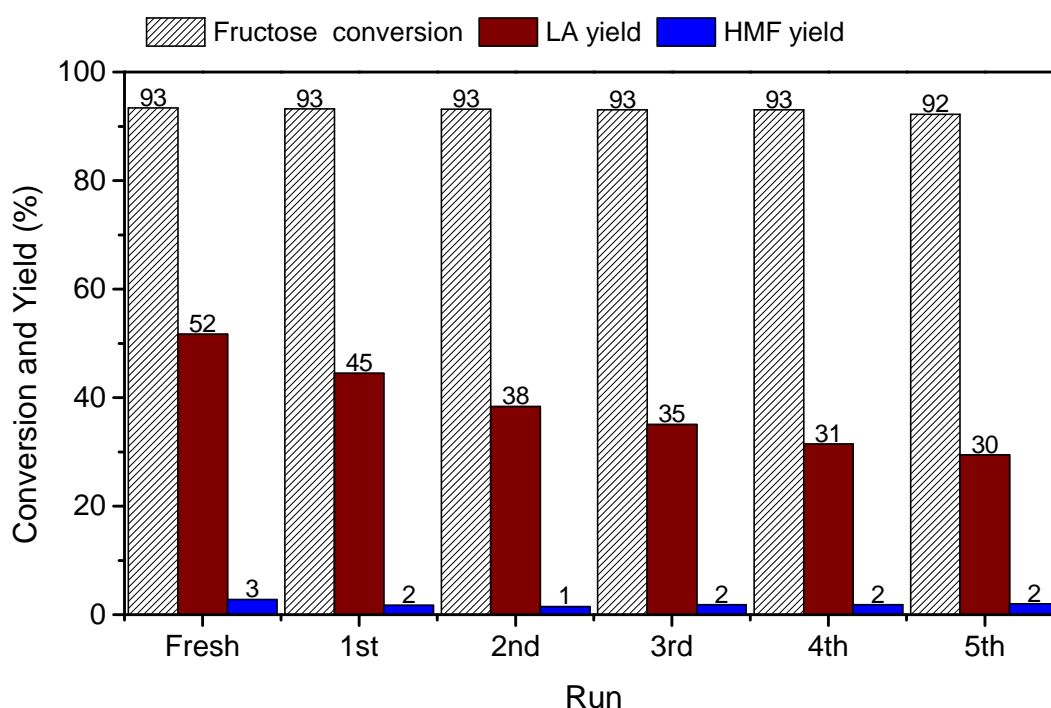


Figure 2.7: Recycling study of Amberlyst-15 in the dehydration of D-fructose to LA. *Reaction conditions:* fructose (0.3 g, 1.67 mmol), water (6 mL), Amberlyst-15 (0.4 g), 120 °C.

tose content was also examined. The results are shown in Table 2.7. The yields of LA decreased gradually with increase in the fructose contents, while the fructose conversions kept high values in all cases (> 90%). It was supposed that a large amount of fructose was decomposed to humins and/or unidentified by-products before which were converted into LA at high concentration. In other words, the ratio of the catalyst to the fructose plays a key factor for inhibition of the side reaction.

Synthesis of LA from other carbohydrate compounds

In this section, the optimum reaction conditions obtained with fructose were attempted to apply for converting various carbohydrate compounds such as C6-sugars (glucose, mannose, galactose), sucrose, cellobiose, inulin and cellulose.

Results in Table 2.8 shows that fructose is very active and easy to be converted into LA, while other hexose sugars, *e.g.* glucose, galactose and mannose (entries 2-4), are quite stable and almost unchanged after 24 h.

Table 2.7: Effect of solution concentration on the fructose conversion over Amberlyst-15.

Entry	Fructose content /%	Fructose Conv. /%	Yield /%		
			LA	FA	HMF
1	5	98	53	69	3
2	10	97	52	59	3
3	20	96	46	53	3
4	30	99	35	41	4
5	40	93	29	37	4
6	50	92	21	29	5

Reaction conditions: Amberlyst-15 (0.4 g), fructose solution volume (4 mL), temperature (120 °C), time (24 h), 500 rpm.

The similar results were observed when performing the reactions with dimer or polymer of hexose sugars as starting materials. Firstly, these compounds were hydrolyzed easily under acidic condition affording corresponding hexose sugars followed by dehydration to generate LA. Degradation of inulin resulted fructose that easily converted completely to LA with 50% yield. Sucrose was hydrolyzed to fructose and glucose, fructose continued to be dehydrated after that to LA while glucose remained 45%. Glucose obtained after the hydrolysis of cellulose and cellobiose also did not react to final product.

Due to the low activity of glucose, galactose and mannose, I attempted to increase reaction temperature and reaction time in order to elevate yield of LA. Reactions were carried out at 150°C. The dependence of LA yields on reaction time was shown in Fig. 2.8.

Obtained results exhibited that Amberlyst-15 could dehydration of glucose, galactose and mannose forming 40-45% yield of LA. However, reactions needed long time to achieve the meaningful conversions of C6-sugars and LA yields. Under these conditions,

Table 2.8: Dehydration of some carbohydrate compounds to LA using Amberlyst-15 at 120 °C

Entry	Substrate	Remaining C6-sugar /%	Conv. /%	LA yield /%
1	Fructose	0	100	52
2	Glucose	95	5	ND
3	Galactose	95	5	ND
4	Mannose	95	5	ND
5 ^a	Sucrose	45 ^b	56	27
6 ^a	Cellobiose	94 ^b	4	ND
7 ^a	Inulin	0 ^c	100	50
8 ^a	Cellulose	93 ^b	3	ND

Reaction conditions: Amberlyst-15 (0.4 g), substrate (0.3 g), water (6 mL), temperature (120 °C), time (24 h), 500 rpm, ^a the values of conversions and LA yields are calculated based on C6-sugar content, ^b glucose, ^c fructose, ND: not detected.

cellobiose and cellulose (dimer and polymer of glucose) also gave 45% and 42% yield of LA, respectively.

2.4 Conclusions

In the presence of solid acid catalysts, HMF could be easily hydrated to LA. The hydration reaction occurred slowly at temperature lower than 100 °C. At 120 °C, reaction took place faster and maximum LA yield (*ca.* 80%) were obtained after 12 and 18 h when using Amberlyst-15 and Nafion-NR50 catalysts, respectively.

For dehydration fructose, various solid catalysts were used. Among tested catalysts, Amberlyst-15 exhibited the most effective solid acid catalyst for converting fructose into LA under mild reaction conditions in water. Under the optimum conditions, 52% yield of LA was obtained. Amberlyst-15 could be used many times without significant loss of its activity.

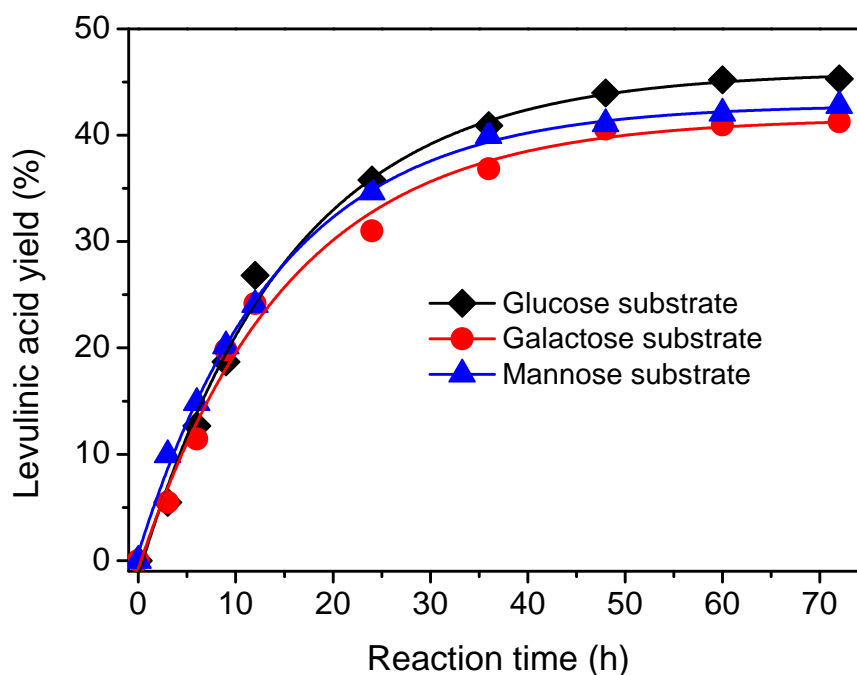


Figure 2.8: Conversion of C6-sugars to LA as function of reaction time. *Reaction conditions:* C6-sugar (0.3 g, 1.67 mmol), water (6 mL), Amberlyst-15 (0.4 g), 150 °C, 500 rpm.

These optimum reaction conditions that were found with fructose above were applied for production of LA from other hexose sugars or its corresponding dimers or polymers. It was found that under these condition, the reaction took place very slowly to give trace contents of product. The significant product amounts were observed when increasing reaction temperature and reaction time to 150 °C and 60 h or higher, respectively.

Despite of less active than fructose, other hexose sugars, especially glucose, prefer to use in industry because of its low cost and availability in nature. The direct transformation of glucose to expected products usually needs harsh conditions. However, the benign reaction conditions are required for saving input energy and reducing the environmental impact. In order to smoothly convert glucose to LA under mild reaction conditions, isomerization of glucose to fructose is necessary. The isomerization of glucose to fructose and conversion of glucose into LA under mild reaction conditions will be discussed in next chapter.

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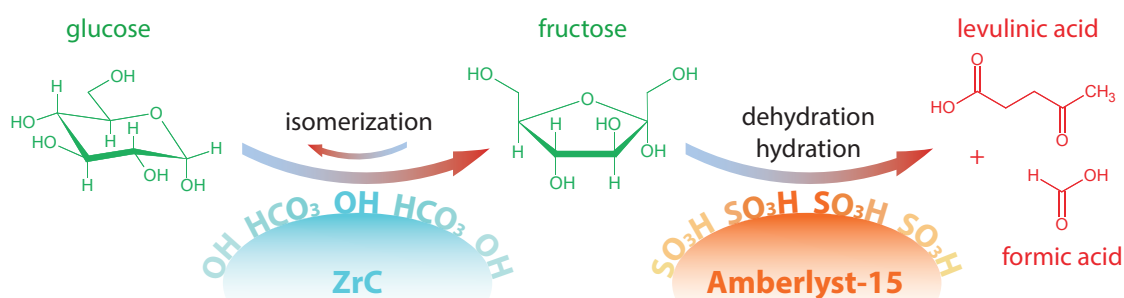
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Chapter 3

Preparation of Zirconium Carbonate as Solid Base Catalyst for Glucose Isomerization and Levulinic Acid Production

Abstract



In this chapter, zirconium compounds were prepared as water-tolerant solid base catalysts by a simple method. The catalytic activities were investigated in aqueous glucose-fructose isomerization reaction. From the effect of catalyst drying temperature and TG results, Zr-OH groups were proposed to be basic sites. The zirconium carbonate (ZrC) catalyst could work in wide range of reaction temperature (80-140 °C) and the maximum glucose conversion reached 45% at 120 °C with 76% selectivity to fructose. The ZrC catalyst was found to remain its activity without significant decrease in the fructose yield after being used for five times. In the one-pot transformation of glucose to levulinic acid (LA), ZrC could be combined with a solid acid catalyst, Amberlyst-15 to afford 17% yield of LA in two steps in water-toluene biphasic solvent after a reaction time of 12 h. The proposed reaction system in water-toluene biphasic solvent occurred faster and gave higher LA yield than that in pure water solvent.

3.1 Introduction

The isomerization reaction of sugars is a key step in the sequential reaction chain of conversion of lignocellulosic materials into value-added fuels and chemicals [1–6]. Among the transformations between sugars, the conversion of glucose into fructose is very important because glucose is the most abundant natural monomer unit of carbohydrates whereas fructose reveals as the most active monosaccharide for production of valuable compounds [1] such as 5-hydroxymethylfurfural (HMF) [7–9] and levulinic acid [10–12]. It is well known that the dehydration of aldohexose sugar (glucose) to HMF and LA is much more difficult than ketohexose sugar (fructose) [1]. Therefore, the direct transformation of glucose to value-added compounds is not as efficient and selective as from fructose. However, glucose is still used in industry as the starting material because its cost is lower than that of fructose [1].

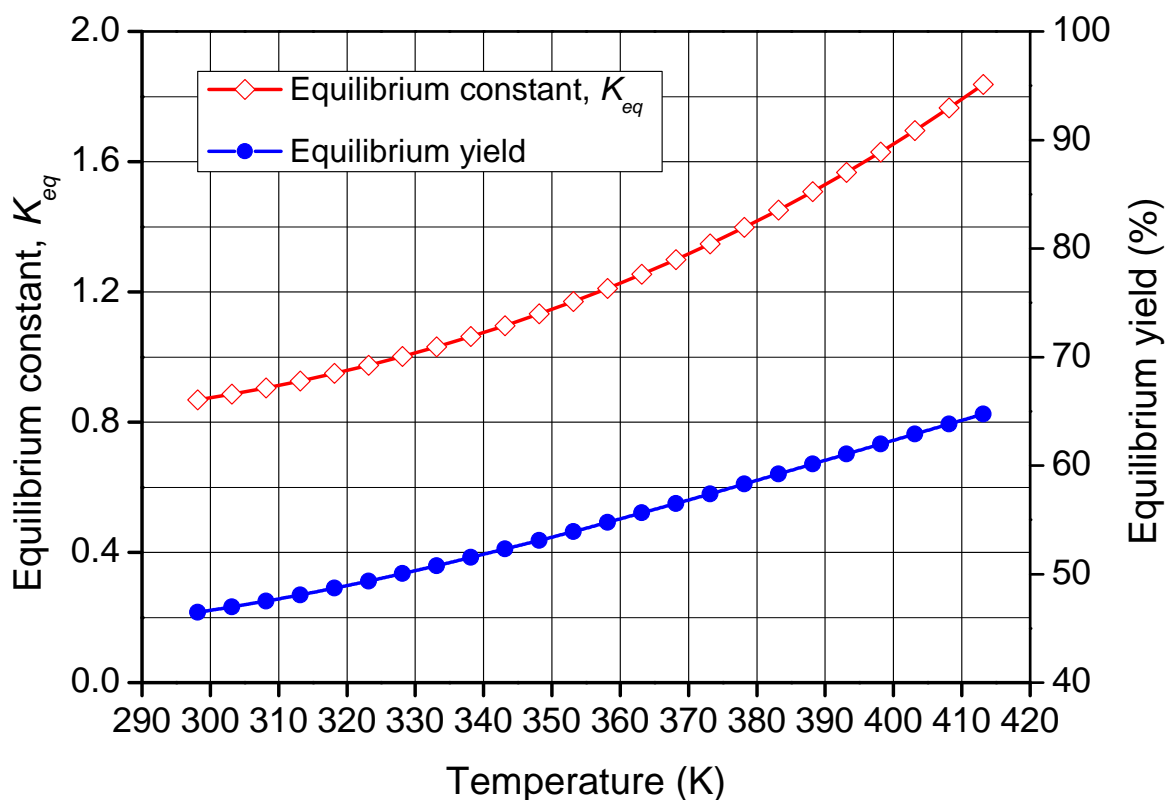


Figure 3.1: The dependences of K_{eq} and equilibrium yield of fructose on temperature

The glucose-fructose isomerization reaction is slightly endothermic and reversible with the equilibrium constant $K_{eq} = 0.87$ and the equilibrium conversion of 46% at 25 °C (Figure 3.1) [13]. The small thermal effect ($\Delta H = 2.78 \text{ kJ mol}^{-1}$) suggests that the K_{eq} increases very slowly when rising up the reaction temperature. In industry, glucose-fructose isomerization reaction is typically catalyzed by an immobilized enzyme at 60 °C resulting 42% fructose yield [14, 15]. In spite of their high performance, enzymes are very expensive and their utilization requires reactant purification, narrow range of operating pH and temperature. These strict requirements make the difficulty for producing chemicals or biofuels from glucose (or other carbohydrate compounds). Unlike enzyme-catalyzed processes, chemical catalytic processes using inexpensive inorganic compounds to promote the isomerization under wider range of reaction conditions have been investigated. Alkaline aqueous solutions is used as homogeneous catalysts for the glucose isomerization [16, 17]. However, the homogeneous processes are facing with severe environmental and technical problems as well as the recovery of the catalysts. In addition, the monosaccharides are unstable under strong basic medium [18, 19]. These reasons have stimulated the search for alternative heterogeneous catalysts for the glucose-fructose transformation.

