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ARTICLE

Supplementary Information for

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

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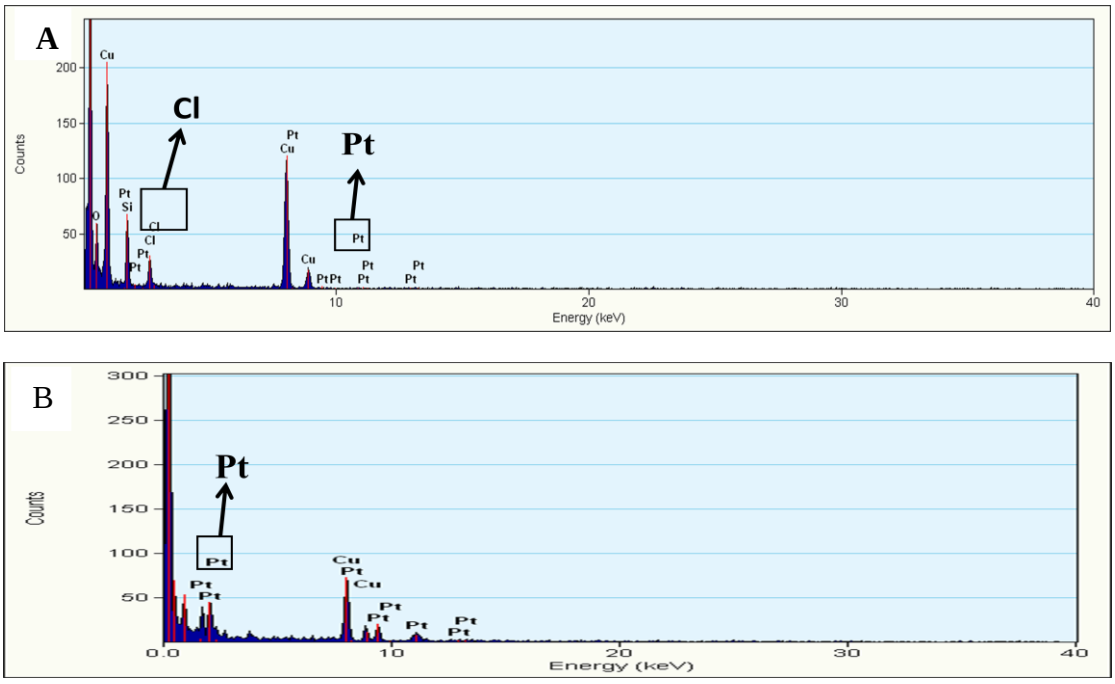


Figure S1 EDX spectra of samples with different treatment: A: UC-5Pt/C catalyst; B: 5Pt/C catalyst

