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Catalytic hydrogenation of ethyl levulinate into γ-valerolactone over commercial Raney Cu catalyst

Yueying Du*, **Chuntao Zhang****, **Yang Li***, **Nahui Zhang***, **Dezhang Ren***,†, **and Zhibao Huo***,**,†

*College of Marine Ecology and Environment, Shanghai Ocean University, 999 Huchenghuan Road, Shanghai, 201306, China
**School of Environmental Science and Engineering, Shanghai Jiao Tong University,
800 Dongchuan Road, Shanghai, 200240, China

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Abstract−An eco-friendly green reaction process was developed to achieve efficient hydrogenation of ethyl levulinate (EL) to γ-valerolactone (GVL) over commercial-available Raney Cu catalyst with H_2 as the hydrogen source. Raney Cu presented higher catalytic activity among a series of Cu based and Raney type catalysts. The maximum yield of GVL was 98.3% at 160 °C for 3 h. It was found that Raney Cu had great reusability and could be used at least three times without loss of activity. Moreover, the results of XRD, XPS and ICP confirmed the high stability of the catalyst. A possible reaction pathway was also proposed. Ethanol was the main byproduct in this reaction; this study therefore provides a green and efficient method for the conversion of EL to GVL.

Keywords: Ethyl Levulinate, γ-Valerolactone, Raney Cu, Catalysis, Hydrogenation

INTRODUCTION

The world is in urgent need of reducing the dependence on fossil resources, and the efficient utilization of biomass resources has become extremely important [1-3]. Levulinic acid (LA) and levulinate esters are regarded as important bio-derived platform molecules, which can be easily obtained from cellulose and hemicellulose [4]. The production of LA and ethyl levulinate (EL) from various biomass has been widely studied, such as spent coffee grounds, waste citrus peels and microalgae [5-8]. Among various useful products of LA and its esters conversion, γ-valerolactone (GVL) is an important chemical that can be used for the production of liquid fuel and polymers, and as the intermediate in the synthesis of fine chemicals [9]. The catalytic hydrogenation of LA and EL to GVL is an efficient way to utilize biomass resources, which has attracted wide attention [10-13].

Up to now, many catalysts have been developed for the hydrogenation of LA or its esters to GVL, such as Pd, Ru, Rh, Cu, Fe, Co and Ni based catalysts [14-25]. Generally, noble metal catalysts have high catalytic activity even under mild conditions. In 2004, Manzer et al. obtained complete conversion of LA and >97% yield of GVL over 5% Ru/C at 150 °C and 500 psig H_2 for 4 h [17]. Compared with other carbon supported catalysts, 5% Ru/C presented better catalytic performance. Al-Shall et al. found that the catalytic activity of Ru/C was much higher than that of Ru/Al_2O_3 or Ru/SiO_2, and 97.5% GVL yield was achieved at room temperature with 12 bar H_2 for 50 h [26]. A recent study by Gao et al. investigated the influence on different CeO_2 morphology of Ru/CeO_2 catalysts of EL conversion [15]. It is evident that studies on hydrogenation of LA and EL to produce GVL over noble metal catalysts have been quite mature. However, the high cost of noble metal catalysts limits their application.

To reduce cost, non-noble metal catalysts have gradually been developed. Chen et al. transformed EL to GVL over Ni supported on equilibrium fluid-catalytic-cracking catalysts, and obtained 96.2% selectivity of GVL at 180 °C for 6 h [20]. Kondeboina et al. produced GVL from EL over Co-based catalysts under atmospheric H_2 pressure in a continuous process [21]. Recently, the same group prepared bimetallic Ni-Co/γ-Al_2O_3 catalyst with a well-built interaction which showed high activity and stability, and 97% yield of GVL was delivered [25]. Although most catalysts have good activity for EL hydrogenation, there are still some shortcomings, such as complex preparation and poor reusability [15,25,27].

In the past several decades, Cu based catalysts have been widely studied in the hydrogenation reactions for their great selectivity for C=O bond [28-31]. In 2012, a study showed that Cu/Al_2O_3 and Cu/ZrO_2 prepared by co-precipitation method presented high activity for hydrogenation of LA and its methyl easter with 90-100% GVL selectivity. The Cu metal leaching was evident visibly of Cu/Al_2O_3 in the water medium [31]. In 2015, Zhang et al. demonstrated a new approach to tailor the Cu/ZnO interface by molecular layer deposition. A 72% yield of GVL was obtained at 240 °C; meanwhile, they indicated that the catalytic activity was correlated with Cu species [30]. Cai et al. reported a bimetallic Cu-Ni catalyst for hydrogenation of EL to GVL. Results showed that 10Cu-5Ni/Al_2O_3 provided a 97% yield of GVL at 150 °C for 12 h [19]. However, the leaching of copper limited the long-term application of Cu-based catalysts in some traditional reactions [30-33]. For this reason, it was urgent to explore a Cu-based catalyst with high stability and activity for EL hydrogenation to GVL. In recent years, we have studied the efficient conversion of EL to GVL with high yield and high selectivity. Based on this, it is desired to continue our previous research [4,34].

