Water as hydrogen source for highly efficient conversion of biomass-derived levulinic acid into γ-valerolactone over Raney Ni catalyst

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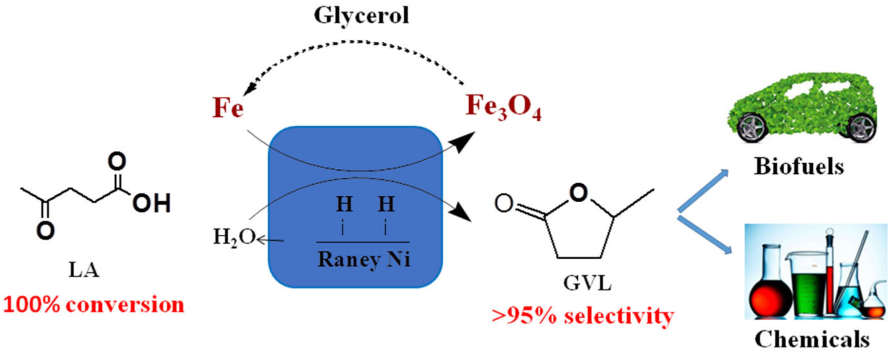
ABSTRACT

Gamma (γ)-valerolactone (GVL) is a promising liquid for energy and carbon-based chemicals. Although many researches regarding the GVL synthesis from carbohydrate biomass, most of them involve the use of noble metals accompanying with the high-purity and high-pressure gaseous hydrogen, existing high cost in large-scale application and safety risk during the transportation and operation process. In this paper, the cheap metal Fe was employed as a reductant for splitting water to produce hydrogen under mild hydrothermal conditions, and commercial Raney Ni was used as a catalyst for in situ hydrogenation of biomass-derived levulinic acid (LA). More than 95% yield of GVL can be attained at 150 ºC for 2 h and ~ 90% yield of GVL was also achieved at 100 ºC by increasing the reaction time to 5 h. Furthermore, Raney Ni remains the stable catalytic activity after being recycled for 4 times at 150 ºC. This work provides a safe and facile process for highly efficient hydrogenation of biomass-derived LA to GVL without precious metals.



Key Words: Biomass conversion; γ-Valerolactone; Levulinic acid; Biofuels; Water hydrogen.

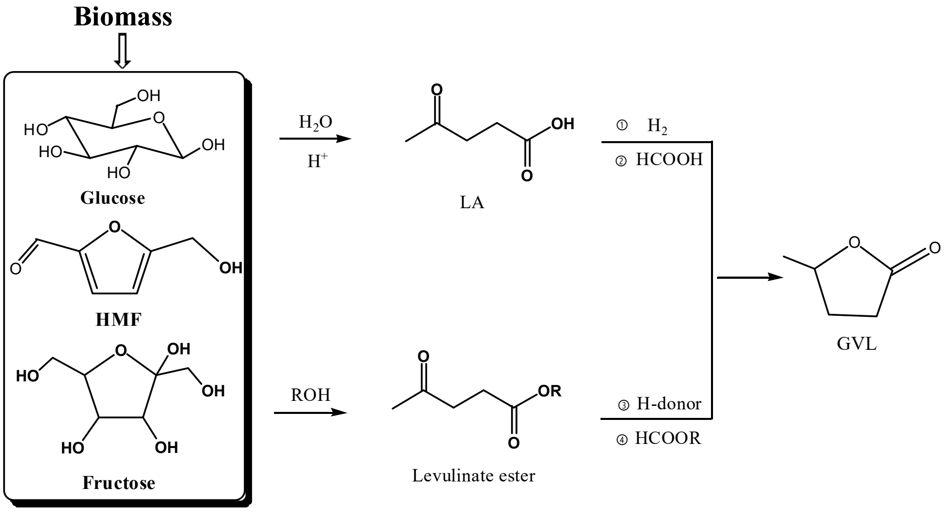
INTRODUCTION

Currently, with the increasing focus on fossil fuel exhaustion and greenhouse gas emission, the explore of green alternative for energy consumption and chemical production is urgently needed. Biomass, the most abundant renewable carbon-neutral resource on Earth, is the only non-fossil carbon-based material which can be converted to fuels and platform chemicals.[1-4] Development of efficient and cost-effective process for biomass conversion to value-added products has attracted extended attention.[5-7] GVL, a sustainable liquid for energy and carbon-based chemicals production possesses excellent properties for energy valorization such as low melting (-31 ºC), high boiling (207 ºC) and open cup flash points (96 ºC). It is low toxicity and diffluent with water and many organic solvents which could be used as eco-friendly solvent.[8-10] Furthermore, GVL can be used as a feedstock for further synthesis of fine chemicals such as liquid alkanes[11] and valeric biofuels. [12, 13] Therefore, production of GVL from biomass was received much attention in the last decades.[10, 14-16]