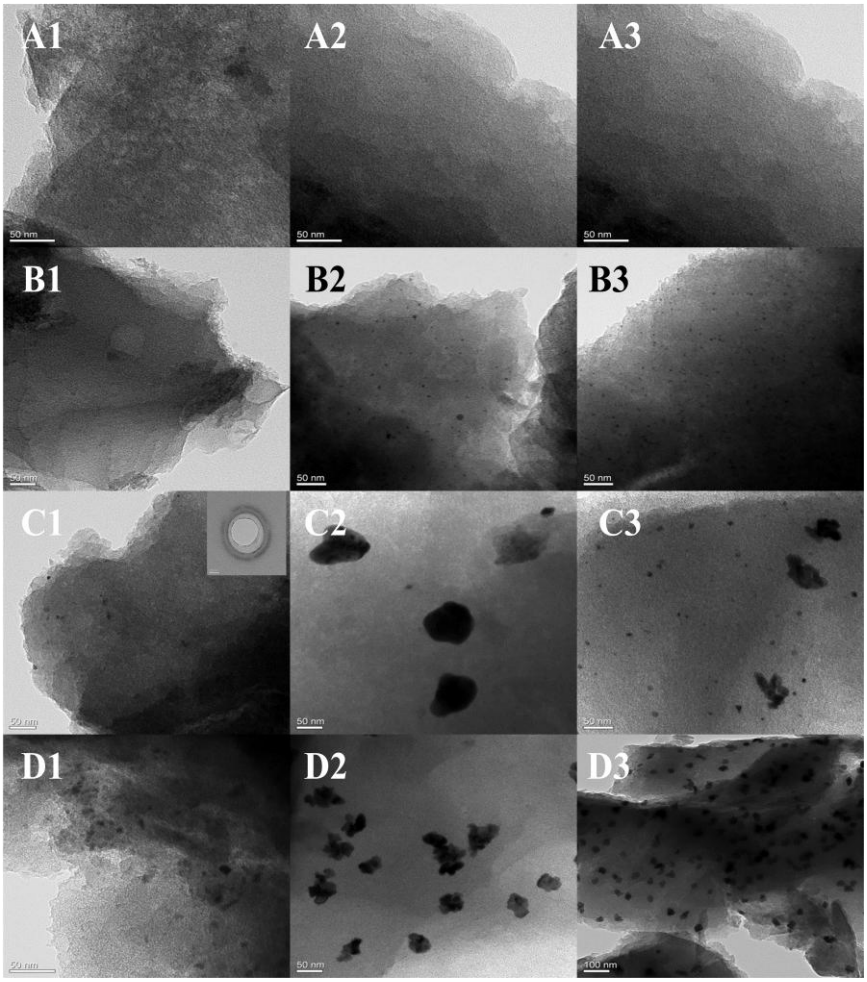


Figure S2 TEM micrographs of different Pt loaded samples with different treatment: A1: UC-0.5Pt/C; A2: UR-0.5Pt/C; A3: 0.5Pt/C; B1: UC-3Pt/C; B2: UR-3Pt/C; B3: 3Pt/C; C1: UC-7Pt/C; C2: UR-7Pt/C; C3: 7Pt/C; D1: UC-11Pt/C; D2: UR-11Pt/C; D3: 11Pt/C;