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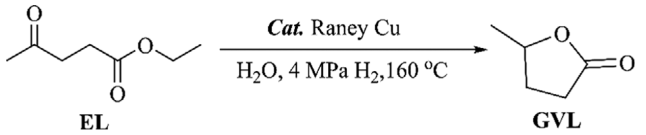
†To whom correspondence should be addressed.
E-mail: dzren@shou.edu.cn, zbhuo@shou.edu.cn



Scheme 1. Hydrogenation of EL to GVL over Raney Cu catalyst.

Among numerous studies, nanocatalysts with high specific surface area show great catalytic activity. As one of them, Raney Cu with low price, simple preparation and good poison proof could be a great hydrogenation catalyst [35-37]. It occurred to us that such a low-cost and efficient catalyst can be used in the hydrogenation of EL to GVL.

In this work, commercial-available Raney Cu was used as the catalyst for hydrogenation of EL to produce GVL with H_2 as the hydrogen donor (Scheme 1). Interestingly, the Raney Cu catalyst could be reused several times with great stability. Besides, the catalyst showed high catalytic activity, the yield and selectivity of GVL could reach 98.3% and 98.7%, respectively.

EXPERIMENTAL SECTION

1. Materials

Ethyl levulinate (EL, 99%) was purchased from Beijing Inoke Technology Co., Ltd. γ-Valerolactone (GVL, 98%), CuAlZn alloy, Cu, CuO, Cu_2O were purchased from Sinopharm Chemical Reagent (China). 1,4-Pentanediol (1,4-PDO) was purchased from Sigma Aldrich Chemical Co., Ltd. Raney Cu, CuAl alloy, Raney Fe, Raney Co, Raney Ni, CuNPore and NiNPore were purchased from Dalian General Chemical Co., Ltd. CuZn alloy was purchased from Changsha Tianjiu Metal Material Co., Ltd.

2. Catalyst Preparation

All the catalysts except CuAlZn-3.5 h were commercial. CuAlZn-3.5 h catalyst was prepared in the following steps: 2 g CuAlZn alloy powder was added into 26 mL 20 wt% NaOH at 5-10 °C under stirring at 700 r/min. After being treated with NaOH solution for 3.5 h, the catalyst was separated.

3. Catalyst Characterization

X-ray diffraction patterns (XRD) of the samples were obtained by Shimadzu XRD-6100 X-ray diffractometer with Cu Kα radiation. The 2θ angle range was 10° to 80° and the rate was 6°/min. X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) spectra were collected on a Thermo Scientific K-Alpha spectrometer with a monochromatic Al Kα X-ray source (h=1,486.6 eV). The kinetic energy was equal to 1,486.6 eV minus the measured binding energy. Inductive coupled plasma emission spectrometer (ICP) was used to analyze the concentration of metal ions in the liquid sample after one reaction to determine whether metal ions were precipitated.

4. Hydrogenation of EL

All the experiments were carried out in a 100 mL PARR 5500 reactor. Typically, 10 mL deionized water, an amount of catalyst and EL was added into the reactor. The reactor was sealed and purged with 1 MPa H_2. Then, a certain pressure of H_2 was introduced to the reactor. After that, the reaction mixture was heated to the desired reaction temperature and kept for a certain time with stirring at 800 rmp/min. After reaction, the reactor was cooled to room temperature; then the liquid samples were collected by filtering with 0.45 μm membrane. The products were analyzed by GC/MS and GC-FID.