Generally, GVL synthesis process from biomass mainly comprises acid-catalyzed hydrolysis of carbohydrate into LA and LA hydrogenation to GVL. Extensive studies on conversion of carbohydrate such as glucose and fructose to LA have been reported (Scheme 1). [17-20] The hydrogenation of LA into GVL with extra hydrogen source was performed in liquid-phase, gaseous-phase or supercritical CO_2 systems by using different metal-based catalysts, such as Pd, Ru, Pt, Rh, Ni, Cu, Al. [5, 10, 14]Recently, formic acid, as a biomass derived, has been regarded as a material of hydrogen storage, which can be easily decomposed to molecule hydrogen at room temperature by catalytic conversion. [21-23]Thus, formic acid as hydrogen source instead of high-pressure H_2 gas for conversion of LA into GVL has been studied.

Water is an important benign protic solvent, exhibits ideal inherent characteristics under hydrothermal conditions, such as low dielectric constant, high ion product (Kw), fewer and weaker hydrogen bonds, which facilitate acid/base autocatalysis reactions without adding any other catalyst. In our previous work,[24] we studied the hydrogenation of $NaHCO_3$ under hydrothermal conditions and found that high-temperature water (HTW) can be acted as H_2 gas source with commercially available and noble-free metals. Thus, the previous work suggests us that the production of

GVL from LA under hydrothermal conditions. However, to the best of our knowledge, the synthesis of GVL from LA by using HTW as both hydrogen source and reaction medium with noble-free metal as reductant has not been performed. Meanwhile, in our previous work, a novel method for highly efficient conversion of LA into GVL in water with zinc as reducing agent over Ni catalyst has been developed, and more than 98% yield of GVL can be obtained under mild reaction conditions. Herein, in this paper, general commercially available Fe as reducing agent to generate hydrogen gas from water to reduction of LA into GVL over Raney Ni catalytic role.



Scheme 1. Synthesis of GVL from LA and its esters

EXPERIMENT SECTION

Materials

Raney nickel (<150 μm) was purchased from Aladdin, Fe powder (325 mesh, 97%) was purchased from Sigma-aldrich. Levulinic acid (LA, 99%) was purchased from J&K chemical, All chemicals were used without further purification. The γ-valerolactone (GVL, 98%) were used as standards for the qualitative analysis of the samples in the liquid products and purchased from Sino-pharm Chemical Reagent Co., Ltd.

Experimental procedure

All of the experiments were performed in a Teflon-lined stainless steel batch reactor with an inner volume of 30 mL. The experimental process is briefly described as follows: the desired amount of LA (10 g/L, 86 mmol/L), Fe powder and Raney Ni were loaded into the reactor with a water filling of 25% (7 mL). Then the reactor was sealed and putted into an oven that had been preheated to the desired temperature. The reaction time was defined as the time that the reactor was placed in the oven. After the reaction, the Teflon reactor was removed out from the oven and cooled to room temperature with an electric fan.

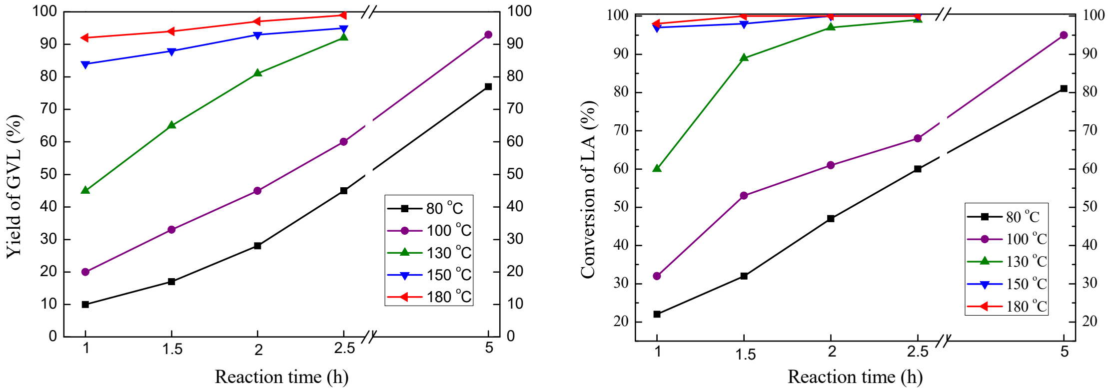
Analysis method

After the reaction, the liquid products were collected by filtering with a 0.22 μm filter membrane, and analyzed using high performance liquid chromatography (HPLC) on Agilent1200LC. Two Shodex KC811 columns were used in series and the 2 mmol/L $HClO_4$ with a flow rate of 1.0 mL/min was employed as mobile phase. Liquid samples were also analyzed by gas chromatography–mass spectrometry (GC–MS) on Agilent 7890A GC system equipped with a 5975C inert MSD. The samples were separated by an HP-Innowax capillary column with helium as a carrier gas. The detail description of the testing conditions have been reported in our previous study.

