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Supported copper catalysts for highly efficient hydrogenation of biomass-derived levulinic acid and γ-valerolactone

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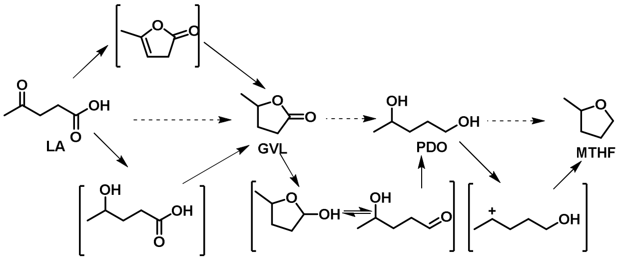
Levulinic acid (LA) is one of the most significant cellulose-derived compounds.γ-Valerolactone (GVL) and 1,4-Pentanediol (1,4-PDO) are considered to be the important chemical intermediates. Direct conversion of LA to GVL and GVL to 1,4-PDO were achieved via chemoselective hydrogenation by supported copper catalysts. We studied the transformation of LA to GVL in water and alcohol, and the pathway of the reaction was also studied. LA was converted to GVL catalyzed by Cu(30%)-WO_3(10%)/ZrO_2-CP-300 catalyst at 413 K in ethanol with 81% yield, while 84% GVL was obtained with Cu(30%)/ZrO_2-OG-300 catalyst in water at 393 K. Furthermore, 1,4-PDO was produced from GVL in excellent selectivities (>90%) using Cu-TiO_2/ZrO_2-CP-600 catalyst.

1. Introduction

Biomass is a carbon-neutral resource. [1] Being regarded as the only renewable resource which can be converted to conventional liquid, solid and gaseous fuels and other chemicals, biomass has a unique advantage in the process of substituting fossil resources. [2, 3] Biomass can be converted to bulk products, such as liquid fuels, or high value-added chemicals include succinic acid, sorbitol and glycerin through bio-refinery process. [4, 5] Biomass-based platform molecules are important bridges linking biomass raw materials and target products.[6] The development of simple, efficient and cost-effective processes for the preparation of platform molecules and their further conversion to fuels and chemicals are crucial to the improvement of the competitiveness of biomass resources relative to fossil resources.

In these lignocellulosic biomass-based chemicals, levulinic acid is an important platform molecule which can be transformed to a variety of derivatives, such as fuel additives, monomer of polymers and other high value-added chemicals. [7, 8] LA can be produced via the dehydration of hexose in acidic aqueous solution or the hydrolysis/alcoholysis of furfuryl alcohol derived from the hydrogenation of pentose. [9, 10] The reduction of levulinic acid could produce γ- valerolactone, which can be used as fuel additives of gasoline and diesel. For example, Horvath *et al.* showed that a mixture of 90% gasoline and 10% GVL has a similar octane value with a mixture of 90% gasoline and 10% ethanol, while GVL improves the burning characteristics of the fuel due to the low vapor pressure of GVL. [11] On the other hand, it is possible to use GVL directly as a liquid fuel due to its similar heating value and higher energy density relative to ethanol. Moreover, GVL has been widely used as precursors in perfumes production, food additives and green solvents. [12] The further conversion of GVL to other chemicals is also valuable (Scheme 1). 1,4-Pentanediol, prepared from GVL, isconsidered to be the monomer of biodegradable polymers, and also an important chemical intermediate.[13] Methyltetrahydrofuran (MTHF) prepared from LA or GVL by hydrogenation is considered as an important solvent and the component of P-series fuels.

Currently, there are many reports about the transformation from LA to GVL. Studies suggest that the hydrogenation of LA to GVL may operate through two main pathways. One is the hydrogenation of LA to γ-hydroxypentanoic acid followed by the intramolecular lactonization to GVL. The other involves the dehydration of LA by acid catalysis to angelica lactone followed by the hydrogenation of lactone to GVL. However, due to the formation of coke by the polymerization of angelica lactone promoted by the acidic catalysis, lower yields of GVL were observed through the second pathway.



Scheme 1. The pathway of the conversion of LA to GVL, PDO and MTHF.

Horváth *et al.* reported a multi-step process for the transformation of LA to GVL, PDO and MTHF by homogeneous

Ru-catalyst systems. [14] Li *et al.* reported that iridium hydride-bipyridine ligand catalysts had a high reactivity for the hydrogenation of LA to GVL. [15] The hydrogenation of LA to GVL using heterogeneous catalysts under gas phase or liquid phase conditions has been extensively studied, and GVL can also be obtained with the external source of hydrogen using supported Ru, Pd, Pt, Ni, Rh, Ir, Au, *.etc*. [16] Among them, supported Ru catalysts showed the highest catalytic activity. Lange *et al.* reported that the continuous hydrogenation of LA using platinum supported on TiO_2 and ZrO_2 resulted in a 95% yield of GVL. [17] In industry, GVL was produced by using heterogeneous metal catalysts and hydrogen for the hydrogenation of LA. For example, the reduction of LA catalyzed by platinum oxide at room temperature with 2~3 atm H_2 gives 87% yield of GVL.

