Supporting Information

Zn-regulated carbon-coated Ni-based carbides for promoting hydrogenation of ethyl levulinate

Siyi Pu, [a‡] Dejin Huang, [a‡] Chunyan Yang, [a] Ying Wang, [a] Chungang Min, [b] Xiaoqin Zou, [c*] Changfu Zhuang [a*]

[a]Key Laboratory of Forest Resources Conservation and Utilization in the Southwest Mountains of China Ministry of Education, Southwest Forestry University, Kunming 650051, P. R. China.

[b]Research Center for Analysis and Measurement, Kunming University of Science and Technology, Kunming 650093, P. R. China.

[c]Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China.

Contents

Experimental Section

Material

$Ni(NO_3)_2·6H_2O$, $Zn(NO_3)_2·6H_2O$ were purchased from Adamas Reagent Co., Ltd. N, N-dimethylformamide, triethylenediamine, benzoic acid, KSCN, Isopropanol and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,3,5-benzenetricarboxylic acid (BTC) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. EL was purchased from Shanghai Titan Technology Co., Ltd. The purity of all chemicals in the experiment was analytically pure and could be used without further treatment.

Synthesis of the precursor Ni_xZn_y-BTC

Ni_xZn_y-BTC was synthesised by hydrothermal method. First, 7.5 mmol of $Ni(NO_3)_2·6H_2O$ and 2.5 mmol of $Zn(NO_3)_2·6H_2O$ were weighed into a round bottom flask, 70 mL of N, N-dimethylformamide was added and stirred until dissolved. Then 5 mmol triethylenediamine and 10 mmol BTC were weighed in a beaker, and 80 mL N, N-dimethylformamide was added to dissolve the solid and transfer it to a round-bottom flask. After cooling to room temperature, the product was separated by filtration, and the sample was washed three times with N, N-dimethylformamide and ethanol, and dried under vacuum at 80 °C for 12 h. The Ni_3Zn_1-BTC was obtained by grinding and homogenising. Ni-BTC, Zn-BTC, Ni_9Zn_1-BTC, Ni_1Zn_1-BTC and Ni_1Zn_3-BTC were also synthesised by the method described above, the total amount of metal was fixed at 10 mmol, then the molar ratio of each metal added was adjusted and the molar ratio of metal to ligand was kept constant. The only difference was the different ratios of the two metals (Ni:Zn= 10:0, 9:1, 7.5:2.5, 5:5, 2.5:7.5 and 0:10) corresponding to a series of Ni_xZn_y-BTC (Ni-BTC, Ni_9Zn_1-BTC, Ni_3Zn_1-BTC, Ni_1Zn_1-BTC, Ni_1Zn_3-BTC and Zn-BTC).

Preparation of Ni_xZn_y@C

About 1g Ni_xZn_y-BTC precursor was put into a magnetic boat, and then placed in a tube furnace. Argon gas was first introduced for 1 h, and the air in the tube was fully eliminated. The precursor was heated to 600 °C at a heating rate of 5 °C min^{-1} and maintained for 2 h, then cooled to room temperature and removed. According to the different components, the material was named Ni_xZn_y@C, which was used for catalytic reaction without further treatment.

Evaluation method of catalytic performance

The reaction of EL catalytic hydrogenation to GVL was carried out in a 25 mL autoclave reactor. 144 mg (1 mmol) EL, 50 mg catalyst and 8 mL isopropanol were added to the reactor. First, H_2 was used for gas exchange three times, and then pressurized to 2 MPa. At a stirring rate of 800 rpm, it was heated to a set temperature at a rate of 5 °C min^{-1} and reacted for 4 h. After the reaction, it was cooled to room temperature, and the liquid sample was separated by filter membrane for gas chromatography test. The products in the liquid phase were distinguished by gas chromatography-mass spectrometry (GCMS-QP2010 SE, Shimadzu), and quantitatively analyzed by GC (GC-7890A, Agilent) equipped with FID detector. The yield of FOL (%) is the product of reactant conversion (%) and product selectivity (%). The reactant conversion and product selectivity are defined as follows:

$$\text{Conversion (\%)} = \frac{\text{Mole of } EL \text{ converted}}{\text{Mole of } EL \text{ loaded}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{Mole of GVL produced}}{\text{Mole of product produced}} \times 100\%$$

Characterization method

Powder X-ray diffraction (XRD) patterns was performed on a Rigaku Ultima X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) analysis was obtained on the PHI5000 VersaProbe-II scanning XPS microprobe system. High-resolution transmission electron microscope (HR-TEM) was performed on a JEM-2100 instrument equipped with an energy dispersive X-ray spectrometer (EDS). Temperature programmed desorption (TPD) of NH_3 and H_2 was performed in an AutoChem1 II 2920. The samples were first pretreated in a He (NH_3-TPD)/Ar (H_2-TPD) gas stream (30 $mL\cdot min^{-1}$) at 150 °C for 60 min, then cooled naturally to 50 °C and saturated with NH_3/H_2 (30 $mL\cdot min^{-1}$) for 1 h. The desorption process was carried out at 600 °C (NH_3-TPD)/800 °C (H_2-TPD) with a heating rate of 10 $°C\cdot min^{-1}$ and detected by TCD.