The solid samples were collected and washed with deionized water and absolute ethanol several times to remove impurities. FT-IR was performed on a Nicolet iS10 FT-IR Spectrometer (Thermo Scientific Instrument) to observe the catalyst. First, 1 mg of sample was mixed with 200 mg of KBr powder, and the mixture was grounded by an agate mortar and pestle. Then 100 mg mixed powder was compressed to create a thin and transparent disk. FT-IR spectra (resolution: 4 cm^{-1}, number of scans: 16, range: 4000-400 cm^{-1}) were taken at a controlled ambient temperature (25 °C). The elemental analysis of the collected catalysts was performed using a Thermo Fisher Scientific FLASH 2000 organic elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA). The X-ray diffraction (XRD) analysis of solid products were conducted on Shimadzu XRD-6100X equipped with Cu $K\alpha$ radiation to detect their phase compositions, employing a scanning rate of 2◦/min and 2θ ranges from 10◦to 80◦. The accelerating voltage was set at 40 KV with a 30 mA flux. Diffraction patterns were compared with reference data in the ICDD PDF-2 database. The quantitative phase analysis was based on the Rietveld calculation using the software MDI Jade 6.

RESULTS AND DISCUSSION

Initially, a series of experiments with Raney Ni and Fe in water were examined by changing a wide range of reaction parameters including reaction temperature and time, Fe amount, the amount of Raney Ni and filling rate of water, respectively. First, to obtain optimal reaction conditions, the reaction temperature and time were performed from 60 min to 150 min at 130 ºC, 150 ºC and 180 ºC, respectively. Figure 1 shows the yield of GVL and conversion of LA was improved with the increased of reaction temperature and time. More than 95% yield of GVL and conversion of LA was achieved at 150-180 ºC for 120-150 min. When the temperature decreased to 100 ºC, the yield of GVL also can be increased to 93% by extending time to 300 min. The results identify the feasibility for reduction LA into GVL in water with Fe as a reductant over Raney Ni catalyst. Meanwhile, indicating a higher temperature is favorable for production GVL and conversion of LA, and higher yield of GVL can be obtained under mild hydrothermal conditions. Furthermore, solid samples after reaction at different reaction time were analyzed by XRD (Figure S1), the observed phenomenon shows the yield of Fe_3O_4 increased with the increased of reaction time from 60 min to 150 min, and the phenomenon will be discussed later.



(a) (b)

Figure 1. Effect of reaction time and temperature on the yield of GVL and conversion of LA ((a) Yield of GVL, (b) Conversion of LA; LA: 86 mmol/L, Raney Ni: 0.2 g, water filling: 25%, Fe: 20 mmol)

Then, the effect of the hydrogen pressure on the yield of GVL and conversion of LA were conducted at 150 °C by changing Fe amount from 10 mmol to 35 mmol. Considering the pressure limitation of the reactor used in this work, experiments with a higher Fe amount were not examined. As shown in Figure 2, the yield of GVL and conversion of LA appears the trend of rising first and then decreasing to 90% approximately. The GVL yield continuously improved to 97% with the increased Fe amount from 10 mmol to 25 mmol. However, then the yield of GVL and conversion of LA began to decline when Fe amount exceed 25 mmol, which is mainly because a higher hydrogen pressure is disadvantage for reduction LA into GVL in water, suggesting superfluous hydrogen amount may restrain the hydrogenation reaction of LA.

