Facile and Selective Conversion of Levulinic Acid into γ-Valerolactone by Low-cost Fe and Ni Catalysts in Water

Xi Chen[1,*], Zhuang Ma[2], Wubin Yan[2] ,Guodong Yao[2,*], Qiuju Li[3], Binbin Jin[2] and Yalin Guo[2]

[1]China-UK Low Carbon College, Shanghai Jiao Tong University, 3 Yinlian Road, Shanghai 201306, China

[2]School of Environmental Science and Engineering, State key lab of metal matrix composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

[3]College of Environmental Science & Engineering, Tongji University, 1239 Siping RD, Shanghai, 200092, China

Email: geode@sjtu.edu.cn; chenxi-lcc@sjtu.edu.cn

Abstract

Renewable chemical production from biomass is desirable for the sustainable development of the society. Levulinic acid (LA) is a common biomass-derived building block that furnishes a suitable source to produce the industrially valuable γ-valerolactone (GVL). In this work, a low-cost, green and effective catalytic system was developed to transform LA into GVL in water by using Fe and Ni, in which the hydrogen source was provided by water splitting. The Fe primarily functioned as the reductant that transformed into Fe_3O_4 species after the reaction, while Ni played the major catalytic role to promote selective LA hydrogenation into GVL. After optimizations, the GVL yield reached the highest of 99% within 2-3 h at relatively low hydrothermal temperature of 230-250 °C. The recycling tests of Ni has suggested negligible decrease of product yield after four runs. This study establishes a green, facile and eco-friendly approach to synthesize GVL from biomass-derived LA.

Keywords: Biomass conversion; Biofuels; Catalytic hydrogenation; γ-valerolactone; Levulinic acid

1. Introduction

Non-renewable fossil resources are heavily consumed and rapidly depleting which induces vital environmental issues such as global warming and compels the scientific community to seek for sustainable alternatives.[1-7] With outstanding merits such as abundant, carbon-neutral, inexpensive, etc., biomass resources have been regarded as promising substitutes for the non-renewable fossil feedstocks to produce energy and chemicals.[8-14] With propitious advancements, extensive studies have been reported to transform various biomass resources into a diversity of chemicals, fuels and materials.[15-22] Levulinic acid (LA) is one of the top valuable chemicals as listed by the US Department of Energy which can be easily and selectively obtained from (hemi)cellulosic biomass via hydrolysis. Moreover, LA is also a versatile building block chemical that can be further upgraded to diverse essential chemicals.[23,24] As a crucial downstream product from LA, the γ-valerolactone (GVL) is a relatively stable, nontoxic and biodegradable cyclic ester with broad applications as food additives, green solvent, lubricants, fuel blends, etc.[25-29] Besides, GVL is a sustainable precursor to synthesize the Nylon monomer adipic acid and other polymer materials. Hence, LA conversion into GVL is an important route to generate diverse, valuable biobased products and has received increasing attentions in the past years.

Heterogeneous and homogeneous metal catalysts have been explored to convert LA into GVL primarily by hydrogenation.[30-38] Compared to the homogeneous catalysts, heterogeneous catalysts boast advantages such as reusable, easier product separation, etc. Supported noble metal catalysts (such as Ru, Pt, Pd, etc.) have been reported to transform LA into GVL in high yields under pressurized H_2 gas.[39-42] However, considering the high costs and deficiency of noble metals, the employment of low-price and ample non-noble metal catalysts is more beneficial for the practical applications of GVL production. Non-noble metal catalysts (such as Zn, Ni, Cu, Zr) on distinct supports have been developed to hydrogenate LA into GVL under different conditions.[43] For example, Cu/Al_2O_3 and Ni/Al_2O_3 has been used to convert LA at 250 °C under 6.5 MPa H_2 gas in water affording GVL in 66% after 5 h and 91% yield after 2 h respectively.[44] Nonetheless, the use of high pressure H_2 gas is associated with some general issues such as increased handling and safety risks, higher requirement on the equipment and elevated costs on H2 transportation and storage. Utilizing a non-noble metal catalytic system to stimulate water splitting as the in-situ hydrogen source and promote LA hydrogenation into GVL may provide a low-cost, green and efficient method to overcome these issues, which would be a more favorable process.[45] Jin's group has reported pioneering and significant works on metal-induced water splitting to in-situ generate H_2 source with hydrothermal technology to promote biomass and CO_2 conversion,[46-54] and excellent performances on the hydrogenation of $NaHCO_3/CO_2$ has been achieved through water splitting with various non-noble metals as both the reductant and catalyst.[55-59] The metals will be oxidized into the corresponding metal oxides during the process, whereas the metal/metal oxide cycle could be constructed by using renewable biomass such as glycerol as the reductant to shift the oxide back into the metal species.