Some results have been reported on the glucose isomerization in the presence of anion-exchange resins (aluminate and hydroxide forms) using fixed bed reactors in water solvent [20, 21]. The fructose yields were 72, 58 and 44% at 2, 25 and 35 °C, respectively; however, the reactions took place too slowly (those needed 1007, 15 and 4 h for good yields, respectively). Recently, many researches have focused on the utilization of inorganic solid bases because they possess high mechanical, chemical and thermal stabilities. Cation-exchanged zeolites and hydrotalcite could catalyze the isomerization reaction in water at 95 °C, and it gave high fructose selectivity (*ca.* 90%) for 15-20% glucose conversions [22, 23]. Glucose was also isomerized to fructose with 35% yield over

rehydrated Mg-Al hydrotalcite catalyst in *N,N*-dimethylformamide at 80 °C for 3 h [24]. Other metal oxides or metals, such as TiO₂ (anatase), ZrO₂ (tetragonal-monoclinic) [25] or Pt nanoparticles [26] were investigated as catalysts for glucose isomerization reaction in aqueous medium. However, these catalysts exhibited good activity only at high temperature (*ca.* 200 °C). Tin-containing zeolite was a highly active catalyst for the glucose isomerization in water, but preparation process of the catalyst was quite complicated and needed very long time (under hydrothermal condition in an autoclave for 25-40 days) [27, 28]. The high yield of fructose (20-39%) was obtained after 2 h when using titanosilicates containing non-framework or framework alkali metals in aqueous phase at 100 °C [29]. More recently, tin-beta zeolite [30] and metal chlorides [31] were utilized as Lewis acid catalysts for glucose-to-fructose transformation step in the production of HMF from glucose using biphasic reactor system in combination with HCl as the dehydration catalyst to afford *ca.* 60% HMF yield. The advantage of these Lewis acids is good working ability in water or biphasic water/alkylphenol media even at low pH, however, the reactions usually need high temperatures (170-180 °C).

In this chapter, I prepared an efficient and recyclable solid base catalyst based on zirconium carbonate (ZrC) and attempted to isomerize glucose to fructose in water in wide range of reaction temperature. The ZrC was also combined with a solid acid catalyst for the one-pot synthesis of LA from glucose. LA has been reported to be synthesized directly from hexose sugars (*i.e.* glucose and fructose) using acid catalysts such as Amberlyst-15 [12, 32], Nafion SAC-13 [33], MFI-type zeolite [11], LZY zeolite [10], and sulfuric acid [34], sulfated-ZrO₂-TiO₂ [35]. The one-pot conversion of glucose into LA in this research comprises base-catalyzed glucose isomerization into fructose, and subsequent acid-catalyzed dehydration of fructose into HMF and hydration of HMF into LA. I found that the use of water/toluene biphasic solvent in the one-pot system gave 17% yield of LA from glucose.

3.2 Experimental

3.2.1 Materials

ZrOCl₂•8H₂O, Na₂CO₃, NaOH and Na₂HPO₄ were supplied by Kanto Chemical Co., Inc. Glucose, fructose, benzoic acid were obtained from Wako Pure Chemical Industries, Ltd. Amberlyst-15, Amberlyst A21 and Amberlyst A26 OH were purchased from Sigma-Aldrich. Hydrotalcite with Mg/Al ratio of 3 (HT3) was served by Tomita Pharmaceutical Co., Ltd. Organic solvents were provided by Wako and Kanto companies. All chemicals were used without any further purification.

3.2.2 Preparation and characterization of solid base catalyst based on zirconium

3.2.2.1 Catalyst preparation

Zirconium carbonate (denoted by ZrC) was prepared as following procedure: 40 mL of 0.5 M ZrOCl₂•8H₂O solution (A) and 100 mL of 0.25 M Na₂CO₃ solution (B) were prepared in individual flasks. The solution (A) was added slowly into the solution (B) by a peristaltic pump with rate of 1 mL min⁻¹. The obtained white gel was aged at 70 °C for 12 h, then the solid was recovered by filtration, washed with 1000 mL of distilled water (till the pH of filtrate reached to *ca.* 7) and dried at different temperatures for 3 h. Zirconium hydroxide (denoted by ZrOH) and zirconium phosphate (denoted by ZrP) were also prepared with the similar procedure described above with 0.5 M NaOH and 0.167 M Na₂HPO₄ solutions instead of Na₂CO₃, respectively.

3.2.2.2 Catalyst characterization techniques

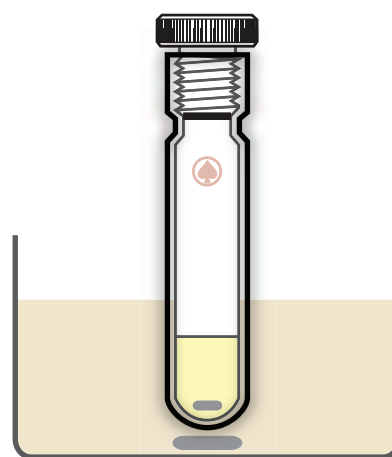
XRD patterns were obtained on a Rigaku-SmartLab diffractometer using the CuK α radiation, $\lambda = 1.5406$ nm with an X-ray generator working at 40 kV and 30 mA. The data were collected from $2\theta = 5 - 80^\circ$ with scanning rate of 2° min^{-1} . Thermogravimetric analysis was performed with TG/DTA 220 SSC/5200 Seiko Instruments using Pt cru-

cible in the temperature range from RT to 750 °C with a heating rate of 10 °C min⁻¹ in N₂ gas flow (40 mL min⁻¹). FT-IR spectra were collected in a range of 500-4000 cm⁻¹ on a Perkin Elmer Spectrum 100 FT-IR Spectrometer. Nitrogen adsorption analysis at 77 K was carried out using BELSORP-max instrument. The samples were degassed at 100 °C for 4 h. BET surface area was calculated by N₂ adsorption in the relative pressure range in 0.05-0.5. The amount of basic sites on the catalysts was estimated by the titration method using benzoic acid as standard solution. Typically, 0.1 g of sample was dispersed in 2 mL of water/ethanol (4/1 V/V) solution including phenolphthalein. Then, the 0.05 M benzoic acid was added into the above solution until its color disappeared. The concentration of basic sites was calculated by the following formula:

$$\text{Basic site content (mmol g}^{-1}\text{)} = \frac{\text{Consumed amount of benzoic acid (mmol)}}{\text{Weight of catalyst (g)}} \quad (3.1)$$

3.2.3 Procedure of catalytic reaction and product analysis

For isomerization reaction, 0.3 g of glucose (1.67 mmol), 0.3 g of catalyst and 3 mL of water were introduced in a closed glass reactor. The reactor was heated in an oil-bath and stirred by a magnetic stirrer (500 rpm) at desired temperatures (typically, 80, 100, 120 and 140 °C). After reaction, the mixture was cooled down, diluted 20 times with water followed by filtration (using 0.2 m Millex filter unit) before analysis.



To estimate the reusability of ZrC catalyst, after each run, catalyst was separated by centrifugation, washed twice with water followed by dry at 80 °C for 1 h before adding a fresh aqueous glucose solution.

The glucose can be converted into LA by the one-pot reaction using pair of solid base

and acid catalysts. Typically, 0.3 g of glucose, certain amount of ZrC, Amberlyst-15 and 3 mL of solvent were introduced into a sealed glass tube reactor. The reactor was put in an oil-bath at desired temperature while keeping constant stir (500 rpm). After the reaction, the reactor was taken out and put in cold water to quench the reaction. The reaction mixture was filtered using 0.2 m Millex filter unit, diluted 20 times with water before HPLC analysis.

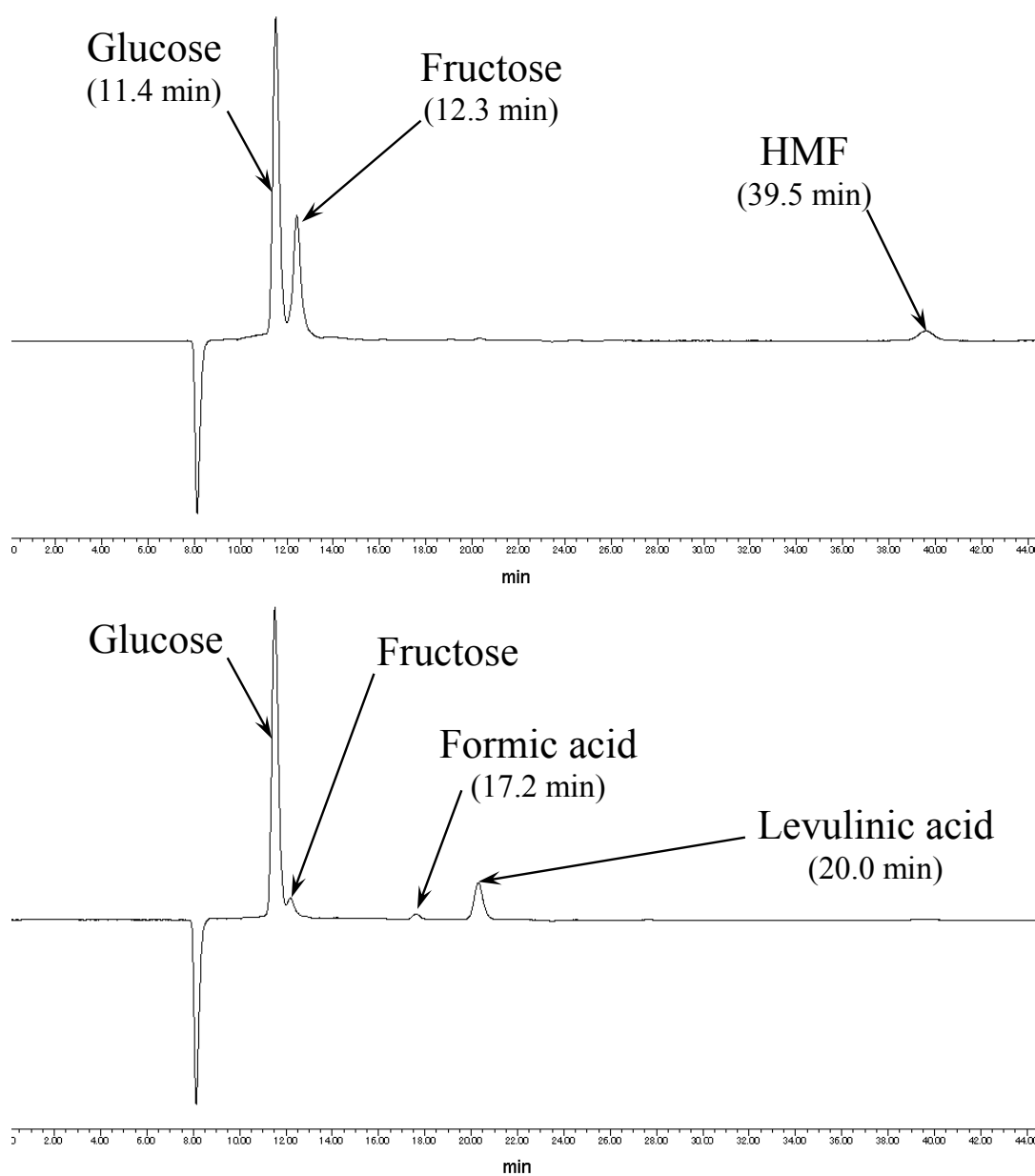


Figure 3.2: Typical HPLC chromatograms.

The amounts of the reactant and products were determined by a high performance liquid chromatograph (HPLC, Waters Co. Ltd.) equipped with Aminex HPX-87H column (Bio-Rad Laboratories, Inc.) and a refractive index detector. The conditions for the analysis were set as follows: 10 mM H₂SO₄ aq. eluent at a flow rate of 0.5 mL min⁻¹, both column and detector were operated at 50 °C. Typically, the retention times of glucose, fructose, formic acid, levulinic acid and 5-hydroxymethylfurfural were obtained on the HPLC charts at 11.4, 12.3, 17.2, 20.0 and 39.5 min, respectively.

3.3 Results and discussion

3.3.1 Catalyst characterization

Powder XRD patterns of the dried samples of ZrC, ZrP and ZrOH were shown in Figure 3.3. All XRD patterns exhibited two broaden peaks in ranges of 15-40° and 40-70° indicating the amorphous phase of solids in these three samples. Some small peaks appeared on the XRD pattern of ZrC sample dried at 250 °C were assigned to ZrO₂ tetragonal phase (JCPDS No. 42-1164). Drying catalyst at high temperatures causes the condensation of Zr-OH group on the surface of catalyst and the formation of ZrO₂ phase. The effect of drying temperature on the catalytic activity will be discussed later.

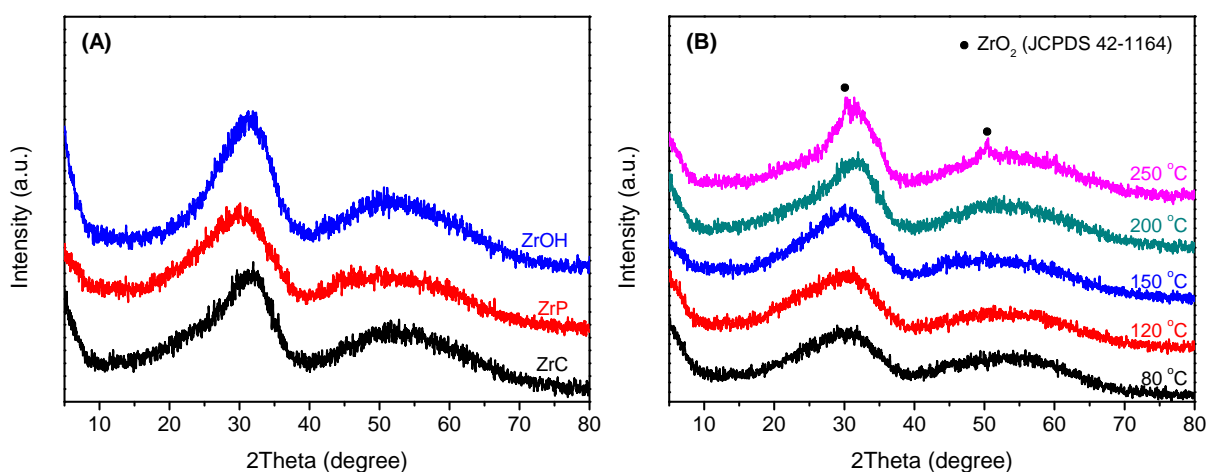


Figure 3.3: XRD patterns of (A) catalyst based on zirconium compounds and (B) ZrC dried at different temperatures

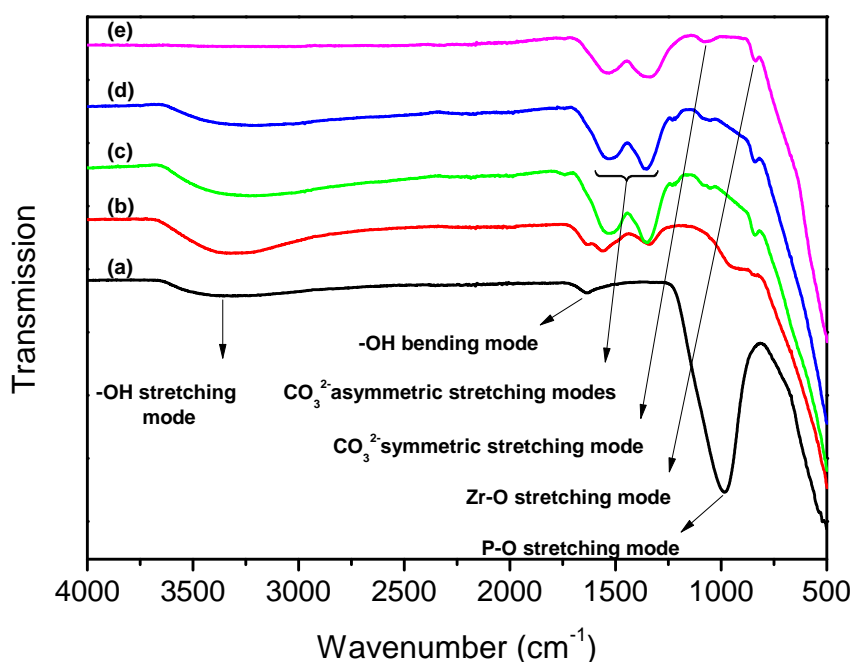


Figure 3.4: FT-IR spectra of (a) ZrP dried at 150 °C, (b) ZrOH dried at 150 °C and ZrC dried at (c) 120°C, (d) 150 °C and (e) 250 °C.