Furthermore, formic acid, the by-product during the preparation of LA, can be decomposed to generate hydrogen in situ. It is more practical that the conversion of LA and formic acid to GVL is achieved without the addition of external hydrogen source. We reported the use of homogeneous and heterogeneous Ru catalysts to prepare GVL from LA and formic acid with 96% yield. [18, 19] Fan *et al.* reported efficient conversion of LA and formic acid to GVL by using Au/ZrO_2 catalyst.[20]

Using heterogeneous non-noble metal supported catalysts is important to reduce the cost of the catalysts. Rode *et al.* reported that LA and its esters could be converted to GVL with a 90~100% selectivity at 473K using Cu/Al_2O_3 in water and Cu/ZrO_2 in methanol. [21] Moreover, Cu-Cr hydrotalcite ($Cu^{+2}/Cr^{+3}=2$) gave 91% yield of GVL in water.[22] Fan *et al.* developed an inexpensive Cu/ZrO_2 catalyst to obtain 100% conversion and 100% selectivity of LA to GVL at 473 K.[23]

At present, 1, 4-PDO and MTHF could be obtained from LA or GVL catalyzed by homogeneous or heterogeneous catalyst in one-step. Leitner *et al.* reported the hydrogenation of LA to MTHF under 8 MPa H_2 at 473 Kusing $Ru(acac)_3/PBu_3/NH_4PF_6$ catalyst, while GVL and PDO were the main products without adding NH_4PF_6 (yield: 37% and 63%, respectively). And if the combination of the ligand of triphos and Ru $(acac)_3$ was used, the yield of 1, 4-PDO increased to 95%. The results reflected the important role of the ligand in homogeneous catalysis.[24, 25] Pravin P Upare used Cu/SiO_2 to catalyze the conversion of LA to MTHF in the gas phase (more than 90% selectivity).[26] Cao and co-workers reported that Cu/ZrO_2 catalyzed the chemoselective hydrogenation of GVL to MTHF or 1, 4-PDO in alcohols. [27]

As shown in previous studies, the transformation of LA to GVL using inexpensive supported metal catalysts (such as supported copper catalysts) in aqueous systems is also attractive. It is worth noted that it still needs to develop a milder reaction conditions in this process. Therefore, it is of great significance to develop efficient and inexpensive supported metal catalysts to achieve the selective conversion from LA to GVL under mild conditions and the subsequent conversion of GVL.

Herein, we prepared and screened a series of supported copper catalysts for the hydrogenation of LA to GVL and the conversion of GVL to 1, 4-PDO. The efficient hydrogenation of LA to GVL under mild conditions (393 K ~413 K) were achieved, and the selective conversion of GVL to 1, 4-PDO were also studied.

2. Experimental

The reagents used in catalyst preparation and reactions were commercially available.

2.1 Catalyst preparation.

WO_3-ZrO_2-CP: $ZrOCl_2$ solution was vigorously stirred at the different concentrations of ammonium metatungstate solution, and then 25% aqueous ammonia was added to adjust the pH to 9, the resulting precipitate was aged at room temperature for 24 h, filtered, washed with deionized water until no Cl^- was detected. Then the precipitate was dried at 383 K for 12 h, and calcined at a certain temperature for 3 h.

Cu/WO_3-ZrO_2-CP: Aqueous solution of copper nitrate, zirconium nitrate and ammonium tungstate were vigorous stirred at 353 K and 0.1 M sodium carbonate solution was added to adjust the pH to 7. The resulting precipitate was aged at room temperature for 24 h, filtered and washed with deionized water. Then the precipitate was dried at 383 K for 12 h, and calcined at a certain temperature for 3 h. The oxides were reduced at 553 K for 3 h with the heating rate 2 ^oC/min and the gas composition was H_2:N_2 (10:90), 100 mL/min.

Cu/ZrO_2-OG: The ethanol solution of copper nitrate, zirconium nitrate and ammonium tungstate were mixed under vigorous stirring, and a 20% excess of alcohol solution of oxalic acid was added rapidly. The mixture were stirred at room temperature for 4 h, filtered, and washed with deionized water. The precipitate was dried at 383 K for 12 h, and calcined at a certain temperature for 3 h. The oxides were reduced same as Cu/WO_3-ZrO_2-CP catalyst.

Cu-TiO_2/ZrO_2-CP: Aqueous solution of copper nitrate, zirconium nitrate and the powder of titanium oxide were vigorous stirred at 353 K and 0.1 M sodium carbonate solution was added to adjust the pH to 7. The resulting precipitate was aged at room temperature for 24 h, filtered, and washed with deionized water. Then the precipitate was dried at 383 K for 12 h, and calcined at a certain temperature for 3 h. The oxides were reduced same as Cu/WO_3-ZrO_2-CP catalyst.

2.2 Catalyst characterization.

The catalyst was characterized by X-ray power diffraction (XRD), transmission electron spectroscopy (TEM), Brunauer-Emmett-Teller (BET), and inductively coupled plasma atomic emission spectroscopy(ICP-AES). The detailed methods were presented in supplementary information.