In this work, we first tested the possibility to convert LA into GVL using the low-cost, widely-available Fe powder as the reductant and catalyst, in which in-situ generated H_2 from water splitting was utilized for the hydrogenation. Under optimal conditions, the GVL yield could achieve ~55% with a high selectivity of about 92% at 250 °C after 2 h in water. Then, the addition of a second metal to further promote the reaction was investigated. After screening, Ni was identified as a distinguishably effective co-catalyst to facilitate LA conversion. Using the Fe and Ni catalytic system, GVL could be produced in the highest yield of ~99% under optimized conditions. Based on XRD analyses and catalytic results, it is deduced that the presence of Ni has not only promoted the process of Fe/Fe_3O_4 shift and thus facilitated the H_2 generation from water which favored the hydrogenation step, but also played an essentially catalytic role on GVL formation. Besides, the recycling tests of the Ni co-catalyst has been conducted and negligible decrease in GVL yield was observed. The reaction pathway of LA conversion into GVL was proposed by using control experiments. This work puts forward a low-cost, simple, green and efficient method to quantitatively transform LA into GVL using a new non-noble metal catalytic system, contributing to the production of value-added chemicals from renewable biomass.

2. Experimental

2.1 Chemicals and materials

Fe powder (325 mesh, 97%) was purchased from Sigma-Aldrich. Levulinic acid (LA, 99%) was purchased from J&K. Ethanol, Fe_3O_4, γ-valerolactone (GVL, 98%) and the co-catalysts of Cu, Co, Mo, Ni, Sn and Cr (AR, 200 mesh) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were directly used as purchased without other treatment.

2.2 General reaction procedures

A stainless-steel batch reactor with a Teflon liner and an inner volume of about 28 mL was used to carry out experiments. At a certain water filling rate (e.g. 25% equals to 7 mL water), the desired amount of LA (e.g. 86 mmol/L), Fe and non-noble metal co-catalysts such as Co, Cu and Ni were added into the reactors in a typical procedure. Then, the closed reactor was transferred to an oven that was pre-heated to the set temperature (e.g. 250 °C) and reacted for a desired period of time. After reaction, the reactor was moved out from the oven and naturally cooled down to ambient temperature. The reaction time was counted at the point when the reactor was put into the oven. After cooling down to room temperature, the liquid solution was gathered by filtering with a membrane filter (0.22-μm diameter). Meanwhile, the solid residues were also gathered and washed for multiple times using both deionized water and absolute ethanol, which were then dried in a vacuum oven for 6 h at 40 °C. For the recycling of the Ni co-catalyst, a magnetic bar was used to separate Ni from the solid residues. The recovered Ni was washed with ethanol for several times by sonication.

2.3 Analysis methods

The high-performance liquid chromatography (HPLC) was employed to quantify the conversion and product yield in the liquid solutions. The HPLC mode is Agilent 1200LC equipped with two Shodex KC811 columns working in series and VWD and RID detectors. The mobile phase is $HClO_4$ (2 mM) with a flow rate of 1 mL/min. Meanwhile, for product identification, gas chromatography-mass spectrometry (GC-MS) was also used (Agilent 7890A mode and a 5975C MS detector). The column for product separation was the capillary column of HP-Innowax with the helium carrier gas. The column can directly analyze the water samples. The detailed conditions of the procedure were described elsewhere.[47,60]

The solid residues collected after the reactions were characterized by the X-ray diffraction (XRD). An X-ray Diffractometer (Shimadzu 6100) was employed which was armed with a Cu K_α radiation (30-mA flux, 40 kV accelerating voltage). A scanning rate of 2 ° per minute was used in the study with a scanning range of 10 to 80 °. The analysis results (diffraction patterns) were compared with the references in the ICDD PDF-2 database, and the MDI Jade 6 software was adopted to conduct the quantitative analysis of crystal phases which was according to the Rietveld calculations.

