Green Chemistry

Accepted Manuscript

Journal Name

ARTICLE

Production of γ-valerolactone via Selective Catalytic Conversion of Hemicellulose in *Pubescens* without Addition of External Hydrogen †

mReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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γ-valerolactone (GVL) is an important chemical, whereas its synthesis directly from raw biomass is challenging because of their complex structure. A three-step method was developed for the selective conversion of hemicellulose in *pubescens* to GVL without addition of external hydrogen in the present work. We achieved a high yield of 20.0 wt % GVL based on the weight of *pubescens* with a high selectivity of 90.5% based on the amount of carbohydrates converted. Pt/C catalyst was prepared by impregnation method and characterized by XRD, TEM, XPS, Boehm titration and H_2 chemisorption. It was indicated that platinum existed in the form of metal Pt^0 and GVL yield was improved on Pt/C catalyst reduced with H_2. Our work also suggested that the platinum species interacted with the carboxylic and lactonic groups of activated carbon, and Pt (220) surface might exhibit high activity for the conversion of LA and FA to GVL (TON=1229.4). Especially, Pt/C catalyst was effective for the *in-situ* generation of hydrogen by high selective decomposition of FA, and for the conversion of an aqueous mixture of monomers and oligomers derived from *pubescens* to GVL without separation of $AlCl_3$, the catalyst for the dissolution of hemicellulose in the first step. The cross-enhancement of different kinds of reactions in the system was significant, which evidenced synergetic effects for the selective production of GVL from multiple reactions.

1. Introduction

With the depletion of fossil resource and concerns for environment, the conversion of biomass to chemicals and liquid fuels has attracted increasing interest worldwide. GVL is a safe, value-added chemical widely used as liquid fuel, solvent, and intermediate in the synthesis of fine chemicals.[1-4] GVL synthesis directly from renewable raw biomass resource therefore represents an attractive avenue of investigation.

The production of GVL from levulinic acid (LA) has been proposed as an efficient approach. Much attention has been paid to the production of GVL from purified LA and hydrogen, where high yields of GVL with high selectivity have been obtained.[5-11] Furthermore, hydrogen has also been used for the catalytic hydrogenation of unpurified LA derived from carbohydrates.[12-14] However, the hydrogen used in this process is usually obtained through the reforming of non-renewable natural gas or petroleum.[15] Minimizing the utilization of external H_2 in the production of GVL would therefore be highly desirable.

Formic acid (FA) has been identified as an attractive source of hydrogen due to its cost-effectiveness and safety.[15-18] The conversion of LA with FA as *in situ* hydrogen source to GVL has been reported.[15-25] Son *et al.*[16] developed one-pot transformation of fructose to GVL over supported metal catalyst, where external FA was added as acid catalyst as well as *in situ* hydrogen source. Heeres *et al.* [14]developed one-pot catalytic synthesis of GVL from C6-sugar sources using an acid catalyst in combination with a hydrogenation catalyst (Ru/C) with the addition of FA. In the conversion of biomass to value-added chemicals such as LA or HMF, a large amount of FA with a higher yield than that of LA is usually obtained as a by-product.[26] Therefore, the synthesis of GVL directly using FA formed from biomass conversion as hydrogen source shows promise as an ideal sustainable protocol.[24-25] Considerable research efforts have been made to convert FA and LA derived by mineral acid hydrolysis and dehydration of carbohydrates(i.e. sugars, starch and cellulose) for the production of GVL.[17, 23-24, 27-28]. Although a high yield of GVL was achieved from carbohydrates, there remains a large gap between the structure of these carbohydrates and the actual lignocellulosic biomass. Thus, the production of GVL directly from raw lignocellulosic biomass with high yield is a key challenge.

Galletti *et al.*[29] developed a catalytic system for the hydrogenation of water slurries from the giant reed with HCl treatment over Ru/C and niobium oxide or niobium phosphate catalyst by the addition of external hydrogen, and obtained a

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

yield of 16.6 wt% to GVL based on the weight of dry biomass. Yuan *et al.*[15] achieved a GVL yield of up to 18.5 wt% (based on the weight of dry biomass) using a "one-pot" copper catalytic conversion of giant reed to GVL by the aid of H_2SO_4. In the process, H_2SO_4 was used as both hydrolysis and dehydration catalyst to obtain LA and FA, so it also needs to be removed before hydrogenation reaction. Although the above research obtained an acceptable GVL yield from raw biomass, the selectivity to GVL needs improvement. The coexistence of products from the simultaneous conversion of hemicelluose, cellulose and lignin in biomass results in the difficult separation of GVL from the aqueous solution containing these products, which limits the further utilization of GVL. Therefore, another key challenge is to develop a novel process for the selective conversion of lignocellulosic biomass to GVL with high yield and selectivity.

Hemicellulose that accounts for 15%-35% of most kinds of biomass is a potential feedstock among the three main components in lignocellulosic biomass for the production of GVL.[30-31] However, the production of GVL from hemicellulose in biomass was rarely reported. Thus, the selective conversion of hemicellulose in raw biomass to GVL with high yield and selectivity would be highly desirable.

In previous work[32], a two-step process was developed for the selective dissolution and conversion of hemicellulose in *pubescens* to obtain an aqueous mixture containing furfural, LA and FA with high selectivity. In the first step, $AlCl_3$ promoted the selective dissolution of hemicellulose in *pubescens*. In the second step, the addition of THF and SiO_2, forming the $AlCl_3$-SiO_2-THF/H_2O system, promoted the conversion of oligomers and monomers derived from hemicellulose to chemicals (furfural, LA and FA) with high selectivity. These chemicals in the aqueous mixture can be further used for the production of GVL. Herein, we report the selective conversion of an aqueous mixture (monomers and oligomers) derived directly from hemicellulose in *pubescens* to GVL without addition of external hydrogen. It provides a clue to how to control a complex system for the selective formation of specific target product.