2.3 Typical experiment and product analysis

A mixture of LA and the pre-reduced supported Cu catalysts, water or ethanol (5 mL) were charged into a 25-mL Hastelloy-C high pressure reactor (Anhui Kemi Machinery Technology Co. Ltd) and stirred at a rate of 600 rpm under 5 MPa H_2 atmosphere for given reaction time. The products were analyzed on a Shimadzu GC-2014 gas chromatograph equipped with DM-WAX (30m×0.25mm) column. The products were identified by GC-MS (Thermo Trace GC Ultra with a Polaris Q ion trap mass spectrometer equipped with a TR-5MS capillary column).

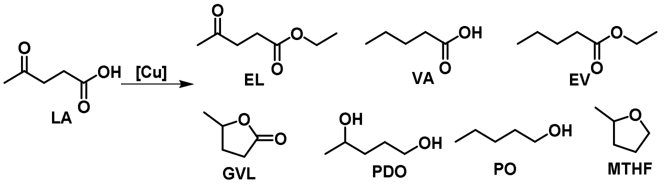
Table 1. Hydrogenolysis of LA into GVL with various supported copper-catalysts in ethanol. [a]

Entry	Catalyst	Conv./%	Yield /%						Total/ %
			GVL	MTHF	PO	PDO	EL	EV+VA	
1	Cu/HZSM-5	100	3	0	0	0	67	0	70
2	Cu/ZSM-5	100	3	0	0	0	58	0	61
3	Cu/SiO$_2$	100	6	0	0	0	74	0	80
4	Cu/ZrO$_2$	100	4	0	0	0	71	0	75
5	Cu/Ta$_2$O$_5$	100	9	0	0	0	70	0	79
6	Cu/γ-Al$_2$O$_3$	100	93	0	0	1	5	0	99
7	Cu/SBA-15	100	20	0	0	0	74	0	94
8	Cu/C	100	22	0	1	0	73	1	97
9	WO$_3$/ZrO$_2$-CP-300	100	2	0	0	0	80	0	82
10	Cu/C+WO$_3$/ZrO$_2$-CP-300	100	18	0	0	1	80	0	99
11	Cu-WO$_3$/ZrO$_2$-CP-300	100	94	0	0	2	0	0	96
12	Cu-WO$_3$/ZrO$_2$-CP-600	100	80	0	0	0	17	0	97
13	Cu/ZrO$_2$-OG-300	100	63	9	0	22	1	0	95
14	Cu/ZrO$_2$-OG-600	100	75	12	0	5	0	1	93
15	Cu-TiO$_2$/ZrO$_2$-CP-300	100	78	1	0	17	0	2	98
16	Cu-TiO$_2$/ZrO$_2$-CP-600	100	40	0	0	6	24	20	90
17[b]	Cu-WO$_3$/ZrO$_2$-CP-300	100	87	0	0	1	10	0	98
18[c]	Cu-WO$_3$/ZrO$_2$-CP-300	100	76	0	0	0	22	0	98

[a] LA 0.25 g, catalyst 0.1 g, 473 K, 6 h, 5 MPa H$_2$. Solvent: ethanol 5 mL. GC Yield. [b] LA 0.5 g. [c] 3 MPa H$_2$. Catalyst (Cu loading: 30 wt%, WO$_3$: 10 wt%, TiO$_2$: 60 wt%, Cu-WO$_3$/ZrO$_2$-CP-300) was prepared by co-precipitation method and the oxide precursors were calcined in air at 573 K, Cu/ZrO$_2$-OG-300 was prepared by oxalate-gel coprecipitation method followed by calcination in air at 573 K.

3. Results and Discussion

3.1 LA to GVL in ethanol



Scheme 2. Hydrogenolysis of LA into GVL with various supported copper-catalysts in ethanol.

First we investigated the effects of the support on the conversion of LA to GVL by using different supported copper catalysts with ethanol as solvent (Scheme 2, Table 1).

At 473 K different supported copper catalysts were screened. The main product was ethyl levulinate (EL, 60~70% yield) by using several common supports such as HZSM-5, ZSM-5, Ta$_2$O$_5$, ZrO$_2$ and SiO$_2$ (Table 1, entries 1-5) and no hydrogenation was observed. The yield of GVL increased slightly (~20%) by using mesoporous silica SBA-15 and activated carbon as supports (Table 1, entries 7-8), but the main product was also EL (~70%). γ--Al$_2$O$_3$ improved the yield of GVL to 93%, which is in consistent with the reported results (Table 1, entries 6). [21]

Subsequently, a series of composite oxide solid acid supported copper catalysts were prepared (Table 1, entries 11-16), and we found that the types of solid acid supports, the preparation methods of the catalysts (e.g. the sol-gel method (OG) and co-precipitation method (CP)) and the calcination temperature of oxide precursor (such as 573 K or 873 K) significantly influenced the conversion of LA to GVL. In particular, Cu (30%)-WO$_3$ (10%)/ZrO$_2$-CP-300 obtained a 94% yield of GVL under 5 MPa H$_2$ (Table 1, entry 11).