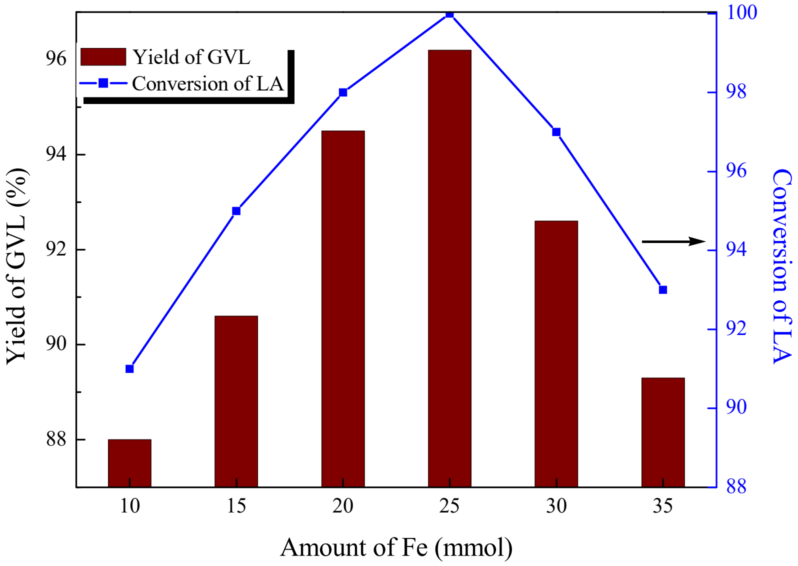


Figure 2. Effect of Fe amount on the yield of GVL and conversion of LA (temperature: 150 °C, time: 90min, LA: 86 mmol/L, water filling: 25%, Raney Ni: 0.2 g)

The amount of catalyst addition is a crucial factor in industrial schemes, then the effect of Raney Ni on the yield of GVL and conversion of LA were investigated under the optimized reaction conditions in hand. As expected, the Figure 3 shows the yield of GVL and conversion of LA increased with increased of Raney Ni amount from 0.01 g to 0.2 g. More Raney Ni should provide plentiful active site to absorb H_2 gas on surface for LA reduction. The results demonstrate Raney Ni played a key role for production of GVL from LA, and more Raney Ni amount is beneficial to promote hydrogenation of LA.

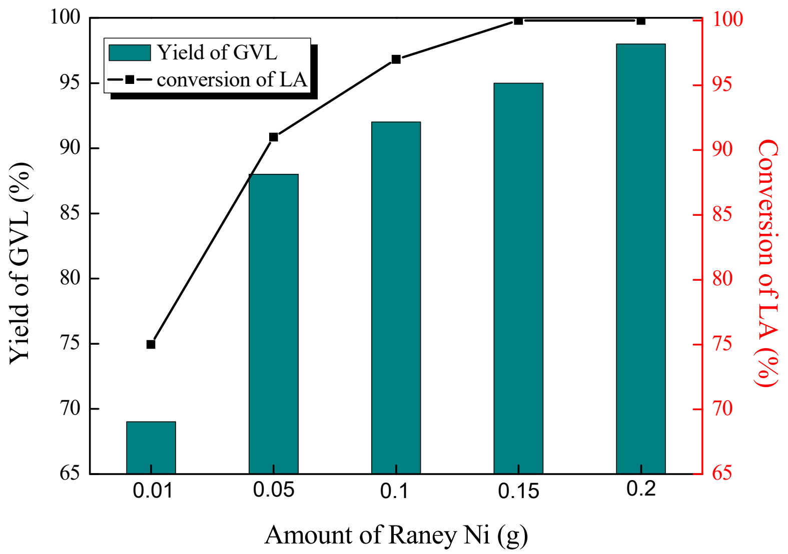


Figure 3. Effect of the amount of Raney Ni on the yield of GVL and conversion of LA (temperature: 150 °C, time: 90 min, Fe: 25 mmol, LA: 86 mmol/L, water filling: 25%)

Subsequently, in the investigation of the effect of reaction pressure on GVL production in water. Noteworthy in Figure 4, when the water filling increased from 25% to 55%, leading to the conversion of LA and yield of GVL were decreased from 97% to 60% roughly, which an increase filling rate lead to decrease in the concentration of LA and Fe. Hence, the results indicate reaction pressure has not accelerate effect for hydrogenation reaction of LA.

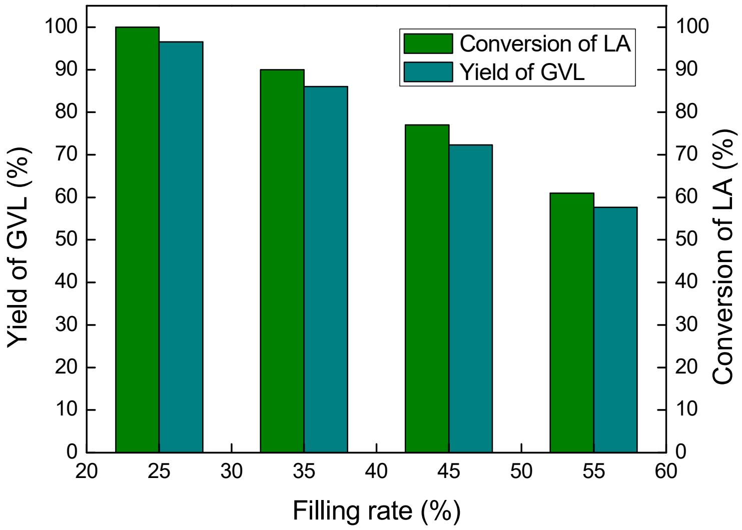


Figure 4. Effect of filling rate of water on the yield of GVL and conversion of LA (temperature: 150 ºC, time: 90 min, Raney Ni: 0.1 g, Fe: 20 mmol)