3. Results and Discussion

3.1 Conversion of LA into GVL by using non-noble Fe metal

Fe is an inexpensive, broadly-available and ample metal species on Earth which was proved capable of generating in-situ H_2 by water splitting under mild hydrothermal conditions. To test the feasibility of using Fe as the reductant and the catalyst for LA conversion, a group of experiments were undertaken without the addition of any co-catalyst. The conversion efficiencies of LA and the GVL yields were examined with the temperature ranging from 200 °C to 250 °C and a reaction time covering 60 min to 210 min (**Fig. 1a & 1b**). In the presence of Fe, the LA could be readily converted into GVL. Both the LA conversion efficiency and the GVL yield were inclined with the increases in reaction temperature and time. About 21% GVL yield was obtained at 250 °C after 210 min. Apart from GVL, no other products were noticed on HPLC or GC-MS in the liquid phase (**Fig. S1**), suggesting a high selectivity of LA conversion to GVL. The results show that the hydrogenation of LA into GVL was able to happen under relatively mild hydrothermal conditions by using Fe, without the use of external H_2 source.

After the reaction, the solid residues were gathered and studied by XRD analysis. The Fe was partially oxidized into Fe_3O_4 (**Fig. S2**), and the amount of Fe_3O_4 was quantified using the MDI Jade software. The formation of Fe_3O_4 was promoted by elevated temperature and prolonged reaction time (**Fig. S3**), indicating that the Fe was gradually oxidize by water to generate H_2 and the process was favored by increased temperature. In our previous work on Fe-promoted $NaHCO_3$ reduction into formic acid,[55] a control experiment has been conducted using the formed Fe_3O_4 and external H_2 gas and found the collected Fe_3O_4 could catalyze the reduction of $NaHCO_3$, despite the yield was much lower than using the Fe system. Possibly, the in-situ formed Fe_3O_4 species here would also play a role on the catalytic LA hydrogenation. The initial studies have proved that the LA conversion into GVL could be achieved in water by adding Fe powder.

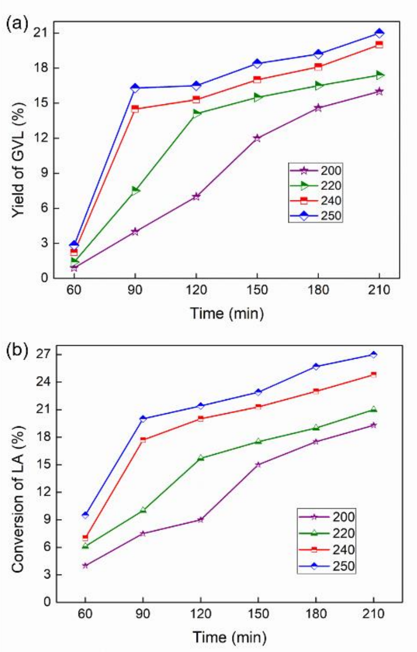


Figure 1. The influences of reaction time and temperature on the GVL yield and LA conversion (a) yield of GVL, (b) conversion of LA (LA: 86 mmol/L; Fe: 10 mmol).

Water splitting is the source of H_2 by using Fe as reducing agent, to further testify the role of the generated H_2 amount on the reduction of LA into GVL, the amount of Fe was varied and the reaction performances were examined at both 200 °C and 250 °C. In principle, higher Fe amount would supply more H_2. As shown in **Fig. 2**, the Fe amount had a pronounced influence on GVL yield and LA conversion. When the addition of Fe increased from 5 mmol to 40 mmol, the yield of GVL significantly enhanced from 8.4% to 35% at 200 °C and from 6% to 55% at 250 °C (nearly 8-time enhancement). The results suggest that sufficient H_2 was necessary to stimulate the LA hydrogenation into GVL and increased Fe amount was beneficial for GVL formation under mild hydrothermal conditions. In addition, the effect of filling rate of water on the yield of GVL was conducted at 200 °C and 250 °C, respectively. The yield of GVL decreased with increased filling rate of water from 20% to 40% (**Fig. S4**). With a higher filling rate, the water volume increased while the concentrations of the Fe and the LA substrate decreased, and the data indicate that low concentrations of LA and Fe have a negative effect on the GVL yield.