The increase of calcination temperature of Cu (30%)-WO$_3$ (10%) /ZrO$_2$-CP led to the decrease of GVL yield (Table 1, entries 11-12). With TiO$_2$ (60%)/ZrO$_2$-CP as the support, the by-products such as PDO and EV increased significantly, while GVL decreased accordingly (Table 1, entries 15-16). Similarly, the yield of GVL significantly decreased and the yield of MTHF and PDO increased by using Cu(30%)/ZrO$_2$-OG catalysts compared to Cu(30%)-WO$_3$(10%) /ZrO$_2$-CP (Table1, entries 13-14). The higher activity of the catalysts presumably results in the over-hydrogenation of GVL. In order to verify the above presumption on Cu (30%)/ZrO$_2$-OG-300 catalyst, the reaction temperature was reduced to 413 K and the yield of GVL increased to 88%, while the over-hydrogenation products were not detected. This result may support partially our explanation. We studied the BET analysis of several catalysts and found that the activity of catalyst was inversely proportional to the surface area of the catalyst by BET (Table 1, Table S8).[28] We found that the BET surface area of Cu-WO$_3$/ZrO$_2$-CP-300 catalyst was the smallest, but the activity was the highest in the five different tested catalysts (Table 1. entry 11, Table S8. entry 1). On the contrary, the Cu/ZSM-5 catalyst had a relatively high specific surface area, but the activity of the catalyst was poor (Table 1, entry 2 and Table S8, entry 5).

Comparied the experimental results, we found that the addition of W in the catalyst gave the higher yield and selectivity of GVL. This may be due to the interaction between Cu and W. The BET surface area of the catalyst decreased after the addition of W and the decreased BET surface area may be beneficial to the product selectivity as the product may be quickly released out of the catalyst surface. At this time, GVL stays relatively longer on the catalyst surface of which BET surface area is higher, leading to further hydrogenation of GVL on the catalyst surface and giving the main byproduct MTHF and PDO. Through the analysis of the pore volume and pore diameter, we found that the selectivity of GVL decreased and over-hydrogenation products were obtained under larger pore volume and pore diameter (Table S8).

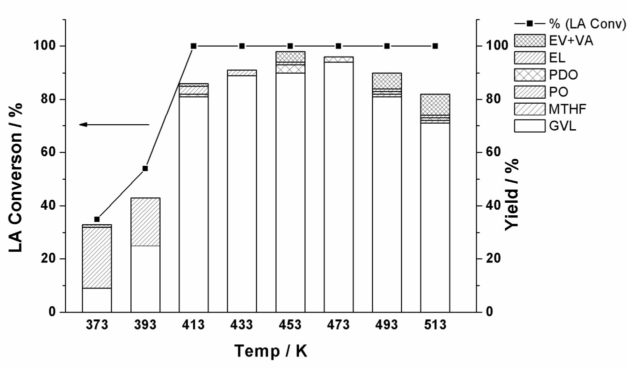


Figure 1. The effect of reaction temperature on the conversion of LA in ethanol. Reaction conditions: LA 0.25 g, Cu (30%)-WO_3 (10%)/ ZrO_2-CP-300 catalyst 0.1 g, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL. GC Yield.

Control experiment showed that EL was the only product with the solid acid support WO_3/ZrO_2-CP-300 as catalyst (Table 1, Entry 9). The mixture of Cu/C with the solid acid support WO_3/ZrO_2-CP-300 (Table1, Entry10) also gave EL as the main product, similar to Cu/C. Through the comparison of the results in ethanol, we found that the addition of W in the catalyst gave the higher yield and selectivity of GVL. This may be due to the interaction between Cu and W. The yield of GVL was very low (only about 2-4%) by using Cu/ZrO_2 and WO_3/ZrO_2-CP-300 catalyst (Table 1, entry 4, 9). It is showed that using one of Cu or W as the sole catalyst could not give a good result. The yield of GVL can reach 18% (Table 1 entry 10) by using Cu/C+WO_3/ZrO_2-CP-300 catalyst. This showed that the physical mixture Cu and W catalyst also have a certain effect. We further used Cu (30%) -WO_3 (10%) /ZrO_2-CP-300 as the catalyst, and the yield of GVL was greatly increased to 94% (Table 1, entry 11). The interaction between W and Cu was enhanced in our prepared catalyst. Experiments with different W loadings of the catalyst were also carried out (Table S6). Through the experiments, we obtained lower yield of GVL and the main by-product was EL at lower W loadings (Table S6, entry 1). The yield of GVL increased with the increase of W loading to 10%(Table S6, entry 2). With further increasing the W loading to 20%, the yield of GVL was not significantly increased (Table S6, entry 3). We found that the yield of GVL decreased slightly when we doubled the concentration of the substrate or reduced the initial hydrogen pressure to 3 MPa. The results showed that the amount of catalyst and hydrogen pressure also partly influenced on the conversion of LA (Table1, entries 17-18).

We studied the effect of reaction temperature (373 K-513 K, Figure 1) on the hydrogenation of LA by using the Cu (30%)-WO_3 (10%)/ZrO_2-CP-300 catalyst. The conversion of LA was 35% at 373 K. It was disappointing that only slight increase of the conversion was observed, even if the reaction time was extended to 24 h. 54% LA conversion was achieved and the main products were GVL and EL at 393 K. LA was completely converted and GVL was obtained with 81% yield at 413 K. The yield of GVL increased at higher reaction temperature. The maximum GVL yield of 94% was obtained at 473 K. With further increase of the reaction temperature, the yield of GVL decreased gradually and the by-products EV and VA were formed, which showed that GVL was over-hydrogenated at higher reaction temperature.

