Supporting information

Sustainable production of γ-valerolactone and δ-valerolactone through the coupling of hydrogenation and dehydrogenation

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1 Materials

Ethyl levulinate (analytical grade, 98%), γ-valerolactone (analytical grade, 98%), 1,5-pentanediol (analytical grade, 98%), δ-valerolactone (analytical grade, 98%) were obtained from Shanghai Aladdin Co., Ltd. $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and Na_2CO_3 were purchased from Sinopharm Chemical Reagent Co., Ltd.. All the above agents were utilized without further purification.

2. Experiments

Preparation of catalyst

The CuZnAl catalysts used in the experiments were prepared via conventional coprecipitated method. In the process, a solution of mixed $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Al(NO_3)_3$ (1 M of total metal ions) was used as metal precursors, with a 1 M Na_2CO_3 solution added as the precipitating agent. During the drop process, the pH value of the mixed solution was kept in the range of 6.0–7.0, and the obtained slurry was further aged for 1 h. Then the suspension was washed with deionized water 3–5 times and filtered. After this, the precipitant was dried in air at 100 °C for 12 h. Subsequently, the obtained precursor was calcined at 450 °C for 4 h in static air.

Activity test and analysis method

The single hydrogenation/dehydrogenation and the coupled reactions were performed in a continuous fixed-bed reactor. The reactor (600 mm long, 12 mm i.d.) was packed with a suitable amount of catalysts (20–40 mesh), which were located in the thermostat segment of the fixed-bed reactors. Velocity of H_2 and substrates were controlled by a mass flow meter and a constant flux pump respectively, so the ratio of hydrogen to reactants (n(H_2):n(Liquid)) can be fixed at a constant value. The catalyst was pre-reduced with H_2 before reaction, and at the same time the temperature was progressively increased from ambient temperature to 260°C. The reactions were performed at different temperatures at 0.2MPa, and the products were collected and then analyzed by a GC instrument with an FID detector.

3. Analysis of products

The products were analyzed using GC (Agilent 7890 A) equipped with AB DM-WAX column (30 m×0.32mm×0.25μm) and a flame ionization detector (FID). The standard solutions were used to obtain the calibration curves to calculate concentrations of the compounds by external standard

method.

The conversion of substrates and the yields or selectivity of the products were quantified according to the following equations:

$$\text{Conversion (\%)} = \frac{\text{Mole of substrates converted}}{\text{Mole of FOL fed (mol)}} \times 100$$

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

$$\text{Yield (\%)} = \text{Selectivity (\%)} \times \text{Conversion (\%)}$$

4. Catalyst characterizations

Thermogravimetric Analysis (TGA)

TGA experiments of precursors were performed on a Mettler Toledo TGA/SDTA 1 instrument with a heating rate of 10°C min^{-1} (air atmosphere).

X-ray diffraction (XRD) measurements

Powder X-ray diffraction (XRD) patterns were obtained on a D8 ADVANCE A25 X-ray diffractometer (Germany), with Cu Kα radiation at 30kV and 10mA. The X-ray patterns were recorded in 2θ values ranging from 10° to 80° with a scanning speed of 4 °/min.

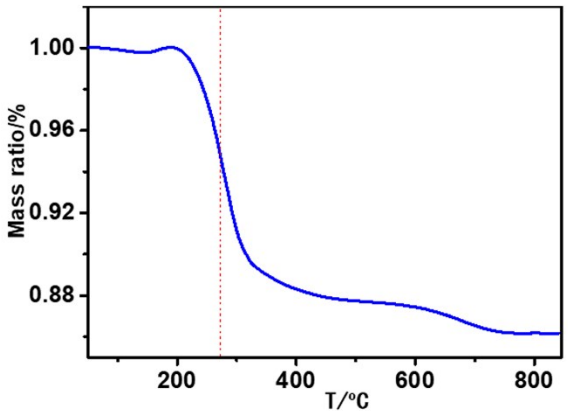

Figure S1 TGA curves of the used CuZnAl catalysts recorded at 10℃/min

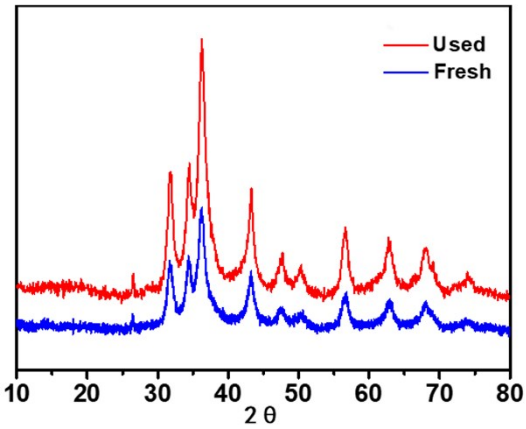

Figure S2 XRD patterns of the fresh and used CuZnAl catalysts