Calculation method

Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) program. The generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) is used to describe the exchange correlation. The plane wave uses a cutoff energy of 400 eV, and the ion positions of all structures are relaxed until the force converges below -0.03 $eV\cdot Å^{-1}$. Using 1 × 2 × 1 group of k points. The vacuum space between the plates along the z direction is set to a minimum of 15 Å.

The adsorption energies (E_{ads}) of EL is defined as:

$$E_{ads} = E_{total} - (E_{slab} + E_g)$$

where E_{total} is the total energy after adsorption; E_{slab} is the energy of a separate clean plate, and E_g is the energy of EL in the gas phase.

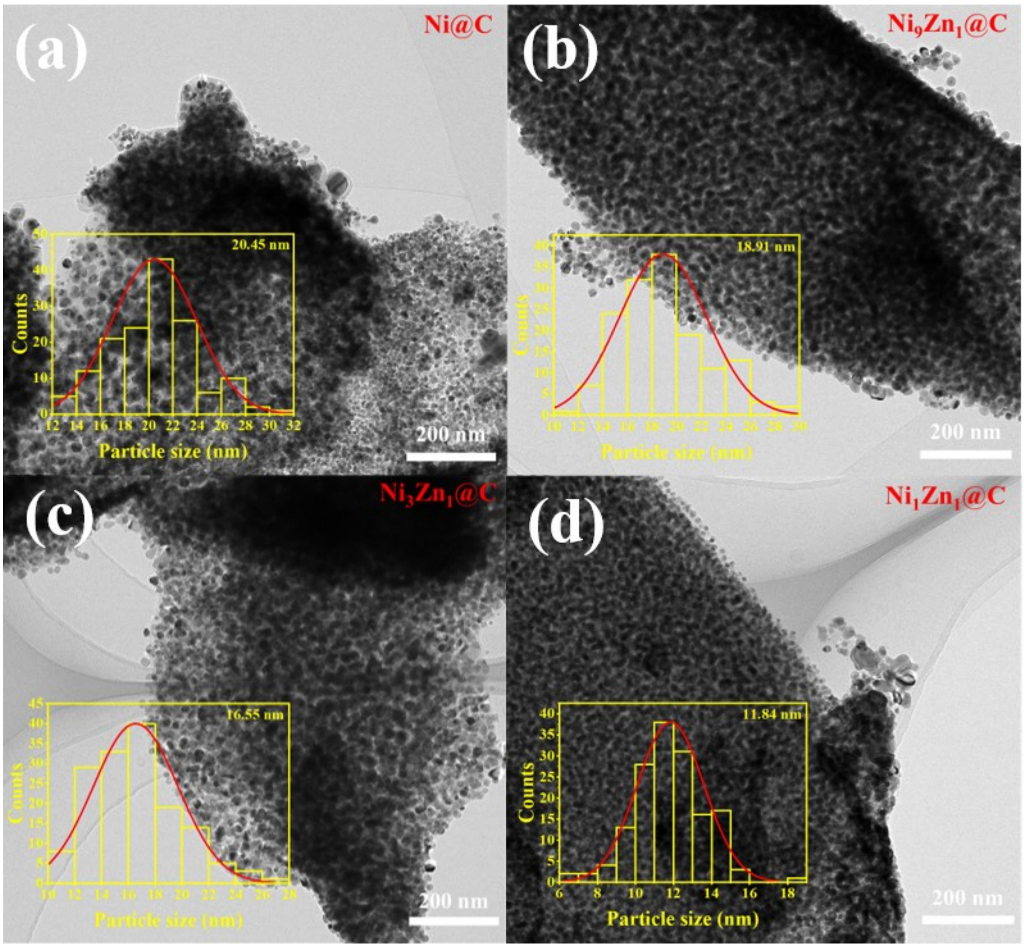

Figure. S1 (a-d) TEM images and particle size distribution of $Ni_xZn_y@C$.