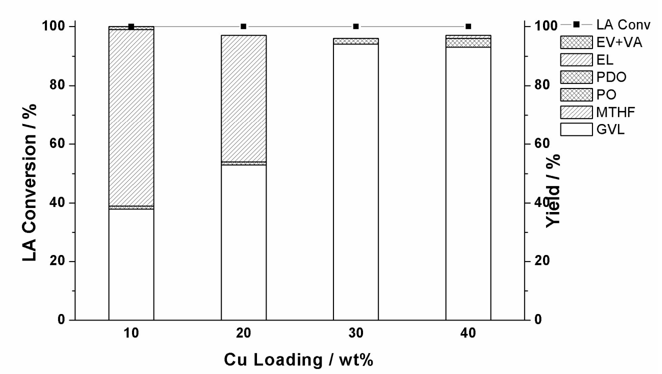


Figure 2. The effect of Cu loadings on the hydrogen conversion of LA. Reaction conditions: LA 0.25 g, Cu-WO_3(10%)/ZrO_2-CP-300 0.1 g, 473 K, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL. GC Yield.

We prepared a series of Cu-WO_3(10%)/ZrO_2-CP-300 catalyst with various Cu loadings (10-40 wt%, Figure 2.) and investigated the effects of copper loadings on the hydrogenation of LA. In each experiment, LA was completely transformed and the products varied considerably for the different loadings. EL was the main product when the copper loading was 10 wt%. As the copper loadings increased, the yield of GVL increased gradually. The highest yield of GVL was 94% when 30 wt% copper was loaded, while a higher copper loading of 40 wt% did not give higher GVL yield. We have also observed a similar trend of product distribution with different Cu loadings under 413 K (Figure S7). With the increased of Cu loadings from 10% to 30%, the yield of GVL increased and the yield of EL decreased.

3.2 LA to GVL in water

It is known that LA is produced from the biomass in aqueous processes. In order to link the preparation process of LA and avoid the extensive use of organic solvents, it is significant to study the conversion of LA to GVL in aqueous system by the supported copper catalysts. The results were shown in Table 2.

A series of experiments using supported Cu catalysts were performed at 413 K with an initial hydrogen pressure of 5 MPa

Table 2. Hydrogenolysis of LA into GVL with various supported copper-catalysts in water.[a]

Entry	Catalyst	Temp./K	Conv./%	Selectivity/%		
				GVL	MTHF	PDO
1	Cu/C	413	2	0	0	0
2	Cu/ZrO_2	413	3	0	0	0
3	Cu/SiO_2	413	4	0	0	0
4	Cu/TiO_2	413	2	1	0	0
5	$Cu/\gamma\text{-}Al_2O_3$	413	5	1	0	0
6	Cu/ZSM-5	413	3	0	0	0
7	Cu/HZSM-5	413	6	0	0	0
8	Cu/SBA-15	413	5	2	0	1
9	$Cu/SBA\text{-}15+SBA\text{-}SO_3H$	413	6	0	0	0
10	$Cu\text{-}WO_3/ZrO_2$-CP-300	413	6	95	0	0
11	$Cu\text{-}WO_3/ZrO_2$-CP-600	413	2	91	0	0
12	$Cu\text{-}TiO_2/WO_3$-CP-300	413	4	92	0	0
13	$Cu\text{-}TiO_2/WO_3$-CP-600	413	3	93	0	0
14	Cu/ZrO_2-OG-300	413	100	88	0	0
15	Cu/ZrO_2-OG-600	413	36	89	0	0
16	$Cu\text{-}WO_3/ZrO_2$-CP-300	473	100	99	0	0
17	$Cu\text{-}WO_3/ZrO_2$-CP-600	473	100	66	0	0
18	Cu/ZrO_2-OG-600	513	100	92	1	0
19[b]	Cu/ZrO_2-OG-300	393	100	84	1	0
20[c]	Cu/ZrO_2-OG-300	413	100	95	0	0
21[d]	Cu/ZrO_2-OG-300	473	3	-	1	2
22[d]	Cu/ZrO_2-OG-600	473	2	-	1	1

[a] LA 0.25 g, catalyst 0.1 g, reaction temperature 413 K, 6 h, 5 MPa H_2. Solvent: water 5 mL. GC Yield. [b] 24 h. [c] 12 h. [d] The substrate was GVL. Catalyst (Cu loading: 30%, WO_3: 10wt%, TiO_2:60wt%, $Cu\text{-}WO_3/ZrO_2$-CP-300) was prepared by co-precipitation method and the oxide precursors were calcined in air at 573 K, Cu/ZrO_2-OG-300 was prepared by oxalate-gel coprecipitation followed by calcination in air at 573 K.