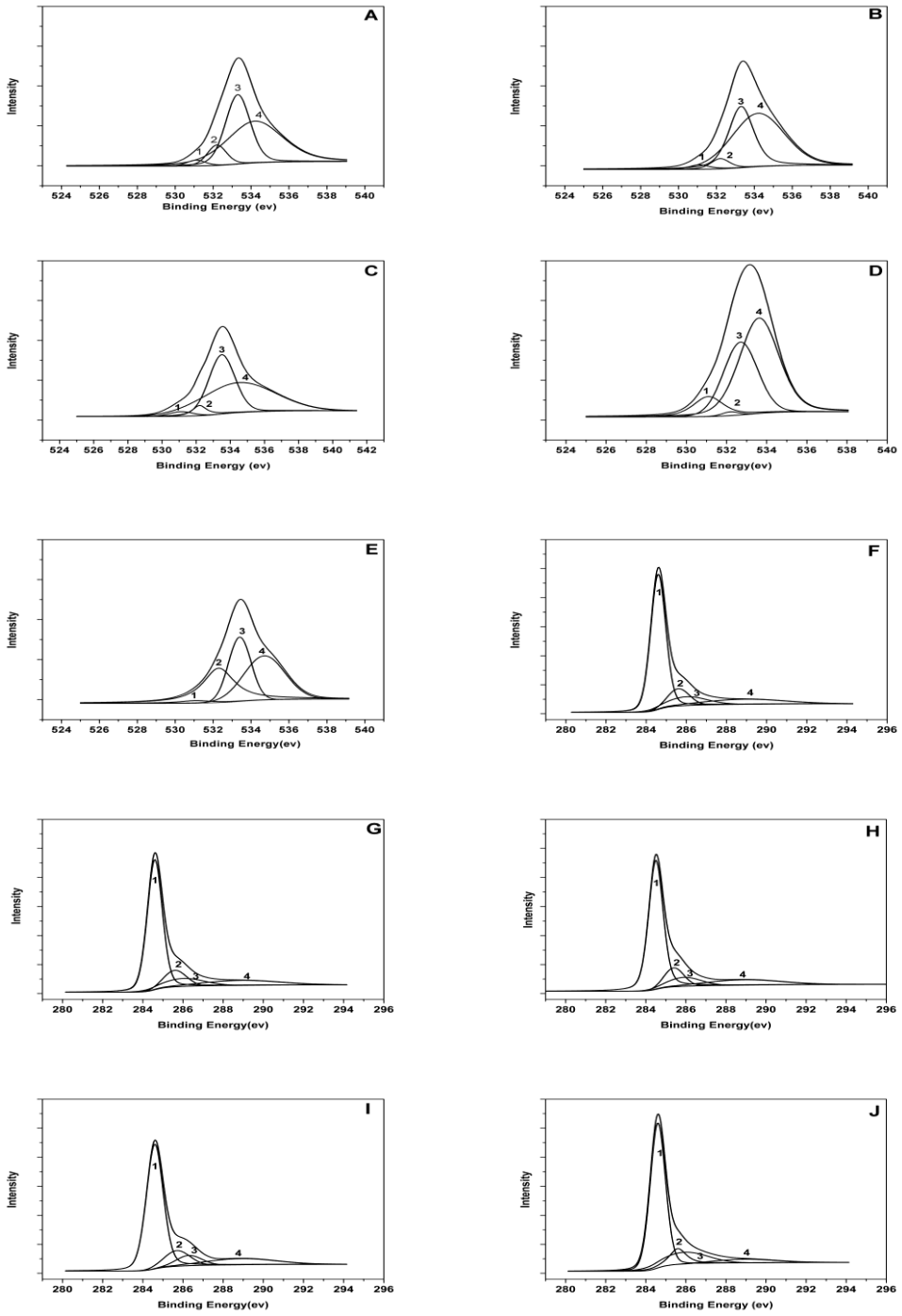


Figure S3 High-resolution XPS O 1s spectra of the samples with different treatment(A:UR-C; B: R-C; C: UC-5Pt/C; D: UR-5Pt/C; E: 5Pt/C). High-resolution XPS C1s spectra of the samples with different treatment (F: UR-C; G: R-C; H: UC-5Pt/C; I: UR-5Pt/C; J: 5Pt/C). Deconvolution of the O 1s species gave four peaks with different binding energies of 531.1, 532.2, 533.3 and 534.2 eV, could be assigned to carbonyl oxygen, phenol oxygen, lactonic oxygen and carboxylic acid oxygen, respectively[S1-S4]. The deconvoluted peaks of C 1s species at the binding energies of 284.5, 285.6, 286.0 and 288.9 eV, respectively, were ascribed to graphite carbon and the contaminant carbon, carbonyl carbon, phenol carbon and carboxylic or lactonic carbon[S5-S8].

