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Catalytic Conversion of Biomass-derived Levulinic Acid into Alcohols over Nanoporous Ru Catalyst

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Catalyst preparation

The precursor alloy consists of desired catalytic metal (Ru) and reactive metal (Al). Firstly, mixture of two metals is heated to designed temperature under the protection of argon in an induction furnace. And then alloy is usually ground and screened. Alloy powder with diameter less than 38 μm was chosen to produce nanoporous material. At last Al was leached out in 20 wt.% NaOH aqueous solution at 90°C for 1 h. Nanoporous Ru was washed with deionized water until neutral solution was achieved. At last, nanoporous Ru was slowly dried and passivated.[1] SEM image of Nanoporous Ru is showed in Figure S1.

5%Ru/AC and 5%Ru/Al_2O_3 are commercial catalysts (Dalian Tongyong Chemical Co., Ltd., China). Powder Ru is also commercial metal powder (Shenyang Zhanyu science and technology development Co., Ltd., China).

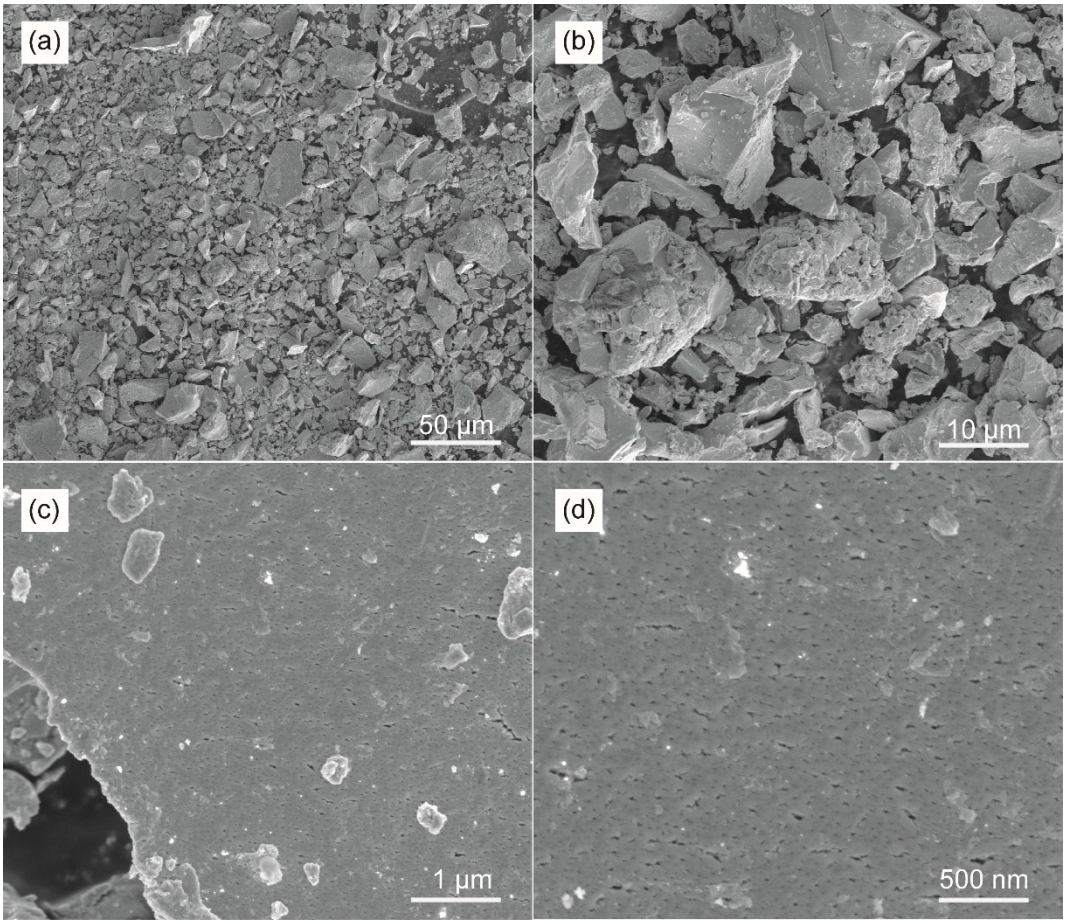

Figure S1. SEM images of Nanoporous Ru

Activity test and product analysis

The catalytic hydrogenation reaction was conducted in a stainless-steel autoclave (75 mL capacity). The 5%Ru/AC and 5%Ru/Al_2O_3 were reduced in H_2 atmosphere for 1 h at 250 °C before test. Typically, levulinic acid (2 mmol), water (20 mL) and nanoporous Ru (0.01 g) were directly added into the reactor, and then it was sealed and purged with N_2 and H_2 for 3 times respectively. The reactor was filled with 6.0 MPa H_2 at room temperature and heated to 120 °C. Finally, 2 mL of the reaction liquid was taken out and tested by ICP-AES (Perkin Elmer, Optima 2000DV).

The effect of agitation speed on LA hydrogenation was investigated and results were shown in Figure S2. The stirring rate was set at 500 rpm in order to exclude the effect of external diffusion.

The effect of catalyst size for LA hydrogenation was investigated and results were shown in in Figure S3. The catalyst with size less than 38 μm was employed in this study in order to exclude the effect of internal diffusion.