for 6 h. The results indicated that the commonly used supported copper catalysts, such as Cu/C, oxide supported copper catalyst Cu/ZrO_2, Cu/SiO_2, $Cu/\gamma\text{-}Al_2O_3$ and Cu/TiO_2, zeolite supported copper catalysts Cu/ZSM-5 and Cu/HZSM-5, mesoporous silicon supported catalysts Cu/SBA-15 and the combination of Cu/SBA-15 and solid acid $SBA\text{-}SO_3H$, showed poor catalytic activity under reaction conditions (Table 2, entries 1-9). Simultaneously, the conversion of LA did not exceed 10%. Four kinds of solid acids supported copper catalysts (Cu(30%)-WO_3(10%)/ZrO_2-CP-300, Cu(30%)-WO_3(10%)/ZrO_2-CP-600, Cu(30%)-TiO_2(60%)/WO_3-CP-300, Cu(30%)-TiO_2(60%)/WO_3-CP-600) with high catalytic activity in ethanol were tried. Unfortunately, although the selectivity of GVL was very high, the conversion of LA was still low (Table 2, entries 10-13). Compared the reaction in water and ethanol (Figure 1 and Table 2), at 413 K, the efficiency was higher in ethanol than that in water. The XRD diffraction peaks of the catalyst collected after reaction in water were more acute than that in ethanol(Figure S8). It showed that the catalyst is easy to reunite and the activity of catalyst reduced in water than that in ethanol. We found that the active component of the catalyst in water was more seriously lost than that in ethanol by analysis of ICP-AES (Table S5 in supporting information), which could also explain the reason that the activity of catalyst in water was not as good as that in ethanol. Due to the high catalytic activity of Cu(30%)/ZrO_2-OG in ethanol, the over-hydrogenation products of MTHF and PDO were observed to form. Surprisingly, the over-hydrogenation was inhibited in aqueous system and Cu(30%)/ZrO_2-OG showed high catalytic activity at 413 K (Table 2, entries 14-15). Cu(30%)/ZrO_2-OG-300 achieved 88% GVL yield. Extending the reaction time to 12 h, 95% yield of GVL was obtained (Table 2, entry 20). Compared to Cu(30%)/ZrO_2-OG-300, Cu(30%)-/ZrO_2-OG-600 showed lower catalytic activity (Table 2, entry 15).

Increasing the reaction temperature to 473 K, Cu(30%)-WO_3(10%)/ZrO_2-CP also showed better catalytic activity (Table 2, entries 16-17). Cu(30%)-WO_3(10%)/ZrO_2-CP-300 gave a 99% yield of GVL, while Cu(30%)-WO_3(10%)/ZrO_2-CP-600 achieved 66% GVL yield. Further increasing the temperature to 513 K, Cu (30%)/ZrO_2-OG-600 also received 92% GVL yield (Table 2, entry 18).

When decreasing the reaction temperature to 393 K and extending the reaction time to the 24 h, a GVL yield of 84% was obtained by using Cu(30%)/ZrO_2-OG-300 as catalyst (Table 2, entry 19). In addition, using GVL as substrate and Cu (30%)/ZrO_2-OG as catalyst, it was found that GVL was hardly transformed under aqueous conditions (Table 2, entries 21-22). This result showed that the product GVL is stable under the reaction condition.

Chosen Cu(30%)/ZrO_2-OG-300 as the catalyst, we investigated the effects of reaction temperature on hydrogenation of LA in aqueous system (373 K-513 K, Figure 3). Only a small amount of LA converted at 373 K, resulting in a low yield of GVL. When the temperature was above 413 K, LA was totally converted and the selectivity of GVL was about 90% (413 K-473 K). Further increasing the reaction temperature (493 K-513 K), the yield of GVL decreased dramatically. Only trace amount of excessive hydrogenation products such as MTHF and PDO was found.

The reusability of Cu (30%)/ZrO_2-OG-300 were studied (Figure S6). The Cu (30%)/ZrO_2-OG-300 used once at 413 K for 6 h was employed under the optimized reaction conditions as Run 1. It can be seen that the yield of GVL decreased slightly after in 5 runs. The results may be explained by the leaching study of Cu (Table S1 in supporting information) and showed good stability of the catalyst in water.

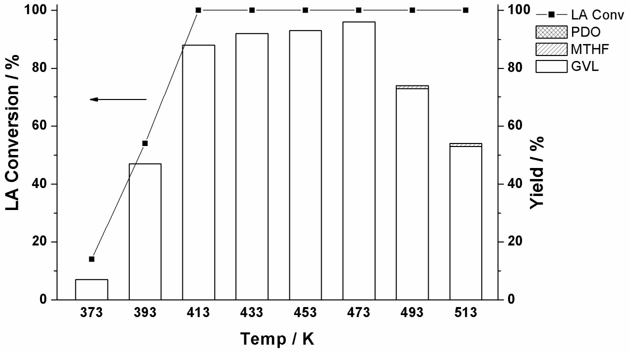
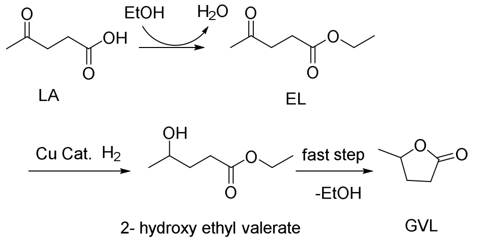


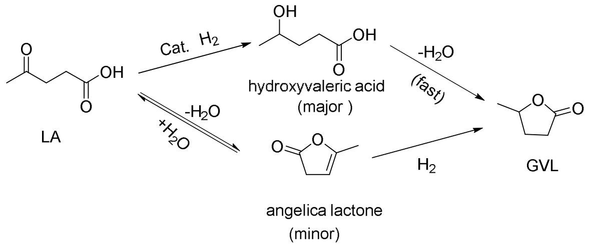
Figure 3. The effect of reaction temperature on the hydrogen conversion of LA in water. Reaction conditions: LA 0.25 g, Cu (30%)/ZrO_2-OG-300 0.1 g, 6 h, 5 MPa H_2. Solvent: water 5 mL. GC Yield.