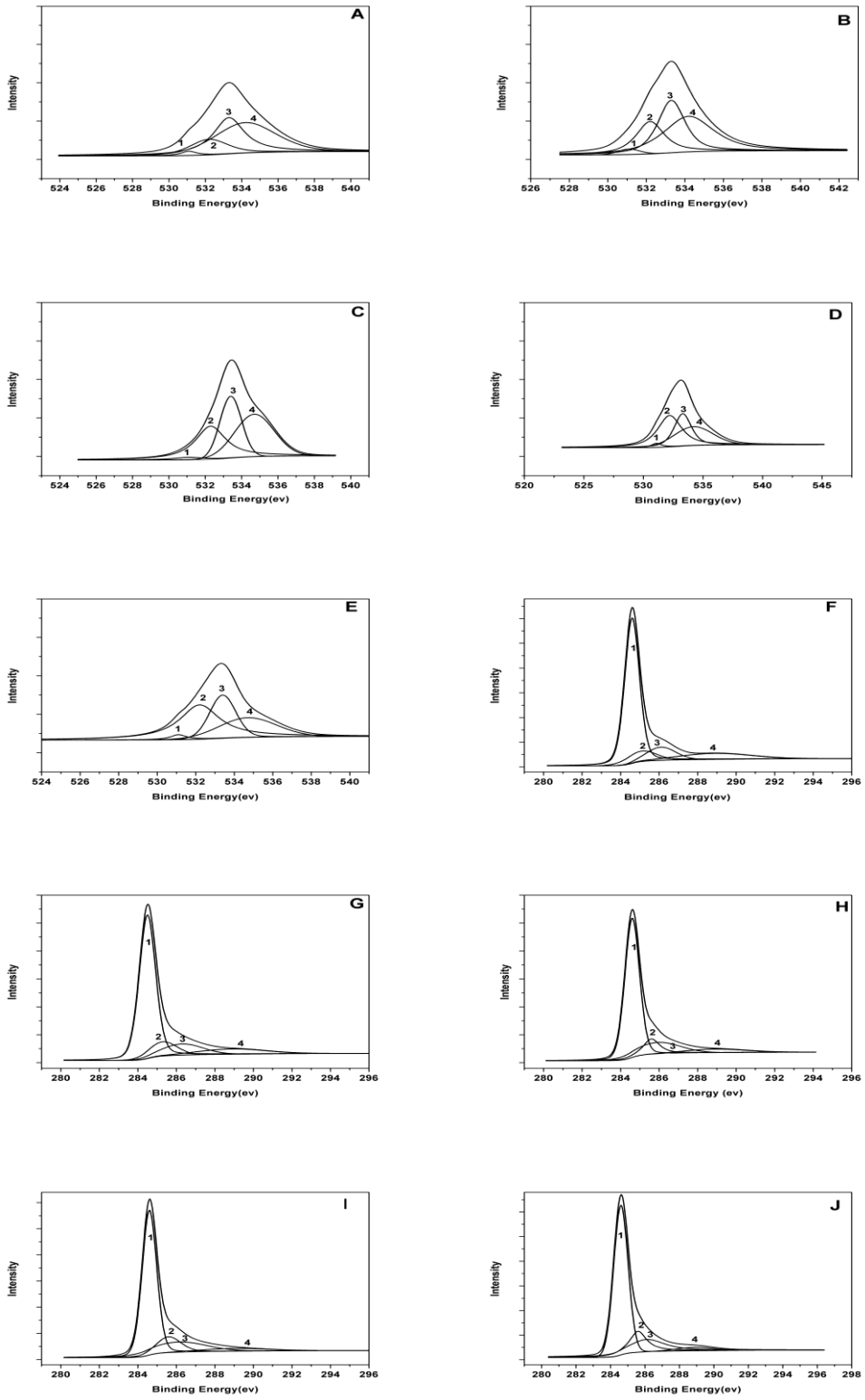


Figure S4 High-resolution XPS O 1s spectra of different samples with Pt loaded on activated carbon after hydrogen treatment (A: 0.5 Pt/C; B: 3Pt/C; C: 5Pt/C; D: 7Pt/C; E: 11Pt/C). High-resolution XPS C1s spectra of different samples with Pt loaded on activated carbon after hydrogen treatment (F: 0.5 Pt/C; G: 3Pt/C; H: 5Pt/C; I: 7Pt/C; J: 11Pt/C).

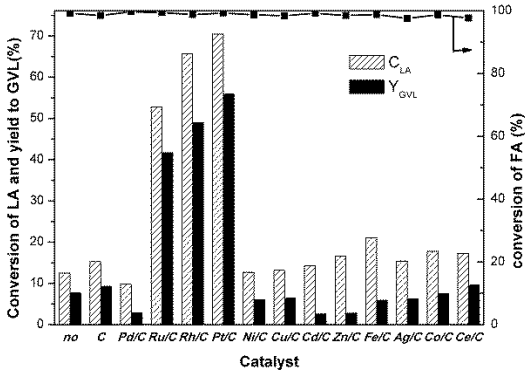


Figure S5 The effect of different metals loaded on activated carbon on the conversion of LA to GVL at 260 ^{o}C for 2 h (The catalysts were prepared by impregnation method. The same preparation method and metal loading (5 wt%) were used for all catalysts.)

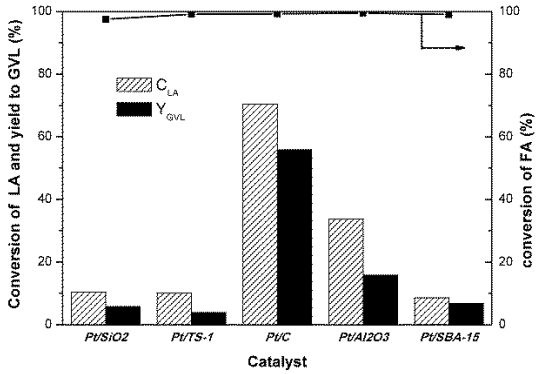


Figure S6 The effect of several typical supports with platinum loaded on the conversion of LA to GVL at 260 °C for 2 h (The catalysts were prepared by impregnation method. The same preparation method and metal loading (5 wt%) were used for all catalysts.)