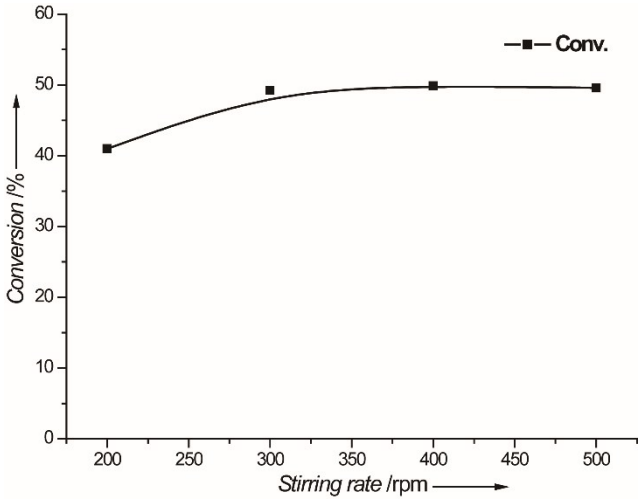

Figure S2. The effect of agitation speed on LA hydrogenation

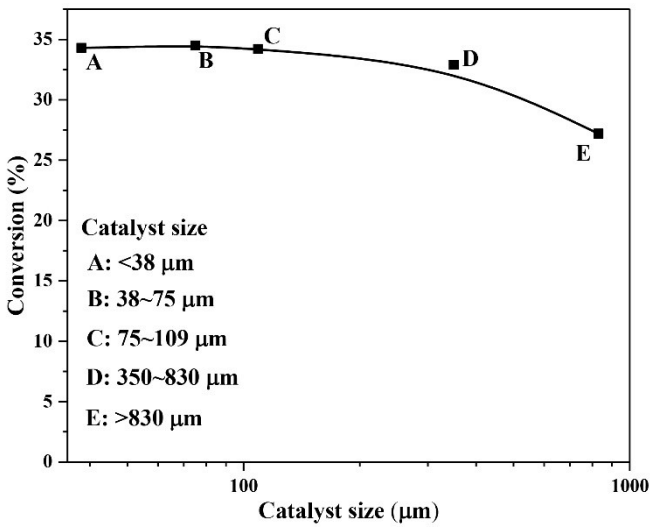

Figure S3. The effect of catalyst size on LA hydrogenation

The products were quantitatively analysed by GC [Techcomp GC 7890F, FID detector, DB-FFAP (30 m×250 μm×0.25 μm) capillary column] and qualitatively analysed by GC-MS (Agilent 5979C). The conversion and selectivity were calculated with internal standard method and carbon balance according to GC-FID results.

The conversion and selectivity were calculated using Eq. (1) and Eq. (2):

$$Conversion = \frac{mole\ of\ LA\ reacted}{mole\ of\ LA\ supplied}$$

Ea.

(1)

$$Selectivity = \frac{mole\ of\ product \times Carbons\ of\ product}{mole\ of\ LA\ reacted \times Carbons\ of\ LA}$$

Ea. (2)

Catalyst characterization

XRD

X-ray diffraction (XRD) patterns for all samples were recorded on a Rigaku D/max-2400 diffractometer (Cu Kα/λ = 0.1541 nm/40 kV/40 mA). The sample was scanned from 10° to 90° at the rate of 10°/min.

TEM

Transmission electron microscopy (TEM) images were obtained with an accelerating voltage of 300 kV (TEM, FEI TF30). Samples were dispersed in alcohol for 1 h and then deposited onto a carbon-coated copper grid for HR-TEM imaging.

XPS

XPS experiment was performed on an Escalab 250Xi spectrometer of Thermo Scientific with an Al anode [Kα (hv = 1486.6 eV) radiation].

N_2 adsorption-desorption

The N_2 adsorption–desorption isotherms were obtained by using a 3H-2000PS1 sorption system [Beishide Instrument-ST (Beijing) Co., Ltd.]. Firstly, sample was dried in vacuum at 200 °C for 6 h. Next, the N_2 isotherms were obtained at -196 °C. The specific surface areas were calculated from isotherms using the Brunauer-Emmett-Teller (BET) method. Pore distribution and cumulative volumes of pores were obtained by the Barrett-Joyner-Halenda (BJH) method from the desorption branches of isotherms.

ICP-AES

The sample was dissolved in aqua regia. And then concentration of metal was tested on an Optimi2000DV.

NH_3-TPD

NH_3-TPD was conducted in TP-5076 (Tianjin Xianquan Industry and Trading Co., Ltd.). At first, sample (0.1 g) was heated to 100 °C in Ar for 3 h. After sample being cooled to 50 °C, Ar was replaced by 5% NH_3-Ar for 15min. After that, sample was heated to 100 °C in Ar for 2h again. The sample was reheated from 100 to 600 °C at the rate of 10 °C/min.

Results

Investigation of Different Nanoporous metal Catalysts

Table S1 Catalytic performance of different nanoporous catalysts on the hydrogenation of LA

Cat.	Leaching (ppm)		Conv. (%)	Sel. (%)[b]					
	Catalytic metal	Al[a]		MTHF	2-BO	2-PO	GVL	PDO	Other
Nanoporous Cu	1.0	0.17	42.8	0	22.9	7.7	100	0	0
Nanoporous Fe	273.5	0.25	50.4	0	10.4	5.0	100	0	0
Nanoporous Co	72.2	0.045	100	0	60.0	15.0	99.8	0	0.1
Nanoporous Ni	11.9	0.048	100	0.1	48.6	19.9	98.8	0.6	0.1
Nanoporous Ru	0.038	0.065	100	2.5	63.6	15.2	4.7	19.2	12.4

Reaction Conditions: 2 mmol LA, 20 mL H_2O, 0.01 g catalyst, 120 °C, initial hydrogen pressure 6.0 MPa, 24 h a Al stands for active metal (aluminum) b selectivity was calculated with internal standard method and carbon balance