2. Experimental Section

2.1 materials

Pubescens sample (80 meshes, Anji county of Zhejiang Province in China) was washed three times with distilled water and dried at 110 °C in an oven overnight before use. The main components of dried *pubescens* were 46.5 wt.% cellulose, 17.9 wt.% hemicellulose and 25.4 wt.% lignin.[32]

Coconut shell activated carbon purchased from Jiangsu Nantong Tongsen Co. (20-40 meshes, S_{BET}=987 m^2g^{-1}) was treated with 4 mol/L NaOH and then 6 mol/L HCl at 110 °C for 5 h, respectively. The sample obtained was denoted as C. Noble metal precursor $H_2PtCl_6·6H_2O$ (Xiya Regent Co.), $PdCl_2$(Sino-Platinum Metals Co.), $RuCl_3·nH_2O$(Institute of Trace Element in China) and $RhCl_3·nH_2O$(Shanghai Regent Co.) were purchased commercially. Other non-noble metal precursor $Ni(NO_3)_2·6H_2O$, $Cu(NO_3)_2·3H_2O$, $CdCl_2·5H_2O$, $Zn(NO_3)_2·6H_2O$, $Fe(NO_3)_3·9H_2O$, $AgNO_3$, $Co(NO_3)_2·6H_2O$ and $Ce(NO_3)_3·6H_2O$ were obtained from Chengdu Kelong Chemical Regent Factory. Levulinic acid (LA, 99%, J&K SCIENTIFIC LTD), formic acid (FA, 97%, Chengdu Kelong Chemical Regent Factory) and γ-valerolactone (GVL, 99%, J&K SCIENTIFIC LTD) were purchased commercially and used without further purification.

2.2 Catalyst preparation

The catalysts were prepared by impregnation method. The processes used for preparation of Pt, Pd, Ru, Rh, Ni, Cu, Cd, Zn, Fe, Ag, Co or Ce supported on activated carbon were the same. Typically, activated carbon support (2 g) was impregnated in aqueous solution containing a desired amount of metal precursors. The slurry was ultrasonically dispersed for 1 h and then set for 24 h at room temperature. Excess H_2O was removed by heating in a water bath at 80 °C. The resultant solid was dried overnight at 80 °C, and then calcined in N_2 flow at 500 °C for 4 h. Prior to the reaction, the obtained catalyst was pre-reduced with H_2 at 450 °C for 2 h and noted as xM/C (x denotes the controlled M content). The method for preparation of Pt supported on SiO_2, TS-1, Al_2O_3 and SBA-15 was the same as the process described above.

2.3 Catalyst characterization

H_2 Chemisorption H_2 chemisorption analyses were performed by Pulse gas chromatography method. The samples were reduced *in situ* at 450 °C for 2 h with a H_2 flow rate of 25 mL/min. After reduction, the H_2 on the metal surface was removed with N_2 at 500 °C for 2 h. The samples were subsequently cooled to ambient temperature under the same N_2 stream. After pretreatments, consecutive 0.07 mL pluses of 5% H_2 were injected into the U-tube, containing the catalyst at ambient temperature, with N_2 as the carrier gas until the H_2 peak area was constant. The amount of chemisorption was calculated by summing up the portions of all pulses consumed. From the chemisorbed H atomic numbers, the exposed Pt atomic numbers were calculated by assuming a Pt/H ratio of 1.

X-Ray Diffraction (XRD) XRD measurements of the samples were performed on DANDONG FANGYUAN DX-1000 instrument using monochromatic Cu Kα radiation (λ=1.542 Å, 40 kV and 25 mA) with a scanning range (2θ) from 10° to 80°.

Transmission electron microscopy (TEM) The mean particles size and surface morphology of the samples were examined by TEM. The measurements were performed on an FEI Company Tecnai G2F20 instrument operated at 200 kV. The samples were ultrasonically dispersed in ethanol at room temperature for 1 h. The as-obtained solutions were deposited onto copper grids for TEM analysis.

Boehm titration The variation of surface groups on samples with different treatments was determined by Boehm titration.[33] The average deviation of titration was less than ±0.1 wt%.

X-ray photoelectron spectroscopy (XPS) XPS was performed using an AXIS Ultra DLD (KRATOS) spectrometer with Al-Kα X-ray radiation. The energy scale was internally calibrated by setting the C 1s peak at 284.6 eV.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) The actual Pt loading of the catalysts and the leaching of Pt in the filtrate liquid were analyzed by ICP-AES using Thermo Elemental IRIS Advantage ER/S spectrometer.

Gel permeation chromatography (GPC) The molecular weight distribution of liquid products was determined by GPC equipped with a Waters 515 pump, UL column (300×7.8 mm) and 2410 refractive index detector. The sample was dissolved in a 1% NaCl solution to a final concentration of 5 mg/mL before measurement. The injection volume was 15 µL, and 1% NaCl was used as an eluent at a flow rate of 0.6 mL/min. Dextranum was used as the standard for molecular weight calibration.

Electrospray ionisation-mass spectrometry (ESI-MS) The liquid products derived from the *pubescens* were also characterized by ESI-MS (Shimadzu).

2.4 Hydrogenation of LA with FA to GVL

Hydrogenation of LA using FA as hydrogen source to GVL was conducted in a 60 mL stainless steel sealed autoclave. In a typical run, 11.25 mmol LA, 11.25 mmol FA, 25 mL water and 0.25 g catalyst were loaded in the reactor (the amount of LA, FA and catalyst were chosen according to the literature [15]). The reactor was then sealed and the inner air was replaced by nitrogen. The initial pressure was added to 1.0 MPa with nitrogen. The reactor was heated from room temperature to the desired temperature and then kept for different time. After the reaction, the reactor was cooled down to room temperature naturally. Gaseous products were collected in a pre-vacuumed gas-bag and analyzed using gas chromatography (GC) with a thermal conductivity detector (TCD). The content in autoclave, a mixture of water, liquid products and solid catalyst, was collected, and the reactor was washed three times with high purity water. The mixture collected was filtered, and the solid catalyst obtained was washed by ethanol and then dried at 80 ^{o}C in an oven for the next run. Liquid products were analyzed by High Performance Liquid Chromatography (HPLC). The yield of GVL was calculated using the molar amount of GVL divided by the initial molar amount of LA. The selectivity to GVL was defined as the molar amount of GVL based on the converted molar amount of LA.