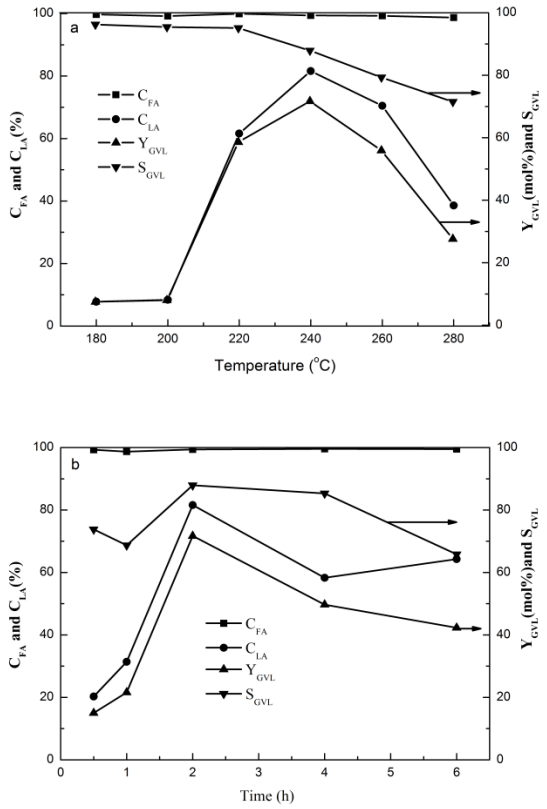


Figure S7 Influence of reaction temperature for 2 h (a) and reaction time at 240 °C (b) on the conversion of LA to GVL with FA

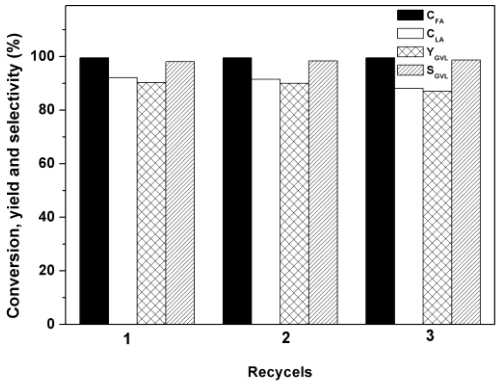


Figure S8 The recyclability of catalysts. (Reaction conditions: LA, 11.25 mmol; FA, 33.75 mmol; H_2O, 25 mL; Catalyst, 0.25 g; N_2, 1MPa. 240 ^oC, 2 h)

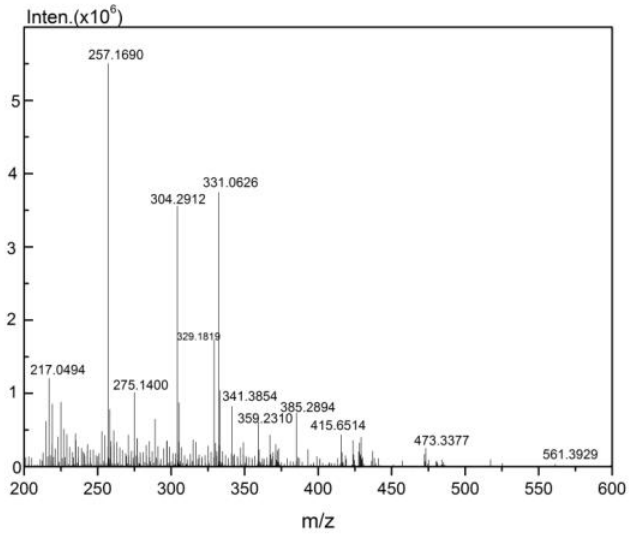
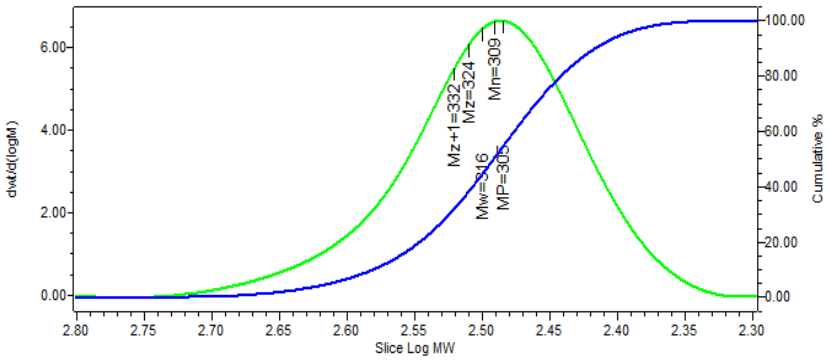


Figure S9 ESI-MS spectra of liquid products in the filtrate obtained from the second-step



GPC Results

	Mw	Mn	Polydispersity
1	3.16e+002	3.09e+002	1.02

Figure S10 GPC results of filtrate obtained from the second-step

Table S1 The metal crystallite size for samples with different Pt loading

samples	0.5 Pt/C	3 Pt/C	5 Pt/C	7 Pt/C	11 Pt/C
metal crystallite size (nm)	-	6.7	9.1	13.9	14.5