Figure 3.4 shows the FT-IR spectra of prepared zirconium compounds. The absorption bands at 3320 and 1640 cm^{-1} were assigned to the asymmetric stretching and bending modes of -OH groups which are present in samples as the basic sites. The weak absorption band at 837 cm^{-1} was attributed to Zr-O stretching mode [36]. Two bands at 1530 and 1356 cm^{-1} belonged to CO_3^{2-} asymmetric stretching modes [37], while a very weak band at 1072 cm^{-1} was assigned to the CO_3^{2-} symmetric stretching mode. These absorption bands demonstrated the presence of carbonate groups in ZrC samples. The FT-IR spectrum of ZrP sample had an absorption band at 986 cm^{-1} that was attributed to the P-O stretching mode [38, 39]. The FT-IR spectra of ZrC samples dried at different temperatures (Figure 3.4 (c)-(e)) showed that, below 150 °C, intensities of the bands at 3320 cm^{-1} (characteristic of -OH group) were almost unchanged, while no band was observed in this region on the spectrum of ZrC dried at 250 °C. This would relate to the decrease in catalytic activity of ZrC dried at high temperature (*vide infra*).

Table 3.1: Basic site amount of ZrC dried at different temperatures

Entry	Drying temperature	Basic site amount
	/°C	/mmol g ⁻¹
1	80	0.15
2	120	0.20
3	150	0.19
4	200	0.07
5	250	0.01

Table 3.2: Lists of the base strength using color indicators and the basic amount using titration method for solid base catalysts

Catalyst	Indicator			Basic site
	Phenolphthalein	Brilliant cresyl blue	2,4-dinitroaniline	amount
	p <i>K</i> _a = 9.2	p <i>K</i> _a = 11	p <i>K</i> _a = 15	/ mmol g ⁻¹
ZrP ^a	+	–	–	0.04
ZrOH ^a	+	–	–	0.05
ZrC ^a	+	+	–	0.19
HT3 ^b	+	+	–	0.21
Amberlyst A21 ^b	+	+	–	0.10
Amberlyst A26 ^b	+	+	+	0.20

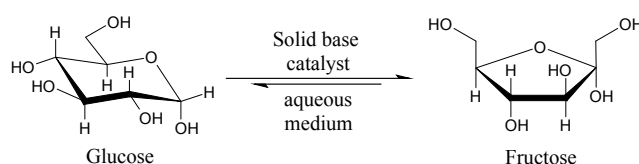
Testing conditions for base strength experiment: catalyst (0.1 g), indicator solution (1 mL), basic color (+), acidic color (–). Solution of each indicator was prepared by dissolving 0.02 g indicator in 100 mL water/ethanol (volume ratio 4:1), ^acatalysts were dried at 150 °C, ^b commercial catalysts.

The amounts of basic site on ZrC catalysts dried at different temperatures were determined by the titration method with 0.05 M benzoic acid solution in the presence of phenolphthalein (p*K*_a = 9.2) as a color indicator (Table 3.1). The result exhibited that the concentration of basic site was changed as the drying temperature, and had the max-

imum value around 120-150 °C. The obtained basic site content of ZrC catalyst died at 150 °C (0.19 mmol g⁻¹) can be comparable with those of HT3 and Amberlyst A26 OH (see Table 3.2). Moreover, it was attempted that the basic strengths of ZrC, ZrP, ZrOH and commercial base catalysts were determined by color indicators having different p*K*_a values. From the obtained results shown in Table 3.2, the order of the basic strength is found to be Amberlyst A26 OH > ZrC, HT3, Amberlyst A21 > ZrOH, ZrP.

3.3.2 Isomerization of glucose to fructose over solid base catalysts

Table 3.3: Glucose-Fructose isomerization over solid base catalysts



Entry	Catalyst	Basic site amount /mmol g ⁻¹	Glucose	Fructose	Fructose
			Conv. /%	Yield /%	Sel. /%
1	ZrC ^a	0.19	45	34	76
2	ZrP ^a	0.05	28	16	58
3	ZrOH ^a	0.04	47	12	25
4	Amberlyst A26 OH	0.20	53	24	46
5	Amberlyst A21	0.10	26	21	80
6	HT3	0.21	26	19	71

Reaction conditions: glucose (0.3 g, 1.67 mmol), catalyst (0.3 g), water (3 mL), reaction temperature (120 °C), time (20 min), 500 rpm, ^a drying temperature (150 °C)

Catalytic activity of the ZrC in the glucose-fructose isomerization reaction was compared to those of HT3, ZrOH, ZrP, and basic Amberlyst catalysts. The results were shown in Table 3.3. All obtained values of selectivity to fructose were less than 100%, but the HPLC chromatographs showed only two peaks that belonged to glucose and fructose with retention time at 11.4 and 12.3 min, respectively. The lower of fructose

selectivities than unit are due to the formation of undesired insoluble-materials, known as humins [18,19], during the reaction.

Among tested solid base catalysts, the ZrC gave the highest fructose yield (34%), which is much higher value than those of ZrOH and ZrP (entries 1-3, Table 3.3). The use of Amberlyst A26 OH, which possesses the strongest basic strength with a large amount of basic sites among those catalysts in listed in Table 3.3, led to the fast degradation of sugars (53% glucose conversion) but gave lower yield and selectivity for fructose than ZrC (entry 4). Amberlyst A21 and HT3 having same basic strength showed the same catalytic activities in the glucose-fructose isomerization reaction (entries 5 and 6, 3.3). Interestingly, though both of ZrC and HT3 had same amount and strength of basic site, the activity for glucose isomerization over HT3 was still poorer than that of ZrC (entries 1 and 4, Table 3.3). It could infer that the basic strength of HT3 seemed to be slightly lower than ZrC. These results suggested that the ZrC became an effective base catalyst for the glucose-fructose isomerization because it possessed the moderate basic strength and the highest amount of basic site.

The changes of catalytic activity on the ZrC versus catalyst drying temperature were also carried out (Figure 3.5). The obtained result showed that the activity of ZrC was almost unchanged when drying temperature reached 150 °C, whereas it decreased significantly if the drying temperature was higher than 200 °C. It suggested that the most of base sites were derived from Zr-OH groups, and which was lost with increasing the drying temperature due to the condensation Zr-OH group together to form ZrO₂ phase (see XRD pattern, Fig. 3.4 B). The decrease in intensity of -OH group on the IR spectra (Figure 3.4) and the change in basic site amount for drying temperature (Table 3.1) were well fitted with these suggestions. A high drying temperature up to 150 °C leads to reduce the amount of base site and catalytic activity, therefore, the best drying temperature selected was 150 °C.

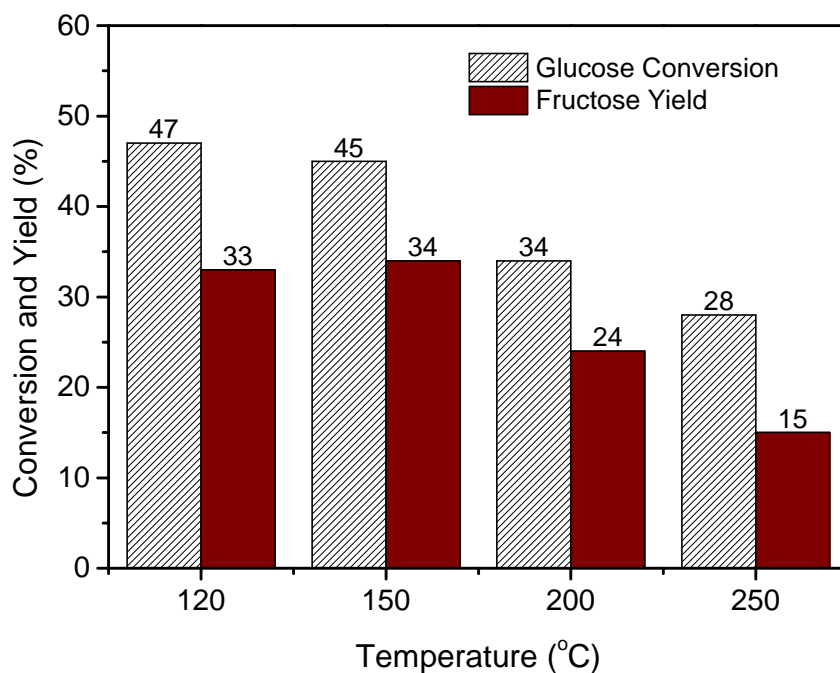


Figure 3.5: The effect of drying temperature of the ZrC catalyst on the reaction performance. Reaction conditions: glucose (0.3 g, 1.67 mmol), ZrC (0.3 g), water (3 mL), time (20 min).

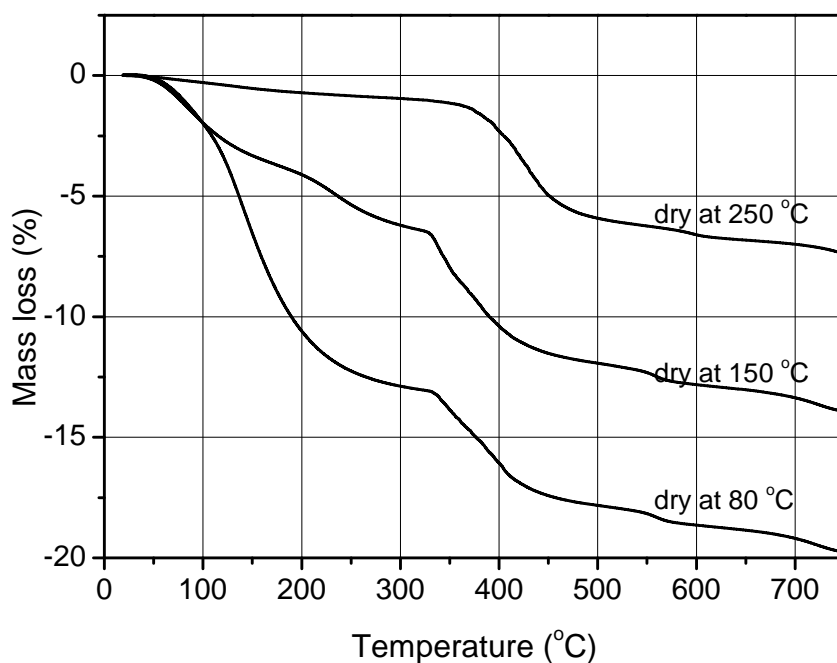


Figure 3.6: The thermogravimetric curves of ZrC catalysts dried at different temperatures.

The thermogravimetric analysis (TG) profiles (Figure 3.6) showed that, the ZrC dried at 80 °C still contained large amount of water (moisture). After dry at 150 °C, the

moisture was lost from catalyst, but the basic sites were retained. Therefore, the catalytic activity almost unchanged when drying catalyst at the temperature in the range of 80-150 °C. The TG curve of ZrC dried at 250 °C almost had no mass variation in RT-350 °C in the TG curve. These results suggested that drying at 250 °C losses the adsorbed moisture and the structured water in preparation. This would concern with the decrease of basic site content in catalyst (Table 3.1) and cause the significant decrease in fructose yield in the case utilizing ZrC dried at 250 °C as catalyst (Figure 3.5). While, the mass losses in TG curves occurred at 300-500 °C and above 550 °C derived from the decomposition of carbonate forms were obtained in all three samples without significant differences. According to these results, it was supposed that the active sites are the Zr-OH groups in ZrC catalyst. The chemical composition of the prepared ZrC is $[\text{Zr}(\text{OH})_2\text{CO}_3]_x \cdot [\text{ZrO}_2]_y$ that possesses higher thermal stability than zirconium hydroxide (ZrOH) [40].

For determining the chemical formula of ZrC catalyst, the data of XPS, TG analyses were used.

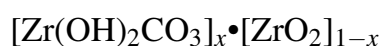
From XPS analysis, the atomic ratio of C : Zr : O was 8.1 : 24.0 : 67.9 or 1 : 3 : 8.4.

Table 3.4: Element content and specific area of zirconium compounds

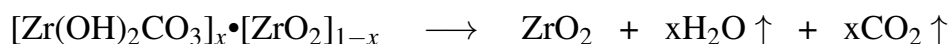
Catalyst	Element content (%) ^a				S _{BET} (m ² g ⁻¹)
	Zr	O	C	P	
ZrOH	45.5	54.5	-	-	25
ZrC	24.0	67.9	8.1	-	48
ZrP	24.1	63.2	-	12.7	30

^a Obtained from XPS analysis

Because ZrC may contain hydroxyl and carbonate groups (according to FT-IR spectrum of ZrC, Figure 3.4), formula of ZrC catalyst is proposed to be



with molecular weight of $(63x + 123) \text{ g mol}^{-1}$. When calcinating, ZrC is decomposed as following reaction:



Total lost mass of H_2O and CO_2 is $62x$. Therefore, the percentage of mass loss is $\frac{62x}{62x+123}$. From TG result (Figure 3.6), the mass loss of ZrC dried at $150 \text{ }^\circ\text{C}$ is 14%. So, we have:

$$\frac{62x}{62x+123} = 0.14 \quad \text{or} \quad x = 0.32$$

Hence, formula of ZrC can be written as $[\text{Zr}(\text{OH})_2\text{CO}_3]_{0.32} \cdot [\text{ZrO}_2]_{0.68}$

With this formula, the atomic ratio of C : Zr : O = 1 : 3.1 : 9.3. This ratio is well agreed with result obtained from XPS analysis.

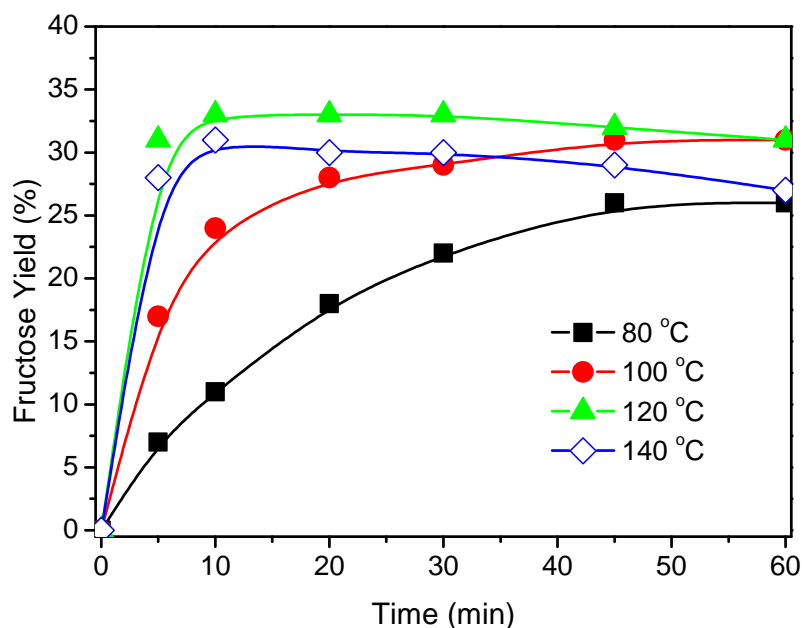


Figure 3.7: Plots of fructose yields from glucose isomerization over ZrC catalyst at the difference reaction temperatures. *Reaction conditions:* glucose (0.3 g, 1.67 mmol), ZrC catalyst (0.3 g), water (3 mL), 500 rpm.