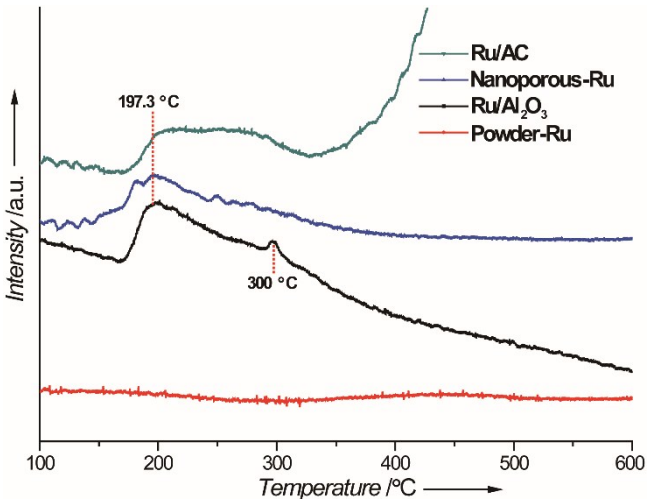

Figure S4. NH_3-TPD of different Ru catalysts

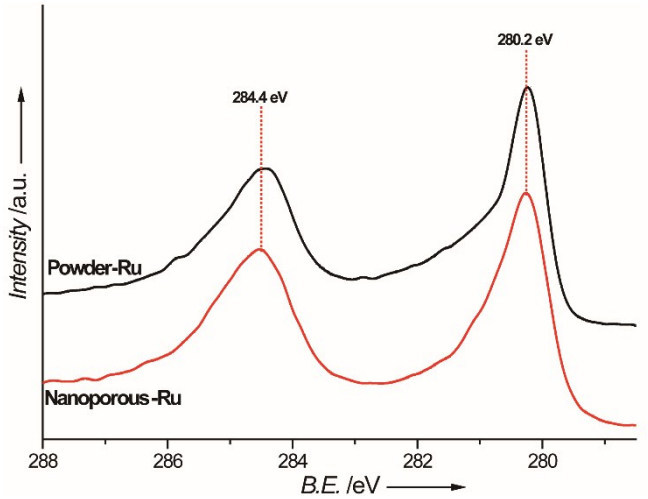

Figure S5. Ru 3d XPS patterns of powder Ru and nanoporous Ru

The Study of Kinetic experiments

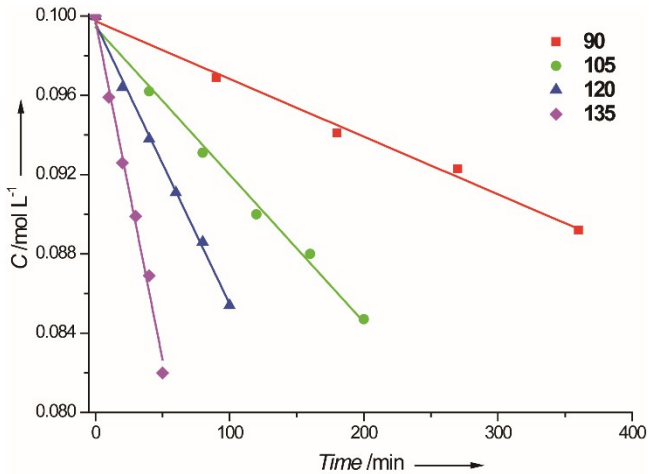

Figure S6. Concentration of GVL versus reaction time with nanoporous Ru

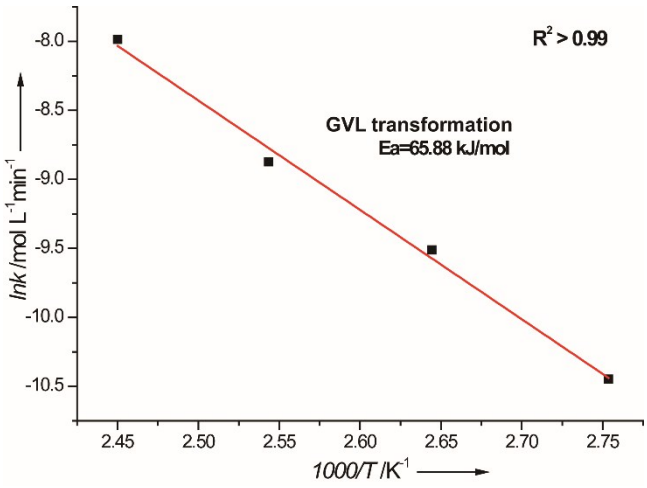

Figure S7. Arrhenius plots of the conversion of GVL to PDO with nanoporous Ru

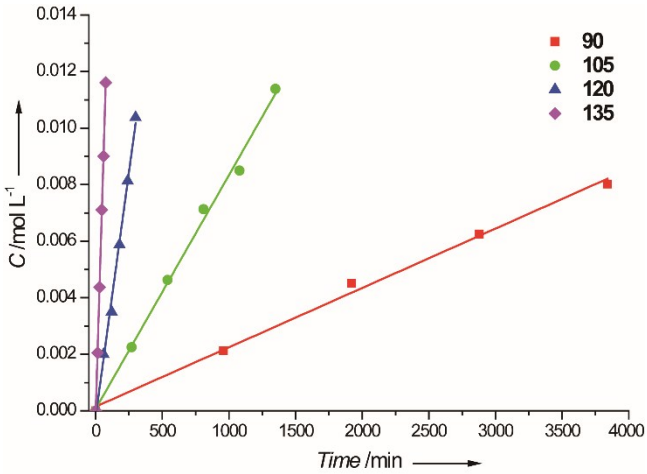

Figure S8. Concentration of 2-BO versus reaction time with nanoporous Ru

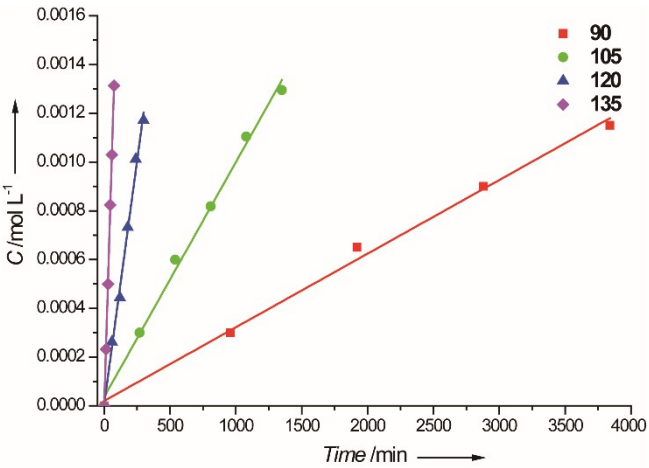

Figure S9. Concentration of 2-PO versus reaction time with nanoporous Ru

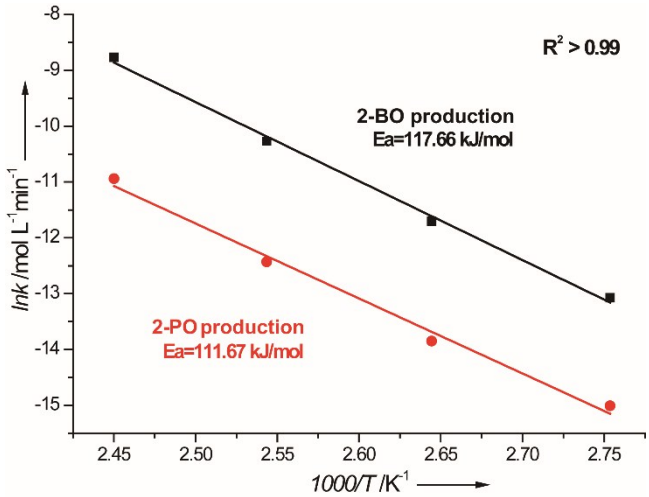

Figure S10. Arrhenius plots of the PDO hydrogenolysis with nanoporous Ru

Table S2 Effect of reaction temperature on the hydrogenation of LA

Temperature (°C)	t (h)	Conv. (%)	BO:PO[a]	Sel. (%)[b]					
				MTHF	2-BO	2-PO	GVL	PDO	Other
100	5	100	2.3	0.4	1.8	1.0	81.1	14.8	0.9
	10	100	2.0	0.6	3.4	2.1	62.3	30.1	1.5
	15	100	2.5	1.6	5.5	2.8	45.5	42.3	2.3
	20	100	2.7	1.9	7.9	3.6	30.8	52.6	3.2
	25	100	3.1	1.6	9.1	3.7	22.5	59.3	3.8
	30	100	3.5	1.5	11.4	4.1	15.9	62.7	4.3
	35	100	3.5	1.8	14.3	5.1	11.0	62.8	4.8
	40	100	3.5	2.2	17.8	6.3	7.5	60.1	6.2
	45	100	3.2	2.6	18.7	7.2	5.6	59.6	6.4
	50	100	3.7	2.5	22.9	7.7	4.1	55.3	7.5
120	5	100	3.2	0.8	8.6	3.4	69.0	15.3	2.9
	10	100	4.1	2.4	23.9	7.3	34.2	25.3	6.9
	15	100	4.2	2.5	33.9	10.2	15.3	28.3	9.8