Noticeably, HPLC spectra shows no other products were detected in liquid samples besides LA and GVL after reaction (Figure S2). Thus, to further investigate whether other products exist in liquid phases, the samples were analyzed by GC-MS (Figure S3). Equally, in addition to GVL and LA, other products, such as acetic acid, propionic acid, pentanoic acid and 2-pentenoic acid were not observed in liquid samples. The existed phenomenon illuminate synthesis of GVL from LA with Fe as reductant presents a excellent selectivity.

To reuse solid products after reaction, Raney Ni and Fe powder were separated using SUS316 screen in reactor before reaction, then the stability and recyclability of Raney Ni were examined. As shown in figure 5, the observed phenomenon indicated that the yield of GVL only mildly decreased from 97% to 82% after being recovered for 4 times at 150 °C, and has hardly effect on the yield of GVL with or without SUS316 screen. These results explain that the Raney Ni can keep a higher activity and stability in the production of GVL from LA. Moreover, in our previous work, reduction of FexOy into zero-valent Fe can be obtained with biomass-derived glycerin under hydrothermal conditions. Thus, the whole procedure would be sustainable by uniting the reduction of Fe_3O_4 into Fe with glycerin and production of GVL from LA with Fe through a Fe−Fe_3O_4 cycle.

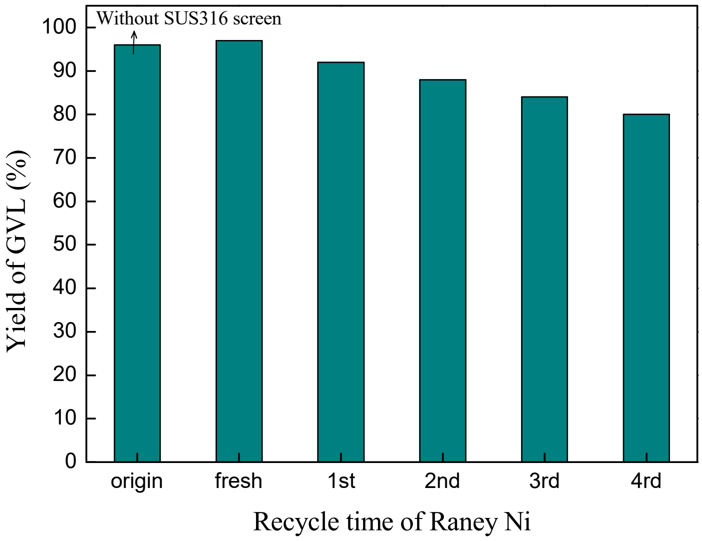


Figure 5. Effect of the Raney Ni recycle time on the yield of GVL (temperature: 150 °C, time: 90 min, LA: 86 mmol/L, Fe: 25 mmol, Raney Ni: 0.2 g)

Proposed Mechanism of Conversion of LA into GVL

In general, galvanic corrosion would occur when two different active metals are present in the electrolyte solution. As far as we know, chemical potential difference and electrolyte solution are two factors that cause galvanic corrosion. As shown in figure S4, the production of Fe_3O_4 appears dramatically distinction after different reaction time under different experimental conditions. Hence, the appearance of primary battery can accelerate the oxidation of Fe. [25] Meanwhile, in our previous research, compared to commercially available Fe_3O_4, in-situ formed Fe_3O_4 under HTW has highly catalytic activity for reduction CO_2 into formic acid. Thus, Fe_3O_4 collected after the reaction in this work can promote production of GVL from LA (Figure 1). The FTIR analysis results of the collected solid products (Figure 6), corresponding enhanced absorption bands were observed, and the absorption strength increased with the increase in reaction time. The bands could be assigned to –OH, -CH_3 and Fe_3O_4 at 3375 cm^{-1}, 1386 cm^{-1}, 570 cm^{-1}, respectively. The results further show the surface of Raney Ni can absorb reactant and intermediate products to promote the reduction of LA to GVL.