2.5 Decomposition of FA in the absence of LA

Decomposition of FA in the absence of LA was conducted in a 60 mL stainless steel sealed autoclave. In a typical run, 11.25 mmol FA, 25 mL water and 0.25 g catalyst were loaded in the reactor. The procedure for treatment and analysis of the products was the same as the process described above.

2.6 The production of GVL with derivatives from *pubescens*

In previous work, [32] a two-step process was developed for the selective dissolution and conversion of hemicellulose in *pubescens* to monomers (furfural, LA and FA). For the conversion of *pubescens* to GVL, the filtrate liquid (FL) obtained from the second-step above was used to complete the hydrogenation reaction directly using FA contained as the hydrogen source. In a typical run, 25 mL FL was filtered before use, then placed in a 60 mL stainless steel sealed autoclave with 0.25 g Pt/C catalyst. The procedure for the treatment and analysis of the products in the hydrogenation reaction was the same as the process described above. Here, the yield of GVL was defined as the weight percentage based on the weight of reactant samples. The selectivity to GVL was defined as the weight percentage based on the weight of converted samples.

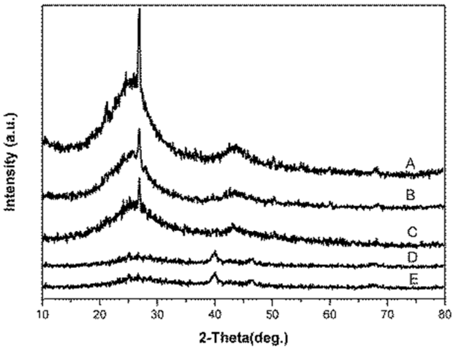


Figure 1 XRD patterns of samples with different treatment. (A: UR-C; B: R-C; C: UC-5Pt/C; D: UR-5Pt/C; E: 5Pt/C)

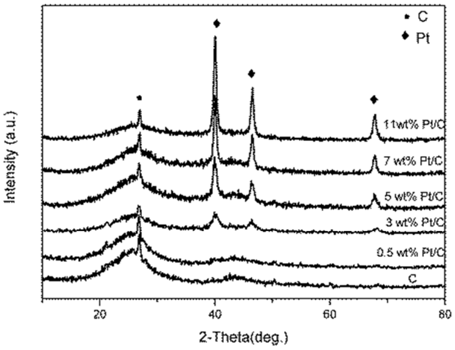


Figure 2 XRD patterns of carbon supports and catalysts with different Pt loading on activated carbon

2.7 Analysis of liquid products

Liquid products were analyzed by Dionex U-3000 High Performance Liquid Chromatography (HPLC) equipped with a dionex PG-3000 pump, an aminex HPX-87 column (Bio-Rad) and a shodex 101 Refractive Index Detector (RID). The temperature of the column oven and detector were 50 ^{o}C and 35 ^{o}C, and the mobile phase was 0.005 M H_2SO_4 solution at a flow rate of 0.6 mL/min. The content of liquid products was quantified by an external standard method. Each sample was tested three times to confirm the reproducibility of the reported results.

3. Results and Discussion

3.1 Catalyst characterization

XRD analysis

XRD patterns of the catalysts with different treatment were shown in Figure 1. Activated carbon before hydrogen reduction (noted as UR-C) presented diffraction peaks at 2θ=26.6^{o} and 44^{o} assigned to graphite.[34] No obvious changes in diffraction peaks were observed for activated carbon after

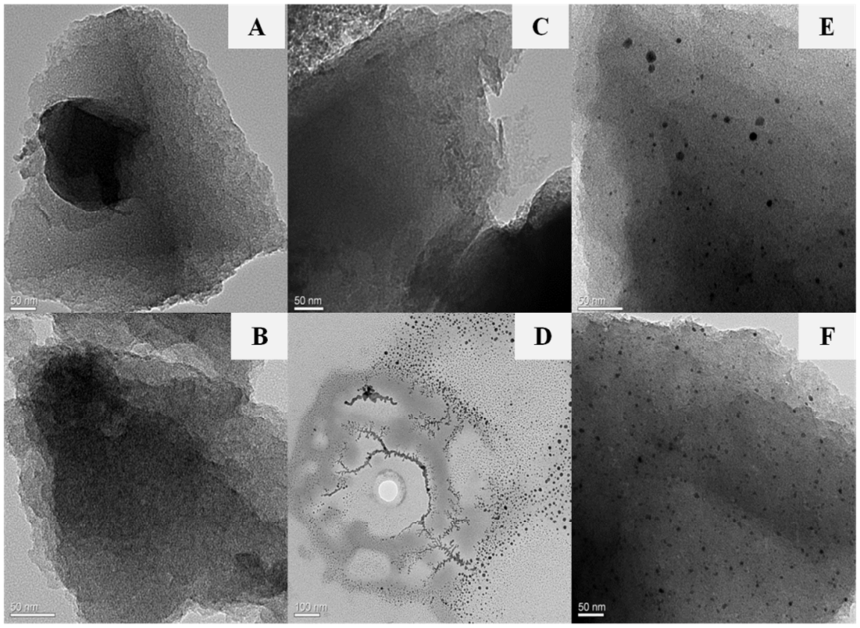


Figure 3 TEM micrographs and EDX spectra of samples with different treatment: A: UR-C; B: R-C; C and D: UC-5Pt/C; E: UR-5Pt/C; F: 5Pt/C.

being reduced with hydrogen (noted as R-C). Activated carbon impregnated with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (noted as UC-5Pt/C, the content of Pt was 5 wt%), presented the same diffraction peaks as UR-C and R-C. In addition, no diffraction peaks from platonic oxide or any related platonic substances were detected. For 5 wt% Pt loaded on activated carbon before reduction (noted as UR-5Pt/C), it exhibited three characteristic diffraction peaks at $2\theta=39.6^o$, 46.3^o and 67.4^o, corresponding to the (111), (200) and (220) lattices planes of face-centered cubic structure (fcc) of Pt.[35] This indicated that platinum existed in the form of metal Pt^0 after calcination, which might be caused by the reduction of carbon in the process. [36] Compared with UR-5Pt/C catalyst, no additional diffraction peaks were observed in 5Pt/C catalyst (The catalyst obtained from UR-5Pt/C was reduced with H_2).