EL conversion, GVL yield and selectivity were calculated using the following equations:

$$\text{EL conversion }(\%) = \left(1 - \frac{\text{Mole of EL}}{\text{Initial mole of EL}}\right) \times 100\%$$

$$\text{GVL yield }(\%) = \frac{\text{Mole of GVL}}{\text{Initial mole of EL}} \times 100\%$$

$$\text{GVI selectivity }(\%) = \frac{\text{Mole of GVL}}{\text{Initial mole of EL} - \text{Mole of EL}} \times 100\%$$

RESULTS AND DISCUSSION

1. Catalytic Activity of Various Catalysts for the Hydrogenation of EL

By reason of the excellent performance of Cu based catalysts in the hydrogenation reaction, various Cu based catalysts and other non-noble metal catalysts were selected for GVL production from EL. As shown in Table 1, the conversion of EL was 8.8% and the yield of GVL was only 2.9% in the absence of catalysts. The slight conversion and yield could probably be due to catalysis of metal on the reactor. Notably, 93.6% conversion of EL and 95.2% selectivity of GVL was observed when Raney Cu was used as the catalyst. Since commercial Raney Cu is usually prepared from CuAl alloy or CuZn alloy, the catalytic activity of CuAl alloy, CuZn alloy and CuZnAl alloy for EL hydrogenation was also investigated, and the yields of GVL were 31.6%, 37.2% and 18.3%, respectively. Compared with CuAlZn-alloy, CuAlZn-3.5 h dealloying in NaOH solution presented much higher activity with 76.4% yield and 90.6% selectivity of GVL, indicating that the metal framework could enhance the catalytic activity. Cu powders and copper oxide were also

Table 1. Catalysts screening

Entry	Catalyst	EL Conv. (%)	GVL Yield (%)	Sel. (%)
1	None	8.8	2.9	- -
2	Raney Cu	93.6	86.1	95.2
3	CuAl-alloy	41.7	31.6	75.8
4	CuZn-alloy	54.5	37.2	68.3
5	CuAlZn-alloy	36.7	18.3	49.9
6	CuAlZn-3.5 h	84.3	76.4	90.6
7	Cu	47.1	34.3	72.8
8	CuO	41.2	14.6	35.4
9	Cu_2O	41.1	18.6	45.2
10	Raney Fe	87.3	67.6	77.5
11	Raney Co	98.5	83.7	85.0
12	Raney Ni	99.0	85.8	86.6
13	CuNPore	55.4	33.7	60.8
14	NiNPore	97.7	81.3	83.2

Reaction conditions: 1 mmol EL, 50 mg catalysts, 10 mL H_2O, 160 °C, 4 MPa H_2, 3 h.

used as the catalysts. Among these Cu based catalysts, Cu powders showed higher selectivity than CuO or Cu_2O, but still lower than Raney Cu. Taking into consideration that other types of non-noble metal nanocatalysts had been used in similar reactions, Raney Fe, Raney Co, Raney Ni, CuNPore and NiNPore were also studied, and 67.6%, 83.7%, 85.5%, 33.7% and 81.3% yields of GVL were obtained, respectively. According to other researches in Table S1, these commercial catalysts had different specific surface areas, which may be one of the key causes for the differences in the EL hydrogenation effect [38,39]. Raney type catalysts with higher specific surface area could result in higher EL conversion and GVL yield than Cu based catalysts. Although Raney Ni, Co and Fe had higher specific surface area, the selectivity was lower than Raney Cu, probably because of over-hydrogenation, leading to by-products, such as 1,4-PDO and the further etherification product 2-methyltetrahydrofuran [25,32,38]. It could be seen that most nanocatalysts had good catalytic activity, except for CuNPore. According to the above analysis, Raney Cu with the highest GVL yield was chosen for further optimization of experimental conditions and catalyst characterization. The GC and GC/MS spectra of EL and GVL with Raney Cu as the catalyst are shown in Fig. S1. Two obvious peaks at 8.46 and 8.67 min could be confirmed as EL and GVL, respectively.

2. Effect of the Various Parameters on Hydrogenation of EL

Since the amount of the catalyst could have a great impact on substrate conversion, the influence of the amount of Raney Cu catalyst on the conversion of EL, the yield of GVL and the selectivity of GVL was explored. The experimental results are shown in Fig. 1(a). Obviously, the yield of GVL increased with the increment of adding amount of Raney Cu. When Raney Cu loading increased from 10 mg to 50 mg, the yield of GVL increased from 83.9% to 98.5% with a growth of 14.6%. However, there was only a small extent of 0.2% increase when catalyst loading increased from 40 mg to 50 mg, indicating that the catalyst loading nearly reached the saturation point. Considering the economic factor and the yield of GVL, 40 mg was selected for the following research.

In this reaction, H_2 was used as the hydrogen donor. Thus, the effect of different H_2 pressure on EL conversion was investigated and the results are shown in Fig. 1(b). It is obvious that H_2 pressure had a significant effect on the yield and selectivity of GVL. The GVL yield revealed a definite trend of fast increase while H_2 pressure increased from 1 MPa to 3 MPa. And the highest 98.3% yield of GVL and 98.7% selectivity were achieved at 4 MPa. However, when further increasing H_2 pressure to 5 MPa, the yield and selectivity of GVL presented a slight decline, probably due to the increase of by-products due to over-hydrogenation. Thus, to obtain the highest GVL yield and remain safe for the reactor, 4 MPa was chosen as the optimum H_2 pressure.

