Electronic Supplementary Material (ESI) for Green Chemistry.

Direct conversion of carbohydrates to γ-valerolactone facilitated by solvent effect

Jinglei Cui,[ab] Jingjing Tan,[ab] Tiansheng Deng,[a] Xiaojing Cui,[a] Hongyan Zheng,[c] Yulei Zhu*[ac] and Yongwang Li [ac]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China.

[b] University of Chinese Academy of Sciences, Beijing, 100049, PR China.

[c] Synfuels China Co. Ltd., Beijing, PR China.

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1. Materials and Methods

1.1 Materials

Cellulose, inulin, starch, sucrose, maltose, glucose, fructose and levulinic acid (LA, 98%) were purchased from Aladdin; γ-valerolactone, γ-butyrolactone, methanol, ethanol and 1, 4-dioxane were purchased from Sinopharm Chemical Reagent Co., Ltd.. All the above agents were utilized without further purification. $RuCl_3 \cdot 3H_2O$, γ-Al_2O_3, SiO_2, ZrO_2, active carbon, TiO_2 (P25 Degussa) and $H_3PW_{12}O_{40}$ (HPA) were purchased from Sinopharm Chemical Reagent Co., Ltd..

1.2 Catalyst preparation

A series of Ru-supported catalysts were prepared by the wet impregnation method. The supports were treated as follows before the wet impregnation: γ-Al_2O_3, SiO_2, ZrO_2, TiO_2 and active carbon were dried at 100 ^oC overnight, followed by the impregnation with an aqueous solution containing $RuCl_3 \cdot 3H_2O$ at room temperature under vigorous stirring for 24 h. The resulting Ru supported catalysts were dried at 100 ^oC for 20 h. All the Ru catalysts except for Ru/C catalyst were calcined in air at 400 ^oC for 4 h. Pure RuO_2 was prepared by the following procedures: taking a certain concentration of $RuCl_3 \cdot 3H_2O$ solution, then 1.0 mol/L ammonia solution was slowly added by a syringe until the pH up to 8. The obtained black sediment was aged under 80 ^oC for 1 h, then the resulting RuO_2 was filtered, washed with water for three times and dried at 120 ^oC under vacuum overnight. Finally, the black solid was calcined in air at 400 ^oC for 4 h.

2 Experiments

2.1 The computational formula

The conversion of sugars and the yield of the products (GVL) were quantified according to the following equations:

$$Conversion = \frac{moles\ of\ sugar(inlet) - moles\ of\ sugar(outlet)}{moles\ of sugar(inlet)} \times 100\%$$

$$Yield = \frac{moles\ of\ GVL\ produced}{moles\ of theoretical\ product\ value} \times 100\%$$

2.2 Procedures for the catalyst recycling

After the first run was completed, adding 5 g fructose into the reaction mixture. The reaction mixture changed into two phases, the top layer of GVL/GBL was collected. The solid Ru/TiO_2 catalyst, water, HPA, fructose and GBL were in the bottom layer. The water and GBL content in bottom layer was analyzed by GC. As the aqueous phase contains 5 g fructose, a certain amount of fresh HPA-Ru/TiO_2 catalysts, water and GBL were added to reach an identical reaction condition to the first run (fructose: HPA: Ru/TiO_2: water (20vol%)/GBL solvent=1 g : 0.4 g : 0.2 g : 10 ml) before each next run. Each recycling run was performed at 130 ^{o}C and 4 MPa H_2 pressure.

3 Catalyst characterizations

3.1 X-ray diffraction (XRD) measurements

Powder X-ray diffraction (XRD) patterns were obtained on a D2/max-RA X-ray diffractometer (Bruker, Germany), with Cu Kα radiation at 30 kV and 10 mA. The X-ray patterns were recorded in 2θ values ranging from 10° to 80° with a scanning speed of 4 °/min.

3.2 Transmission electron microscope (TEM)

TEM measurements were performed with a field-emission transmission electron microscopy (FETEM, JEM-2011F) operating at 200 kV voltages. The reduced samples were suspended in ethanol with an ultrasonic dispersion for 30 min and deposited on copper grids coated with amorphous carbon films.

3.3 N_2 adsorption-desorption isotherms of the Ru based catalysts

The catalysts were measured at -196 ^{o}C using a Mrcriomeritics ASAP2420 instrument after degassing at 300 ^{o}C to remove physically absorbed impurities for 8h in vacuum.