XRD patterns of the samples with different Pt loading on activated carbon were shown in Figure 2. No obvious diffraction peaks of face-centered cubic crystalline Pt was observed with Pt loading of 0.5 wt%, likely due to small particle size of Pt with such a low loading. Pt loading increase from 3 wt% to 11 wt%, increased the three characteristic diffraction peaks corresponding to the face-centered cubic structure of Pt. The average crystalline size of Pt particles for different samples, as calculated by the Sherrer formula at $2\theta=39.6^o$, is provided in Table S1. Metal crystallite size increased with increased Pt loading from 0.5 to 11wt%. These results were in agreement with the findings of Aristizábal et al.[37]

TEM analysis

TEM was used in order to observe the morphology change of samples with different treatments (Figure 3). The morphology of activated carbon before and after hydrogen treatment was similar, which indicates that hydrogen treatment would not impact the structural integrity of carbon (Figure 3(A) and 3(B)). While for UC-5Pt/C, no metal particles were observed on carbon support (Figure 3(C)). However, some particles were observed in areas other than on the surface of carbon support (Figure 3(D)). EDX spectra of UC-5Pt/C confirmed the presence of chlorine, which suggests that Pt species may interact with Cl^- (Figure S1(A)). The individual metal particles were present on UR-5Pt/C with a size distribution between 14nm-17nm, which suggests that Pt particles were not well-distributed over the carbon support for UR-5Pt/C(Figure 3(E)). The results also suggested that Pt particles were present on the support after calcination. The TEM morphology of 5Pt/C is shown in Figure 3(F), which displays a mean Pt particles size concentrated around 9.1 nm comparable to that determined from XRD. Pt particles on carbon support were better distributed than UR-5Pt/C. It indicated that a well dispersion of Pt particles on carbon support was achieved by H_2 treatment. TEM micrographs of different Pt loading samples with different treatments showed that a better Pt dispersion was observed on Pt/C samples, even those with higher Pt loading (Figure S2). However, even with hydrogen treatment, some aggregated particles were observed when Pt loading was over 5 wt%.

Table 1 Results of Boehm titration of sample with different treatment

Samples	The amount of surface species (mmol/g)				
	Carboxyl	Lactonic	Phenolic	Carbonyl	Total
UR-C[a]	0.15	0.17	0.27	0.56	1.15
R-C[b]	0.05	0.09	0.04	0.57	0.75
UC-5Pt/C[c]	0.62	0.33	0.28	0.74	1.97
UR-5Pt/C[d]	0.18	0.15	0.08	0.64	1.05
5Pt/C[e]	0.01	0.02	0.05	0.56	0.64

[a] Carbon support was dried overnight at 80 °C. [b] Carbon support was reduced with H_2 at 450 ^oC for 2 h. [c] Carbon support was impregnated with aqueous liquid of $H_2PtCl_6 \cdot 6H_2O$ to obtain one catalyst. [d] The catalyst obtained from *c* was calcined with N_2 at 500 ^oC for 4 h. [e] The catalyst obtained from *d* was reduced with H_2 at 450 ^oC for 2 h.

Table 2 The relative concentration of different surface oxygen species on different samples after deconvolution

Samples	Binding Energy/eV and the corresponding composition/%			
	531.1	532.2	533.3	534.2
UR-C	2.4	8.5	37.1	52.1
R-C	2.4	4.5	36.1	55.6
UC-5Pt/C	2.6	5.3	40.1	52.6
UR-5Pt/C	10.1	0.8	33.9	55.2
5Pt/C	2.4	32.1	29.1	36.4

Table 3 The relative concentration of different surface carbon species on different samples after deconvolution

Samples	Binding Energy/eV and the corresponding composition/%			
	284.5	285.6	286.0	288.9
UR-C	66.1	11.2 (33.0)[a]	10.6 (31.3)	12.1 (35.7)
R-C	66.7	11.6 (34.8)	10.1 (30.3)	11.6 (34.8)
UC-5Pt/C	67.6	11.6 (35.0)	9.3 (28.1)	12.2 (36.9)
UR-5Pt/C	68.5	11.7 (36.9)	7.7 (24.3)	12.3 (38.8)
5Pt/C	66.8	10.6 (32.0)	15.9 (48.0)	6.6 (20.0)

[a] The values in parentheses were obtained by renormalization of the three species (phenol carbon, lactonic carbon, and carboxylic carbon.

While metal particle size increased with increased Pt loading, the treatment with hydrogen decreased the mean particle size. It was obvious that the increase of particle size was influenced more significantly by the increase of Pt loading. These results were in accord with the XRD data.

Consistent with what was reported by Coloma et al [38], a better dispersion of Pt particles on carbon support was achieved by H_2 reduction. Furthermore, adequate dispersion of Pt particles on carbon support is highly important for increasing catalyst activity.[39] The conversion of LA into GVL over different catalysts with different treatments were studied. The results indicated that GVL yield was improved on Pt/C catalyst reduced with H_2 (Table S2). Therefore, high dispersion of Pt particles on carbon support is one of the crucial factors to realize a high yield to GVL.