	20	100	4.5	2.3	42.5	11.9	6.5	24.6	12.1
	25	100	4.5	2.5	48.6	13.5	3.1	18.6	13.7
	30	100	4.7	2.3	52.5	14.0	0.9	15.3	15.1
	35	100	4.8	2.2	56.2	14.7	0.2	9.6	17.0
	40	100	4.9	2.9	58.2	14.9	0.0	6.3	17.6
	45	100	4.9	3.0	59.2	15.2	0.0	5.0	17.5
	50	100	5.0	2.7	60.0	15.0	0.0	4.5	17.8
	55	100	5.1	2.5	61.0	15.0	0.0	3.3	18.2

Reaction Conditions: 2 mmol LA, 20 mL H_2O, 0.01 g catalyst, initial hydrogen pressure 6.0 MPa a n(2-BO):n(2-PO) b Yield was calculated with internal standard method and carbon balance

i-PrOH was chosen as control solvent of H_2O and PDO was used as a starting substrate (Table S3). Results showed that ratio of BO to PO dramatically decreased from 7.9 to 2.7, indicating solvent effect played a significant role in controlling selectivity of products. However, 2-BO as a main product remained unchanged, thus solvent effect did not act as a major factor to determine the selectivity of products.

Table S3 Test of PDO conversion with isopropanol as solvent

Solvent	Catalyst (g)	Time (h)	Conv. (%)	Sel. (%)			BO/PO
				2-BO	2-PO	Others	
H_2O	0.01	24	69.5	70.3	8.9	20.7	7.9
i-PrOH	0.03	10	21.5	60.5	22.8	16.7	2.7

Reaction Conditions: 2 mmol PDO, 20 mL solvent, nanoporous Ru, 120 °C, initial hydrogen pressure 6.0 MPa

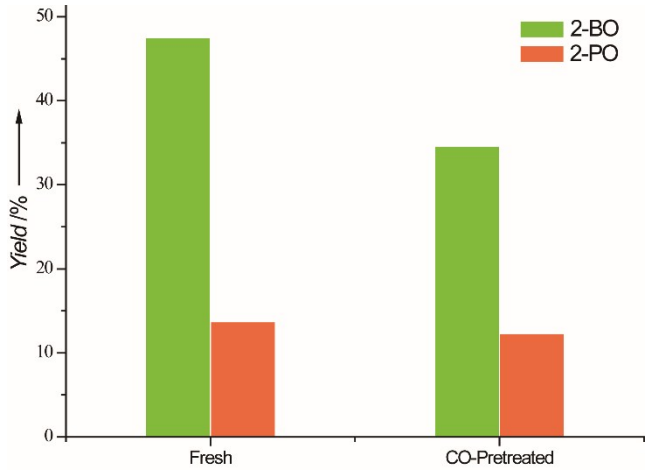

Figure S11. Performance of fresh and CO-pre-treated nanoporous Ru [a] 2 mmol LA, 20 mL H_2O, 0.01 g catalyst, 120 °C, initial hydrogen pressure 6.0 MPa, 24 h