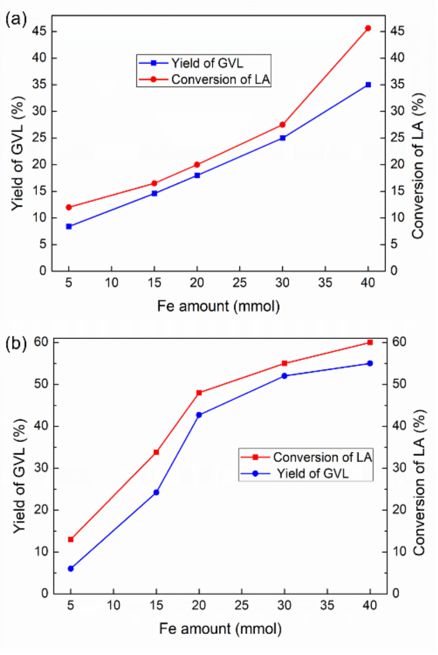


Figure 2. The influence of Fe amount on GVL yield and LA conversion (a) 200 °C, 120 min. (b) 250 °C, 120 min.

3.2 Conversion of LA to GVL with the addition of a non-noble co-catalyst

After validating the feasibility of LA conversion into GVL by using Fe in water, the additions of a second metal catalyst to further boost the product yield were attempted. Several low-cost non-noble metal species including Ni, Co, Cu, Mo, Cr, and Sn were investigated. From the data in **Table 1**, the addition of Mo and Sn led to decreasing LA conversion and GVL yield compared to the contrast experiment (without the addition of a second metal), which exhibited inhibitory effect on the reaction. Conversely, the addition of Ni, Co, Cu and Cr generally facilitated the LA conversion and GVL formation. Particularly, Ni and Co displayed exceptional promotive effect resulting in dramatically improved GVL yield to 90.4% and 88.6% respectively which were more than two-fold values as that of the contrast experiment. Besides, the selectivity to GVL also reached 99% by adding Ni as a co-catalyst. After the reaction, the solid residues were collected and analyzed by XRD (**Fig. 3**). According to the results, the second metals remained their crystal structure whereas the Fe powder was fully transformed into Fe_3O_4 with the addition of a co-catalyst as the XRD signals of Fe was no longer observed. It infers that the presence of a metal co-catalyst commonly promoted the shift of Fe into Fe_3O_4 releasing more H_2 gas for the hydrogenation. More H2 generation is beneficial for the LA hydrogenation, nonetheless, the catalytic role of the metal species was more paramount to the reaction because only Ni and Co led to very high GVL yield. After the screening, Ni was selected as an effective, abundant and cheap co-catalyst to promote LA conversion into GVL.

Table 1. The influence of different non-noble metals as the co-catalyst on the yield of GVL[a].

Co-catalyst	GVL yield (%)	LA conversion (%)
contrast	42%	60%
Ni	90.4%	91.5%
Co	88.6%	90.3%
Cu	55.8%	60.5%
Mo	31.2%	38.2%
Cr	47.9%	50.5%
Sn	23.1%	30.4%

[a] Reaction conditions: 86 mmol/L LA solution, 20 mmol Fe, 250 °C, 120 min, 0.5 g of the co-catalysts (Ni, Co, Cu, Mo, Cr, Sn).

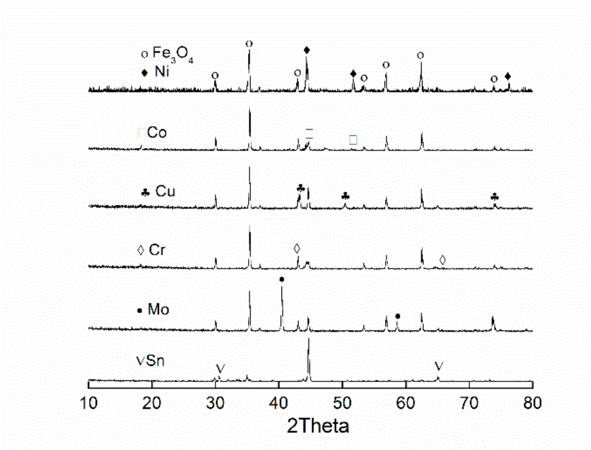


Figure 3. XRD signals of solid residues after the LA reduction reactions with Fe and various co-catalysts. Reaction conditions: 86 mmol/L LA, 250 °C, 120 min, 20 mmol Fe, 0.5 g of co-catalysts, water filling rate of 25%.