As mentioned in the introduction section, the isomerization reaction was strongly influenced by the reaction temperature. To estimate the effect of temperature, the reaction was carried out at different temperatures from 80 to $140 \text{ }^\circ\text{C}$. The time profile for each

reaction temperature was shown in Figure 3.7. The reaction took place very fast at 120 °C and 140 °C. The maximum fructose yield was reached only after 10 min of the reaction. After that, the fructose yields decreased gradually because fructose was degraded partly at high temperature as reported in references [18, 19, 27]. At temperatures below 100 °C, the reaction was slower and needed longer time (more than 60 min) to reach the maximum fructose yield. Therefore, 120 °C is the optimum temperature for isomerization of glucose by ZrC catalyst. This temperature was suitable for further upgrading reaction of fructose to higher valuable compounds, such as LA [12] (*vide infra*).

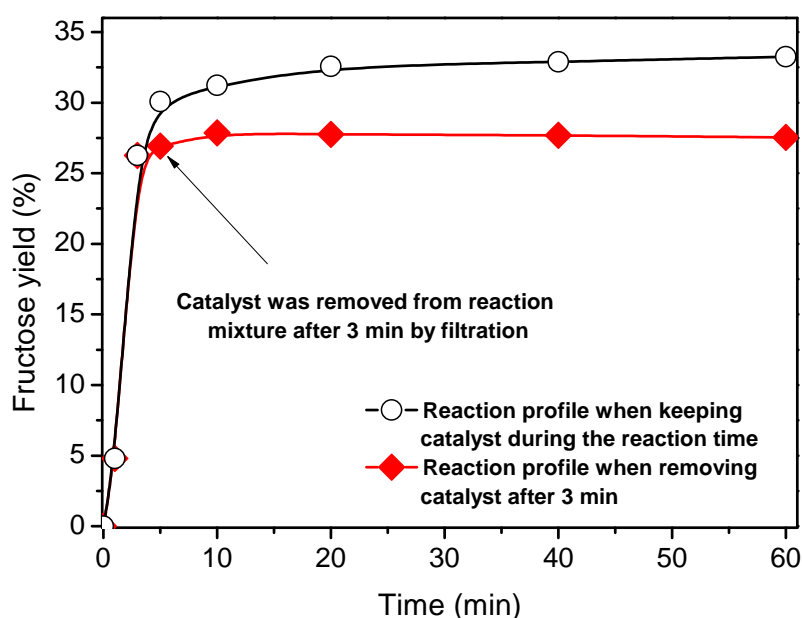


Figure 3.8: Experiment for checking the heterogeneous nature of ZrC catalyst. *Reaction conditions:* glucose (0.3 g, 1.67 mmol), ZrC (0.3 g), water (3 mL), reaction temperature (120 °C), 500 rpm, fructose yield with catalyst, fructose yield by removing catalyst after 3 min.

In order to check the heterogeneous nature of ZrC-catalyzed glucose isomerization reaction, the catalyst was removed from reaction mixture at time of 3 min. The filtrate was continued to react at same conditions to monitor the changes of glucose conversion and fructose yield. The results (Figure 3.8) showed that the fructose yield no longer increased alongside the reaction time (keep almost unchanged at 28%) when the catalyst was removed after 3 min. This result confirmed that the isomerization reaction catalyzed

In a one-pot reaction producing LA from glucose, ZrC would act as solid base catalyst for the transformation of glucose to fructose before acid-catalyzed fructose dehydration and successive hydration of HMF to LA (Scheme 3.1). As a solid catalyst, I employed Amberlyst-15 because it could effectively convert fructose to LA in the presence of water [12].

Table 3.6: Conversion of glucose into levulinic acid over different catalyst systems

Entry	Glu	Fruc		HMF		LA		FA	
	Conv.	Yield	Sel.	Yield	Sel.	Yield	Sel.	Yield	Sel.
	%	%	%	%	%	%	%	%	%
1	28, 44 ^a	0, 6 ^a	0, 14 ^a	0, 0 ^a	0, 0 ^a	4, 4 ^a	15, 8 ^a	10, 8 ^a	35, 19 ^a
2b	45	34	76	0	0	0	0	0	0
3c	11	0	0	0	0	0	0	0	0
4d	0	0	0	0	0	0	0	0	0

Reaction conditions: glucose (0.3 g, 1.67 mmol), ZrC catalyst (0.3 g), Amberlyst-15 (0.3 g), water (3 mL), reaction temperature (120 °C), 500 rpm, reaction time (24 h), ^a Amberlyst-15 (0.1 g), ^b without Amberlyst-15, reaction time (20 min), ^c without ZrC catalyst, ^d blank.

In this reaction, there is FA as a co-product of LA and HMF as an intermediate. The results of reactions with or without catalysts were listed in Table 3.6. According to the LA formation mechanism from HMF, the obtained amount (in mole) of LA and FA should be same [41]. However, the obtained amount (in mole) of FA is usually slightly higher than that of LA. This phenomena was also reported in some literatures [11, 42]. Without both catalysts and either ZrC or Amberlyst-15 (entries 2-4, Table 3.6), LA did not form. Only glucose-fructose isomerization reaction occurred when using solid base catalyst ZrC alone (entry 2), it showed 45% conversion of glucose to produced 34% yield of fructose (76% selectivity). When the ZrC catalyst was combined with Amberlyst-15, LA (4% yield) and FA (10% yield) were obtained (entry 1 and 1a). It indicated that the one-pot conversion of glucose into LA is possible in this catalytic system. The increase

in the amount of Amberlyst-15 scarcely influenced yield of LA and FA (entry 1).

Table 3.7: The one-pot synthesis of LA from glucose with various co-solvents having different dielectric constants and solubilities in water.

Co-solvent with water	Dielect. const.*	Polarity *	Solubility in water *	Glucose Conv. /%	Yield (Selectivity) /%			
					Fruc	HMF	LA	FA
Water	80.1	Polar protic	-	23	0 (0)	0 (2)	4 (18)	4 (18)
Dimethyl sulfoxide	47.2	Polar aprotic	Miscible	29	0 (0)	5 (18)	5 (19)	5 (19)
<i>N,N</i> -dimethylacetamide	37.8	Polar aprotic	Miscible	41	9 (22)	2 (4)	0 (0)	0 (0)
Acetonitrile	36.6	Polar aprotic	Miscible	27	0 (0)	4 (15)	0 (0)	0 (0)
Dichloromethane	8.9	Non-polar	Insoluble	24	0 (0)	0 (1)	7 (29)	7 (29)
Chloroform	4.8	Non-polar	Insoluble	18	0 (0)	0 (2)	8 (44)	9 (47)
Toluene	2.4	Non-polar	Insoluble	26	0 (0)	0 (1)	11 (43)	12 (46)
1,4-Dioxane	2.3	Non-polar	Miscible	46	0 (0)	2 (5)	14 (31)	15 (32)
Petroleum ether	2.1	Non-polar	Insoluble	19	0 (0)	0 (1)	6 (32)	6 (32)

* Dielectric constant (ϵ), polarity and solubility in water data were taken from references [43, 44]. *Reaction conditions:* glucose (0.3 g, 1.67 mmol), ZrC catalyst (0.3 g), Amberlyst-15 (0.3 g), reaction temperature (120 °C), 500 rpm, time (24 h), solvent system (1.5 mL of water + 1.5 mL of another solvent).

To improve the LA yield, I investigated a biphasic solvent system of water and toluene for the one-pot synthesis of LA with ZrC and Amberlyst-15 catalysts. In order to select the effective organic solvent, various polar and non-polar organic compounds such as dimethyl sulfoxide, *N,N*-dimethylacetamide, acetonitrile, dichloromethane, chloroform, toluene, 1,4-dioxane, and petroleum ether were tested for the reaction. These results were shown in Table 3.7. Co-solvents possessing high dielectric constant gave low LA yields, while non-polar solvent with low dielectric constant resulted in higher LA yield [45, 46]. Therefore, it was supposed that in the presence of non-polar solvent, the co-operation between solid base and solid acid catalysts took place better than in polar organic solvents. The reaction had higher glucose conversion but lower LA selectivity in water/1,4-dioxane than in water/toluene solvent system. Therefore, I selected

toluene as co-organic solvent for the one-pot synthesis of LA. The results obtained with different volume ratios of water/toluene were also examined as shown in Table 3.8. In comparison with pure water solvent, the water/toluene biphasic solvent system afforded the higher yield and selectivity of products in all cases. The lower water/toluene ratio yielded the higher glucose conversion and LA, however, the water/toluene ratio was limited till 1:1 because reactants could not dissolved well in high content of organic solvent. Thus, the best volume ratio of water/toluene was found to be 1:1.

Table 3.8: Transformation of glucose to levulinic acid in biphasic solvent system of water/toluene with different volume ratios

Entry	Solvent		Glu	Fru		HMF		LA		FA	
	Water /mL	Toluene /mL	Conv. /%	Yield /%	Sel. /%	Yield /%	Sel. /%	Yield /%	Sel. /%	Yield /%	Sel. /%
1	3.0	0.0	23	0	0	0.3	2	4	17	3	13
2	2.5	0.5	16	0	0	0.4	3	7	44	6	35
3	2.0	1.0	18	0	0	0.4	3	8	44	6	32
4	1.5	1.5	26	0	0	0.4	2	11	43	7	26

Reaction conditions: glucose (0.3 g, 1.67 mmol), ZrC (0.3 g), Amberlyst-15 (0.3 g), reaction temperature (120 °C), 500 rpm, time (24 h).

Finally, the one-pot reaction was carried out with two consecutive steps. In the first step, the isomerization reaction was catalyzed by ZrC until the fructose yield reached maximum (20 min). After that, Amberlyst-15 was added to the reaction mixture to convert fructose to LA via HMF formation. The time profiles of reactions in water and water/toluene (1:1 volume ratio) solvents were plotted in Figures 3.9. In both solvents, the yield of fructose formed by the isomerization (32% after 20 min) immediately decreased by adding Amberlyst-15 in the reaction system to form HMF and LA. HMF disappeared during the initial stage of the reaction. In the case of the reaction in pure water solvent, the rate of LA production was slower than that in biphasic water/toluene

solvent. In water, the LA yield increased gradually to 15% after 24 h reaction time. In contrast, the LA yield reached maximum value (*ca.* 17%) after only 12 h. Therefore, the presence of non-polar organic solvent enhanced the dehydration step of fructose to HMF that led the faster formation of final product, LA.

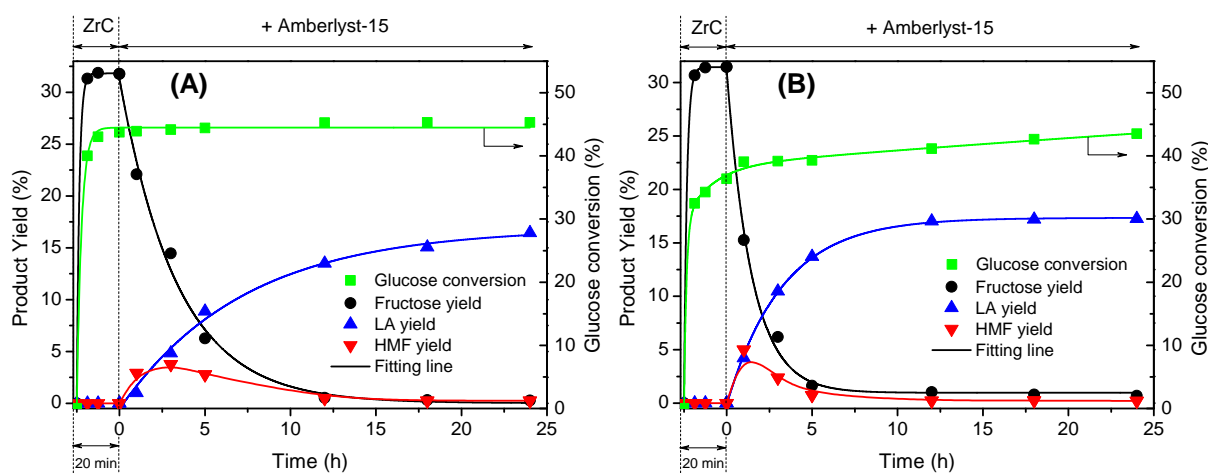


Figure 3.9: Time profile of reactions occurring in water (A) and in water/toluene (B). *Reaction conditions:* (A) water (3 mL), (B) water/toluene (1.5/1.5 mL/mL); glucose (0.3 g, 1.67 mmol), ZrC catalyst (0.15 g), Amberlyst-15 (0.3 g) was added after 20 min isomerization with ZrC, reaction temperature (120 °C), 500 rpm.

The use of water/toluene biphasic solvent accelerated acid-catalyzed reactions since fructose yield in the initial 20 min did not change in both solvents (pure water and water/toluene). In biphasic solvent system, catalysts and sugars were distributed in water phase, while formed HMF moved into toluene phase. These phenomena pushed dehydration reaction of fructose in water phase to shift toward HMF formation [45, 46]. The utilization of pure organic solvents for transform of sugars to LA is not necessary to be investigated because the rehydration of HMF to LA is prohibited in the absence of water.

These results implied that solid base ZrC catalyst could work together with solid acid Amberlyst-15 catalyst. In the case of pure water solvent, the glucose conversion did not change significantly after adding Amberlyst-15 whereas the glucose conversion gradually increased with the reaction time in the biphasic system. The ZrC still acted as solid base catalyst in the presence of Amberlyst-15 in the water/toluene biphasic system.

3.4 Conclusions

The preparation and the utilization of water-tolerant solid base catalyst zirconium carbonate for glucose isomerization to fructose in water are described. Zirconium carbonate (ZrC) can act as heterogeneous and reusable base catalyst for the aqueous glucose-fructose isomerization in wide range of temperature (80-140 °C). At 120 °C, the reaction occurs quite fast (20 min) to afford 34% yield of fructose. The solid base catalyst ZrC is also used with the solid acid catalyst in the same reactor to convert glucose to LA under mild reaction conditions without isolation and purification of intermediates. ZrC catalyst takes part in the glucose isomerization to fructose, a monosaccharide that is more active than glucose for the production of LA. The results also show that in the presence of non-polar co-organic solvents the reaction takes place faster and gave higher LA yield than in pure water.

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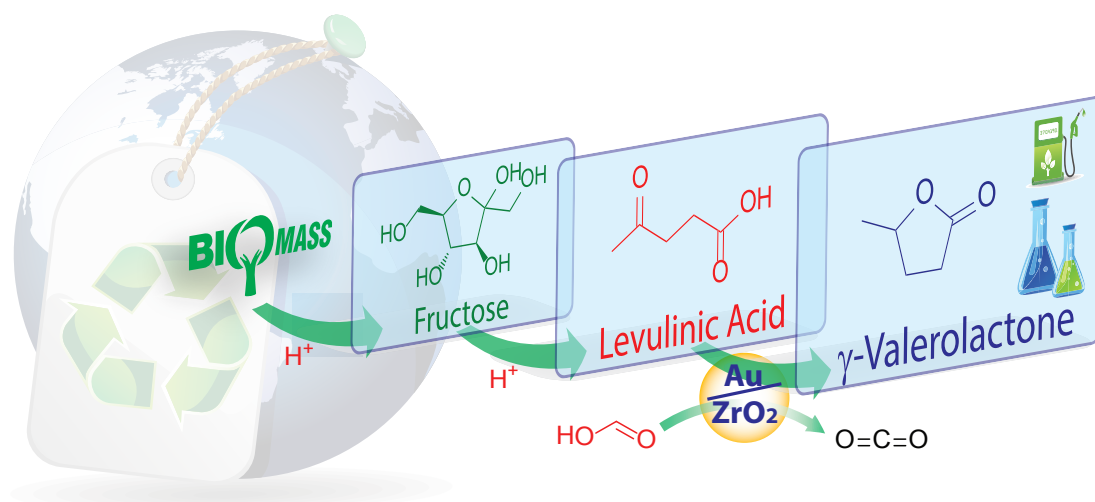
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Chapter 4

Production of γ -Valerolactone from Biomass-Derived Materials using Supported Metal Catalysts

Abstract



γ -Valerolactone (GVL) is a key intermediate for production of fuels and chemicals. In this chapter, GVL is synthesized from biomass-derived compounds using formic acid (FA) as a hydrogen source over various supported metal catalysts which are prepared by a simple impregnation or co-precipitation method. Under optimum conditions, levulinic acid (LA) is almost converted to GVL by Ru/C, Ru/SBA, Au/ZrC and Au/ZrO₂ catalysts with above 90% yield in water solvent. Especially, the Au/ZrO₂ showed excellent activity and recyclability; the Au/ZrO₂ catalyst can decompose completely FA to CO₂ and H₂, which gives high yield of GVL (*ca.* 97%) from hydrogenation of LA, and can retain its activity for at least 5 recycle runs. GVL is also obtained from one-pot dehy-

dration/hydrogenation reaction of fructose in water solvent. In this reaction, FA plays two roles: an acid catalyst for dehydration of fructose to LA, and a hydrogen source for hydrogenation of the obtained LA over supported metal catalysts. The Au/ZrO₂ is the best catalyst for dehydration/hydrogenation reaction with overall GVL yield of 48% and can be reused several times.