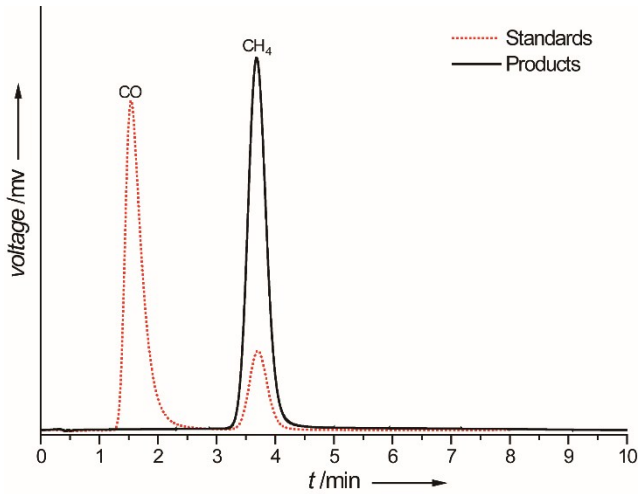

Figure S12. The chromatogram for gas products

Test of Recycling time with Leaching

Table 1 showed that Ru slightly dissolved in the reaction liquid. So the activity of dissolved Ru was investigated in the following test (Figure S13). First of all, the catalytic test was performed at 120 °C and 6.0 MPa for 5 h. Then 10 mL of reaction solution was separated without catalyst and added into a new reactor to react for another 10 h. And the rest was continued to react for 10 h too. All of results were listed in Table S3. After 5 h, GVL (69.1%), PDO (17.3%) and monohydric alcohol (10.9%) were obtained with full conversion of LA in step-1. The result of step-2 without catalyst was almost the same as that of step 1. It meant that little dissolved Ru in the water was inactive for the reaction.

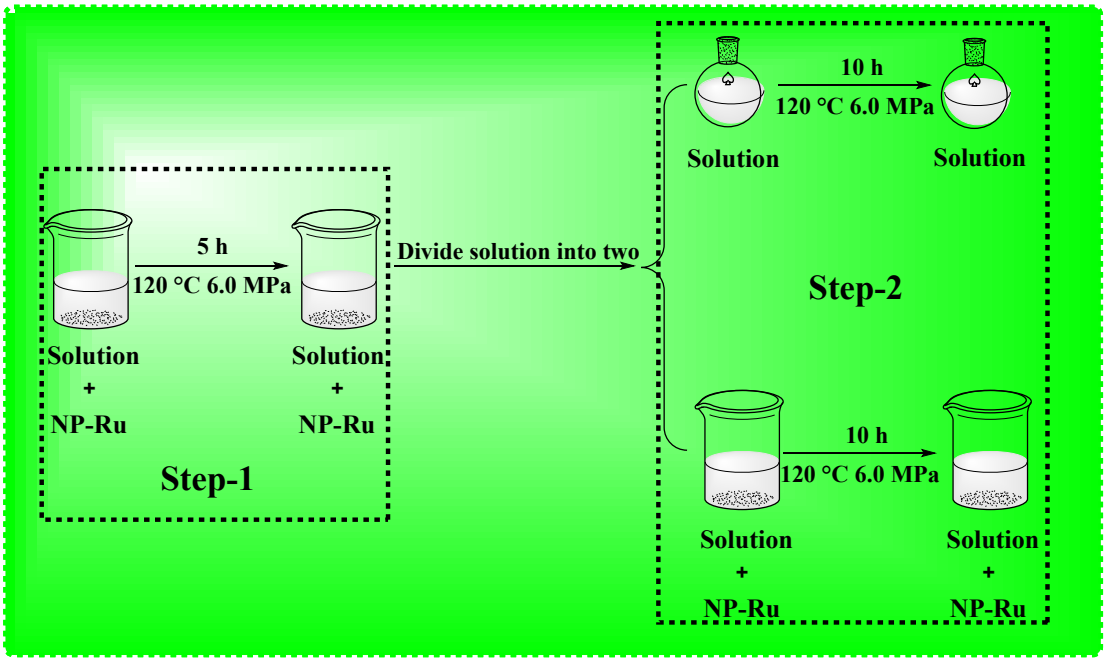

Figure S13. Test about leaching of nanoporous Ru during hydrogenolysis of LA

Next, the stability of NP-Ru was studied (Table S4). Firstly, the catalytic test was performed at 120 °C and 6.0 MPa for 10 h with 0.03 g catalyst. Then, the used catalyst was washed with deionized water for three times at ambient conditions and recycled in the following catalytic tests.

Table S4 Test about leaching of nanoporous Ru during hydrogenation of LA

Step	Conv. (%)	Sel. (%)[a]					
		MTHF	2-BO	2-PO	GVL	PDO	Other
1	100	0.5	7.3	3.6	69.2	17.3	2.1
2-Solution	100	0.6	7.3	3.5	69.1	17.3	2.2
2-Solution+catalyst	100	2.8	41.7	19.6	5.5	18.3	12.1

Reaction Conditions: 2 mmol LA, 20 mL H_2O, 0.01 g catalyst, 120 °C, initial hydrogen pressure 6.0 MPa a selectivity was calculated with internal standard method and carbon balance

Table S5 Test of recycling time with leaching results

Recycling time	Leaching (ppm)[a]		Conv. (%)	Sel. (%)[b]					
	Ru	Al		MTHF	2-BO	2-PO	GVL	PDO	Other
1st	0.011	0.038	100	2.6	48.6	19.9	0.5	14.1	14.2
2nd	0.0059	0.033	100	2.7	45.1	19.9	1.1	17.9	13.4
3rd	0.0028	0.037	100	3.5	49.0	20.2	0.5	12.5	14.3
4th	0.0055	0.037	100	3.6	46.5	19.8	1.0	15.4	13.7
5th	0.0091	0.034	100	3.4	46.4	20.5	1.0	15.2	13.6
6th	0.010	0.046	100	4.1	42.2	19.0	0.3	22.4	11.9
7th	0.053	0.031	100	3.3	35.3	15.5	1.5	34.0	10.4
8th	0.045	0.036	100	2.9	31.5	13.1	3.8	39.5	9.3

Reaction Conditions: 2 mmol LA, 20 mL H_2O, 0.03 g catalyst, 120 °C, initial hydrogen pressure 6.0 MPa, 10 h a Ru strands for catalytic metal (ruthenium), Al stands for active metal (aluminum) b selectivity was calculated with internal standard method and carbon balance

Product analysis

The products were quantitatively analyzed by GC [Agilent 7890A, FID detector, DB-FFAP (30 m×250 μm×0.25 μm) capillary column] and qualitatively analyzed by GC-MS (Agilent 5979C).