3.4 Inductively coupled plasma optical emission spectrometry (ICP-OES)

The content of phosphorus and tungsten in the GBL/GVL layer was analyzed by PerkinElmer Optima 2100 DV.

4. The direct conversion of fructose to GVL

Table S1 The direct conversion of fructose to GVL on combined HPA and various supported Ru catalysts [a]

Entry	Catalyst	LA yield/mol%	GVL yield/mol%
1	HPA-Ru/C	5.1	0.5
2	HPA-Ru/ZrO_2	6.6	10.2
3	HPA-Ru/Al_2O_3	7.5	3.5
4	HPA-Ru/SiO_2	0.8	11.4
5	HPA-Ru/TiO_2	4.8	16.3

a: 0.2 g of 2 wt% Ru/support catalyst, 180 ^oC, H_2, 4 MPa ; 1 g D-fructose, 20 ml water, reaction for 10 h, 0.2 g of HPA; no fructose was detected after the reaction in all experiment runs.

Table S2 The effect of acid amount on GVL yield in aqueous reaction [a]

Entry	T/^{o}C	HPA/g	GVL yield%
1	180	0.8	40.3
2	180	1.0	36.5
3	150	0.8	22.5
4	150	1.2	35.5
5	150	1.6	32.3
6	130	0.4	trace
7	130	0.8	22.6
8	130	1.2	41.8
9	130	1.6	39.6
10	120	1.2	17.5
11	120	1.6	29.1

a: 0.2 g of 2 wt% Ru/TiO_2 catalyst; H_2, 4 MPa, 1 g D-fructose, 20 ml water, reaction for 10 h; no fructose or LA was detected in each reaction run.

5. The results of catalyst characterization

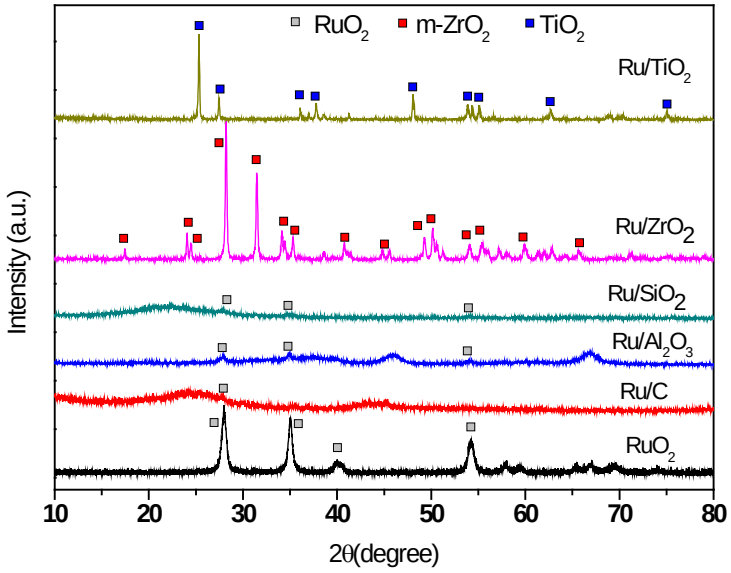


Figure S1 The XRD patterns of supported Ru catalysts

Table S3 Surface area (S_{BET}), average pore diameters (D_{pore}) and average pore volumes (V_{pore}) of Ru-support catalysts

Entry	Catalyst (2 wt%)	S_{BET} (m^2/g)	D_{pore} (nm)	V_{pore} (cm^3/g)
1	Ru/Al_2O_3	159.57	16.42	0.65
2	Ru/SiO_2	336.52	10.89	0.92
3	Ru/ZrO_2	2.68	69.03	0.05
4	Ru/TiO_2	4.34	30.43	0.03
5	Ru/C	1206.1	1.91	0.57