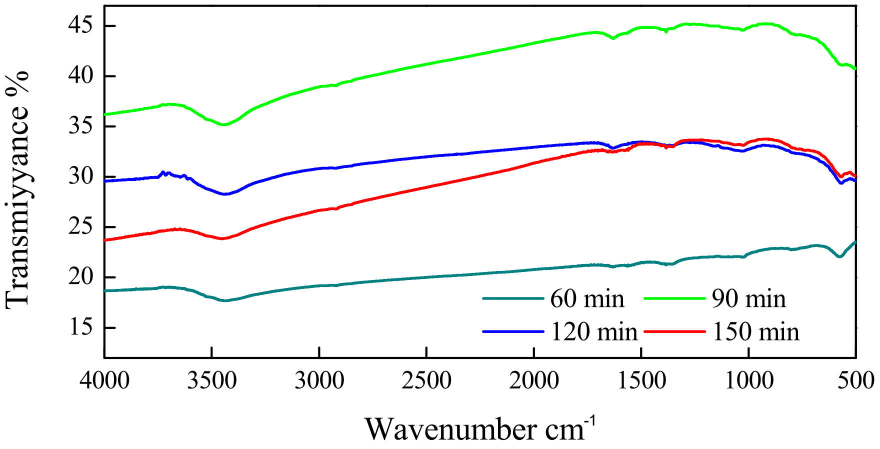
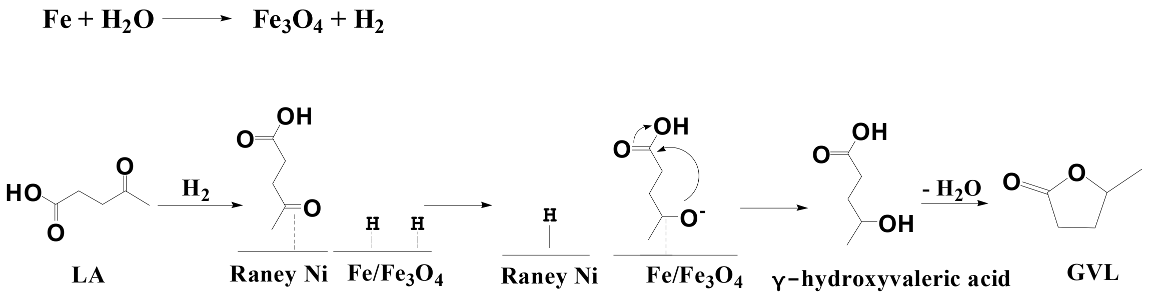


Figure 6. FTTR absorption spectra of solid products after the reaction (LA: 86 mmol/L, temperature: 150 °C, Fe: 20 mmol, Raney Ni: 0.2 g, filling rate: 25%)

On the basis of obtained experimental results and some reported knowledge, a possible reaction mechanism for the reduction of LA to GVL by using Fe as reducing agent over Raney Ni was proposed in scheme 2. Initially, hydrogen was formed from water and Fe was converted into Fe_3O_4 under HTW conditions. Then, in-situ formed Fe_3O_4 and Raney Ni played a catalytic role in absorbing hydrogen atoms on its surface. At the same time, carbonyl group (C=O) of LA was absorbed on the surface of Raney Ni. Then, the activated hydrogen attacks the carbon of the C=O absorbed on the surface of Raney Ni, and double band is reduced. Finally, the formed O^- attacks the carbon of carboxyl group(COOH) and γ-hydroxyvaleric acid is formed. [26-28]According to γ-hydroxyvaleric acid is unsteadiness under hydrothermal conditions, subsequently, quickly generate dehydration and esterification reaction to form GVL. Moreover, the results also explain why γ-hydroxyvaleric acid has been detected in HPLC and GC-MS at any experimental conditions.



Scheme 2. Proposed Mechanism of Synthesis of GVL from LA with Fe as the Reductant

CONCLUSION

In summary, a highly efficient Raney Ni catalyzed hydrogenation of LA into GVL has been explored under mild hydrothermal conditions by applying Fe as reductant. Moreover, water as protic solvent, not only act as hydrogen source, but also is advantage for reduction LA. More than 95% yield of GVL can be achieved at 150 ºC. Also, a considerably high GVL yield can be obtained at 100 ºC by prolong reaction time. Furthermore, a significantly selective production of GVL from LA can be observed. The novel process not only offers a method for producing GVL but also provides a possibility of using this method in the large-scale industrial production of GVL from LA even directly from actual biomass.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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Supporting Information