With Fe and Ni as the new catalytic system, the reaction parameters were optimized such as the Fe and Ni amount, water filling rate, reaction time, temperature, etc. By introducing Ni, a different trend of Fe amount on product yield was observed (**Fig. 4a**). The highest GVL yield and LA conversion were realized with 10 mmol Fe powder of 92.5% and 95.3%, which were then declined with further increase in Fe amount. Presumably, the presence of Ni has efficiently promoted the catalytic hydrogenation of LA into GVL with a low requirement on H2 amount and thus reduced Fe amount. The overloaded Fe powder might compete with Ni on H2 and substrate adsorption which resulted in reduced GVL yield and LA conversion. With Fe amount fixed at 10 mmol, the effect of Ni amount was examined (**Fig. 4b**). When the Ni amount rose from 0.1 g to 0.5 g, both the LA conversion and the GVL yield enhanced steadily showing the significant role of Ni on GVL formation. Increased Ni probably provided more activity sites that absorbed hydrogen atom from water to promote the reduction of LA into GVL. Meanwhile, increasing the water filling rate from 25% to 65% would lead to gradually decreased GVL yield (**Fig. 4c**) possibly due to the decreased concentrations of the catalysts, which was in agreement with previous findings.

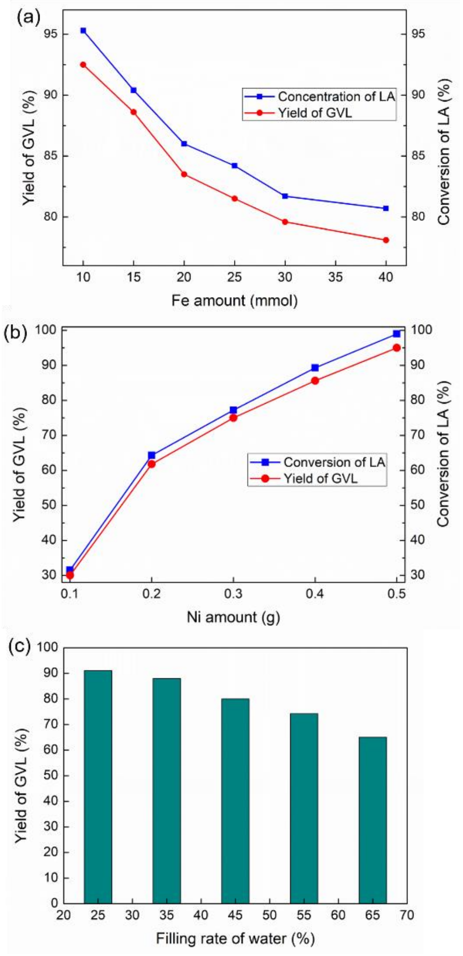


Figure 4. The influence of Fe amount (a), Ni amount (b), filling rate of water (c). Basic reaction conditions: 86 mmol/L LA, 250 °C, 120 min, 10 mmol Fe, 0.5 g Ni, 25% water filling rate.

Next, the influence of reaction temperature and time on GVL yield and LA conversion was studied with a wide range from 180 °C to 250 °C and 60 min to 180 min using Fe and Ni. As shown in **Fig. 5a & 5b**, the reaction temperature and time imposed a remarkable impact on the GVL yield and LA conversion. Higher temperature and prolonged reaction time generally favored GVL production. The highest GVL yield was obtained of 99.9% at 250 °C after a reaction time of 150 min.

3.3 The recyclability of Ni catalysts

As aforementioned, the Fe/Fe_3O_4 cycle could be potentially constructed by using a waste biomass such as glycerol as a reductant.[61] In the study, the recyclability tests of the co-catalyst Ni have been investigated. After the reaction, the Ni was collected by using a magnetic bar and re-added into the reaction system for another four runs. **Fig. 6** shows that only slight drop in the GVL yield happened (from 92% to 85%) during the four-run recycling experiments at 230 °C. These results indicate that the Ni co-catalyst largely maintained its catalytic reactivity during the recycling tests. As a result, combined with a recovery treatment on the Fe powder by using glycerol as a reductant, the catalytic system of Fe and Ni could be in principle recyclable in the reaction process to be self-sustained.

