

Electronic Supplementary Information (ESI)

Selective hydrogenation of butyl levulinate to γ -valeractone over sulfonated activated carbon-supported SnRuB bifunctional catalyst

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Experimental

Materials

Butyl levulinate (BL, 98%), 1,4-pentanediol (1,4-PDO, 98%) and NaBH₄ (98%) are purchased from Aladdin Reagent Co. Ltd. (Shanghai, China); γ -valerolactone (GVL, 98%) and Stannous chloride (SnCl₂ · 2H₂O, 99%) are obtained from Macklin biochemical Co. Ltd. (Shanghai, China); Ruthenium (II) chloride trihydrate (RuCl₃ · 3H₂O) is purchased from Energy Chemical Reagent Co., Ltd. (Shanghai, China). n-Butyl alcohol (n-BuOH) and absolute ethyl alcohol (EtOH) are purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sulfuric acid (SA) is purchased from Guangzhou Chemical Reagent Factory. Activated carbon (AC) is provided by ZHONGKE New Energy Technological Development Co., Ltd (Huai-An, China). All reagents are used without any further purification.

Catalyst preparation

The commercial AC was used as feedstock to prepare SAC by excessive sulphuric acid sulfonation method. First of all, 5 g AC and 27.2 mL SA with a solid-liquid mass ratio of 1:10 were added into a three-necked flask which was inserted by a thermometer and reflux condensation device. The flask was placed in an oil bath to conduct the sulfonation reaction at 160 °C for 5 h under constant stirring with a rate of 200 rpm. And then, the flask was transferred into an ice-water bath to terminate the reaction and two times volume of deionized water was added. The samples were filtered and washed until the filtrate was neutral. The filter cake was dried in an air dry oven at 100 °C overnight to obtain SAC.

The SAC supported SnRuB catalysts with different Sn/Ru mass ratio were prepared by an

impregnation-reduction method using NaBH_4 as the reduction agent¹. Typically, for the preparation of SAC supported 20Sn1RuB catalyst, firstly, 1.93 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 2.57 g RuCl_3 aqueous solution with a mass fraction of 3.24 wt% were dissolved thoroughly in a beaker. And then, 3 g SAC and 3.29 g deionized water were slowly added to the beaker and mixed homogeneously, subsequently, impregnated under vacuum at room temperature for 24 h. The catalyst precursor gel was dried at 105 °C overnight and then squashed and sieved to powder with particle size of larger than 100 mesh. The precursor powder was reduced by adding dropwise 18.01 g of NaBH_4 and NaOH mixed aqueous solution with respective mass fraction of 7.5 wt% and 0.73 wt% under vigorous stirring and continuous nitrogen flow in an ice-water bath. The stirring lasted for 3.0 h to ensure the complete reaction of metallic ions impregnated on SAC. The precipitate was washed with deionized water several times until the filter liquor was neutral, followed by washing with absolute ethyl alcohol three times to remove residual water and water-soluble impurities¹. The obtained catalyst was named as 20Sn1RuB/SAC and kept in absolute ethyl alcohol for future use. For comparison, other catalysts including 1RuB/SAC, 5Sn1RuB/SAC, 13Sn1RuB/SAC, 25Sn1RuB/SAC and 20SnB/SAC were also prepared according to the above procedure through changing the concentration of metallic ions and NaBH_4 solution. In addition, the 20Sn1RuB/SAC catalyst was also dried at 120 °C under flowing N_2 for 2 h and further reduced by H_2 with a flow rate of 50 mL/min for 3 h at 300 and 500 °C in a quartz tube, and the obtained samples are named as 20Sn1RuB/SAC-H300 and 20Sn1RuB/SAC-H500, respectively.