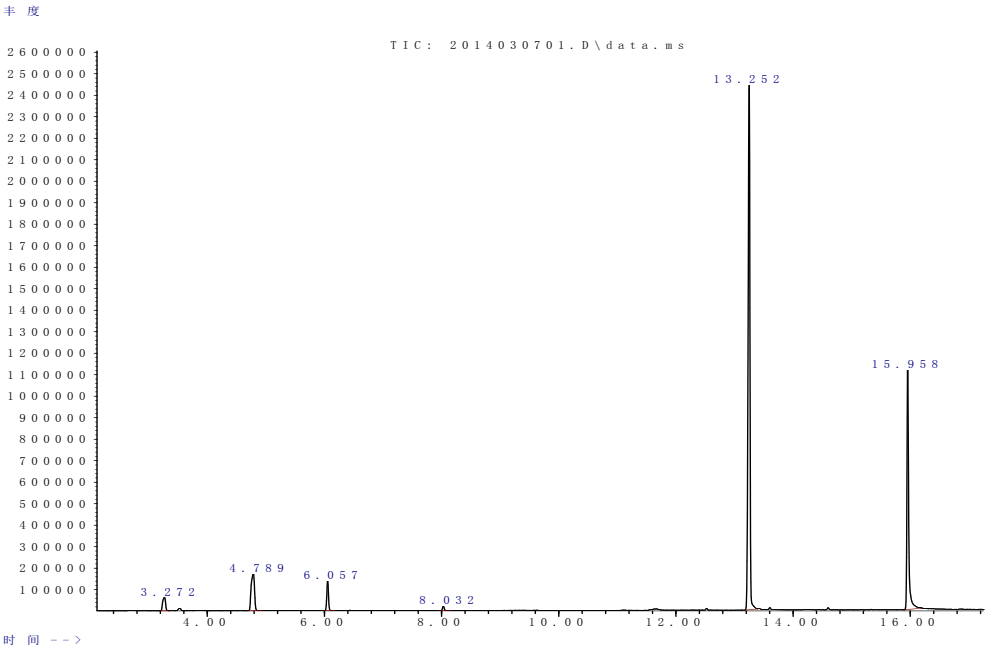

Figure S14. The chromatogram for hydrogenation of LA

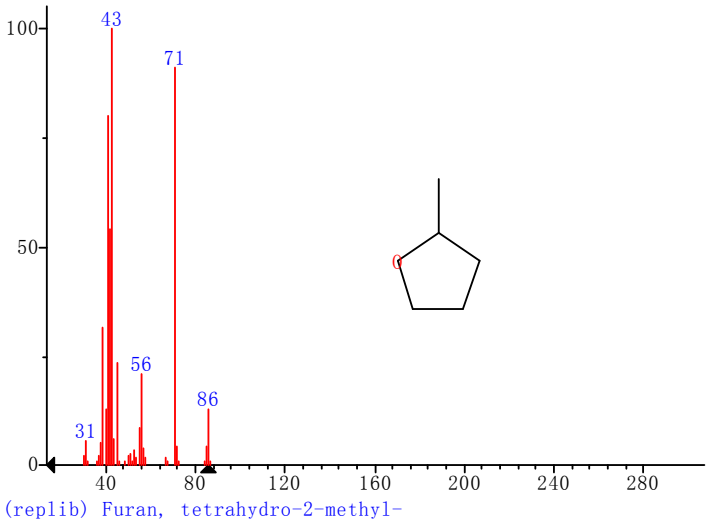

Figure S15. The mass spectrum for 2-methyltetrahydrofuran

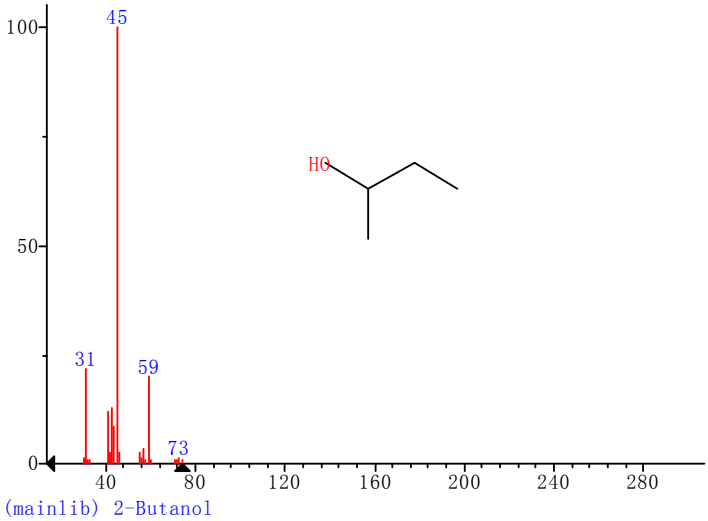

Figure S16. The mass spectrum for 2-butanol

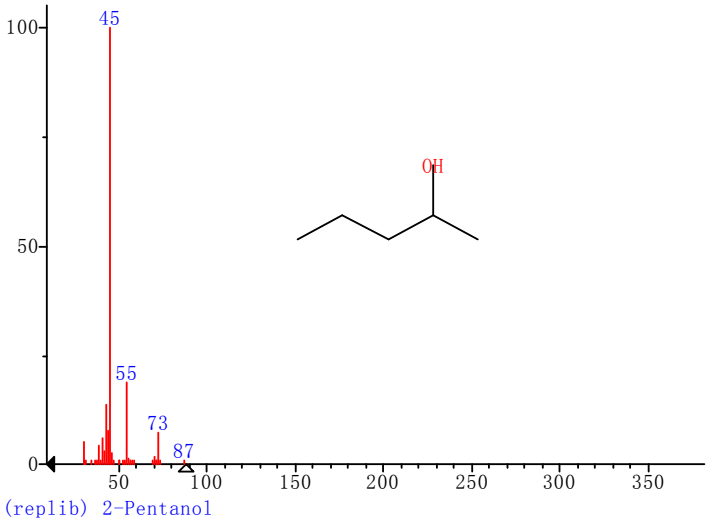

Figure S17. The mass spectrum for 2-pentanol

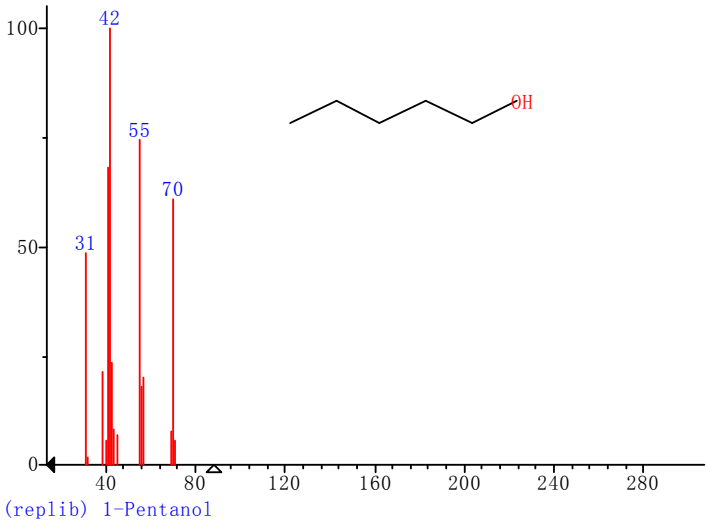