Boehm titration of the samples

Surface functional groups on carbon materials play a major role in the Pt-carbon interaction.[39] In order to study Pt-carbon interaction, we measured the change of surface functional groups on carbon for samples with different treatments via Boehm titration (Table 1). Compared with the UR-C catalyst, R-C catalyst possessed decreased amount of carboxyl, lactone, and phenolic groups. For the UC-5Pt/C catalyst, the amount of carboxyl, lactone and carbonyl groups greatly increased. This may be due to the adsorption of H_2PtCl_6 on the surface of activated carbon after impregnation, which increases the support's acidity. [40] Therefore, the titration method could not give accuracy data for UC-5Pt/C. For UR-5Pt/C catalyst, the amount of phenolic groups significantly decreased compared with UR-C catalyst. This is suggestive of the presence of platinum species in coordination with phenolic groups after calcination. Compared with UR-5Pt/C catalyst, 5Pt/C catalyst possessed decreased amount of carboxyl and lactonic groups (decreased sharply from 0.18 and 0.15 mmol/g to 0.01 and 0.02 mmol/g, respectively). In addition, 5Pt/C catalyst also possessed decreased amount of carboxyl and lactonic groups compared with R-C catalyst. This demonstrates that platinum species have a strong interaction with the surface carboxyl and lactonic groups by H_2 treatment. As reported by Vedrine et al., [41] the Pt-carbon support interaction enhances the catalytic properties. This result also suggests that the interaction of both the carboxyl and lactonic groups with platinum species may enhance the catalytic performance for the hydrogenation of LA to GVL.

XPS analysis

The change in the surface composition for samples with different treatments was investigated with XPS. The O1s peak and C1s peak of different samples are shown in Figure S3. For UR-C samples, the deconvolution of the O 1s species gave four peaks with binding energies of 531.1, 532.2, 533.3 and 534.2 eV, corresponding to carbonyl oxygen, phenol oxygen, lactonic oxygen and carboxylic acid oxygen, respectively.[39, 42-43] Deconvoluted peaks of C 1s species at 284.5, 285.6, 286.0 and 288.9 eV, respectively, corresponded to graphite carbon and the contaminant carbon, carbonyl carbon, phenol carbon and carboxylic or lactonic carbon.[44-47]

The relative concentration of different surface oxygen species and carbon species are shown in Table 2 and Table 3. For the O1s peak, the relative concentration of the oxygen group was lower in R-C samples compared with UR-C samples, which indicates that hydrogen treatment led to decomposition or reduction of oxygen-containing functional groups.[39] Impregnating Pt on activated carbon (UC-5Pt/C) decreased the amount of phenolic groups from 8.5% to 5.3%, which indicates the presence of interactions between Pt species and phenolic groups. Furthermore, there was a large decrease in phenolic groups from 8.5% in UR-C to 0.8% in UR-5Pt/C. This phenomenon implies that platinum species anchor on the phenolic site after impregnation and calcination. A comparison of UR-5Pt/C with 5Pt/C showed that the relative concentration of peaks at 533.3 eV and 534.5 eV decreased from 33.9% and 55.2% to 29.1% and 36.4%, respectively. Peaks at 533.3 eV and 534.2 eV also exhibited a dramatic decrease from R-C to 5Pt/C. The results of C1s peak listed in Table 3 presented a similar trend as the results of O1s peak. This implies that hydrogen treatment led to stronger platinum species interactions with carboxylic and lactonic groups. XPS results of Pt/C samples with different Pt loading with hydrogen treatment (Table S3 and Table S4) indicate stronger platinum-carbon species interactions with increased Pt loading. As reported by Yu *et al.*,[39] some oxygen-containing groups such as carboxylic groups are more effective for the anchorage of platinum particles, thereby improving the catalytic activity. In this work, high yields of GVL obtained over the 5Pt/C catalyst may be attributed to the interaction of platinum species with the carboxylic and lactonic groups of activated carbon. Furthermore, these results matched well with the results of Boehm titration.

3.2 Hydrogenation of LA with FA to GVL

The effect of different metals loaded on activated carbon on the conversion of LA to GVL is shown in Figure S5. These results suggested that Pt was highly active for the hydrogenation of LA to GVL under the conditions tested in the present work. We screened for the effect of support, such as SiO_2, TS-1 and SBA-15, on the activity, and found that activated carbon provided an excellent catalyst support (Figure S6). Within the catalysts tested in the present work, Pt/C was the best candidate for the conversion of LA to GVL. The Pt/C catalyst had high activity at 160 °C for the direct decomposition of FA to H_2 and CO_2. Furthermore, the robust Pt/C catalytic activity was likely due to the inhibition of CO formation at a higher temperature of 240 °C (Table S5). The hydrogenation of LA with addition of H_2 at 240 °C produced a higher yield of GVL in the presence of Pt/C catalyst compared with that in the absence of the catalyst (Table S6). This suggested that the Pt/C catalyst was effective for both the decomposition of FA to H_2, and then the *in situ* hydrogenation of LA to GVL.

Characterization of Pt loading on the conversion of LA to GVL with FA revealed that the catalytic performance was strongly dependent on the Pt content (Table 4). Increasing Pt loading from 0.5 wt% to 5 wt% increased LA conversion, GVL yield, and selectivity to GVL. The highest yield of GVL was achieved over 5 wt% Pt/C catalyst. When Pt loading was further increased to 11 wt%, LA conversion and the yield and selectivity to GVL decreased seriously. As listed in Table 4, the percentage of Pt surface atoms gradually decreased with increased Pt loading. 5 wt% Pt/C catalyst showed the highest TON of 758.8 compared to other catalysts with different Pt loading, which indicated that the reaction was structure sensitive. This result was in agreement with what previously reported in the literatures.[15, 37] A comparison of the metal crystallite size of the samples with different Pt loading indicated that a proper metal crystallite size may be more beneficial for the hydrogenation of LA to GVL (Table S1). The relative intensity of lattice planes in face-centered cubic structure of Pt for samples with different Pt loading was shown in Table S7. The relative intensity of the (220) lattice plane for 5 wt% Pt/C catalyst was stronger than that for all other catalysts. These results suggest that Pt (220) surface might exhibit high activity for the production of GVL.