4.1 Introduction

The rapid developments of industry and transportation actions all over the world have led to a drastic increase in the demand of fuels. Currently, over 84% of this demand is based on the burning of fossil fuels – non-renewable resources (oil 34%, gas 28% and coal 22%), but these resources are finite and becoming more expensive. Furthermore, the combustion of fossil fuels for the production of heat and power is associated with a worldwide increase in greenhouse gas levels which is considered the main cause of climate change [1–4].

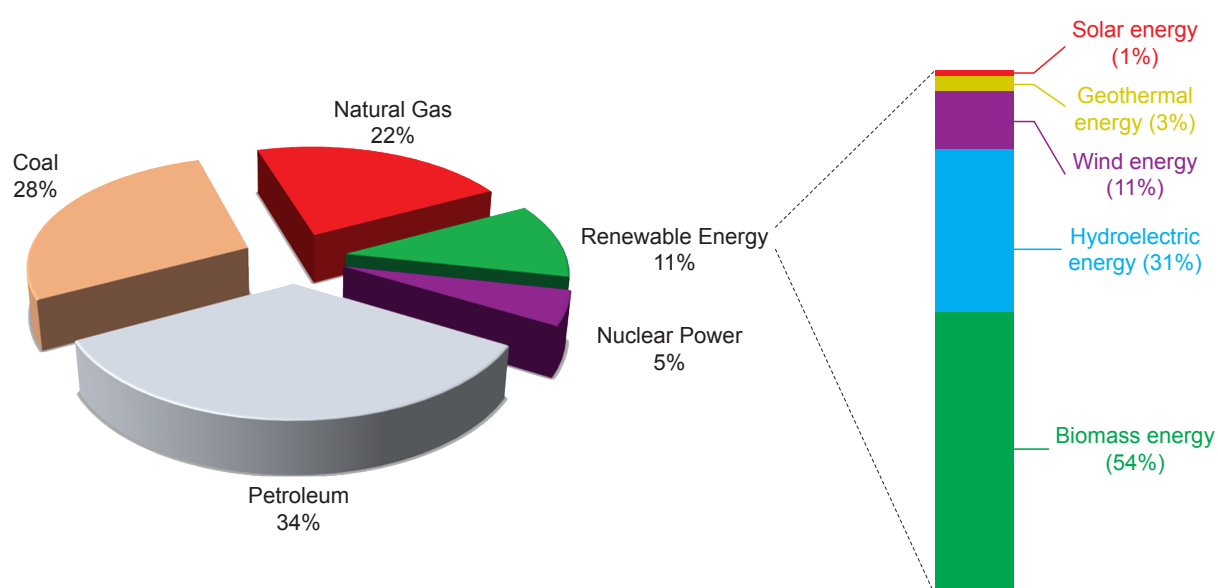
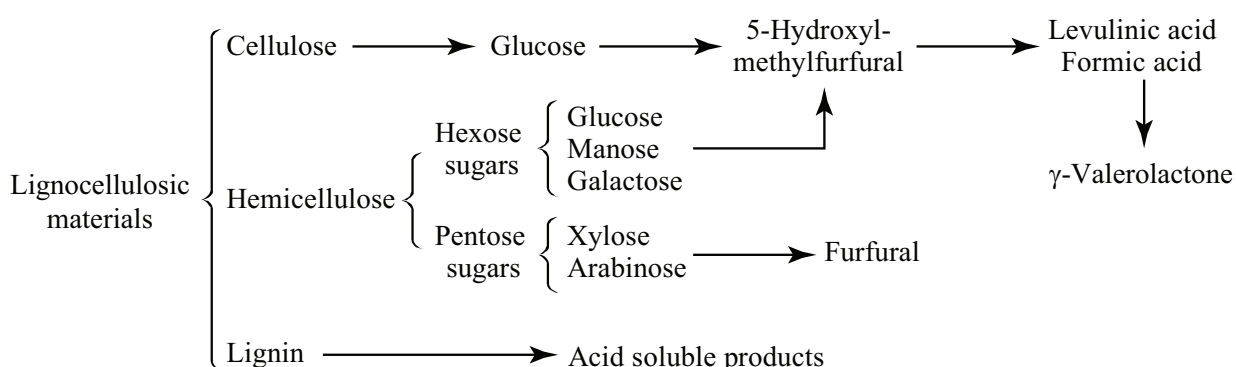


Figure 4.1: World energy consumption in 2010 (Data taken from [4])

Diminishing fossil resource reserves and degradation of the environment are strong

driving forces for the search for sustainable and renewable resources [4]. Various alternative energy sources have been developed, such as hydroelectric energy, wind power, geothermal energy, solar energy, and so on. Since the application of those energy sources might take longer than they are expected, the development of efficient processes to convert biomass resource into liquid fuels and valuable chemicals is a key research area in the next few decades [5–11]. Biomass is an abundant and renewable alternative resource that is the best candidate to replace fossil fuels for the sustainable production of energy [1–3, 12, 13] as well as chemicals [13–17].

Some of the most important characteristics for an expected ideal platform chemical include the possibility to use it for production of both energy and carbon-based products, renewable, easy and safe to store and move in large quantities, low melting point, high boiling and flash points, low or non-toxicity, easy for bio-degradation [5]. Because of its versatile properties, GVL is considered as one of the most promising platform molecules that satisfy above requirements. GVL can be converted into fuels, fuel additives [18, 19], green solvents [13, 20], food additives, and intermediates for chemicals and pharmaceutical industries [2, 21, 22].



Scheme 4.1: Pathway for conversion of lignocellulose into γ -valerolactone

One of the main challenges in converting lignocellulosic biomass is producing chemicals or fuels at high selectivities and yields at economical costs. Single-step methods,

like pyrolysis, rely on high temperatures to deconstruct the lignocellulosic biomass and lead to lower costs due to the lack of pretreatment steps. However, the produced liquid is a mixture of hundreds of compounds, which makes separations difficult prior to upgrading to targeted chemicals or fuels. Therefore, the transformation of lignocellulosic materials usually undergoes the hydrolysis process affording highly functionalized and reactive molecules (mainly C6 and C5 sugars). These sugars are processed at mild conditions to obtain intermediate molecules followed next catalytic conversion into levulinic acid and γ -valerolactone [13, 15, 22, 23].

One of the most effective methods than can be used for production of GVL is the hydrogenation of levulinic acid (LA) which can be obtained from the hydrolysis followed by dehydration of biomass-derived compounds in acidic media [24, 25]. LA can be converted into GVL through hydrogenation process over supported metal catalysts [22].

There are multiple pathways to produce GVL (Scheme 1.9, Chapter 1, p. 20). Starting from LA, hydrogenation produces 4-hydroxyvaleric acid, an unstable intermediate, which ring-closes by intramolecular esterification and loses a water molecule spontaneously to produce GVL. A second possible pathway starts with LA dehydration to form angelica lactone followed by hydrogenation to produce GVL. In the case of levulinic acid esters, the reaction proceeds in a similar way as LA: first, the ester is hydrogenated to make the hydroxy levulinic ester, which ring-closes by intramolecular transesterification to produce GVL and the corresponding alcohol.

An overview of GVL production from hydrogenation of LA was introduced in Table 1.4, Chapter 1. Most studies focus on the hydrogenation by hydrogen gas as the reductant. The hydrogenation of LA in vapor phase takes place at an atmospheric pressure of hydrogen and gives high yield of GVL [26–28] Nevertheless, vapor phase reactions need huge amount of energy for vaporization of reactants and are not suitable for the

LA product mixtures obtained from carbohydrate feedstocks. Hydrogenation of LA in liquid phase is more common; however, the reaction usually requires high pressure of H₂ gas (1.2–5.5 MPa). In liquid phase, hydrogenation reaction of LA can occur in the presence of either heterogeneous or homogeneous catalysts. The homogeneous catalysts are usually complexes of Ru and Ir [29–32]. These homogeneous catalysts have high activities but are difficult to separate from reaction mixture.

Many supported metal catalysts have been developed for liquid phase hydrogenation of LA under high pressured H₂, for example [33–35]. In these works, various metal such as Ir, Rh, Pd, Ru, Re, Ni, *etc.* on different supports such as carbon and metal oxides have been screened. The results showed Ru catalyst supported on carbon always gave the highest yield of GVL; however, a weak point of Ru/C is its recyclability. The reaction of carbohydrate compounds usually generates huge amount of undesired solid known as humins that deactivate the catalysts. The reuse of catalyst, therefore, needs calcination at high temperature of catalyst to combust humins. Under this condition, the Ru/C is destroyed completely.

Up to now, however, most studies have been used hydrogen gas that is a non-sustainable source for hydrogenation of LA, there have been few researches focusing on the utilization of the alternative hydrogen source, such as formic acid, *iso*-propanol, *etc.* These are some advantages when using formic acid (FA) as the hydrogen source compared with hydrogen gas because FA is cheaper, safer, giving higher atomic efficiency, and needing less instrumental requirements [32, 36–40].

The first purpose of this chapter is to synthesize GVL from LA using FA as a hydrogen source and heterogeneous catalysts in water solvent. I found that Ru/SBA-15 had good activity as well as Ru/C. Besides Ru/SBA, Au/ZrO₂ and Au/ZrC acted as acid-tolerant catalysts with excellent catalytic activities for production of GVL from LA using FA as a hydrogen source. The second topic of this chapter is one-pot dehydra-

tion/hydrogenation of fructose to GVL over supported metal catalysts in water solvent. To the best of our knowledge, this is the first report on production of GVL *via* dehydration/hydrogenation of fructose in the absence of mineral acid catalysts.

4.2 Experimental

4.2.1 Materials

Metal supported catalysts, metal oxide, salts used in present work including 5wt% Ru/C, 5wt% Ru/Al₂O₃, 5wt% Pt/C, 5wt% Pd/C, RuCl₃·3H₂O, HAuCl₄·4H₂O, Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Ni(NO₃)₂·6H₂O, activate carbon, mordenite zeolite (hydrogen form), formic acid (FA), and naphthalene were supplied from Wako Pure Chemical Ind., Ltd. Fructose, acetone, TiO₂, ZrO₂, Al₂O₃, ZrOCl₂·8H₂O, and Na₂CO₃ were obtained from Kanto Chemical Co., Inc. Levulinic acid (LA) and IrCl₃·3H₂O were bought from Tokyo Chemical Industry Co., Ltd. Tri-block co-polymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (P123, (EO)₂₀(PO)₇₀(EO)₂₀, *M* = 5800), tetraethylorthosilicate (98%, TEOS), and γ -valerolactone (GVL) were purchased from Sigma Aldrich.

4.2.2 Catalyst preparation

Preparation of supported metal catalysts by impregnation method

This method is used for preparation of Ru, Pd, Pt, Ir or Au supported on mesoporous silica (SBA-type), TiO₂, ZrO₂, Al₂O₃, C, mordenite (hydrogen form), and ZrC (as-prepared zirconium carbonate according to the reference [41]). Typically, 0.2 g of supporting material and 20 mL of water were introduced into a round-bottom flask, and then the mixture was stirred (500 rpm) at room temperature. Thereafter, a desired amount of metal precursor was added and the mixture was kept at same condition for 2 h (in case of Au catalysts, the pH of mixture was adjusted to 10 by an ammonia solution). Subse-

quently, the mixture was refluxed at 140 °C for 4 h. After cooling to room temperature, the obtained solid was collected by filtration and washed with 1 L of water followed by drying at 100 °C overnight.

Co-precipitation method for preparation of metals supported on ZrO₂

Metals (Ru, Au, Cu, and Ni) supported on ZrO₂ were prepared by co-precipitation method. Typically, a 50 mL of 0.25 M Na₂CO₃ solution was added slowly (1 mL min⁻¹) into a round-bottom flask containing 20 mL of 0.5 M ZrOCl₂•8H₂O solution including the desired amount of metal precursor. The obtained gel was kept at room temperature under violent stir for 2 h followed by aging at 140 °C for 12 h. The solid was recovered by filtration, extensively washed with 2 L of distilled water and dried 100 °C. After ground to fine powder, the solid was calcined at 500 °C for 4 h.

4.2.3 Reaction procedure

Hydrogenation of levulinic acid to γ -valerolactone

Typically, 2 mmol (0.232 g) of levulinic acid, 4 mmol (0.184 g) of formic acid, 1 mL of water, and 20 mg of supported metal catalyst were introduced into a glass tube sealed by teflon and silicon-lined plastic cap (5 mL vol.). The reactor was heated and kept at desired temperature (110-170 °C), followed by cooling to room temperature. Reaction mixture was diluted in acetone, filtered and analyzed by GC using naphthalene as an internal standard.

One-pot dehydration/hydrogenation of fructose to γ -valerolactone

2 mmol (0.36 g) of fructose, 4 mmol (0.184 g) of formic acid, 1 mL of water, and 20 mg of supported metal catalyst were introduced into a glass tube sealed by teflon and silicon-lined plastic cap (5 mL vol.). Dehydration stage of fructose to LA was carried out at 120 °C for 3 h. In this step, FA acted as an acid catalyst for dehydration of fructose to HMF and consecutive rehydration of HMF to LA. After that, reaction temperature was

elevated to 150 °C in order to decompose FA over supported metal catalyst into CO₂ and H₂ that participated in hydrogenation of LA to generate GVL. Reactor was heated and kept at desired temperature followed by cooling to room temperature. Reaction mixture was diluted in acetone, filtered and analyzed by GC using naphthalene as an internal standard.

4.2.4 Analyses

The reaction mixture after reaction was diluted by acetone and analyzed by GC with naphthalene used as an internal standard. GC-17A instrument (Shimadzu) was equipped an Agilent DB-1 column (30 m × 0.32 mm × 0.25 mm), a FID detector, and an injection port working at 280 °C with split ratio 100 : 1. The temperature program for a column is described as follows: 40 °C isothermal for 0.5 min, 20 °C min⁻¹ to 200 °C, 7 °C min⁻¹ to 250 °C, and isothermal at 250 °C for 2 min. Retention times of acetone, GVL, LA, and naphthalene are observed at 1.5 min, 3.7 min, 4.6 min, and 5.7 min, respectively. The amounts of fructose and FA were determined by a high performance liquid chromatograph (HPLC, Waters Co., Ltd.) equipped with an Aminex HPX-87H column (Bio-Rad Laboratories, Inc.) and a refractive index detector. 10 mM H₂SO₄ aq. was used as an eluent at a flow rate of 0.5 mL min⁻¹. Both column and detector were operated at 50 °C. Typically, fructose, FA, and HMF were obtained in the HPLC chart at 12.3 min, 17.2 min, and 39.5 min, respectively.