Total pages: 6

Total number of Figures: 4

Total number of Tables: 1

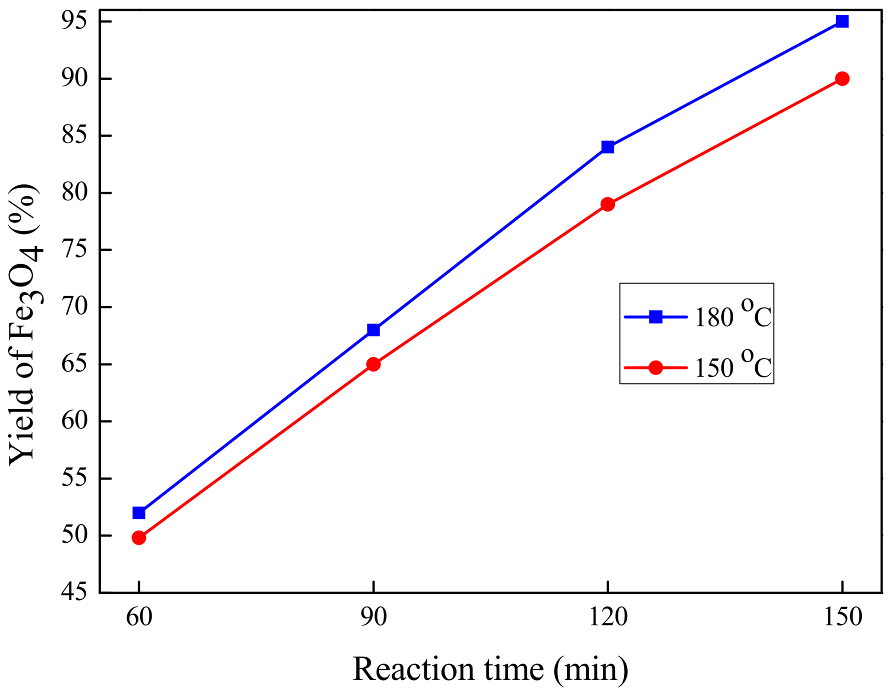

Figure S1. Oxidization of Fe after the GVL production reactions at different reaction time (Fe: 20 mmol/L, Raney Ni: 0.2 g, filling rate: 25%, LA: 86 mmol/L)

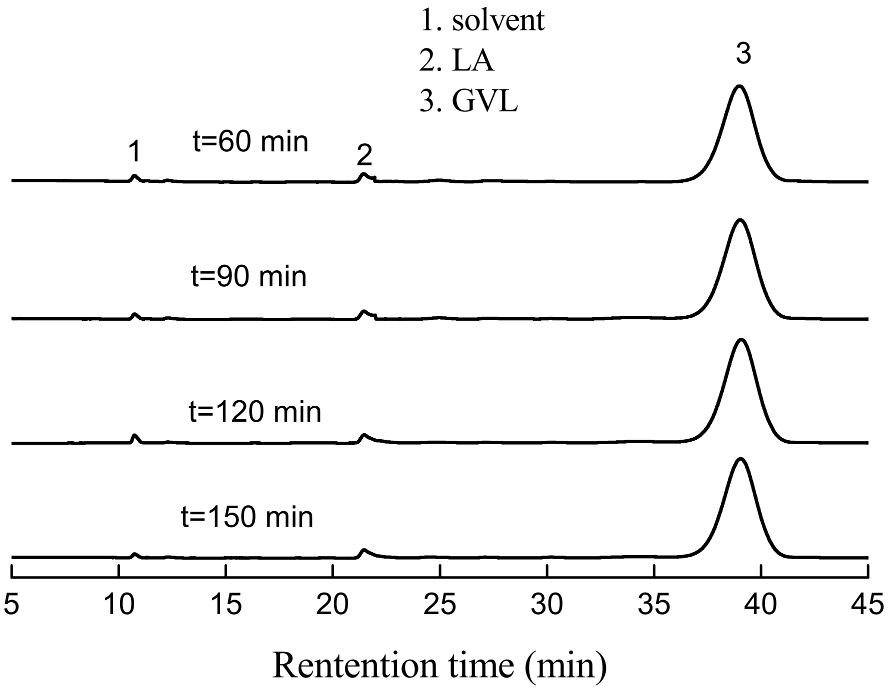

Figure S2. HPLC spectra of the liquid samples after reaction at different reaction times (temperature: 150 °C, LA: 86 mmol/L; water filing: 25%, Fe: 20 mmol, Raney Ni: 0.2 g)