Table 4 The effect of Pt loading on the conversion of LA to GVL at 260 °C for 2 h[a]

Catalyst	A_{Pt} (wt%)[b]	C_{FA} (%)	C_{LA} (%)	Y_{GVL} (%)	S_{GVL} (%)[c]	D_{Pt}[d]	TON[e]
0.5Pt/C	0.4	98.8	9.6	3.4	35.8	45.4	164.3
3.0Pt/C	2.9	99.0	42.6	30.9	72.6	35.9	251.9
5.0Pt/C	5.2	99.3	70.5	55.9	79.3	12.4	758.8
7.0Pt/C	7.5	99.2	30.1	19.3	63.9	11.2	201.2
11.0Pt/C	10.6	99.3	25.0	18.8	75.3	9.9	152.1

[a] Reaction conditions: LA, 11.25 mmol; FA, 11.25 mmol; H_2O, 25 mL; Catalyst, 0.25 g; N_2, 1MPa. [b] The actual Pt content measured by ICP-AES. [c] GVL selectivity based on LA conversion. [d] The percentage of the number of Pt surface atoms to total number of Pt atoms obtained by H_2 chemisorption analysis. [e] Turnover number (TON) is defined as mole of GVL formed per actual mole of active Pt site.

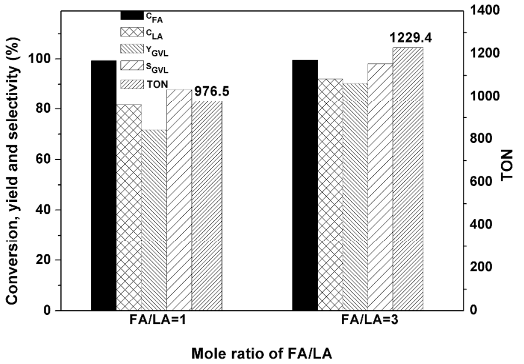


Figure 4 Effect of FA/LA molar ratio on the hydrogenation performance

GVL yield from the hydrogenation of LA to GVL with FA is dependent on reaction temperature (Figure S7 (a)). A higher yield of 71.7% GVL was obtained at 240 °C. However, the yield of GVL was only 6.3 % for the conversion of LA with 0.5 MPa H_2 (Table S6). We found that FA, which produces hydrogen *in situ* for the hydrogenation of LA, is more efficient than H_2, as a greater amount of H_2 is required to obtain a higher yield of GVL on Pt/C catalyst. The results were in accordance with Deng's work[24], which showed that CO_2 produced in the decomposition of FA may be one factor for the production of GVL with high yield. Furthermore, we also studied the effect of reaction time on the hydrogenation of LA to GVL with FA (Figure S7 (b)). The conversion of LA reached 81.6% after only 2 h reaction in this system, which indicated that Pt/C catalyst was highly active for the conversion of LA with FA. The conversion of LA decreased gradually from 2 h to 6 h, while the yield of GVL decreased from 71.7% to 42.3%. This decrease in the conversion of LA and the yield of GVL may be attributed to the instability of intermediate from LA and the further hydrogenation of GVL to methylte-trahydrofuran (MTHF) or

Table 5 The production of GVL directly from xylan and microcrystalline cellulose

Samples	Yield[e]/%						
	Fur	FA	AA	HMF	LA	Lac	GVL
Xylan[a]	47.4	16.4	-	-	3.0	10.4	-
FL+Pt/C[b]	1.0	5.9	15.2	-	4.7	5.6	10.1
Cellulose[c]	-	24.6	-	22.4	12.8	2.1	-
FL+Pt/C[d]	-	2.8	4.0	-	10.7	4.1	6.7

[a] Reaction conditions: 0.2 g xylan, 1.00 g SiO_2,0.08 g $AlCl_3$, 80 mL THF, 20 mL water. T=180 °C, t=2 h. [b] The filtrated liquid obtained from *a* was used for further hydrogenation at 240 °C for 2 h with 5 wt% Pt/C catalytst. [c] Reaction conditions: 0.2 g microcrystalline cellulose, 1.00 g SiO_2, 0.08 g $AlCl_3$, 80 mL THF, 20 mL water. T=220 °C, t=4 h. [d] The filtrated liquid obtained from *c* was used for further hydrogenation at 240 °C for 2 h with 5 wt% Pt/C catalytst. [e] Yield was calculated based on the weight of samples. Fur, FA, AA, HMF, LA, and Lac were the abbreviation of furfural, formic acid, acetic acid, 5-hydroxymethyl furfural, levulinic acid and lactic acid.