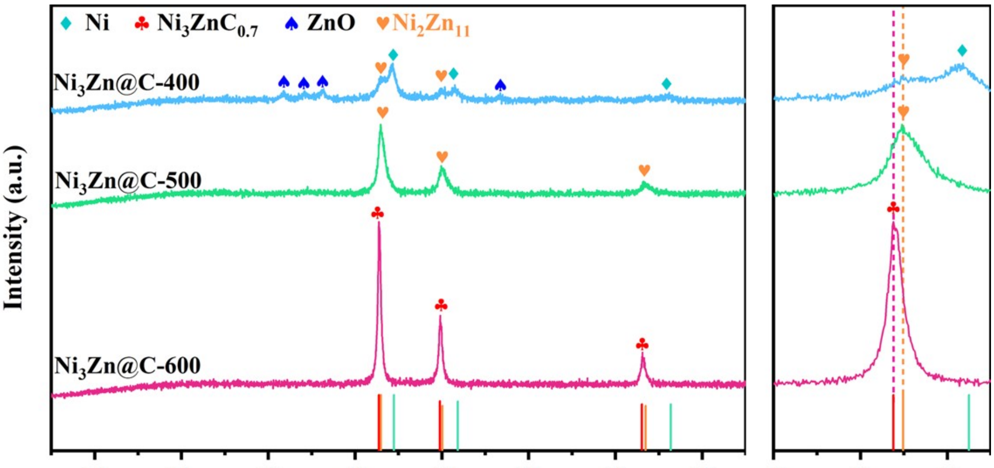

Figure. S2 Powder XRD patterns of $Ni_3Zn@C$ at different temperatures.

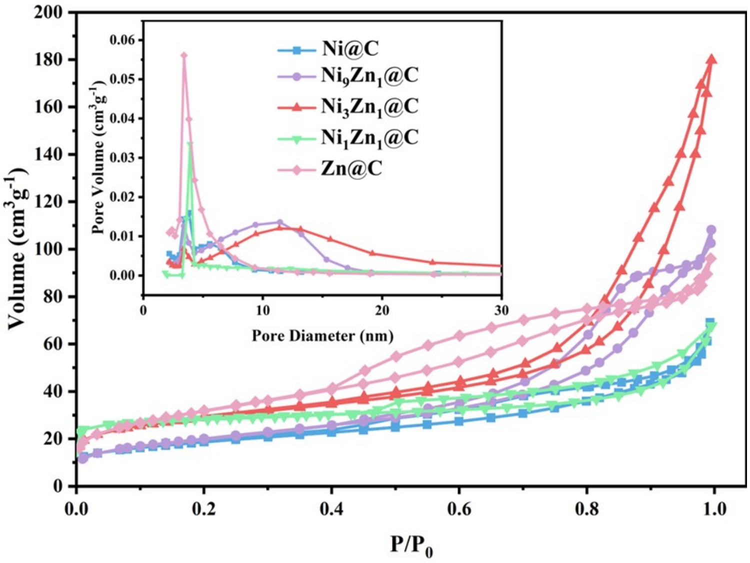

Figure.S3 Nitrogen adsorption-desorption curves and pore size distribution of Ni_xZn_y@C catalyst samples