The conversion (Conv.) of reactant, yield and selectivity (Sel.) of product are calculated by following formulas:

$$\text{Conv. (\%)} = \frac{\text{reacted moles of reactant}}{\text{initial moles of reactant}} \quad (4.1)$$

$$\text{Yield (\%)} = \frac{\text{obtained moles of product}}{\text{initial moles of reactant}} \quad (4.2)$$

$$\text{Sel. (\%)} = \frac{\text{obtained moles of product}}{\text{reacted moles of reactant}} \quad (4.3)$$

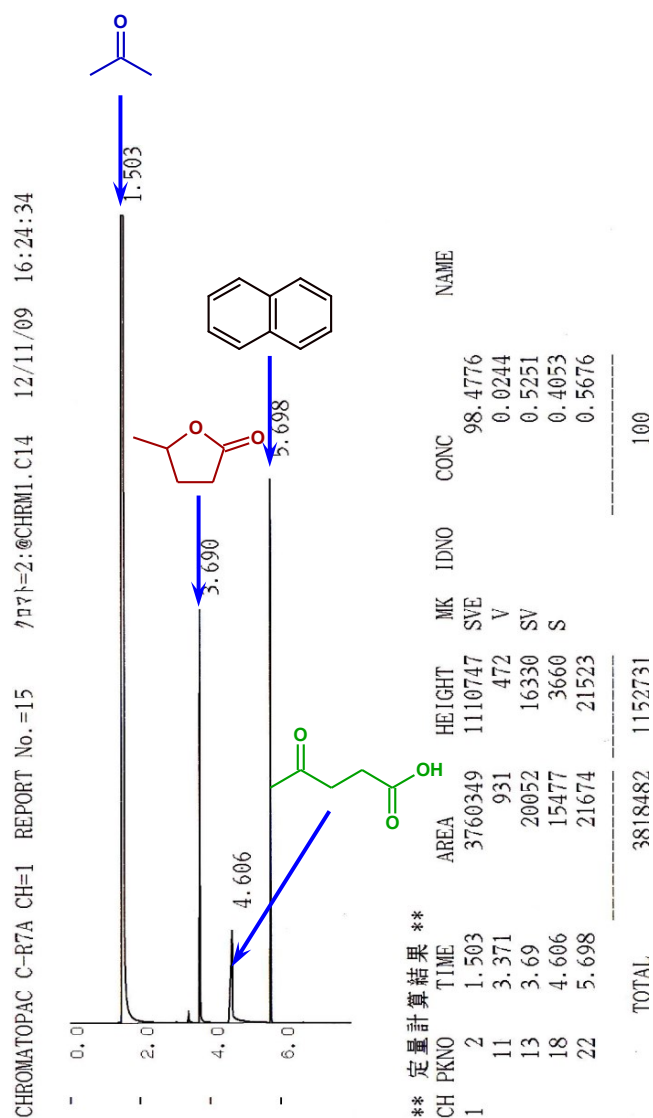


Figure 4.2: A typical GC chromatogram of reaction mixture

Metal content in the catalyst was measured by inductively coupled plasma-atomic emission spectroscopy (ICPS-7000 Ver.2, Shimadzu Co., Ltd.). All samples was dissolved in aqua regia before ICP measurement.

In this chapter, turn over number (TON) for GVL is defined as mole of formed GVL per actual moles of supported metal.

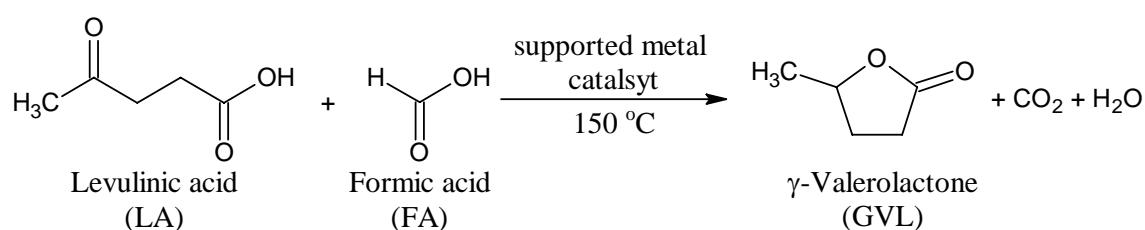
$$\text{TON} = \frac{\text{Obtained moles of GVL}}{\text{Actual moles of metal}} \quad (4.4)$$

The particle size was studied using Transmission Electron Microscope (TEM), model Hitachi H-7100 operating at 100 kV.

X-ray Photoelectron Spectroscopy (XPS) was measured on a Shimadzu Kratos AXIS-ULTRA DLD spectrometer using Al target at 15 kV and 10 mA. The binding energies were calibrated with C 1s level (284.8 eV) as an internal standard reference.

4.3 Results and discussion

Hydrogenation of levulinic acid



Scheme 4.2: Hydrogenation of LA using FA as a hydrogen donor source.

The reaction route of GVL preparation from LA hydrogenation is shown in Scheme 4.2. In this pathway, FA is decomposed to CO_2 and H_2 by supported metal catalyst. Subsequently, H_2 takes part in the hydrogenation of LA to generate GVL.

Firstly, the reaction was carried out with 1/1 mole ratio of FA/LA at 150 °C using Ru-supported on carbon as catalyst because Ru/C is the most common catalyst for hydrogenation of LA using H_2 gas as reductant [33, 35, 42–44]. The conversion and yield were monitored as functions of time (Fig. 4.3). The difference between conversion and yield may be caused by the formation of intermediates or unidentified compounds formed during the reaction. The obtained result showed that the reaction occurred quite fast within 5 h and almost reached maximum performance after that. Therefore, 5 h of reaction time was applied for next experiments.

In order to estimate the effect of support materials on the activity, the impregnation method was used for grafting Ru on various supports such as C, SBA-15 (ordered mesoporous SiO_2), TiO_2 , ZrO_2 , and Al_2O_3 to afford Ru/C, Ru/SBA-15, Ru/ TiO_2 , Ru/ ZrO_2 , and Ru/ Al_2O_3 , respectively. The activities of these catalysts were listed in Table 4.1.

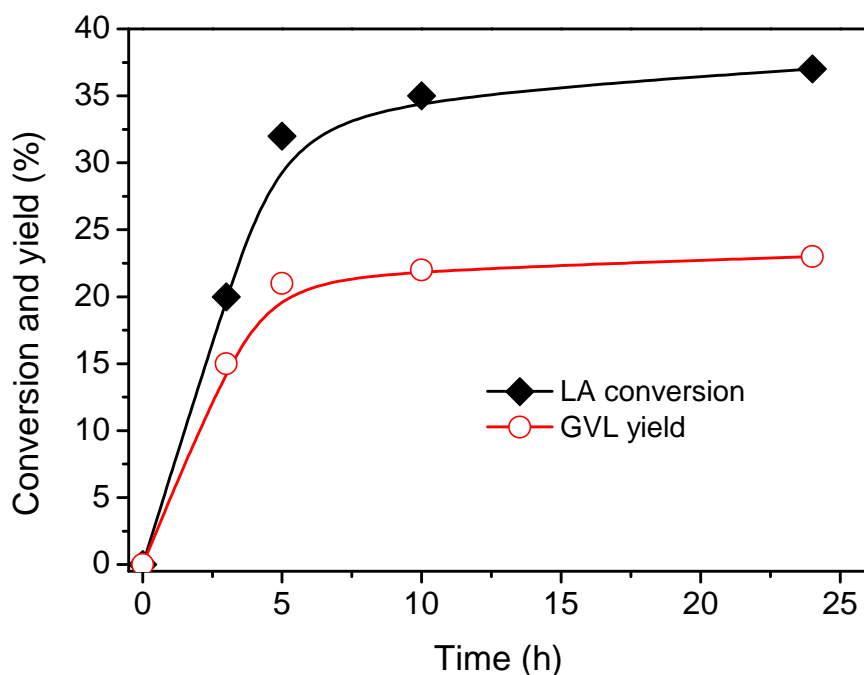


Figure 4.3: LA conversion (*black diamond*) and GVL yield (*open circle*) as functions of reaction time. Reaction conditions: LA (2 mmol or 0.232 g), FA (2 mmol or 0.092 g), 5wt% Ru/C (0.02 g), water (1 mL), temperature (150 °C).

Obtained results showed the similar activities of C and SBA-15 supported Ru catalysts (21-22% GVL yield, entries 1 and 2), while metal oxide supported Ru catalysts had much lower activities with trace amount of product (GVL yields were below 3%, entries 3-5). Because of good support for Ru catalyst, C support was also used for preparation of other catalyst such as the Pt/C, Pd/C, and Au/C; nevertheless, the activities of these catalysts were much lower than that of the Ru/C (12% GVL yield, entries 6-8). The screen of metals and supports exhibited that Ru/C and Ru/SBA-15 are the best catalyst for hydrogenation of LA to GVL using FA as hydrogen donor source.

Interestingly, Ojeda and Iglesia reported that well-dispersed Au species could selectively decompose gaseous FA [45]. The obtained small Au clusters had very high activity in FA dissociation reaction and even better than some well-known catalysts such as Pt or Ru. In this chapter, various supported Au catalysts were also examined for hydrogenation of LA to GVL using FA as a hydrogen source (Figure 4.4). Among tested catalysts,

Table 4.1: Hydrogenation of LA using various supported metal catalysts

Entry	Catalyst	LA conv. /%	GVL yield /%	GVL sel. /%
1	Ru/C	29	21	73
2	Ru/SBA-15	31	22	71
3	Ru/Al ₂ O ₃	16	3	17
4	Ru/TiO ₂	10	2	20
5	Ru/ZrO ₂	11	2	18
6	Pt/C	13	2	13
7	Pd/C	9	2	17
8	Au/C	13	1	9

Reaction conditions: LA (2 mmol or 0.232 g), FA (2 mmol or 0.092 g), 5 wt% supported metal catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).

the Au/ZrO₂ and Au/ZrC possessed the highest activity with 77% yield of GVL. Other metal supported on ZrO₂ were prepared by co-precipitation method. Activities of the these catalysts were quite low compared with that of Au (1-2% GVL yield, Table 4.2). These results indicated that both of the noble metal and the nature of the support played important roles in the catalytic activity of LA hydrogenation to GVL using FA as a hydrogen source.

The influence of FA/LA mole ratio on LA conversion and GVL yield was investigated on 5 wt% Ru/C and 5 wt% Au/ZrO₂ catalysts (Figure 4.5). In case of 5 wt% Ru/C catalyst, the hydrogenation reaction is proportional to the initial amount of FA. With FA/LA mole ratio of 1, GVL yield was only 21%, while LA was converted completely giving 90% GVL yield when the FA/LA mole ratio changed to 3. At every FA/LA mole ratios, the Au/ZrO₂ catalyst was more efficient than the Ru/C for hydrogenation of LA. 77% GVL yield was obtained over 5 wt% Au/ZrO₂ at mole ratio of FA/LA = 1, while there was no significant difference in reaction performances with FA/LA mole ratios of 2

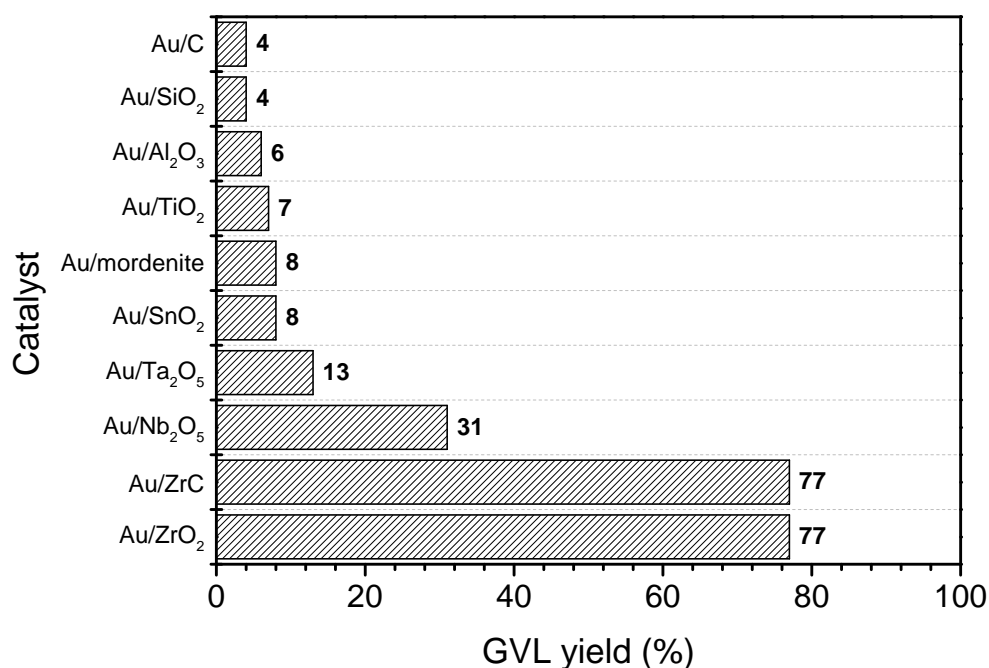


Figure 4.4: GVL yield from LA hydrogenation over 5 wt% Au catalyst on various supports. *Reaction conditions:* LA (2 mmol or 0.232 g), FA (2 mmol or 0.092 g), 5 wt% Au-supported catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).

and 3 (94-97% GVL yield). Therefore, the best FA/LA mole ratio for 5 wt% Ru/C and 5 wt% Au/ZrO₂ were 3 and 2, respectively. Higher activity of the Au/ZrO₂ than Ru/C was due to the differences in their decomposition ability of FA (Table 4.3 and 4.4); FA was decomposed completely at all investigated amounts with the Au/ZrO₂ catalyst, whereas Ru/C converted only 56%, 49%, and 43% FA when using 2 mmol, 4 mmol, and 6 mmol of FA, respectively. It seems that the Au/ZrO₂ was very stable in presence of FA, but the Ru/C was deactivated gradually by FA during the reaction. Indeed, Ru/C almost lost its activity after the first run and could not be recycled, in contrast to Au/ZrO₂ (*vide infra*).

The hydrogenation of LA using FA as a hydrogen source strongly depended on reaction temperature. Three represented catalysts for this experiment were Ru/C, Au/ZrO₂, and Au/ZrC (Table 4.3). At temperatures lower than 120 °C, GVL yield was less than 15% in both cases (entries 1-3, 7-9) but increased gradually when rising reaction temperature higher than 130 °C. At 150 °C, GVL yield suddenly achieved more than 90%. These results showed that at low temperatures (below 130 °C), FA was not decomposed

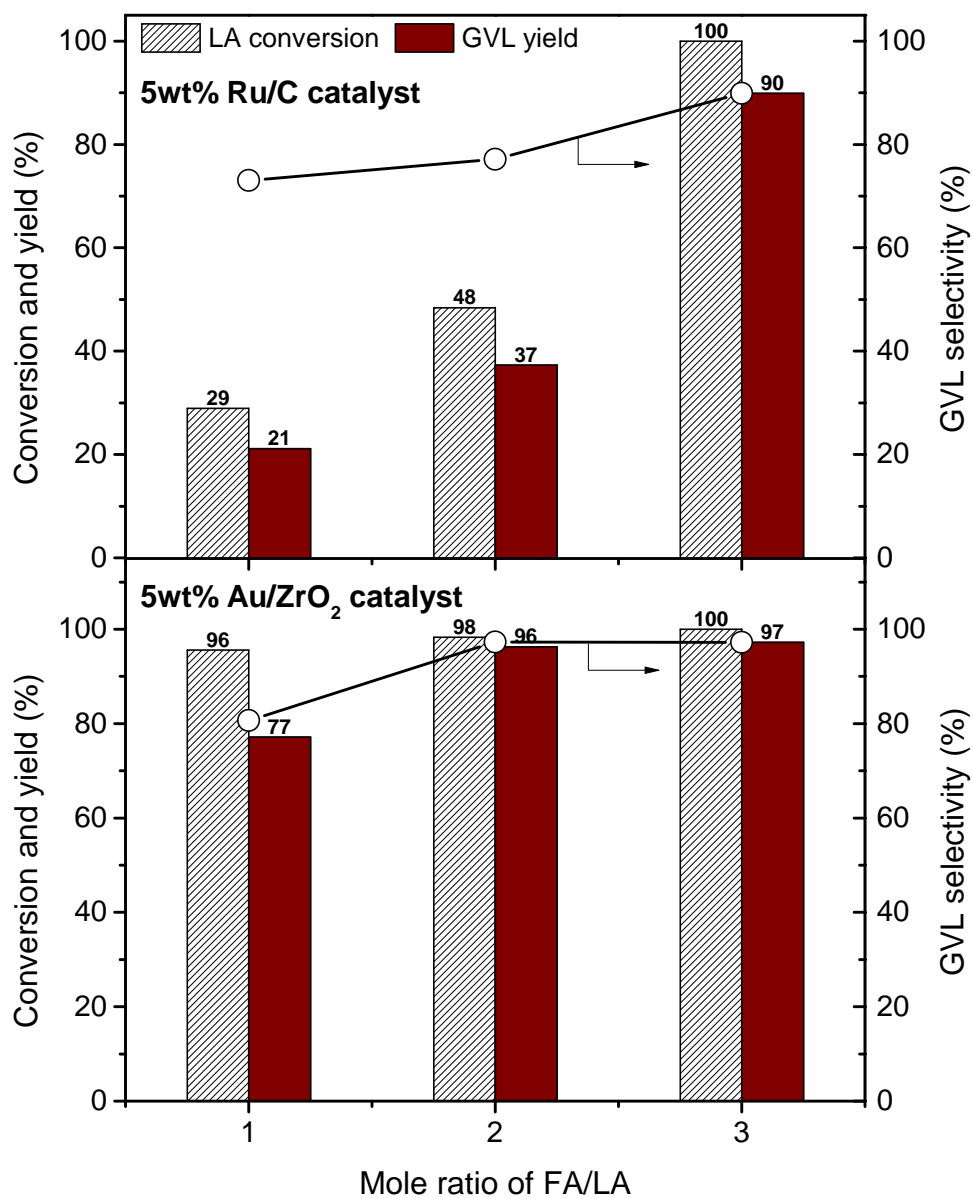


Figure 4.5: Effect of FA/LA mole ratio on the hydrogenation performance. Reaction conditions: LA (2 mmol or 0.232 g), catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).