Catalyst characterization

The bulk composition of the catalysts was detected by the OPTIMA 8000 inductively coupled plasma–optical emission spectroscopy (ICP-OES) (PerkinElmer). The Brunauer–Emmett–Teller

surface area (S_{BET}), total pore volume (V_p), and average pore diameter (D_p) of the supports and catalysts were determined by N_2 adsorption/desorption isotherms at 77 K using a Model ASIQMO002-2 analyzer (Quantachrome, USA). The samples were degassed at 80 °C for 6 h before measurement. X-ray diffraction (XRD) patterns of the supports and catalysts were measured using a D/max-RA X-ray diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) operated at 40 kV and 40 mA on a 2θ range of $5^\circ - 80^\circ$. Fourier transform infrared spectroscopy (FTIR) spectra of AC, SAC and SAC supported SnRuB catalyst were recorded with a Frontier FTIR spectrometer (Perkin-Elmer, Germany) in the range of $4000\text{-}500 \text{ cm}^{-1}$. X-ray photoelectron spectroscopy (XPS) measurement of fresh and used catalysts was carried out on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, Inc., USA) with $\text{Al K}\alpha$ radiation to determine the surface atomic ratios and valence states of elements. The C1s peak has been fixed at a binding energy (BE) of 284.8 eV to subtract the surface charging effect. High-resolution transmission electron microscopy (HRTEM) analysis and selected-area electron diffraction (SAED) were performed on a Model JEM-2100F microscope (JEOL, Japan) operating at 200 kV. The element distribution was detected by Energy Dispersive Spectrometer (EDS) mapping. A small amount of sample was dispersed in ethanol under ultrasonication before testing and several droplets of dispersion liquid were placed on carbon-coated copper grids.

NH_3 - temperature programmed desorption (NH_3 -TPD) of support and catalyst was carried out using a ChemBET Pulsar-1 automated chemisorption analyzer (Quantachrome, US) from 50 to 800 °C. The desorbed ammonia was recorded by a thermal conduct detector (TCD). FTIR of pyridine adsorption technique was performed on a Frontier FTIR spectrometer (Perkin-Elmer, Germany) equipping with an in-situ pool. Before adsorption, the samples were heated at 350 °C for

2 h in vacuum to remove water adsorbed on the surface, and then cooled to room temperature. Afterwards, the samples were exposed to liquid pyridine for 30 min. The total acid and strong acid spectra were recorded after desorption pyridine at 150 and 350 °C, respectively.

Catalytic tests and product analysis

The BL hydrogenation reaction was carried out in a 100 mL YZPR-100 (M) stainless steel autoclave. In a typical catalytic test, BL (2 mL, 1.938 g), 20Sn1RuB/SAC catalyst (0.464 g) and cyclohexane (23 mL) were introduced into the reactor. The autoclave was first purged by repetitively filling N₂ four times and H₂ three times, and then filled with 3.0 MPa H₂ and heated to 180 °C with a stirring rate of 800 rpm. After reaction for 3 h, the used catalyst and liquid product were separated by vacuum filtration. The spent catalyst was washed by cyclohexane and absolute ethyl alcohol respectively for three times, subsequently was stored in absolute ethyl alcohol for next use. The obtained liquid product was qualitatively analyzed by a TRACE 1300-ISQ gas chromatography - mass spectrometry (GC-MS) (Thermo Fisher Scientific Inc, US) equipped with an Agilent HP-5 MS column (5% phenyl methyl silox, 30 m × 0.25 mm × 0.25 μm). Helium (99.999%) was used as the carrier gas. The column temperature was programmed from 50 °C to 250 °C at 10 °C/min and held for 5 min. The components were identified through a mass spectral library (NIST 2014). The liquid product was then quantitatively analyzed on a 7890A gas chromatograph (Agilent, US) equipped with a FFAP column (30 m × 0.25 mm × 0.25 μm) and flame ionization detector (FID). Helium (99.999%) was used as the carrier gas with a flow of 30 mL/min. The injector temperature was 230 °C and detector temperature was 250 °C. The oven temperature was programmed from 60 to 230 °C at a rate of 10 °C /min. The BL conversion (C_{BL}), selectivity (S_M) and yield (Y_M) of M product were calculated according to Eqs. (1)-(3), respectively.

$$C_{BL}(\text{mol}\%) = \left(1 - \frac{n_{0BL}}{n_{tBL}}\right) \times 100\% \quad (1)$$

$$S_M(\text{mol}\%) = \frac{n_{tM}}{n_{0BL} \times C_{BL}} \times 100\% \quad (2)$$

$$Y_M(\text{mol}\%) = C_{BL} \times S_M \times 100\% \quad (3)$$

Where n_{0BL} , n_{tBL} and n_{tM} stand for the molar concentration of initial BL, final BL and final M product, respectively.

