Supporting information

1. Materials and Methods

1.1 Materials and analysis

Ethyl laevulinate (99%), Furfuryl alcohol (98%), 5-(Hydroxymethyl)furfural (HMF, 98%), acetonylacetone (>99%), CeO_2, TiO_2 were supplied by aladdin reagent co. ltd. Aluminium nickel (Al-Ni 50/50), was obtained from J&K chemical co. Itd.. Pt/C (5wt %), Pd/C (5wt %), Ru/C (5wt %) , Amberlyst-15, (3-mercaptopropyl) trimethoxysilane and D-fructose were purchased from Alfa Aesar. Pluronic P123, sodium metasilicate nonahydrate were purchased from Sigma. The other reagents, diethylene glycol dimethyl ether (AR Grade), NaOH (AR Grade), concentrated hydrochloric acid, anhydrous ethanol (AR Grade) 2-butanol (AR Grade), cyclohexanol (AR Grade),1-propanol (AR Grade) and isopropanol (AR Grade) were supplied by sinopharm chemical reagent co. ltd..

The reaction mixture was sampled, diluted 10 times in ethyl acetate and analyzed by GC-MS (Thermal Trace GC Ultra with a PolarisQ ion trap mass spectrometer) with either a TR-35MS or a TR-5MS capillary column (30m×0.25mm×0.25μm) and a shimazu GC equipped a AT-65 capillary column. Autosampler was used and split injection was performed at a split ratio of 50 using helium as carrier gas. Identification of compounds was carried out by comparison mass spectrum and retention time of pure chemical.

1.2 Preparation of solid catalysts

Preparation of Raney Ni[1]: Raney Ni catalyst was prepared by the following method: 10.0 g of Ni–Al alloy (weight ratio of 50 : 50) was slowly added to an aqueous solution of NaOH (6.0 M, 50 mL) under stirring over the ice water and control the temperature between 10-20℃ in 1 h. When finished, the solution was raised to room temperature. After half an hour, the reaction solution was heated to 90℃ slowly and stirred for 2 h until no H_2 bubbles. Then the mixture was cooled and the black precipitate was washed with distilled water to PH=7 and kept in water (or subsequently washed with anhydrous isopropanol to remove the water). The as-prepared Raney Ni catalyst was kept in anhydrous isopropanol or water.

Preparation of Ni/C, Ni/TiO_2, Ni/CeO_2[2]: supported Ni catalysts were prepared with Ni loading of 5 wt% by an impregnation method. A mixture of support and an aqueous solution of Ni nitrates were stirred for 12h, followed by drying at 90°C for 12 h, calcination in air at 350°C for 4 h, and reduction in H_2 at 500°C for 30 min. These catalysts were used for reaction without being exposed to air.

Preparation of AC-SO_3H[3]: Typically, the activated-carbon (1.0 g) was added into concentrated H_2SO_4 (18 mol/L, 20 mL) and heated under argon flow (40 ml/min) at 423 K (5 K/min) for 16 h. The resultant AC-SO_3H was washed repeatedly with hot distilled water (3 L) at 353 K. Furthermore, the black powder was hydrothermally pretreated at 473 K for 3 h and then washed again with the hot distilled water until sulfate ions are no longer detected in the wash water, to prevent elution of SO_4^{2-} ions under hydrothermal reaction media around 423 K.

Preparation of SBA-15-SO_3H[4]: Pluronic P123 (8.0 g) was dissolved in concentrated hydrochloric acid (81.0 g, 37 wt%) and the mixture heated at 40 °C. An aqueous solution of sodium metasilicate nonahydrate (21.8 g) in water (250 g) was added to the surfactant solution followed by (3-mercaptopropyl)trimethoxysilane, 3-MPTMS (1.0 g). The reaction gel mixture was then mechanically stirred at 40 °C for 24 h, transferred into a polypropylene bottle and aged at 100 °C for

24 h. The solid product was filtered off and washed with copious amount of water and ethanol separately, where after the surfactant was removed by Soxhlet extraction with ethanol for 24 h. The extracted material was oxidated with 30 wt% aqueous hydrogen peroxide (10.0 g per 0.3 g of catalyst) at room temperature for 24 h under argon atmosphere, filtered off and washed several times with water and ethanol. The wet material was finally suspended in 1 M sulfuric acid for 2 h, collected by filtration, washed with water and ethanol and dried at 60 °C under vacuum for several hours to obtain the final product SO$_3$H-SBA-15.

2   Experiment section

2.1   Catalytic Transfer hydrogenation of ethyl levulinate to GVL:

Ethyl laevulinate (1 mmol), Raney Ni catalyst (freshly prepared, wet, 0.1 g), 2-propanol (10 ml) were mixed in the schlenk tube and the mixture was vigorously stirred at room temperature under Ar atmosphere. The products were exampled and analyzed by gas chromatography, using diethylene glycol dimethyl ether as the internal standard.