In addition, the influences of reaction temperature and time were investigated. The reaction was conducted over Raney Cu by changing the reaction temperature at an interval of 10 °C from 140 °C to 180 °C (Fig. 1(c)). At 140 °C, 92.6% conversion of EL, 72.3% yield and 78.1% selectivity of GVL were obtained after 3 h. When the temperature was increased from 140 °C to 150 °C, the

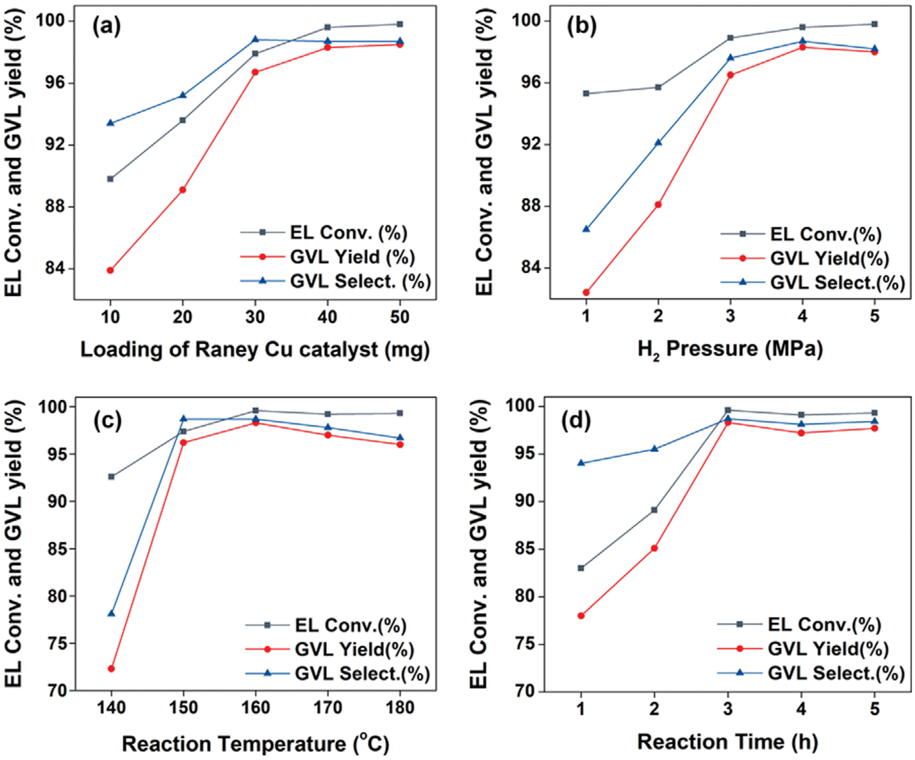


Fig. 1. EL conversion and GVL yield under different (a) loading of Raney Cu, (b) H_2 pressure, (c) reaction temperature and (d) reaction time. Reaction conditions: 0.4 mmol EL, 4 mL H_2O, (a) 4 MPa H_2, 160 °C, 3 h, (b) 40 mg Raney Cu, 160 °C, 3 h, (c) 4 MPa H_2, 40 mg Raney Cu, 3 h, (d) 4 MPa H_2, 40 mg Raney Cu, 160 °C.

EL conversion increased to 97.4%, and the GVL yield was 96.2% with a significant increase of 23.9%. Similarly, the selectivity of GVL also increased by 20.6%. The highest yield of 98.3% could be reached at 160 °C, and the selectivity of GVL remained stable. However, when the temperature continued to rise to 170 °C and 180 °C, the yield of GVL began to decrease slightly, indicating that higher temperature was not conducive to the catalytic hydrogenation of EL to GVL over Raney Cu catalyst. Therefore, the optimum reaction temperature for this reaction was 160 °C.

The appropriate reaction time could inhibit the formation of by-products, so that the target product could be obtained more efficiently. Fig. 1(d) reveals the influence of reaction time on the EL hydrogenation at 160 °C. Noticeably, the EL conversion was 83% and the GVL yield was 78% after 1 h, indicating that Raney Cu had high catalytic efficiency for the reaction. Further increasing the reaction time led to a continuous transformation of EL to GVL. However, the catalytic efficiency of the catalyst decreased slightly when the reaction time increased to 4 h or 5 h. The catalytic effect had reached the maximum and promoted the further hydrogenation of GVL into 1,4-PDO.