At present, the pathway of LA to GVL in water and alcohol solution is still controversial. We found that the conversion of LA to GVL in ethanol obtained the EL as the major product with 5 MPa N_2(Table S7, entry 2).[29] Direct reaction of EL can obtain almost equivalent GVL. The EL converted to 2-hydroxy ethyl valerate through the carbonyl hydrogenation and the GVL was obtained by rapid lactonization of the unstable 2-hydroxy ethyl valerate. The 2- hydroxy ethyl valerate was too unstable to be detected. Therefore, the possible pathway of LA to GVL in ethanol may conduct as follows:



Scheme 3. The possible pathway of LA to GVL in ethanol.

We detected the reaction liquid (water solvent, H_2, 20 min) by the gas phase chromatograph and found that the major product was GVL and accompanied a small amount of angelica lactone. We all know that the conversion of LA to angelica lactone is a reversible reaction in the water, and the angelica lactone is more inclined to LA in the water. Then we found that the reaction of LA was not converted in 5 MPa N_2(Table S7, entry 3), and no angelica lactone was detected. It can be explained that the main intermediate of LA to GVL in water may be not angelica lactone. Under our experimental conditions, the carbonyl is easily hydrogenated to alcohol by using Cu based catalyst. The hydroxyvalerate, which is further hydrogenated to GVL, is not stable and difficult to be detected in the reaction liquid. The possible pathway of LA to GVL in water may be as follows:



Scheme 4. The possible pathway of LA to GVL in water

Table 3. Conversion of carbohydrates [a] and subsequent reduction of LA with formic acid (FA) by Cu (30%)/ZrO_2-OG-300.[b]

Entry	Carbohydrate	Yield		
		LA[mol]	FA[mol]	GVL[mol] (Sugar 100%)[c]
1	Glucose	52	56	45
2	Fructose	53	58	46
3	Sucrose	60	63	53
4	Cellobiose	57	60	50
5	Starch	51	55	45
6	Cellulose	30	36	26

[a] 2 g of Carbohydrate, 20 mL water, 1 g H_2SO_4(98%), 443 K, 1 h; [b] biomass-derived LA and FA (5 mL), Cu(30%)/ZrO_2-OG-300 0.1 g, 6 h, 5 MPa H_2. GC Yield; [c] The yields were based on the conversion of sugar.

In order to link up with the preparation process of LA, we used the hydrolysis solution of LA as the substrate for the reaction. The selected sugars included glucose, fructose, sucrose, cellobiose, starch and cellulose. Sulfuric acid was used as an acid catalyst for the hydrolysis of sugars in aqueous system at 443 K for 1 h and the hydrolysate containing LA and HCOOH was obtained (Table 3). Cu(30%)/ZrO_2-OG-300 was used as the catalyst for the hydrogenation of the hydrolysate.

Table 4 Hydrogenolysis of GVL into 1, 4-PDO or MTHF with various supported Cu-catalysts in ethanol. [a]

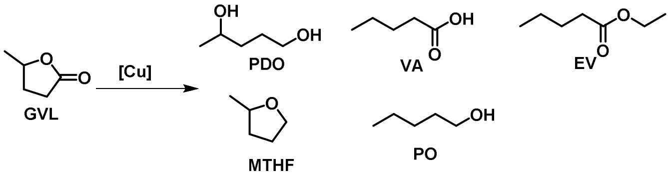
Entry	Cat.	Conv./ %	Selectivity/ %			
			MTHF	PO	PDO	EV+VA
1	Cu/TiO_2	45	12	1	84	2
2	Cu/CeO_2	41	0	0	11	1
3	Cu/ZrO_2	4	0	0	34	9
4	Cu/SBA-15	42	0	0	2	1
5	Cu/HZSM-5	51	0	2	0	4
6	Cu/γ-Al_2O_3	9	89	0	0	3
7	Cu/SiO_2	58	0	0	0	0
8	Cu/Ta_2O_5	17	1	0	1	1
9	Cu/β-zeolite	16	55	0	5	1
10	Cu/α-Al_2O_3	14	0	0	0	46
11	Cu/C	4	8	0	0	0
12	WO_3/ZrO_2-CP-300	5	0	0	0	0
13	Cu/C+WO_3/ZrO_2-CP-300	3	16	0	8	17
14	Cu-WO_3/ZrO_2-CP-300	9	5	0	56	2
15	Cu-WO_3/ZrO_2-CP-600	21	1	0	94	3
16	Cu-TiO_2/ZrO_2-CP-300	45	15	0	82	1
17	Cu-TiO_2/ZrO_2-CP-600	27	3	0	96	1
18[b]	Cu-WO_3/ZrO_2-CP-300	21	11	0	9	53

[a] GVL 0.25 g, catalyst 0.1 g, Cu Loadings (30 wt%), 473 K, 6 h, 5 MPa H_2. Solvent: ethanol 5 mL; [b] 513 K.