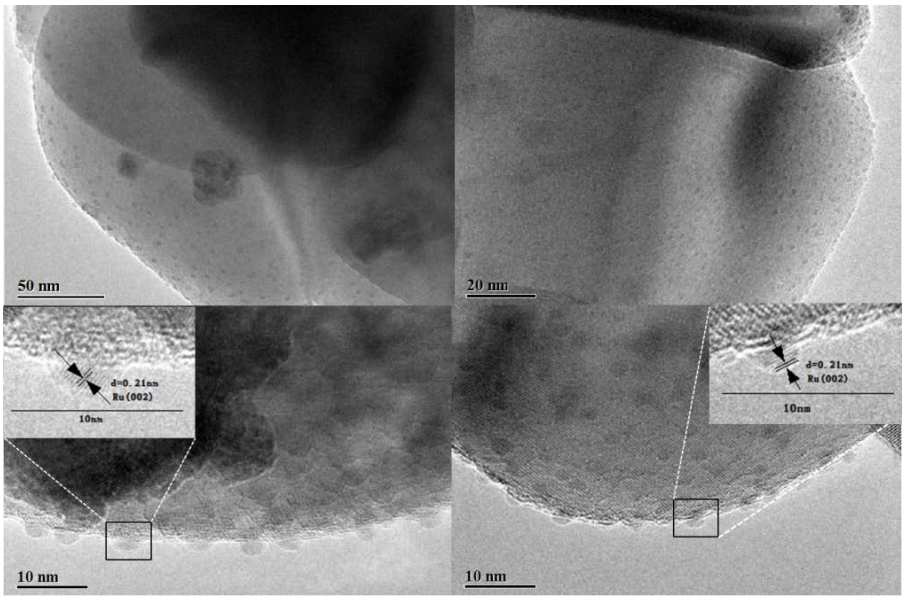


Figure S2 The TEM images of 2 wt% Ru/TiO_2 catalyst

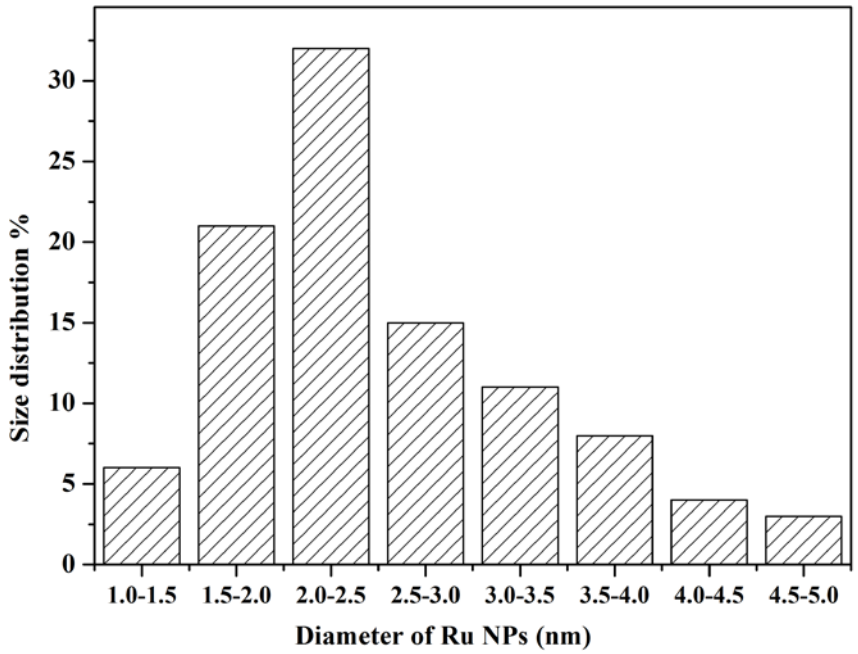


Figure S3 Size distribution of Ru nanoparticles

6. The comparison of reaction rate in water and water/GBL mixture

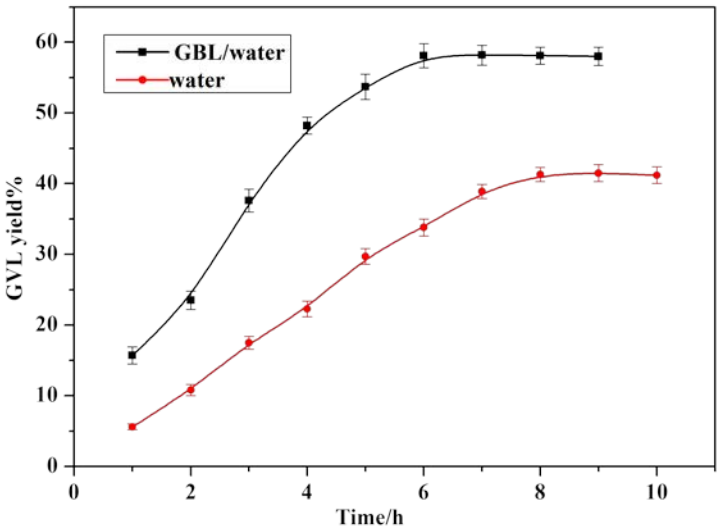


Figure S4 The conversion of fructose to GVL in water and water/GBL mixture. Reaction conditions: 1 g fructose, 130 ^{o}C, H_2, 4 MPa; HPA, 0.4 g; 20 ml solvent, 20 vol% water content for GBL/water mixture.