Figure S18. The mass spectrum for 1-pentanol

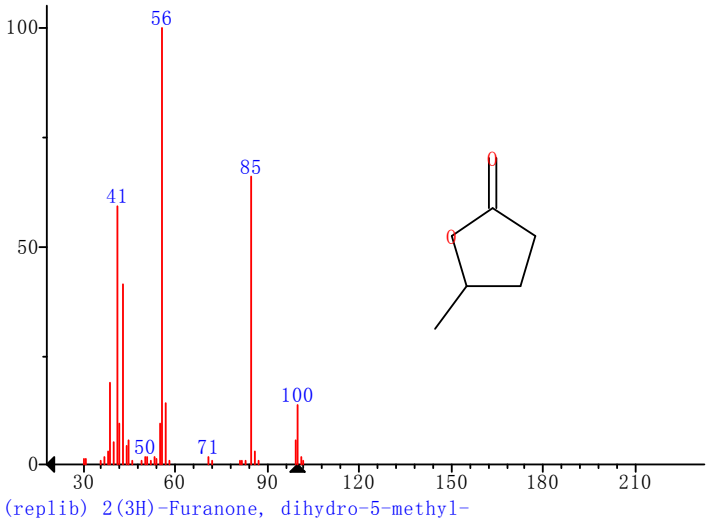

Figure S19. The mass spectrum for γ-valerolactone

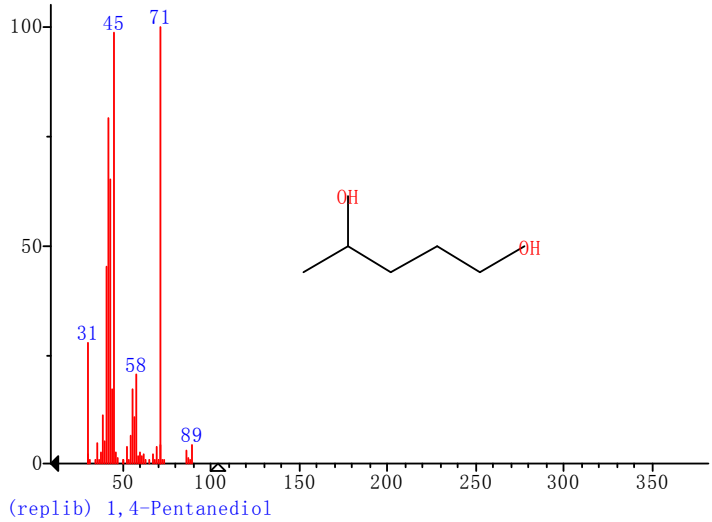

Figure S20. The mass spectrum for 1, 4-pentadiol

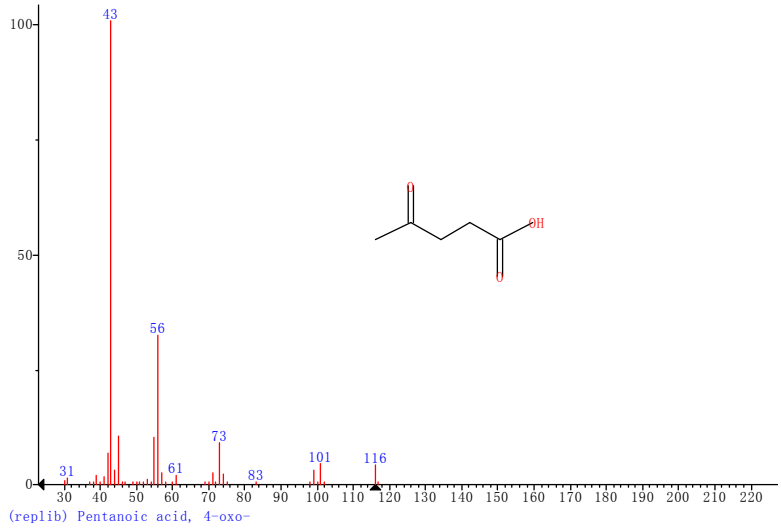

Figure S21. The mass spectrum for levulinic acid

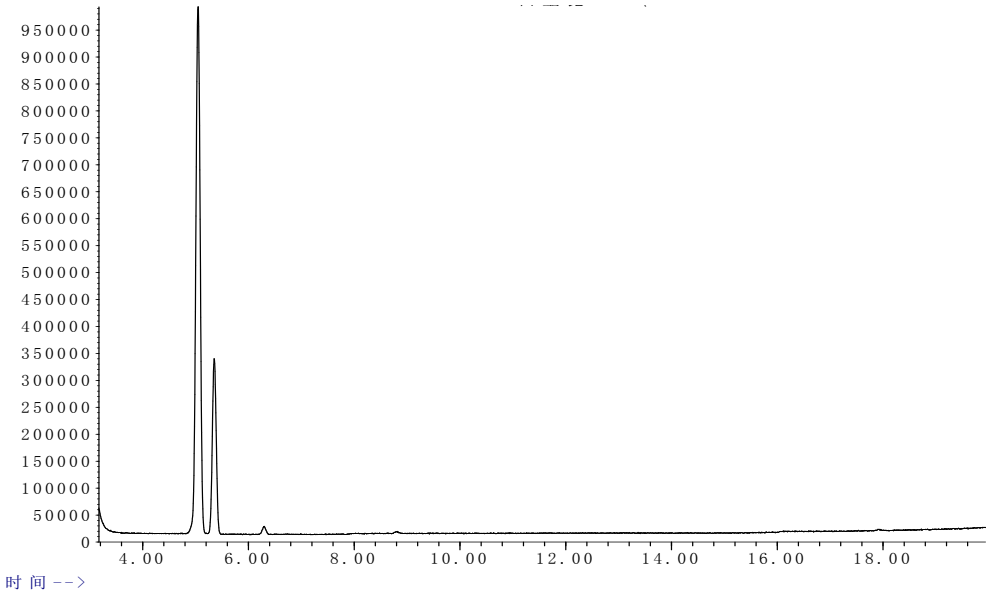

Figure S22. The chromatogram for gas products