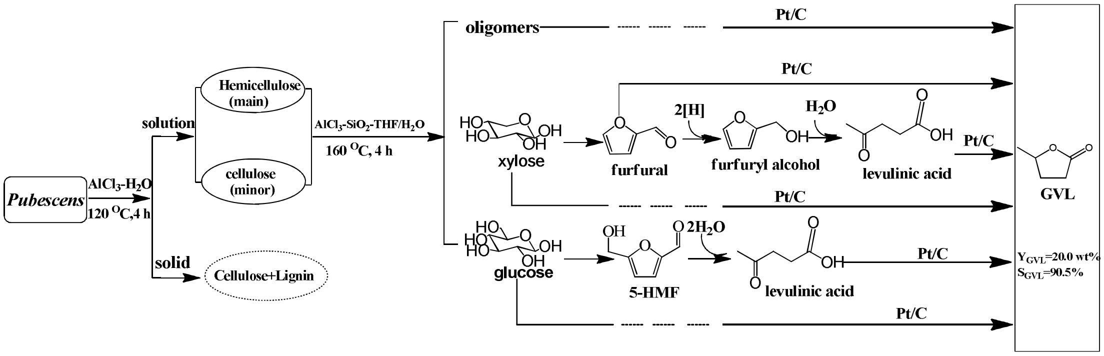
pentanoic acid.[14, 48] Therefore, we identified that a reaction time of 2 h was optimal for the conversion of LA to GVL. As reported by Son et al.,[16] the hydrogenation reaction is proportional to the initial amount of FA. To obtain a higher yield of GVL with high selectivity, the influence of the FA/LA molar ratio on the hydrogenation performance was investigated (Figure 4). At a molar ratio of FA to LA of 1, the yield to GVL was 71.7% (TON=976.5), while 18.4% LA was still not converted, although FA was almost completely converted. When the molar ratio of FA/LA was increased to 3, the conversion of LA was 92.1% and the yield of GVL was 90.3%. The TON was 1229.4 (TOF=617.4 h^{-1}) under the optimal conditions, while the results in literature[49] showed a TOF of 166, 131, 4.8, and 29 h^{-1} respectively corresponding to 0.8% Au/ZrO_2, 3% Au/ZrO_2, 20% Cu/ZrO_2 and 10% Ag-20%Ni/ZrO_2 catalyst with formic acid as hydrogen source. However, the reaction conditions are different. So it is hard to compare directly these results. The selectivity to GVL was improved from 87.9% at a molar ratio of FA/LA=1 to 98.1% at a molar ratio of FA/LA=3. Du *et al.* [17] obtained a high yield of GVL with high selectivity at a lower temperature of 150 °C over Au/ZrO_2 catalyst, while it need a long reaction time of 6 h. A reaction temperature of 240 °C was required for the production of GVL in this work, but a shorter reaction time of 2 h was needed. Braden *et al.* [19] achieved high selectivity of GVL (>95%) over RuRe/C catalyst in the presence or absence of sulfuric acid at 150 °C, but the conversion of levulinic acid was only 15%-40%. Therefore, we can only say that the Pt/C catalyst showed an acceptable selectivity to GVL in the conversion of LA with FA.

The experiment about the recovery of the catalyst was carried out. As shown in Figure S8, the yield of GVL was 90.3% over fresh catalyst. The second run gave out a GVL yield of 90.0%. A slight decrease of GVL yield from 90.0% to 87.0% was observed in the third run, while both the conversion of FA and the selectivity to GVL remain unchanged within the 3 runs. The results showed that the catalyst recycling was successful. The possible leaching of Pt was also investigated by analyzing the filtrate liquid. After each run, the Pt concentration in the aqueous phase was found to be below the detection limits of ICP analysis. This indicated that the leaching of Pt/C catalyst was neglectable.

3.3 The production of GVL with derivatives from *pubescens*

Previous work has demonstrated a two-step process for the selective dissolution and conversion of hemicellulose in *pubescens* to chemicals (furfural, LA and FA) with high selectivity and the yield of FA was much higher than that of LA and furfural. [32] This mixture was possible to be converted to GVL. Herein, the filtrate obtained from the second-step above (6.3 wt% LA, 5.1 wt% furfural, 8.1 wt% FA and followed with about 1.5 wt% of HMF, glucose and xylose, based on the weight of biomass), was used directly to produce GVL at 240 °C for 2 h over Pt/C catalyst. We obtained a high yield of GVL (20.0 wt%, based on the weight of biomass) mainly from hemicellulose in *pubescens* with a selectivity of 62.7% (based on the weight of *pubescens* converted). We have observed that in the first step of *pubescens* conversion, easily degradable lignin component, ashes and other components such as proteins, lipids, and resins were also included. Thus the selectivity to GVL would be as high as 90.5% based on the amount of converted carbohydrates. In addition, a small amount of lactic acid, AA and LA was still present in the liquid products.

Compared with carbohydrates, raw biomass is more structurally complex, and is composed of hemicellulose, cellulose and lignin. In order to further study the origin of GVL from biomass, a two-step method was used for the conversion of carbohydrates with typical structures, such as xylan and cellulose, to GVL (Table 5). Using xylan as the starting material, the main products were furfural (47.4%), FA (16.4%), 3.0% LA and 10.4% lactic acid in the $AlCl_3$-SiO_2-THF/H_2O (1:4) system. The yield of furfural and FA were significantly decreased and 10.1% GVL was obtained by the further reaction of filtrated liquid in the presence of Pt/C catalyst. As reported by Dumesic *et al.*[50] and Fu *et al.*[51], furfural can be hydrolyzed to furfuryl alcohol, which can be further hydrogenated to LA. Bui *et al.*[52] developed a catalytic process for the efficient production of GVL from furfural, through a transfer hydrogenation reaction. This suggested that the production of GVL from xylan may come from the hydrogenation of furfural using FA as hydrogen source. A control experiment using purified furfural as a starting material was carried out, which produced 3.7% LA and 1.6% GVL. Using cellulose as the starting material, the main products obtained were 24.6% FA, 22.4% HMF, and 12.8% LA, with lactic acid as a byproduct. 6.1% GVL was obtained using Pt/C catalyst in the second step. Francesca Liguori *et al.*[49] suggested the production of GVL can be from both C5 sugars and C6 sugars in plant biomass. The results of the present work implied that Pt/C exhibited dual catalytic performance for the production of GVL from both C5 sugars and C6 sugars without addition of external hydrogen. It was also observed that the relative yield of FA derived directly from raw biomass was higher than that from pure xylan and microcrystalline



Scheme1. The origin of GVL from a aqueous mixture derived from hemicellulose in *pubescens*

cellulose. This suggested that the interaction between the components in actual biomass might promote the formation of FA, which is favourable for the hydrogenation.

If the aqueous mixture of LA and furfural in the filtrate can be completely converted to GVL, the theoretical yield of GVL is only about 10.7 wt%. However, 20 wt% GVL was obtained in this system. The liquid products in the filtrate obtained from the second-step above were analyzed by electrospray ionisation-mass spectrometry (ESI-MS) and gel permeation chromatography (GPC). ESI-MS results confirmed that oligomers were present in the filtrate obtained from the second-step and the molecular weights of oligomers were concentrated around 300 Da (Figure S9). The GPC results also confirmed the formation of oligomers with a polydispersity of 1.02 (Figure S10). In the filtrate obtained from the second-step, weight-average molecular weights (Mw)=316 Da and number-average molecular weights(Mn)=309 Da were obtained, which were close to the weight of two molecules of xylose. Monosaccharides such as xylose and glucose in the filtrate were also detected by HPLC. Therefore, oligomers or monosaccharides from hemicellulose, or small amount of extracted cellulose may contribute to the production of GVL.