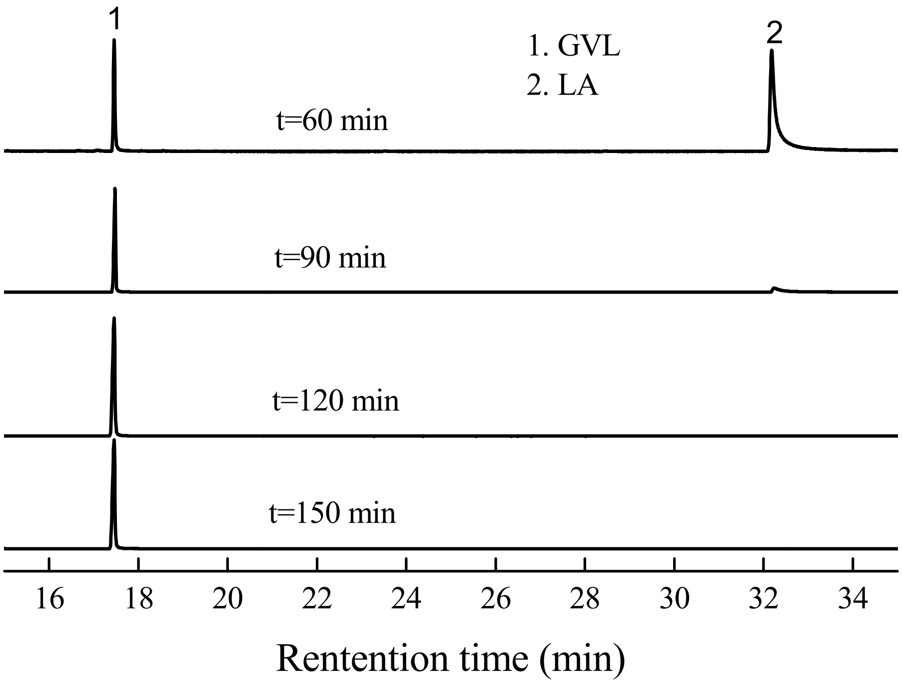

Figure S3. GC-MS spectra of the liquid samples after reaction at different times (temperature: 150 °C, LA: 86 mmol/L; water filing: 25%, Fe: 20 mmol, Raney Ni: 0.2 g)

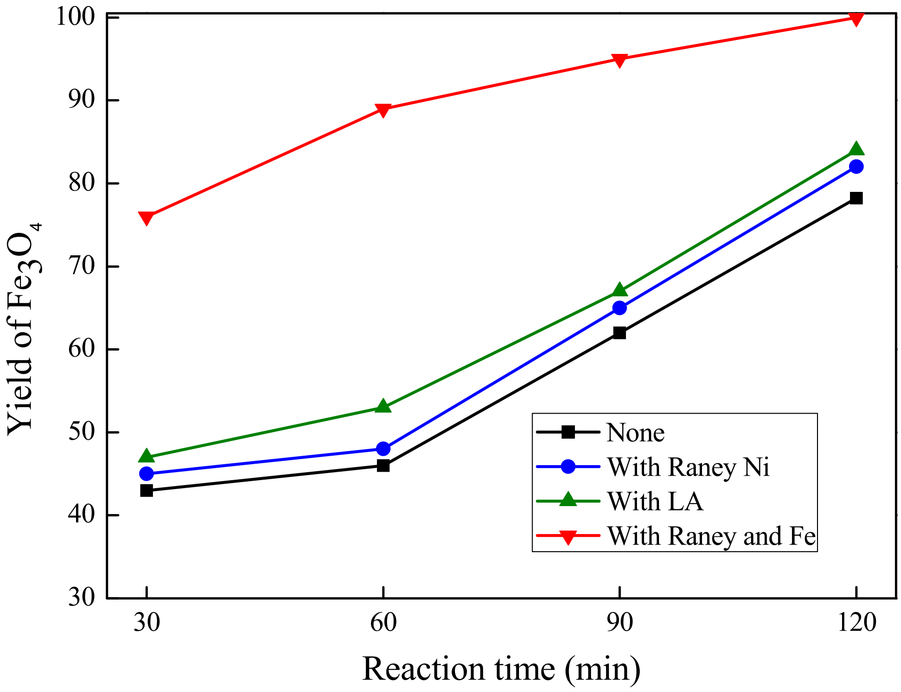

Figure S4. Oxidation of Fe in HTW in the presence and absence of Raney Ni and LA (temperature: 150 ^{o}C, water filling: 25%, Fe: 20 mmol, LA: 86 mmol/L, Raney Ni: 0.2 g)

Table S1. The assignment of the main characteristic absorption bands.

IR wavenumber (cm^{-1})	Assignment
3375	-OH
1386	$-CH_3$
570	Fe_3O_4