As a result, under the optimum conditions of 0.4 mmol EL, 4 mL H_2O, 40 mg Raney Cu, 4 MPa H_2, 160 °C and 3 h, the highest 99.6% conversion of EL and the highest 98.3% yield of GVL could be achieved.

3. Reusability of the Raney Cu Catalyst

The reusability of catalyst is an important index to evaluate the activity of catalyst, and it also affects the economic benefit of catalyst applied in industry. Therefore, the cyclic stability of Raney Cu catalyst was tested. After reaction, the mixture was centrifuged and the catalyst was washed with deionized water and ethanol several times, then dried with N_2. The results are shown in Fig. 2. It was noticed that EL conversion and GVL yield remained basically unchanged after used three times.

The above results indicate that Raney Cu had high reusability and could be used three times without loss of catalytic activity. Meanwhile, XRD characterization was carried out and the XRD patterns of fresh catalyst and spent catalyst used three times are shown in Fig. 3. The diffraction peaks at 2θ=43.2°, 51.1° and 75.8° were attributed to metallic Cu (JCPDS 04-0836). Additionally, the weaker diffraction peak next to the highest peak corresponded to Cu_9Al_4 (JCPDS 24-0003), and no Cu_xO (X=1, 2) was observed [36]. Moreover, there was no significant difference between the two XRD patterns.

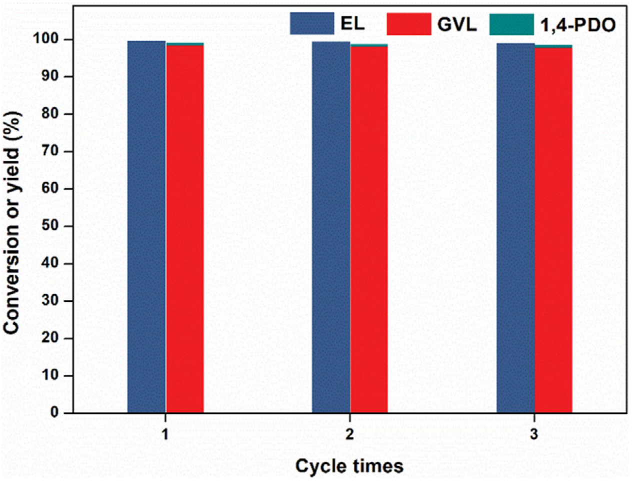


Fig. 2. Reuse stability of the Raney Cu (0.4 mmol EL, 40 mg Raney Cu, 4 mL H_2O, 4 MPa H_2, 160 °C, 3 h).

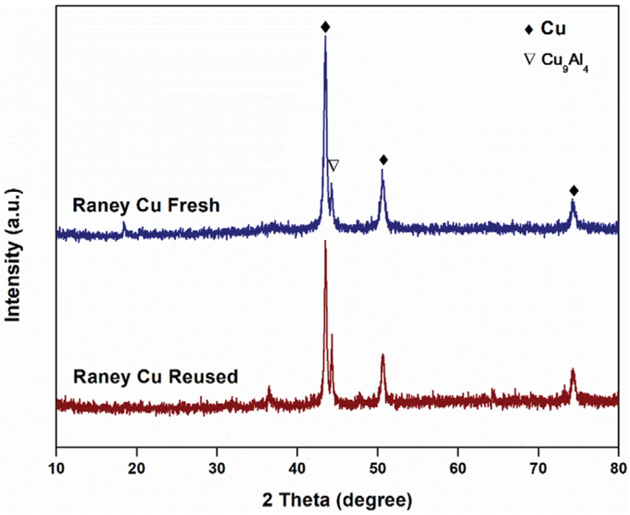


Fig. 3. XRD images of fresh Raney Cu and reused Raney Cu.

XPS was used to analyze the components and chemical states of fresh and spent Raney Cu. As shown in Fig. S2, the peaks of Cu, O, C and Al can be seen. By integrating the spectral peak area, the proportion of Cu, Al and O atoms was summarized in Table S2. The ratio of Cu atom was almost the same. The content of Al increased a little, and the content of O showed a slight decrease. As shown in Fig. 4(a), the peak with binding energy (BE) at about 934.0 eV in the spectra of Cu XPS 2p3/2 region corresponds to Cu^{2+} species and the peak at about 932.6 eV corresponds to Cu^+ or Cu^0 species. The ratio of Cu^+ and Cu^0 in fresh Raney Cu and reused Raney Cu was 74.9% and 80.9% (Table S3). The slight increase of the ratio of Cu^+ and Cu^0 is probably because of the reduction of Cu in the hydrogenation reaction. The detailed Cu status, however, cannot be ascertained by Fig. 4(a) due to closeness in binding energies of Cu^+ and Cu^0 (~0.1 eV) [40]. Therefore, the Cu LMM Auger transition profiles (Fig. 4(b)) were obtained. Herein, the peaks with the kinetic energy of ~916.8 eV were assigned to Cu^+, and the peaks located at ~918.7 eV were attributed to Cu^0. The kinetic energy of Cu^+ and Cu^0 of fresh Raney Cu was virtually the same with reused Raney Cu. The Cu XAES spectra showed no significant change. Similarly, Al 2p spectra showed no significant change (Fig. 4(c)).