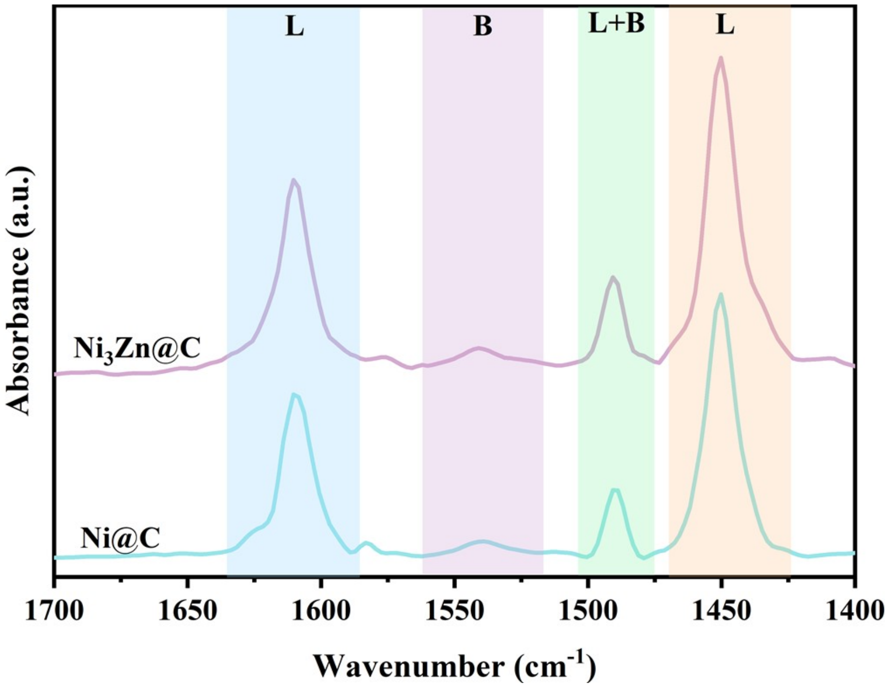

Figure.S4 Pyridine infrared spectra of Ni_3Zn@C and Ni@C

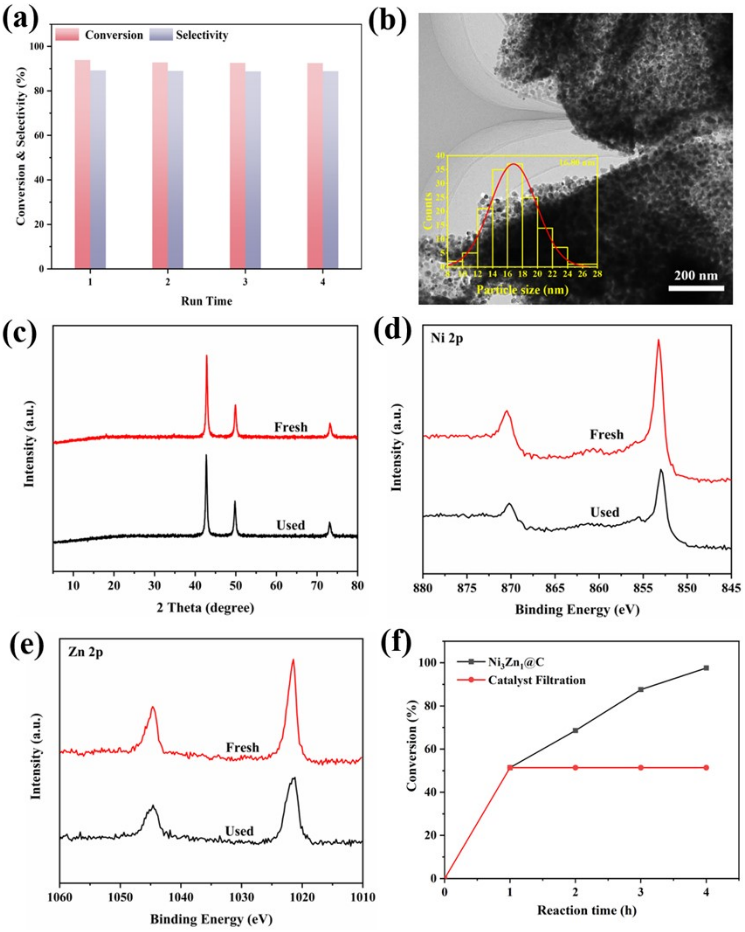

Figure S5 (a) Reusability of Ni_3Zn_1@C in EL hydrogenation (Reaction conditions: 1 mmol EL, 8 mL isopropanol, 50 mg catalyst, 6 h, 2 MPa H_2, 150 °C), (b) TEM image and particle size of used Ni_3Zn_1@C, (c) XRD of fresh and used Ni_3Zn_1@C, (d)-(e) XPS spectra of Ni 2p and Zn 2p of fresh and used Ni_3Zn_1@C, (f) metal leaching experiment of Ni_3Zn_1@C.

Table S1 Structural parameters of Ni_xZn_y@C catalyst samples

Sample	S_{BET}^{a} (m^2 g^{-1})	Pore Size^{a} (nm)	Pore Volume^{a} (cm^3 g^{-1})	Metal particle size^{b} (nm)
Ni@C	65.44	7.89	0.10	20.45
Ni_9Zn_1@C	72.44	8.22	0.17	18.91
Ni_3Zn_1@C	100.36	13.6	0.27	16.55
Ni_1Zn_1@C	109.15	9.31	0.10	11.84
Zn@C	114.23	5.62	0.14	--

a: by ASAP 2020 Plus. b: by TEM.

Table S2 Hydrogen consumption of different catalysts in H_2-TPD.

Entry	**Catalyst**	**Temperture (℃)**	**Quantity(mmol/g)**
1	Ni@C	159	0.003
		414	0.047
2	Ni_3Zn_1@C	161	0.005
		476	0.068

Table S3 The acid content of different catalysts in NH_3-TPD.

Entry	**Catalyst**	**Temperture (℃)**	**Quantity(mmol/g)**
1	Ni@C	124	0.001
		438	0.085
2	Ni_3Zn_1@C	200	0.014
		549	0.254

Table S4 Quantitative Py-IR acidic site data for Ni_3Zn@C and Ni@C

Sample	**B acidic/μmol g^{-1}**	**L acidic/μmol g^{-1}**	**Total/μmol g^{-1}**	**Ratio of B to L acidic**
Ni_3Zn@C	3.87	34.52	38.39	0.11
Ni@C	3.77	29.53	33.30	0.13