Table 4.2: Various metals supported on zirconia for hydrogenation of LA

Entry	Catalyst	GVL Yield (%)
1	Au/ZrO ₂	77
2	Ru/ZrO ₂	2
3	Fe/ZrO ₂	1
4	Co/ZrO ₂	1
5	Ni/ZrO ₂	1
6	Cu/ZrO ₂	1
7	Ag/ZrO ₂	1

Reaction conditions: LA (2 mmol or 0.232 g), FA (2 mmol or 0.092 g), 5wt% supported metal catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).

significantly, but violently decomposed when reaction temperature was higher than 140 °C to release sufficient amount of hydrogen for the hydrogenation reaction. LA conversion only reached 100% when reaction temperature was elevated to 150 °C (entries 6 and 12). Therefore, the suitable temperature for decomposition of FA and consecutive hydrogenation of LA was 150 °C. Gold on zirconium carbonate (Au/ZrC) was also estimated (entries 13-18). Au/ZrC also revealed the similar activity with that of Au/ZrO₂. Therefore, the compounds of zirconium can be selected as excellent support materials for gold catalyst in the FA decomposition reaction and hydrogenation reaction to GVL.

The activities of various contents of Au catalyst on ZrO₂ were tested (Table 4.5). The increase in percentage of Au led the rise of product yield. However, above 3 wt% of Au, the active sites on ZrO₂ support became saturation leading to the unchanged GVL yield with 96-97%. The highest TON value of 630 was obtained with 3 wt% Au/ZrO₂ catalyst.

In order to investigate the recycling properties of the catalyst, the Au/ZrO₂ or Au/ZrC was removed from the reaction mixture by centrifugation, washed with acetone, dried

Table 4.3: Hydrogenation of LA to GVL at different reaction temperatures^a

Entry	Catalyst	React. Temp. (°C)	LA Conv. (%)	GVL Yield (%)	GVL Sel. (%)	FA Conv. (%)
1	5wt%	100	7	2	29	13
2	Ru/C ^a	110	16	5	30	16
3		120	30	12	39	19
4		130	35	22	62	33
5		140	50	32	63	37
6		150	100	90	90	43
7	5wt%	100	7	2	28	10
8	Au/ZrO ₂ ^b	110	19	11	56	24
9		120	21	14	67	32
10		130	40	26	67	52
11		140	73	66	91	100
12		150	100	97	97	100
13	5wt%	100	5	2	34	14
14	Au/ZrC ^b	110	17	8	49	19
15		120	21	11	55	30
16		130	41	22	54	49
17		140	76	62	82	98
18		150	100	96	96	100

^aReaction conditions: LA (2 mmol or 0.232 g), FA (^a 6 mmol or 0.276 g, ^b 4 mmol or 0.184 g), catalyst (0.02 g), water (1 mL), time (5 h).

Table 4.4: Decomposability of FA over Ru/C and Au/ZrO₂ in hydrogenation reaction of LA

Entry	Catalyst	FA amount (mmol)	FA decomposition (%) ^a
1	5wt% Ru/C	2	56
2		4	49
3		6	43
4	5wt% Au/ZrO ₂	2	100
5		4	100
6		6	100

^aReaction conditions: LA (2 mmol or 0.232 g), catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h). ^a Estimated by HPLC

Table 4.5: Hydrogenation of LA over various contents of gold on zirconia

Entry	Actual metal content (%) ^a	Catalyst	GVL Yield (%)	TON ^b
1	1.01	1wt% Au/ZrO ₂	14	276
2	1.89	2wt% Au/ZrO ₂	36	355
3	3.02	3wt% Au/ZrO ₂	96	630
4	3.89	4wt% Au/ZrO ₂	97	478
5	4.89	5wt% Au/ZrO ₂	97	382

Reaction conditions: LA (2 mmol or 0.232 g), FA (4 mmol or 0.184 g), catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h), ^a determined by ICP, ^b see equation 4.4 - p. 100.

at 80 °C for 2 h before subjected to further catalytic reaction. As a result, I found that the Au catalysts could be recycled at least five times without significant loss of catalytic activity (Figure 4.6).

The TEM images and Au particle size distributions of Au-supported catalysts were shown in Figure 4.7. In fresh catalysts, Au particles were around 4 nm. However, particle size increased to 5.3-5.8 nm after 5 recycle runs. The increase in particle size might lead to the decrease in catalytic activity as recycle catalyst.

In order to test the leaching of metal from catalyst during reaction, the content of

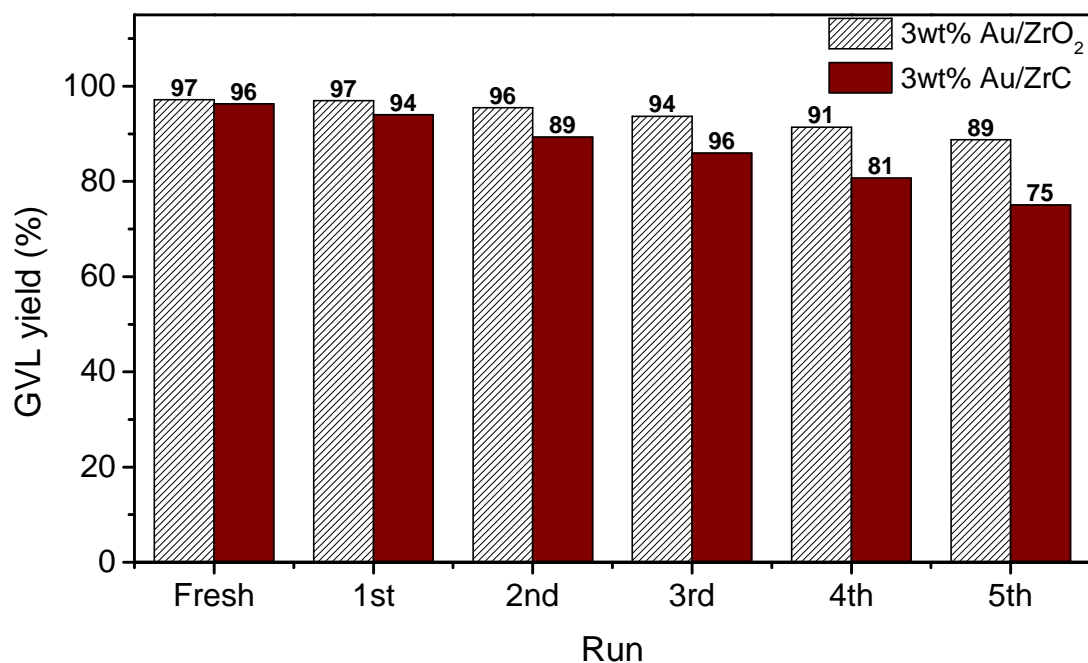


Figure 4.6: Recycling properties of 3 wt% supported gold catalysts in the production of GVL *via* hydrogenation of LA with FA as hydrogen source. *Reaction conditions:* LA (2 mmol or 0.232 g), FA (4 mmol or 0.184 g), 3 wt% Au-supported catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).

Table 4.6: Leaching test for Au-supported catalysts

Entry	Catalyst	Weight of catalyst	Concentration	Metal content
		(mg) ^a	(ppm)	(wt%) ^b
1	Fresh 3wt% Au/ZrO ₂	16.7	10.09	3.02
2	Recycled 3wt% Au/ZrO ₂ ^c	8.5	4.63	2.72
3	Fresh 3wt% Au/ZrC	16.3	9.17	2.81
4	Recycled 3wt% Au/ZrC ^c	16.5	8.93	2.71
5	Reaction mixture ^d	-	0.01	-

^a Solid was dissolved in 2 mL of aqua regia followed by dilution to 50 mL, ^b determined by ICP, ^c catalysts were collected after 5 recycle runs, ^d solids were removed from reaction mixture by 2 μ m Millex filter unit.

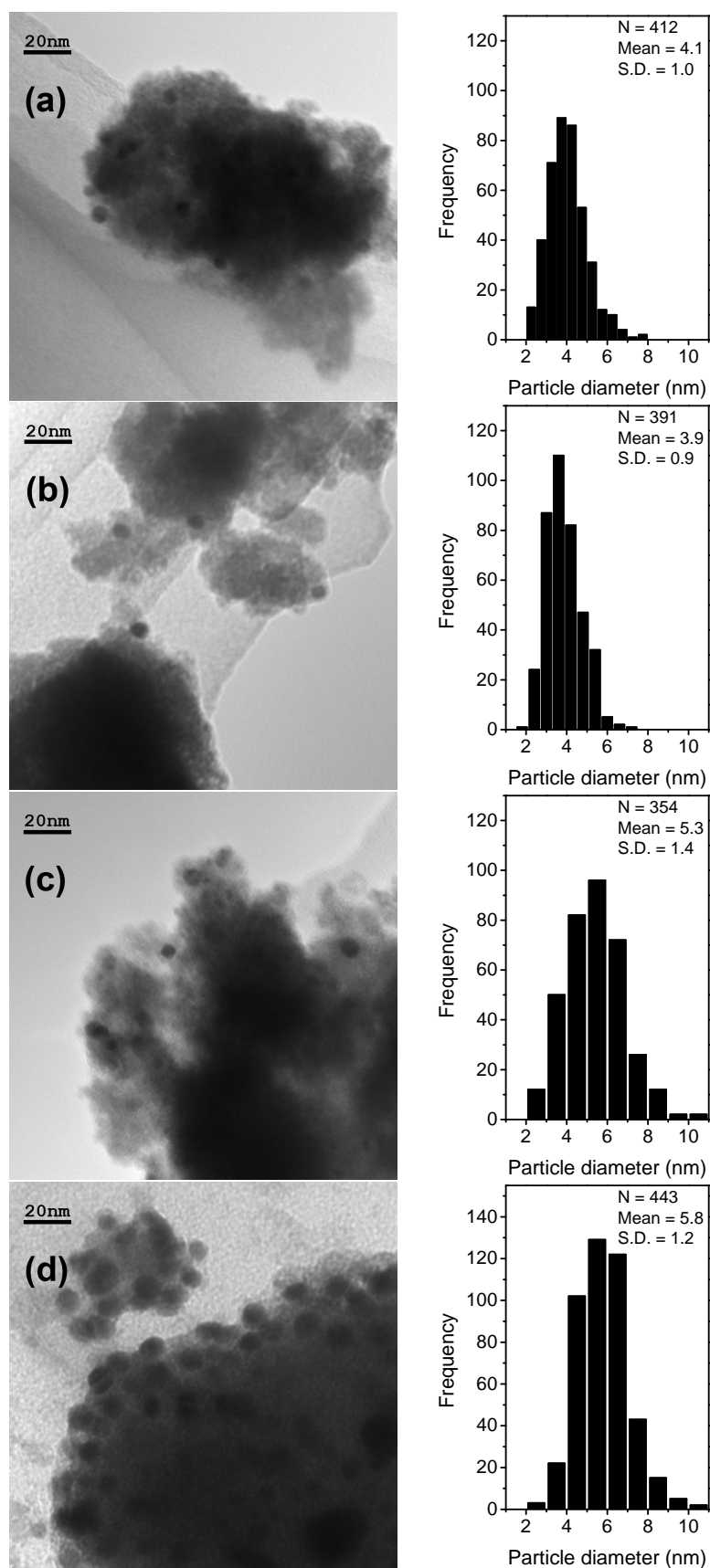
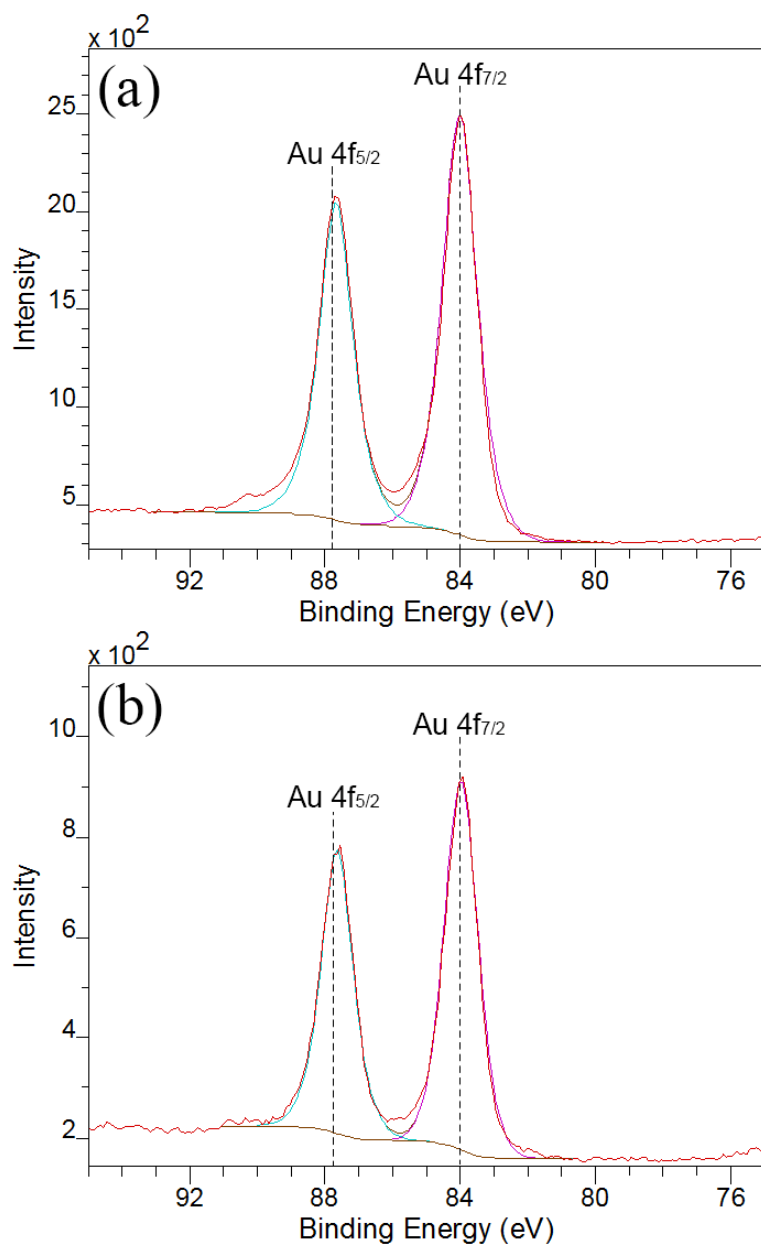


Figure 4.7: TEM images of fresh catalysts (a) Au/ZrO₂, (b) Au/ZrC and catalysts after 5 times of recycle (c) Au/ZrO₂, (d) Au/ZrC and their size distributions.