The chemical states of O on fresh and reused catalysts were also evaluated by XPS. As shown in Fig. 4(d), O 1s XPS spectra is deconvoluted into two peaks of fresh Raney Cu. The peak at the lower binding energy is related to lattice oxygen ($O_{lattice}$), and the peak at 532.0 eV corresponds to surface oxygen ($O_{surface}$). For reused Raney Cu, the added peak at 533.3 eV was assigned to the oxygen species bonded to the organic compounds adsorbed on the reused catalyst. The density of surface oxygen vacancies was evaluated by the ratio of $O_{surface}/(O_{lattice}+O_{surface}+O_{others})$. Related data is summarized

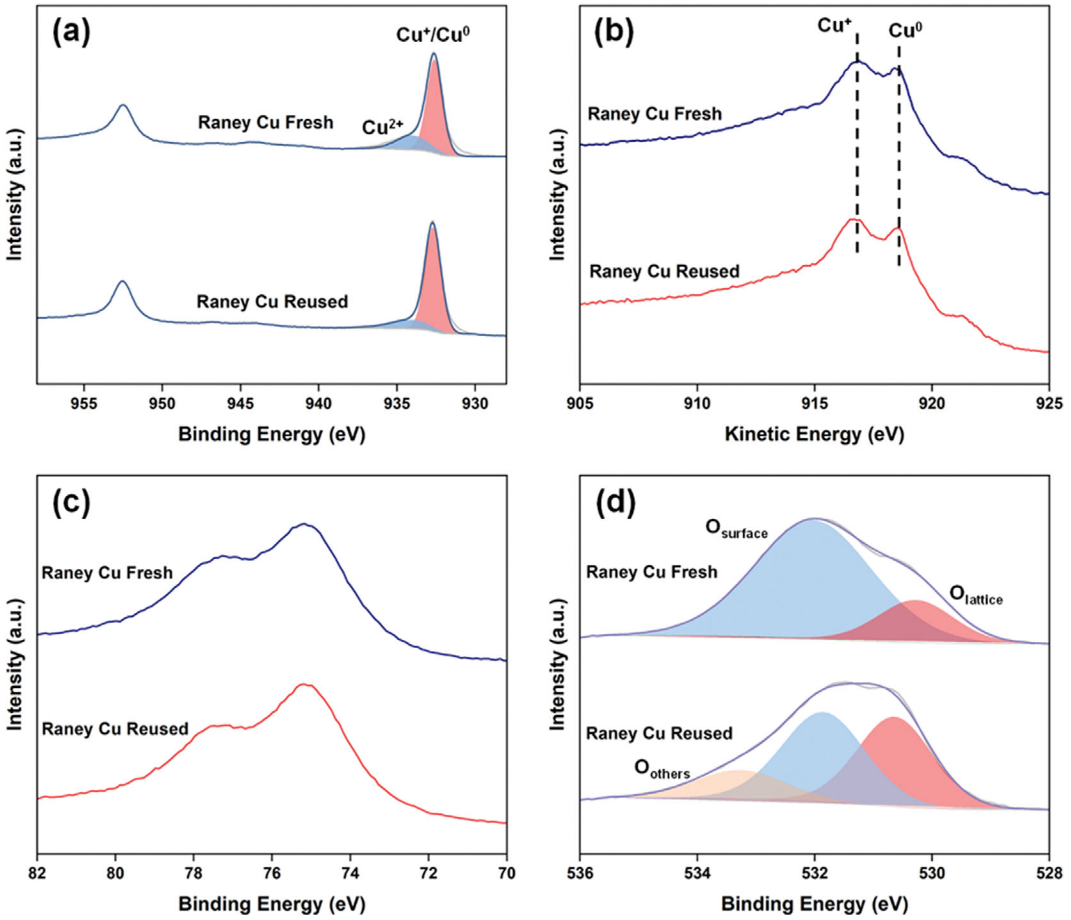


Fig. 4. XPS spectra of (a) Cu 2p, (b) Cu LMM, (c) Al 2p and (d) O 1s of catalysts.