Direct hydrogenation of untreated hydrolysate did not achieve a good yield of GVL (< 5%). We presumed that the introduction of sulfuric acid improved the acidity of hydrolysate and reduced the activity of copper catalyst in hydrogenation process. In order to verify this assumption, we firstly tested the pH value of the mixture of LA and HCOOH (1:1 molar, 5 wt %, pH=1.91). The pH of the hydrolysate from fructose, sucrose, glucose and cellobiose were 1.28, 1.30, 1.33 and 1.40, respectively. It was obvious that the acidity of hydrolysate was higher than that of the mixture of LA and HCOOH. Furthermore, we added sulfuric acid in the mixed solution of LA and HCOOH (4 wt%) to adjust the pH to 1.30, and GVL was not detected after hydrogenation. The results suggested that the introduction of sulfuric acid had a negative effect on the catalytic activity of copper catalyst. In order to solve the above problems, we used $NaHCO_3$ to neutralize sulfuric acid in the hydrolysate until pH=3. The neutral hydrolysate was hydrogenated with Cu (30%)/ZrO_2-OG-300 and found that GVL was obtained with a yield of 88% in terms of LA.

3.3 GVL to PDO

Based on the conversion of LA to GVL, we studied the supported copper catalyzed conversion of GVL to MTHF and PDO (Scheme 5, Table 4). Firstly we screened several common supports (e.g. TiO_2, CeO_2, ZrO_2, SBA-15 and HZSM-5) with the hydrogen pressure of 5 MPa at 473 K (Table 4, entries 1-5). The conversion of GVL was not high and TiO_2 showed a high selectivity to 1, 4-PDO (84%). After using the solid acid support HZSM-5, the conversion of GVL had increased. Some other supports, such as γ-Al_2O_3, SiO_2, Ta_2O_5, β-zeolite, α-Al_2O_3 and activated carbon were conducted. γ-Al2O3 showed a high selectivity to MTHF (89%), but GVL conversion was low (Table 4, entries 6-11). It was also found that GVL was not converted under the reaction conditions by using WO_3 (10%)/ZrO_2-CP-300 catalyst in the blank experiment (Table 4, entry 12). The physical mixture of Cu/C and WO_3 (10%)/ZrO_2-CP-300 showed a similar result with Cu/C (Table 4, entry 13).



Scheme 5. Supported copper catalysts catalysed conversion of GVL.

Then, we used two types of supported copper Cu-WO_3/ZrO_2 and Cu-TiO_2/ZrO_2 catalysts for the hydrogenation of GVL (Table 4, entries 14-17). Although the GVL conversion was not high, the catalysts gave high selectivity to PDO except Cu-WO_3/ZrO_2-CP-300. PDO selectivity of 94% and 96% were achieved by using Cu (30%)-TiO_2 (60%)/ZrO_2-CP-600 and Cu (30%)-WO_3 (10%)/ ZrO_2-CP-600, respectively. Increasing the temperature to 513 K with Cu-

WO_3/ZrO_2-CP-300 catalyst, the GVL conversion increased slightly and the main products were EV and VA.

4. Conclusion

In summary, we have demonstrated simple yet versatile supported copper catalysts for the hydrogenation of LA to GVL and the conversion of GVL to PDO. LA was catalyzed by Cu (30%)-WO_3 (10%)/ZrO_2-CP-300 at 413 K in ethanol and 81% yield of GVL was obtained. The maximum GVL yield of 94% was obtained at 473 K. Moreover, Cu (30%)/ ZrO_2-OG-300 catalysed the hydrogenation of LA to give 84% yield of GVL in water at 393 K. A higher yield of GVL obtained at a higher temperature (95% yield at 413 K). For Cu-catalyzed conversion of LA to GVL, these reaction conditions were the mildest reported by now. The reusability experiment of Cu (30%)/ZrO_2-OG-300 showed good stability of the catalyst in water and a direct hydrogenation of the hydrolysates containing LA and HCOOH from sugars achieved a good yield of GVL. Furthermore, it is feasible to convert GVL to PDO in excellent selectivity using the supported copper catalysts in ethanol. The findings in this work will inspire the development of efficient conversion of platform molecules into fuel additives and higher value-added chemicals with economic heterogeneous catalytic systems.

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Notes and references

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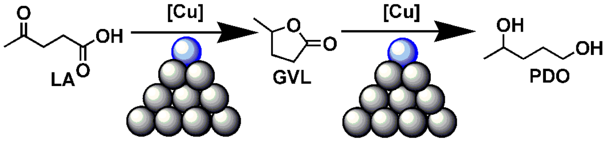

Direct conversion of cellulose-derived levulinic acid into γ-valerolactone and γ-valerolactone into 1,4-pentanediol were carried out by chemoselective hydrogenation catalyzed through supported copper-catalyst.