Table S2 Conversion of LA into GVL over different catalyst with different treatment [a]

Catalyst	C_{FA} (%)	C_{LA} (%)	Y_{GVL}(%)	S_{GVL}(%)[b]
UR-C[c]	96.6	8.0	7.2	89.9
R-C[d]	98.4	6.6	5.8	89.0
UC-5Pt/C[e]	99.2	53.5	50.0	93.5
UR-5Pt/C[f]	99.0	53.7	51.6	96.1
5Pt/C[g]	99.4	81.6	71.7	87.9

[a] Reaction conditions: LA, 11.25 mmol; FA, 11.25 mmol; H_2O, 25 mL; Catalyst, 0.25 g; N_2, 1MPa; T=240 °C for 2 h. [b] GVL selectivity based on LA conversion. [c] Carbon support was dried overnight at 80 °C. [d] Carbon support was reduced with H_2 at 450 °C for 2 h. [e] Carbon support impregnated with aqueous liquid of $H_2PtCl_6 \cdot 6H_2O$ to obtain the catalyst. [f] The catalyst obtained from *e* was calcined with N_2 at 500 °C for 4 h. [g] The catalyst obtained from *f* was reduced with H_2 at 450 °C for 2 h.

Table S3 The relative concentration of different surface oxygen species after deconvolution on activated carbon samples with different Pt loaded after hydrogen treatment

Samples	Binding Energy/eV and the corresponding composition/%			
	531.1	532.2	533.3	534.2
0.5Pt/C	2.1	15.8	36.5	45.6
3Pt/C	2.1	22.7	33.0	42.2
5Pt/C	2.4	32.1	29.1	36.4
7Pt/C	2.4	40.4	27.9	29.3
11Pt/C	2.6	46.1	26.3	25.0

Table S4 The relative concentration of different surface carbon species after deconvolution on activated carbon samples with different Pt loaded after hydrogen treatment

Samples	Binding Energy/eV and the corresponding composition/%			
	284.6	285.6	286.1	288.9
0.5Pt/C	68.1	8.8(27.6)[a]	11.0(34.5)	12.1(37.9)
3Pt/C	68.3	10.5(33.1)	12.1(38.2)	9.1(28.7)
5Pt/C	66.8	10.6(32.0)	15.9(48.0)	6.6(20.0)
7Pt/C	65.1	12.8(36.8)	16.7(48.0)	5.3(15.2)
11Pt/C	62.7	15.7(42.2)	18.0(48.4)	3.5(9.4)

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

Table S5 The decomposition of FA and gas product distribution over different catalysts

Catalyst	Conditions	C_{FA} (%)	H_2 (%)	CO_2 (%)	CO (%)	CH_4 (%)
NO	160 ^{o}C, 2 h	14.4	49.7	50.3	-	-
NO	240 ^{o}C, 2 h	99.7	68.1	28.2	3.6	-
C	160 ^{o}C, 2 h	14.0	27.5	64.2	-	8.4
Pt/C	160 ^{o}C, 2 h	95.9	41.5	53.0	-	5.5
Pt/C	240 ^{o}C, 2 h	99.9	63.7	30.8	0.4	5.3

Table S6 The conversion of LA with H_2 at 240 ^{O}C for 2 h

Catalyst	H_2 (MPa)	C_{LA} (%)	Y_{GVL} (%)[a]	S_{GVL}(%)[b]
no	0.5	15.0	0.1	0.8
Pt/C	0.5	39.5	6.3	16.0

[a] The yield of GVL was calculated through the molar amount of GVL divided by the initial molar amount of LA.

[b] GVL selectivity based on LA conversion.

Table S7 The relative intensity of lattice plane in face-centered cubic structure of Pt for samples with different Pt loading

Relative intensity (%)	0.5 Pt/C	3 Pt/C	5 Pt/C	7 Pt/C	11 Pt/C
(111)	-	54.6	55.8	55.8	56.5
(200)	-	26.0	23.7	26.4	25.8
(220)	-	19.4	20.5	17.8	17.7

Table S8 The effect of $AlCl_3$ on the conversion of LA with FA to GVL at 240 ^{O}C for 2 h

Samples	$AlCl_3$	Y_{GVL}(%)
fufural	-	1.3
fufural	+	1.6
LA	-	71.7
LA	+	67.7

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