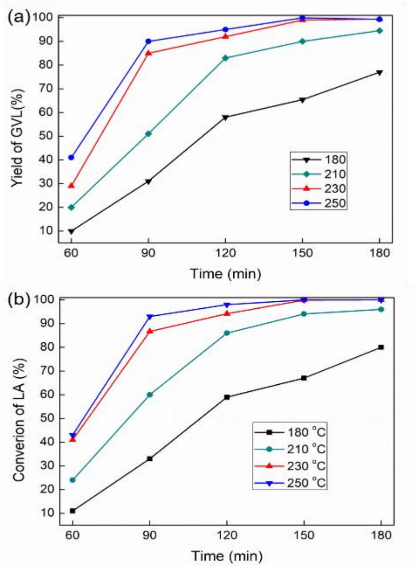


Figure5. The influence of reaction time and temperature on the yield of GVL and conversion of LA. Reaction conditions: 86 mmol/L LA, 10 mmol Fe, 0.5 g Ni, 25% water filling rate.

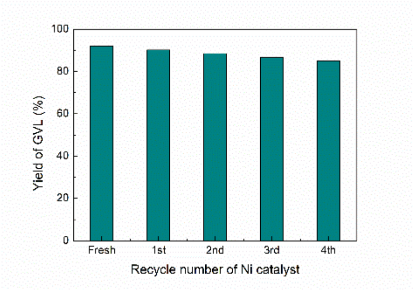
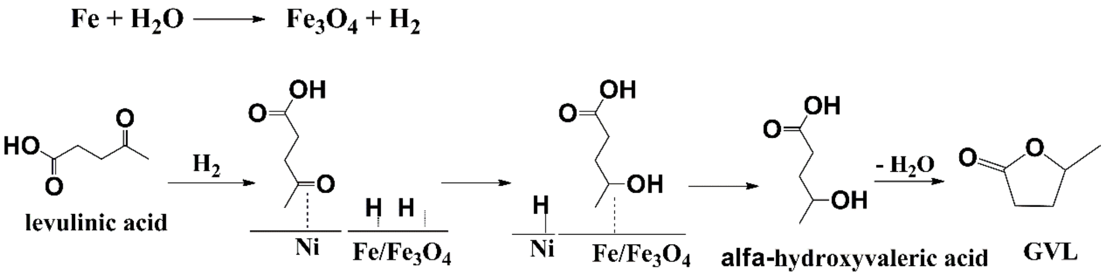


Figure 6. The recyclability tests of the Ni co-catalysts. Reaction conditions: 86 mmol/L LA, 10 mmol Fe, 0.5 g Ni, 230 °C, 120 min.

3.4 Proposed reaction pathway of LA conversion into GVL

In the reaction system, it is deduced that the addition of a metal co-catalyst has significantly facilitated the Fe/Fe_3O_4 shift and promoted H_2 generation for LA hydrogenation. Pyruvic acid (PA) that has a similar structure to LA has been adopted as the starting material under identical reaction conditions, and the major product was identified to be lactic acid in this control experiment. It infers that the in-situ generated H_2 attacked the C=O group of PA and hydrogenation reaction happened. **Scheme 1** displays the proposed possible reaction route of LA conversion into GVL by using the Fe and Ni catalytic system in water. During the reaction, the Ni facilitated the Fe shift to Fe_3O_4 meanwhile water splitting was promoted to generate in-situ H_2. A portion of the H_2 that produced by water splitting might absorb on the surface of the metal catalyst to provide active H for hydrogenation. Under the catalysis of Ni and Fe_3O_4, the C=O group of LA has been hydrogenated into the -OH group. Finally, the esterification of the -OH group and -COOH group happened to form the ring of GVL product.



Scheme 1. Possible reaction route of LA conversion into GVL by using the Fe and Ni catalytic system in water.

4. Conclusion

In this paper, the conversion of LA into GVL in water by using Fe and Ni as the catalysts has been reported for the first time. Water splitting through the Fe/Fe3O4 cycle provided the H2 source for the LA hydrogenation, without the need for external H2 supply. A high GVL yield of about 99.9% was realized under relatively low hydrothermal temperature and with a relatively short reaction time. In the reaction system, the Fe mainly functioned as a reductant to facilitate water splitting while the Ni played a primary catalytical role on selective LA hydrogenation into GVL. The combinational use of Fe and Ni has been proved remarkably efficient, and the non-noble metals are cheap, abundant and easily attainable. Besides, the Fe can be potentially recovered by using waste biomass such as glycerol and the Ni can be reused for more than four times without remarkable yield drop. With the low capital costs, environmentally friendly and facile process, the established method can be widely applied and holds the potentials to scaling-ups which steps forward for GVL production from renewable biomass resources.

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Conflict of interest

We declare that we have no financial and personal relationships with other people or organizations.

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