7. The carbon yield and relative carbon selectivity of various reactions

Table S4 The carbon yield and relative carbon selectivity in aqueous reaction [a]

Entry	T/°C	Carbon yield	Relative carbon selectivity %				
		mol%	GVL+FA	LA	HMF	DMF	Furan
1	180 [b]	22.3	76.2	17.9	-	3.7	2.2
2	180	28.6	95.6	-	-	2.1	2.3
3	180 [c]	41.8	96.4	-	-	2.5	1.1
4	150 [c]	23.6	95.8	-	0.6	1.7	1.9
5	130 [c]	23.1	96.8	-	0.9	2.3	-

a: 0.2 g of 2 wt% Ru/TiO_2 catalyst, 0.4 g $H_3PW_{12}O_{40}$; H_2, 4 MPa, 1 g D-fructose, 20 ml water, reaction for 10 h; b: 0.2 g $H_3PW_{12}O_{40}$; c: 0.8 g $H_3PW_{12}O_{40}$.

Table S5 The carbon yield and relative carbon selectivity in water/organic solvent [a]

Entry	Solvent	Carbon yield	Relative carbon selectivity %		
		mol%	GVL+FA	DMF	Furan
1	Methanol/water	16.8	98.5	1.1	0.4
2	Ethanol/water	23.6	98.2	0.9	0.9
3	1,4-dioxane/ water	42.1	98.8	0.3	0.9
4	GBL/Water	61.2	98.7	1.0	0.3
5	GBL/Water [b]	68.8	98.9	0.9	0.2

a: 0.2 g of 2 wt% Ru/TiO_2 catalyst, 0.4 g $H_3PW_{12}O_{40}$; H_2, 4 MPa, 1 g D-fructose, 20 ml 20 vol% water/organic solvent, 130 ^oC, reaction for 10 h; b: 10 ml 20 vol% water/GBL solvent.

8. LA hydrogenation in different solvents

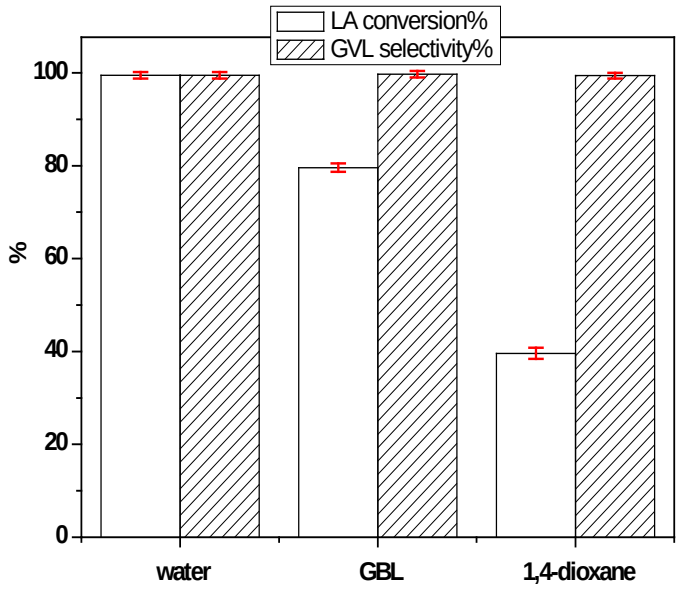
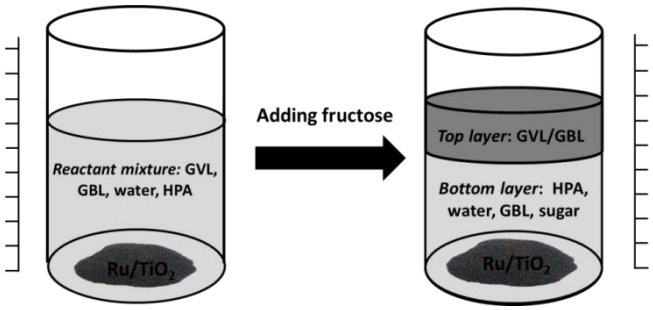


Figure S5 LA hydrogenation in different solvents. Reaction conditions: 1 g LA, 10 ml solvent, 130 ^{o}C, H_2 4 MPa, 0.2 g of 2 wt% Ru/TiO_2, reaction for 30 min.