Figure 4.8: XPS spectra of (a) fresh and (b) recycled Au/ZrO₂ catalysts.

facilitate the decomposition of FA to H₂, followed by hydrogenation of LA obtained in previous step to GVL. Consequently, it is expected that this multi-step-reaction can be done in a one-pot manner. In this work, instead of utilization of mineral acids (H₂SO₄, HCl, *etc.*), FA was attempted to use as both an acid catalyst for dehydration of fructose step at low temperature (120 °C) and a hydrogen source for hydrogenation step that occurred over supported metal catalysts at higher temperature (150 °C).

A preliminary experiment was carried out to estimate the performance of hydration of fructose by FA: a mixture including 16 mmol of fructose and 48 mmol of FA was heated at 120 °C for 3h. HPCL analysis showed the complete conversion of fructose affording 50% LA yield and huge amount of undesired solid compounds, known as humins as side products in this reaction.

Table 4.7: One-pot transformation of fructose to GVL over supported metal catalysts

Entry	Catalyst	Actual metal content (wt%) ^a	GVL Yield (%)	TON ^b
1	Au/ZrO ₂	3.02	48	317
2	Au/ZrC	2.81	47	307
3	Ru/SBA-15	2.63	26	87
4	Ru/C	2.68	21	71

Reaction conditions: Fructose (2 mmol), FA (4 mmol), 3wt% supported metal catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h), ^a determined by ICP, ^b see equation 4.4 - p. 100.

Four catalysts were selected for one-pot dehydration/hydrogenation of fructose included Au/ZrO₂, Au/ZrC, Ru/SBA-15, and Ru/C. For direct conversion of fructose to GVL, the Au/ZrO₂ exhibited an excellent catalytic activity with 48% yield of GVL (TON = 317). Result from Table 4.7 also showed that Au/ZrC might be another potential candidate of catalyst for this reaction, since activity of the Au/ZrC could be comparable to that of the Au/ZrO₂. Ru catalysts had lower activities in this one-pot reaction (entries 3 and 4). The recyclability of Au/ZrO₂, Au/ZrC, and Ru/SBA-15 catalysts were also

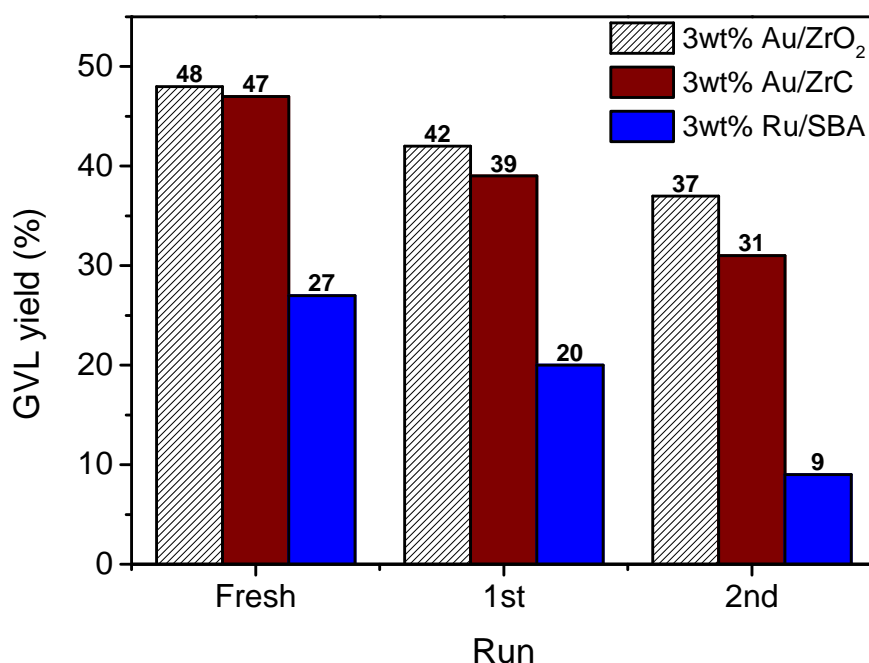


Figure 4.9: Recyclability of 3wt% Au/ZrO₂, 3wt% Au/ZrC and 3wt% Ru/SBA in dehydration/hydrogenation reaction of fructose to produce GVL. Reaction conditions: Fructose (2 mmol), FA (4 mmol), catalyst (0.02 g), water (1 mL), temperature (150 °C), time (5 h).

tested. After the reaction, reaction mixture was separated by centrifugation to collect solid that contained both catalyst and humins. To remove humins and other products deposited on the catalysts, the solid was calcined at 500 °C for 4 h. Calcined Au/ZrO₂, Au/ZrC, and Ru/SBA-15 were used for the next run. After 3 runs, activities of the Au/ZrO₂ and Au/ZrC decreased gradually from 48 to 31%, while the Ru/SBA-15 lost its activity faster than the gold catalysts (only 9% GVL yield was obtained for the 3rd run) (Figure 4.9). The recycle experiment showed that Au catalysts were more stable than Ru catalyst. Therefore, the gold catalysts were still reused for several times though it was partly deactivated.

4.4 Conclusions

γ -Valerolactone (GVL) can be obtained from hydrogenation of levulinic acid (LA) using formic acid (FA) as hydrogen source and supported metal catalysts in water. For Ru catalyst, the best supports include carbon or mesoporous silica (SBA-15). Under optimized

reaction conditions, the reaction with these catalysts can give at least 90% GVL yield. Au supported on zirconia and zirconium carbonate (denoted as Au/ZrO₂ and Au/ZrC) are also found to be excellent catalysts for decomposing FA and hydrogenating LA to produce GVL with 97% yield. The Au/ZrO₂ is found to be a highly stable, acid-tolerant catalyst and can be reused for 5 recycles without significant loss of its activity. In the one-pot transformation of fructose to GVL, FA acts as an acid catalyst for dehydration reaction of fructose to LA at 120 °C before participating in the hydrogenation stage as a hydrogen source at higher temperature (150 °C) to afford GVL. In this reaction, the Au/ZrO₂ is also the best catalyst for one-pot synthesis of GVL from fructose in water which provides 48% yield of GVL.

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Chapter 5

General Conclusions

5.1 General summary

A substantial amount of research activities is currently carried out worldwide to identify attractive chemical transformation for the conversion of biomass to bio-fuels and green added-value chemicals. LA and GVL have been identified as platform chemicals for the synthesis of various organic chemicals with applications in polymers, fuels, fuel additives and organic solvents. This research specifically focuses on the conversion of the C6-sugars to LA through an acid-catalyzed hydrolysis/dehydration reaction and GVL through dehydration/hydrogenation reaction using formic acid as the alternative hydrogen source. The water-tolerant solid base catalyst for glucose isomerization and production of LA (combination with solid acid catalyst) is found, while Au supported on zirconium compounds are good catalysts for producing GVL using FA as hydrogen source.

Chapter 1 gave the definition, composition, source and potential application for fuels and chemicals of biomass. The characterization and application of heterogeneous for production of value-added compounds from biomass were presented. The author also reviewed the literatures about the syntheses of LA and GVL and their derivatives to show that these two important compounds have potential to become the platform molecules for production of various chemicals and liquid fuels. From this overview, the author showed the weak points of these researches and proposed the objectives of present thesis.

In Chapter 2, the author described the conversion of HMF and C6-sugars to LA in

aqueous medium under mild reaction conditions. These are most active starting materials for hydration/dehydration reaction to LA. Among tested solid acid catalysts, Amberlyst 15 exhibited the highest performance. Under optimum reaction temperature (120 °C), Amberlyst 15 could convert 96% HMF to LA with 82% yield after 18 h, while Nafion 50 and SBA-SO₃H gave lower LA yields (78% and 63%, respectively). The effect of dehydration reaction conditions of fructose over solid acid catalysts was studied. Maximum LA yield was 52%. In this reaction, large amount of undesired solid compounds, known as humins, formed. After filtration to remove solids, LA could be easily isolated by vacuum rotary distillation method giving 47% isolated yield. Reuse experiments show the slight decrease in activity of Amberlyst 15. After 6 runs, the LA yield decreased from 52 to 30%. These same reaction conditions were applied to hydrolysis and dehydration of other carbohydrate compounds (glucose, mannose, galactose, sucrose, cellobiose, inulin, cellulose). The hydrolysis of dimers or polymers to monosaccharides was quite easily. However, the conversion of glucose to LA at 120 °C took place very slowly and faster when increased reaction temperature to 150 °C. This problem showed that glucose is more stable than fructose in the dehydration reaction to LA and the isomerization of glucose to fructose is necessary for production of LA from glucose with benign conditions.

In Chapter 3, zirconium carbonate (ZrC) as water-tolerant solid base catalyst was prepared by a simple method. XRD, FT-IR, TG and titration methods have been used to determine the characteristics of obtained catalysts. The results showed that Zr-OH groups play as basic sites, the basic site amount of ZrC could be comparable with those of hydrotalcite and anionic ion-exchanged resin (Amberlyst A26OH). But ZrC gave the highest performance in the glucose to fructose isomerization reaction with 34% fructose yield (at 45% glucose conversion). Hot filter method was used to estimate the heterogeneity of catalyst. The recycling experiment showed that ZrC could retain its activity

after reaction, the fructose yield did not decrease significantly for 5 runs. ZrC could work together with acid catalyst for one-pot transformation of glucose to LA. In this reaction, ZrC participated in the isomerization stage to afford fructose from glucose before fructose was dehydrated over solid acid catalyst to get final product, LA. In the presence of ZrC, glucose could be converted to LA more easily even at mild reaction conditions (In chapter 1, glucose almost did not react under the promotion of Amberlyst 15 at 120 °C). In the presence of biphasic solvent water/toluene, the reaction took place faster than in pure water solvent affording 17% LA yield.

The main works of Chapter 4 were syntheses of γ -valerolactone (GVL) from hydrogenation of LA and dehydration/hydrogenation of fructose using FA as hydrogen source. In the first reaction, FA was utilized as hydrogen donor source, while it played two functions in the second reaction: acid catalyst and hydrogen source. At low temperature (120 °C), FA catalyzed the dehydration of fructose to LA before was decomposed by metal catalysts at higher temperature (150 °C) providing hydrogen to hydrogenation of LA that was obtained from previous step yielding final product, GVL.

The screening metals and supports showed carbon and SBA-15 are the best supporting materials for Ru catalysts in the hydrogenation reaction of LA to GVL. I found that gold catalysts can decompose completely FA to CO₂ and H₂. They also possess good ability of LA hydrogenation to GVL. Under optimized conditions (FA/LA = 2, 150 °C and 5 h), Au/ZrO₂ and Au/ZrC could enhance the hydrogenation of LA resulting 97% GVL yield. Recycling experiments show that Au-supported zirconium compounds have excellent recyclability. Gold metal is not leached from solid catalysts during reaction. Au-supported zirconium compounds are acid-tolerant catalysts and can be reused at least 5 times without significant loss of their catalytic activities. In the one-pot manner for production of GVL from fructose, Au catalysts also exhibit the better activity than Ru catalysts. The transformation of fructose by Au catalysts gave 48% GVL yield and

recovered catalysts could be reused several times.

Generally, the present thesis exposes that solid acid catalysts are potential candidates for replacing homogeneous acid catalysts for hydrolysis, hydration and dehydration of biomass-derived compounds for production of LA. These catalysts could be easily separated from the reaction mixture and reused without significant decrease in their activity. The use of solid base catalyst for isomerization of monosaccharide is necessary for smooth transformation carbohydrate compounds to LA under mild reaction conditions. For production of GVL from biomass-derived compounds, the utilization of FA as both acid catalyst and hydrogen source for hydration and hydrogenation steps, respectively, opens the ability to perform the one-pot of dehydration/hydrogenation reaction.

5.2 Prospect of thesis

From results achieved in the present thesis, this author suggests further progresses for upgrading of biomass-derived compounds to higher valuable chemicals as follows.

1. Application of solid acid catalyst for hydrolysis followed by dehydration reaction of lignocellulosic materials to LA at high temperature (150-200 °C). Combination of solid base and solid acid catalysts in an one-pot reaction to synthesis LA. The use of biphasic solvents (water-organic) may facilitate the reaction to occur faster toward the formation of product than in pure water solvent (as mentioned in Chapter 3).
2. SBA-15 has a potential to be used as support for grafting both of acidic site and basic site on its surface. This type of catalyst can act as duality acid-base catalyst and it is expected to have high efficiency for multiple-step reactions that require both of acid and base catalysts.
3. For the production of GVL, Ru/C has high activity and are well-known. However

the application of this catalyst is restrained because it is easily poisoned by contaminations (humins) formed during the reaction. The regeneration of this catalyst usually required calcination in air and Ru/C is burnt under this condition. Ru/SBA has high activity that can comparable with that of Ru/C. Moreover, Ru/SBA possesses highly thermal stability that makes Ru/SBA easily to be regenerated by calcination. Consequently, Ru/SBA becomes greatly alternative candidate for replacing Ru/C in industry. Au supported on zirconia and zirconium carbonate are also potential catalysts for decomposition of FA and hydrogenation of LA because of its excellent activity and recyclability. Further studies are needed to understand clearly the effect of support to the activities of metal catalysts.

List of Publications and Presentations

Publications

1. Pham Anh Son, Shun Nishimura, and Kohki Ebitani
“Production of γ -Valerolactone from Biomass-derived Compounds using Supported Metal Catalyst and Formic Acid as Hydrogen Source”
RSC Advances, **2014**, *4*, 10525-10530.
(DOI: 10.1039/C3RA47580H)
2. Pham Anh Son, Shun Nishimura, and Kohki Ebitani
“Preparation of Zirconium Carbonate as Water-Tolerant Solid Base Catalyst for Glucose Isomerization and One-pot Synthesis of Levulinic Acid with Solid Acid Catalyst”
Reaction Kinetics, Mechanisms and Catalysis, **2014**, *111*, 183-197.
(DOI: 10.1007/s11144-013-0642-6)
3. Pham Anh Son, Shun Nishimura, and Kohki Ebitani
“Synthesis of Levulinic Acid from Fructose using Amberlyst-15 as a Solid Acid Catalyst”
Reaction Kinetics, Mechanisms and Catalysis, **2012**, *106*, 185-192.
(DOI: 10.1007/s11144-012-0429-1)

Presentations

International conference

1. Kohki Ebitani, Hemant Choudhary, Jaya Tuteja, Pham Anh Son, and Shun Nishimura
“Transformations of Biomass-derived Compounds into Useful Chemicals using Heterogeneous Catalytic Systems”

International Conference on Advances in Biothechnology and Bioinformatics (ICABB 2013), Pune, India, 25 Nov. 2013 (Oral-invited).

2. Pham Anh Son, Shun Nishimura, and Kohki Ebitani

“Preparation of Zirconium Carbonate as Solid Base Catalyst for Glucose Isomerization and Production of Value-added Compounds”

44th IUPAC World Chemistry Congress, Istanbul, Turkey, 13 August 2013 (Oral Presentation).

3. Pham Anh Son, Shun Nishimura, and Kohki Ebitani

“Preparation of Zirconium Carbonate as Solid Base Catalyst for Aqueous Glucose-Fructose Isomerization and One-pot Conversion of Glucose into Levulinic Acid”

7th International Symposium on Acid-Base Catalysis (ABC-7), Tokyo, Japan, 13 May 2013 (Poster presentation, No. RRR008).

4. Shun Nishimura, Hemant Choudhary, Pham Anh Son, and Kohki Ebitani

“Synthesis of Biomass-derived Organic Acids from Furan compounds in Aqueous Media with Heterogeneous Acid Catalyst”

7th International Symposium on Acid-Base Catalysis (ABC-7), Tokyo, Japan, 13 May 2013 (Poster presentation, No. PA-069).

Domestic conference

1. Pham Anh Son, Shun Nishimura, and Kohki Ebitani

“Synthesis of Levulinic Acid from D-Fructose using Solid Acid Catalyst”

Hokuriku Research Conference - Japan Chemical Society, Kanazawa University, Ishikawa, Japan, 18 November 2011 (Poster presentation, No. J10).