According to the literatures [50-52] and our above findings, the high yield of GVL with high selectivity obtained in our reaction system was likely obtained through three avenues (Scheme 1). GVL could have been produced via the hydrogenation of LA with FA derived from hemicellulose, or a small amount of extracted cellulose. GVL could also have been produced via the reduction of furfural with FA also derived from hemicellulose. The production of GVL may also have arisen from oligomers or monosaccharides derived from hemicellulose or cellulose. However, the mechanism for the production of GVL directly from the oligomers and monosaccharides or from their conversion byproducts in this actual biomass conversion system requires further study.

In the previous study investigating the production of GVL from raw biomass, [15, 29] mineral acid (HCl or H_2SO_4) was used as both hydrolysis and dehydration catalyst to obtain FA or LA. The deactivation of hydrogenation catalyst was occurred due to the presence of mineral acid [14, 53]. So the removal of the catalysts was necessary before hydrogenation reaction. In this work, LA, FA and furfural were obtained by the treatment of $AlCl_3$. Without the separation of $AlCl_3$, the liquid filtrate obtained from the second-step above was used to complete the hydrogenation reaction with Pt/C catalyst. So a small amount of $AlCl_3$ (0.01 g) co-existed with the Pt/C catalyst in the conversion of *pubescens* to GVL. The effect of $AlCl_3$ on the production of GVL using purified furfural or LA as raw materials was explored (Table S8). The results suggested that $AlCl_3$ slightly inhibits the hydrogenation reaction. In the actual system, $AlCl_3$ exhibited good performance on the selective conversion of oligomers or monosaccharides to monomers. [54-55] We also found that Pt/C catalyst was effective for both the decomposition of FA to H_2, and then the *in situ* hydrogenation of LA to GVL. According to literature [54-55] and our previous work, [32] we speculate that $AlCl_3$ play an important role in the conversion of oligomers or monosaccharides from hemicellulose with Pt/C catalyst coexisted in the hydrogenation reaction. The cross-enhancement of different kinds of reactions catalyzed by $AlCl_3$ and Pt/C in the actual system was significant, which facilitate the production of GVL. While the GVL obtained may further promote the shift of reaction toward its formation. So a high yield of GVL was obtained in raw biomass conversion system. These results demonstrated a multifunctional catalytic system for one-pot conversion of aqueous mixture to GVL with high yield and high selectivity, which evidenced synergetic effects for the selective production of GVL from a complex system. The findings also give a clue to make a complex catalytic system act possibly like the function of enzyme to improve the yield and selectivity to target product by adjusting and controlling the function of different catalysts. Li *et al.*[56] studied the recyclability of the aqueous phase contained $AlCl_3$ in a similar system. The results indicate that the reaction system could be reused for at least four times. Therefore, the recyclability of $AlCl_3$ is possible. On the one hand, further reaction of the products in the reaction mixture could produce fuels, leaving the aqueous solution containing $AlCl_3$, the later could be used further for the first step reaction. On the other hand, GVL obtained could be separated through extraction. Therefore, aqueous phase remained could be reused with the addition of biomass.

The results implied that a multifunctional catalytic system was developed for one-pot conversion of aqueous mixture to GVL with high yield. Importantly, we obtained an acceptable yield and high selectivity compared to GVL than previous studies investigating the production of GVL from raw biomass[15, 29]. The effective utilization of hemicellulose in *pubescens* to GVL was achieved in the process, while the reaction residue contained mainly cellulose and lignin could be further used as feedstock to produce fuels and chemicals. The results also demonstrated that it was an effective route to the production of GVL mainly from hemicellulose in *pubescens*.

4. Conclusions

In summary, we have demonstrated the production of GVL with high yield and selectivity directly from *pubescens* without addition of external hydrogen. Acceptable selective conversion of hemicellulose to GVL was realized, while the significant conversion of cellulose and lignin was avoided. The approach is beneficial for the full utilization of raw biomass, and avoids the subsequent separation process. With no requirement of external hydrogen, our process relies simply on the use of FA originated directly from raw biomass in the first two steps, which produces hydrogen *in situ* for the hydrogenation of the components in the aqueous mixture to GVL. The selective production of GVL from a mixture of a series of reactants including different monomers and oligomers is achieved, which provides a clue to how to control a complex system for the selective formation of specific target product. The present findings open the possibility of developing a novel catalytic system for a one-pot conversion strategy, via the control of different catalytic processes giving out synergetic effects.

Acknowledgements

This work is financially supported by National Basic Research Program of China (973 Program, No.2013CB228103) and the Special Research Fund for the Doctoral Program of Higher Education ofChina (No.20120181130014). The characterization of catalysts and liquid products from Analytical and Testing Center of Sichuan University and Chengdu Branch, Chinese academy of sciences are greatly appreciated.

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Journal Name

ARTICLE

Production of γ-valerolactone via Selective Catalytic Conversion of Hemicellulose in *Pubescens* without Addition of External Hydrogen †

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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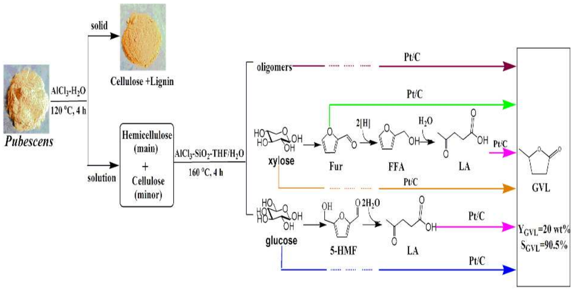

A process was developed for the conversion of *pubescens* to GVL with high yield (20.0 wt%) and selectivity(90.5%).