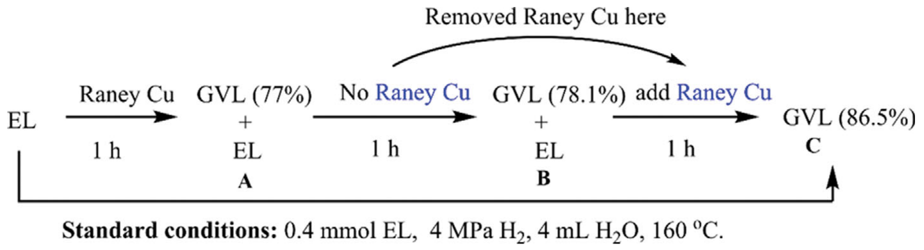


Fig. 5. Step diagram of the experiment.

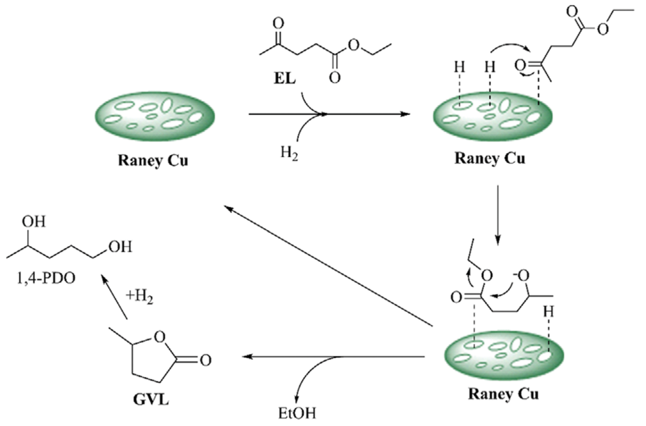
in Table S4. The density of surface oxygen vacancies of Raney Cu decreased after being used for three times, and the peak of O_{others} was added due to the adsorption of organic compounds on the catalyst surface. In summary, the components and chemical states of fresh and spent Raney Cu have no significant change.

Furthermore, to investigate whether Cu would strip during the reaction and whether the stripped Cu could catalyze the production of GVL, we designed a systematic experiment as shown in Fig. 5. First, the reaction was carried out under the following conditions: 0.4 mmol EL, 4 MPa H_2, 40 mg Raney Cu, 4 mL H_2O and 160 °C. After 1 h, a little reaction solution (**A**) was removed to perform GC analysis, and the yield of GVL was 77%. Next, the Raney Cu was taken out, and the rest of the solution continued to react for 1 h. 78.1% yield of GVL was obtained in solution (**B**). Finally, the removed Raney Cu was added into the reactor, and the solution (**C**) after 1 h came to 86.5% GVL yield, which was similar to the GVL yield (85.1%) of direct reaction for 2 h. This experiment proved that Raney Cu was the effective catalyst for the hydrogenation of EL to GVL.

Meanwhile, ICP analysis of the solution after the reaction illustrated that the stripping phenomenon of Raney Cu was negligible with low concentration of 1.062 ppm of Cu (Table S5). It was also one of the reasons why Raney Cu could be reused and the catalytic activity did not decrease, and also the GVL yield was almost unchanged from solution **A** to solution **B** in Fig. 5.

4. The Proposed Mechanism

According to the above results and previous studies [41-43], a possible mechanism of catalytic hydrogenation of EL to GVL by



Scheme 2. The proposed pathway for the hydrogenation of EL over Raney Cu.

Raney Cu was proposed, as shown in Scheme 2. Since no obvious intermediates were detected even though the reaction time was very short, we speculated that the experimental process was as follows: both the acetyl group of EL and the external molecular H adsorbed on the surface of Raney Cu, then the active H species attacked the acetyl group to form an extremely unstable γ-hydroxypentanoic ester [42]. Finally, a molecule of ethanol was removed and the target product GVL was formed. Meanwhile, GVL would further acquire additional hydrogen to form trace 1, 4-PDO.