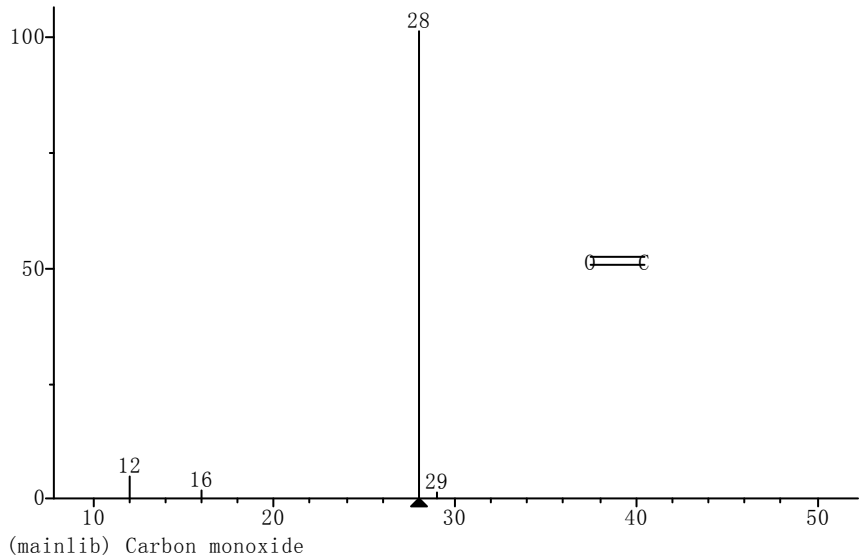

Figure S23. The mass spectrum for carbonic oxide

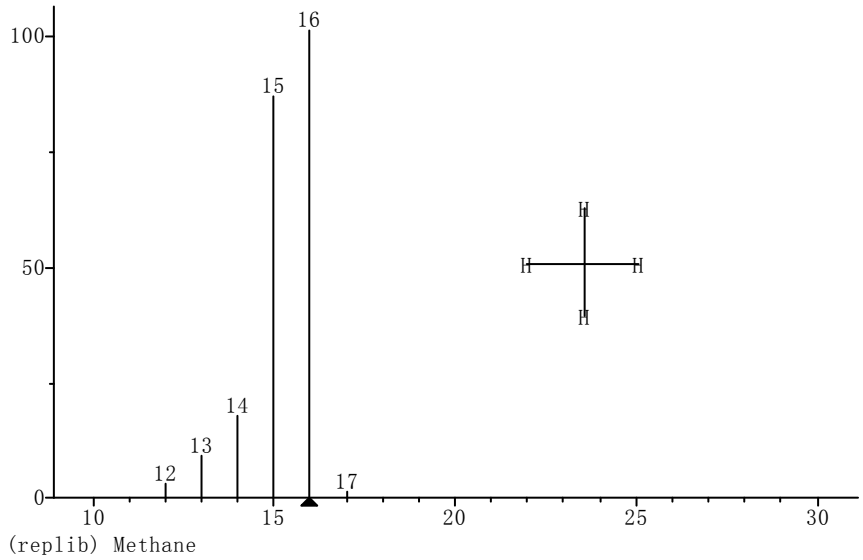

Figure S24. The mass spectrum for methane

[1] a) K. Urabe, T. Yoshioka, A. Ozaki, *J. Catal.* **1978**, *54*, 52; b) A. J. Smith, D. L. Trimm, *Annu. Rev. Mater. Res.* **2005**, *35*, 127; c) A. J. Smith in *Surface and Nanomolecular Catalysis*, Taylor & Francis Group, **2006**, p. 141-159.