The turnover frequency (TOF) of BL hydrogenation to GVL was calculated according to the equation (4) as reported in our previous work ²:

$$\text{TOF} = \frac{n \times Y}{N \times t} \quad (4)$$

Here n is the molar amount of BL used in the reaction feedstock, Y the yield of GVL, N the number of surface Sn and Ru atoms and t the reaction time. The unit of TOF is per hour (h^{-1}). N was calculated by the equation (5):

$$N = (n_{Sn} + n_{Ru}) \times D \quad (5)$$

, here n_{Sn} and n_{Ru} is the mole amount of Sn and Ru in the catalyst, respectively. D is the dispersion of SnRuB active site and is calculated according to the statistical size of SnRuB particles from HRTEM.

Table S1. Comparison of hydrogenation performances of levulinic acid and its esters to GVL using H₂ in batch reactor.

Substrate	Catalyst	Catalyst dosage ^a (wt%)	Solvent	Temperature (K)	Pressure (MPa)	Time (h)	Conversion (%)	GVL yield (%)	Reference
Levulinic acid	4.5Ir/CNT	8.3	CHCl ₃	323	2	1	93	91	3
	1Ru/ZSM-5	12.0	Dioxane	473	4	4	100	50	4
	5Pt/HAP	5.0	H ₂ O	343	0.5	4	42	37	5
Methyl levulinate	5Ru/C	12.6	methanol	403	3.45	2	95	91	6
Ethyl levulinate	1Ru/CeO ₂ -rod	3.5	H ₂ O	373	4	15	100	99.4	7
	2Ni/AC	34.7	isopropanol	523	1	2	99.7	79.8	8
	5Ru/C	12.6	ethanol	403	3.45	2	98	78.4	6
	2.8Cu-3.5Fe/SBA-15	69.4	hexane	413	3	3	97	95.8	9
Butyl levulinate	Cu _{0.5} Ni ₁ Co ₃ B	3.0	cyclohexane	473	3	3	99.7	89.5	10
	20Cu _{0.25} Mo _{0.25} Ni ₁ Co ₁ B/H ⁺ -PAL	15.0	cyclohexane	473	3	1	100	95.7	2
	5Ru/C	12.6	butanol	403	3.45	2	97	58.2	6
	20Sn1RuB/SAC	23.9	cyclohexane	453	3	3	99.2	83.1	This work

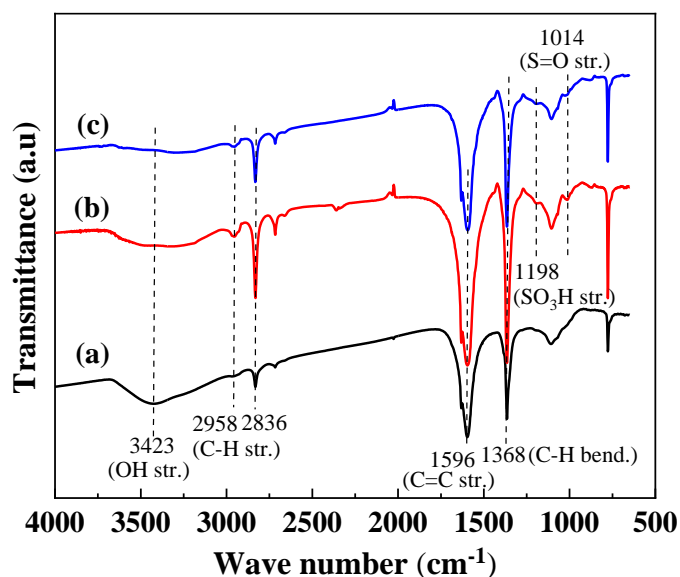


Fig. S1 FTIR spectra of (a) AC, (b) SAC and (c) 20Sn1RuB/SAC.

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