2.2   Catalytic Transfer hydrogenation of ethyl levulinate to GVL

A. Alcoholysis of platform molecules to ethyl levulinic in the presence of solid acid catalyst:

The procedure for the alcoholysis of furfural alcohol is as follows: furfural alcohol (98 mg, 1 mmol), ethanol (2 mL), and solid acid catalyst such an Amberlyst-15 (30 mg), were added to a thick-walled cylindrical pressure-resistant bottles (15 ml). The mixture was heated at 120℃ under vigorous stirring for 20 h. After that, the mixture was analyzed by gas chromatography, using acetonylacetone as the internal standard. The procedure for the alcoholysis of HMF and D-fructose is the same as furfuryl alcohol.

B. Conversion of ethyl levulinate to GVL:

After alcoholysis, the mixture was cooled to room temperature. The sample was filtered by a hydrophobic microporous membrane (45 μm) to separate the solid acid catalyst. Then the catalyst Raney Ni (wet, 0.1 g) and 2-PrOH were added to the filtrate, the mixture was stirred at room temperature under Ar atmosphere for 9 h. The mixture was analyzed by gas chromatography, using diethylene glycol dimethyl ether as the internal standard.

To improve the GVL yield, the ethyl levulinate solution was separated with a rotary evaporator under reduced pressure. The solvent EtOH and ethyl levulinate was distilled by evaporation and remained insoluble humins and other by products in the flask. After that, ethyl levulinate was transferred into a schlenk tube filled with Ar. Then the catalyst Raney Ni (wet, 0.1 g) was added to tube, the mixture stirred at room temperature under Ar atmosphere for 9h. The mixture was analyzed by gas chromatography, using diethylene glycol dimethyl ether as the internal standard.

2.3 Recovery and reuse Raney Ni catalyst

The Raney catalyst was filtered and washed with isopropanol for three times. Then the catalyst was used for next run. The filtrate were collected and further analyzed by gas chromatography, using diethylene glycol dimethyl ether as the internal standard.
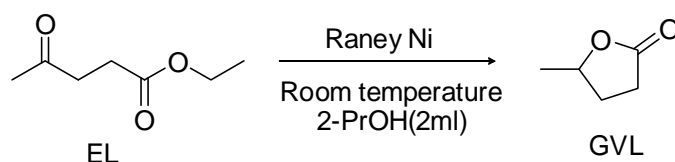
3. Optimization of the reaction

3.1 Optimize the reaction time:

EL → GVL
Raney Ni(0.1 g)
Room temperature
2-PrOH(2ml),Ar
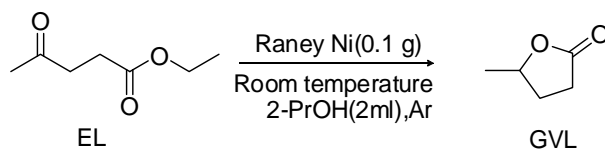
Entry	t/h	GC Yield(%)
1	0.5	46
2	1	67
3	2	87
4	3	89
5	6	93
6	9	>99
7	12	>99

Condition: EL (1mmol), Raney Ni (freshly prepared and kept in 2-PrOH, wet), Ar.

3.2 Optimize the other reaction conditions:

EL → GVL
Raney Ni
Room temperature
2-PrOH(2ml)

Entry	Raney Ni/g	Reaction condition	T/℃	t/h	GC Yield(%)
1	0.1	Under air	r.t.	9	69
2	0.1	Under air	40.	9	92
3	0.1	Under air	60	9	95
4	0.1	Under air	80	9	99
5	0.2	Under air	r.t.	9	85
6	0.2	Under air	r.t.	18	99
7	0.1	Under Ar	r.t.	9	99
8	0.05	Under Ar	r.t.	9	95

Condition: EL (1mmol), Raney Ni (freshly prepared and kept in 2-PrOH, wet).

3.3 Recovery and reuse of Raney Ni for catalytic transfer hydrogenation of ethyl levulinate:

Recycle times	1	2	3	4	5
GVL yield (%)	99	95	89	84	84

Condition: EL (1mmol), Raney Ni (freshly prepared and kept in 2-PrOH, wet, 0.1g), r.t., 9h, Ar.

3.4 Conversion of lignocellulosic derivatives to levulinate esters by using Amberlyst-15 as the acid catalist for the first step and using Raney Ni for catalytic transfer hydrogenation of the levulinate esters from the first step:

| First step | | | Second step | |
Substrate	Solvent	Yield(%)	T/℃	Yield(%)
Furfural alcohol	EtOH	95	r.t.	6
			100	92
			r.t.	86[a]
HMF	EtOH	74	r.t.	9
			100	63
			r.t.	66[a]
Fructose	EtOH	55	r.t.	2.4
			100	49
			r.t.	50[a]

Condition: (first step) substrate (1mmol), Amberlyst-15 (30 mg), EtOH (2 ml), 120ºC, 12h; (second step) Raney Ni (freshly prepared and kept in 2-PrOH, wet, 0.1g), 2-PrOH (2ml), r.t., 9h, Ar. [a] EL was separated by vacuum distillation and used in the second step

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