9. The recycle of HPA and Ru/TiO_2 catalyst



(a)

(b)

Figure S6 The picture of reaction mixture separation: reaction mixture before separation (left sample), reaction mixture after adding 5g fructose (right sample).

Table S6 The compositions of the separated layers [a]

	Weight of adding fructose /g											
	2			3			4			5		
Weight/ Composition	*Layer Weight /g*	*GBL wt%*	*GVL wt%*	*Layer Weight /g*	*GBL wt%*	*GVL wt%*	*Layer weight /g*	*GBL wt%*	*GVL wt%*	*Layer Weight /g*	*GBL wt%*	*GVL wt%*
Top layer	2.1	72.1	12.1	1.8	73.2	15.2	1.6	75.5	19.9	1.4	73.9	23.8
Bottom layer	9.8	60.4	1.1	11.1	54.9	0.7	12.3	51.1	0.4	13.5	47.9	0.1
a: The weight and composition of original reactant mixture: 10 g, 20.5 wt% of water, 75.1 wt% of GBL, 3.4 wt% of GVL.												

Table S7 The content of lost $H_3PW_{12}O_{40}$ in the GBL/GVL layer [a]

Entry	Weight of adding fructose/g	Content of P μg/g	Content of W μg/g	W / P [b]	$H_3PW_{12}O_{40}$ in GBL/GVL layer /total $H_3PW_{12}O_{40}$ % [c]
1	2	12.9	882.7	68.4	0.89
2	3	12.2	891.3	73.1	0.68
3	4	11.3	785.1	69.5	0.52
4	5	<1	17.8	-	trace

a: The content of P and W was analyzed by ICP-OES; b: The W/P value of $H_3PW_{12}O_{40}$ is 71.2; c: the value of $H_3PW_{12}O_{40}$ in GBL/GVL layer / total $H_3PW_{12}O_{40}$ was calculated according the content of W.

10. The conversion of sucrose in GBL/water

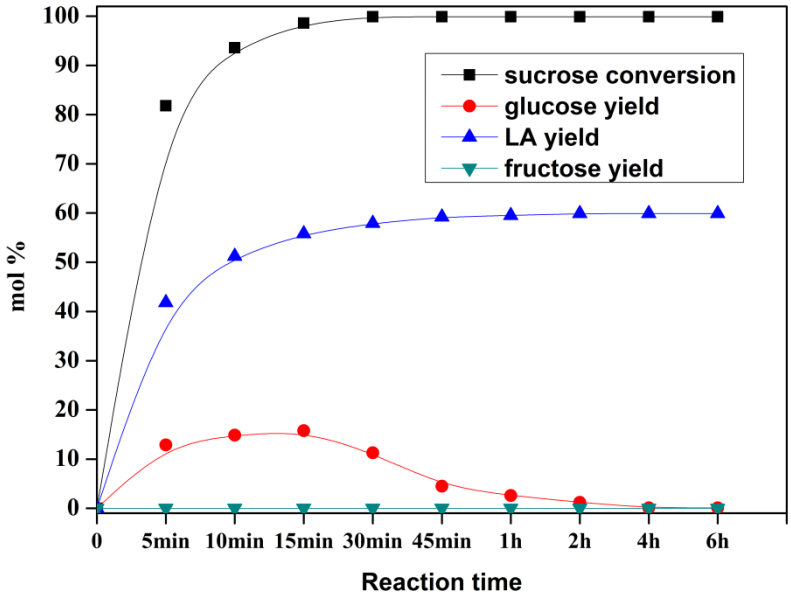


Figure S7 The conversion of sucrose in GBL/water. Reaction conditions:150 ^{o}C, 1 g sucrose, 0.4 g HPA, 10 ml 20 vol% water/GBL solvent.