CONCLUSIONS

We developed a green process to use commercially available Raney Cu as a catalyst for EL hydrogenation to GVL with H_2 as the hydrogen source. The catalytic activity of various catalysts was investigated, and 98.3% yield and 98.7% selectivity of GVL were successfully obtained at the optimized reaction conditions: 40 mg Raney Cu, 4 MPa H_2, 160 °C and 3 h. Moreover, it was found that the catalytic activity of Raney Cu remained unchanged during the reusability test. A systematic experiment was designed to analyze the catalysis of Raney Cu and its leaching; the results indicated that Raney Cu maintained high stability in the hydrogenation of EL to GVL. A possible mechanism was proposed, and ethanol and trace 1,4-PDO as byproducts were obtained. The work provides a new route for the conversion of EL to GVL and also possible industrial application prospects.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Catalytic hydrogenation of ethyl levulinate into γ-valerolactone over commercial Raney Cu catalyst

Yueying Du*, Chuntao Zhang, Yang Li*, Nahui Zhang*, Dezhang Ren*,†, and Zhibao Huo*,**,†**

*College of Marine Ecology and Environment, Shanghai Ocean University, 999 Huchenghuan Road, Shanghai, 201306, China
**School of Environmental Science and Engineering, Shanghai Jiao Tong University,
800 Dongchuan Road, Shanghai, 200240, China
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Table S1. The specific surface areas of different commercial catalysts

Entry	Catalyst	Specific surface area (m^2/g)	References
1	Raney Cu	10.5	Rong et al. [1]
2	Cu	0.1	Iwamoto et al. [2]
3	CuO	0.7	Iwamoto et al. [2]
4	Cu_2O	0.8	Iwamoto et al. [2]
5	Raney Fe	25.7	Rong et al. [1]
6	Raney Co	13.2	Rong et al. [1]
7	Raney Ni	55.9	Rong et al. [1]

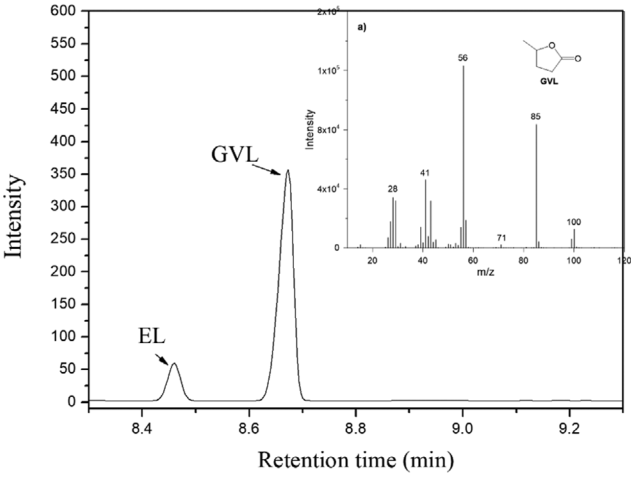

Fig. S1. GC spectra of products and GC/MS spectra of GVL.

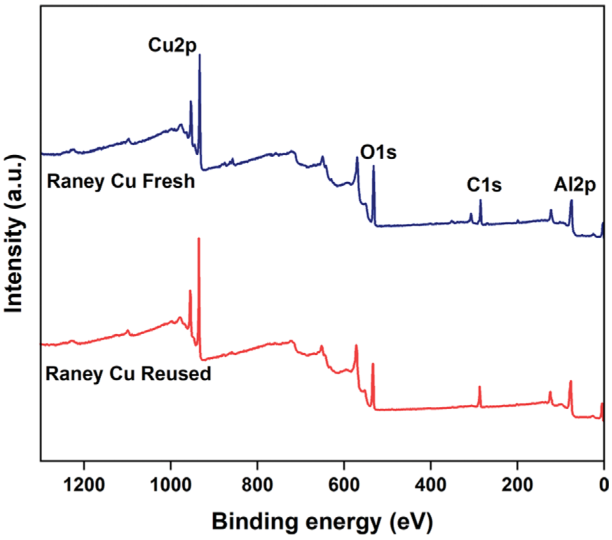

Fig. S2. XPS spectra of fresh Raney Cu and reused Raney Cu.

Table S2. Proportion of surface elements of fresh and reused Raney Cu

Samples	Cu (%)	Al (%)	O (%)
Raney Cu Fresh	10.6	66.3	23.1
Raney Cu Reused	10.9	69.9	19.2

Table S3. XPS analysis of Cu

Samples	BE (eV)		Content (Cu^++Cu^0)	KE (eV)	
	Cu^{2+}	Cu^++Cu^0		Cu^+	Cu^0
Raney Cu Fresh	934.0	932.6	74.9%	916.9	918.7
Raney Cu Reused	933.8	932.7	80.9%	916.8	918.7

Table S4. XPS analysis of O

Samples	BE (eV)			$X(O_{surface}/O_{all})$
	$O_{lattice}$	$O_{surface}$	O_{Others}	
Raney Cu Fresh	530.3	532.0	-	81.1%
Raney Cu Reused	530.6	531.9	533.3	44.4%

Table S5. ICP analysis

Element	Concentration (ppm)
Cu	1.062

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