

## Supporting Information

### **Nanofibers and amorphous Ni/Al<sub>2</sub>O<sub>3</sub> catalysts — Effect of steric hindrance on hydrogenation performance**

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## Experimental

### Materials

All the chemicals used in this study were analytical grade. Furfural, 5-hydroxymethylfurfural (HMF) and polyvinyl pyrrolidone (PVP,  $(C_6H_9NO)_n$ , Relative molecular mass =  $1.3 \times 10^6$ , K88-96) were purchased from Shanghai Macklin Biochemical Co., Ltd. Nickel nitrate hexahydrate, aluminium nitrate nonahydrate, ethanol and N,N-dimethylformamide were purchased from Sinopharm Chemical Reagent Co., Ltd.

### Catalysts preparation

The amorphous Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by an incipient wetness impregnation method. Before the impregnation, the carrier of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Zibo HANLU Environmental Protection Technology Co., Ltd.; Specific surface area: 230.7 m<sup>2</sup>/g; Water absorption capacity  $\geq$  49%; Particle size: 0.5–1.0 mm) was washed several times with distilled water to remove dust and impurities from the surface. A certain amount of nickel (II) nitrate hexahydrate was dissolved in distilled water (accurately calculated based on the water absorption capacity of alumina). After that, the carrier was mixed with the solution and placed at room temperature for the liquid to fully fill the pores of the carrier. After the step of aging, the catalyst precursors was firstly placed in the oven (105°C). Until the moisture absorbed by the catalyst was completely evaporated, the samples were then calcined in the muffle furnace at 600°C for 2 h in static air to obtain the amorphous Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

The nanofibrous Ni-Al<sub>2</sub>O<sub>3</sub> catalyst was synthesized by a electrospinning method. The mixture of C<sub>3</sub>H<sub>7</sub>NO/C<sub>2</sub>H<sub>6</sub>O with the volume ratio of 4 was used as a solvent. PVP was added into the mixture of C<sub>3</sub>H<sub>7</sub>NO/C<sub>2</sub>H<sub>6</sub>O to increase viscosity of the solution. After that, a certain amount of nickel (II) nitrate hexahydrate and aluminium nitrate nonahydrate (the Ni content of 20%) were added and the salt concentration was maintained at 8%. Finally, the solution was gently stirred at room temperature for 12 h. Ucalery ET-2535H (Beijing, China) was used for the electrospinning experiment. The voltage applied on the syringe tip and collector were 18.5 kV and -5 kV, respectively. The liquid was propelled at a speed of 0.02 mL/min under the control of the electrospinning machine and the collector was placed 20 cm from the syringe tip.

After that, the catalyst was calcined at 800°C for 2 h to obtain the nanofibrous Ni-Al<sub>2</sub>O<sub>3</sub> catalyst.

### **Catalytic tests**

The hydrogenation experiments were carried out in an autoclave with a volume of 10 mL. In the hydrogenation experiment, the reduced catalyst (reduced at 600°C for 1 h in 50 vol% H<sub>2</sub>/N<sub>2</sub> before the use) of 15 mg was used in each run. The concentration of the reaction solution (furfural and 5-hydroxymethoxyfurfural (HMF)) was 2.5 wt% with water as the reaction medium. After assembling the reactor, the reactor was purged with high-purity hydrogen for three times to remove the air residual inside. Before the hydrogenation experiments, the reactor was pressurized again with a high-purity hydrogen to 3 MPa and the reactor was maintain at 25°C for 120 min with a stirring rate of 400 rpm for the hydrogenation reactions. The reactor is equipped with a cooling circulating water device, and the reaction temperature is maintained at 25°C by circulating water and a heating jacket.

The recycle tests of hydrogenation of furfural and HMF were also carried out in an autoclave with a volume of 10 mL. The specific conditions were as follow: T = 25°C; time of each test = 120 min; number of recycle tests = 5; P = 3 Mpa; Catalyst loading = 15 mg. The spent catalysts after every hydrogenation reaction was separated by centrifuge, and the catalyst was washed by ethanol. After drying, the spent catalyst was used to the next hydrogenation reaction.

### **Characterization**

The liquid products were analysed by using GC/MS (7890A GC plus with a 5975C MS detector; capillary column (DB-Wax); length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 μm). The temperature of the column (Wax type; Length = 30.0 m; Internal diameter = 0.25 mm; Film thickness = 0.25 μm) was firstly hold at 50°C for 3 min (Oven temperature: 50°C; Carrier gas: helium; Carrier gas flow rate: 4 mL/min), and then the temperature was increased to 250°C with the heating rate of 20 °C/min for 15 min. The concentration of the sample was diluted to 3 wt.% in ethanol for the analysis. The conversion of furfural and HMF was calculated according to the following equations:

$$\text{The conversion of Furfural} = \frac{\text{Mole of Furfural consumed}}{\text{Mole of Furfural loaded}} \times 100\%$$

$$\text{The conversion of HMF} = \frac{\text{Mole of HMF consumed}}{\text{Mole of HMF loaded}} \times 100\%$$

Crystal phase of the nickel-based catalyst was characterized with X-ray diffraction (XRD) characterization (X-ray diffractometer; Rigaku Ultima IV,  $\lambda = 1.5406 \text{ \AA}$ , Cu K $\alpha$  target). The operating conditions of XRD were listed as follows: Scanning range = 20.0 to 80.0°; Scanning rate = 20°/min; Operating voltage = 40 kV; Current = 40 mA. Meanwhile, the particle size of nickel and nickel oxide were calculated by using Debye–Scherrer equation.

The interaction between nickel species and the carrier was analysed with Temperature Programmed Reduction (TPR; Vodo VDSorb–91x instrument) characterization. The calcined catalysts were accurately weighed (5 mg) and placed in a U-tube reactor. The specific conditions of TPR were listed as follows: Temperature range: 25 to 900°C; Heating rate: 20 °C/min; Flow gas: 5 vol% H<sub>2</sub>/Ar; Flow rate: 10 mL/min. The change in the gas signal was monitored by a TCD.

H<sub>2</sub>-Temperature Programmed Desorption (H<sub>2</sub>-TPD; Vodo VDSorb–91x instrument) was conducted to analyse nickel dispersion on the catalysts. The reduced nickel-based catalyst was accurately weighed (30 mg) and placed in a U-tube reactor. The specific condition of H<sub>2</sub>-TPD was as follows: Temperature range = 25 to 900°C; Heating rate = 20 °C/min; Adsorbed gas = high-purity H<sub>2</sub> (30 mL/min; Room temperature; Holding for 30 min); Carrier gas = high-purity Ar (20 mL/min). The change in the gas signal was recorded with a TCD.

The pore structure of nickel-based catalysts was analysed by using BET method (Micromeritics ASAP–2010 instrument). Nitrogen was used as the adsorbate and helium was used as the carrier gas. The two gases were mixed in a certain ratio to reach the specified relative pressure and then flowed through the sample. By changing the mixing ratio of nitrogen and helium, the adsorption amount of nitrogens under relative pressure can be measured, and the specific surface area can be calculated according to the BET formula.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1) P}{V_m C P_0}$$

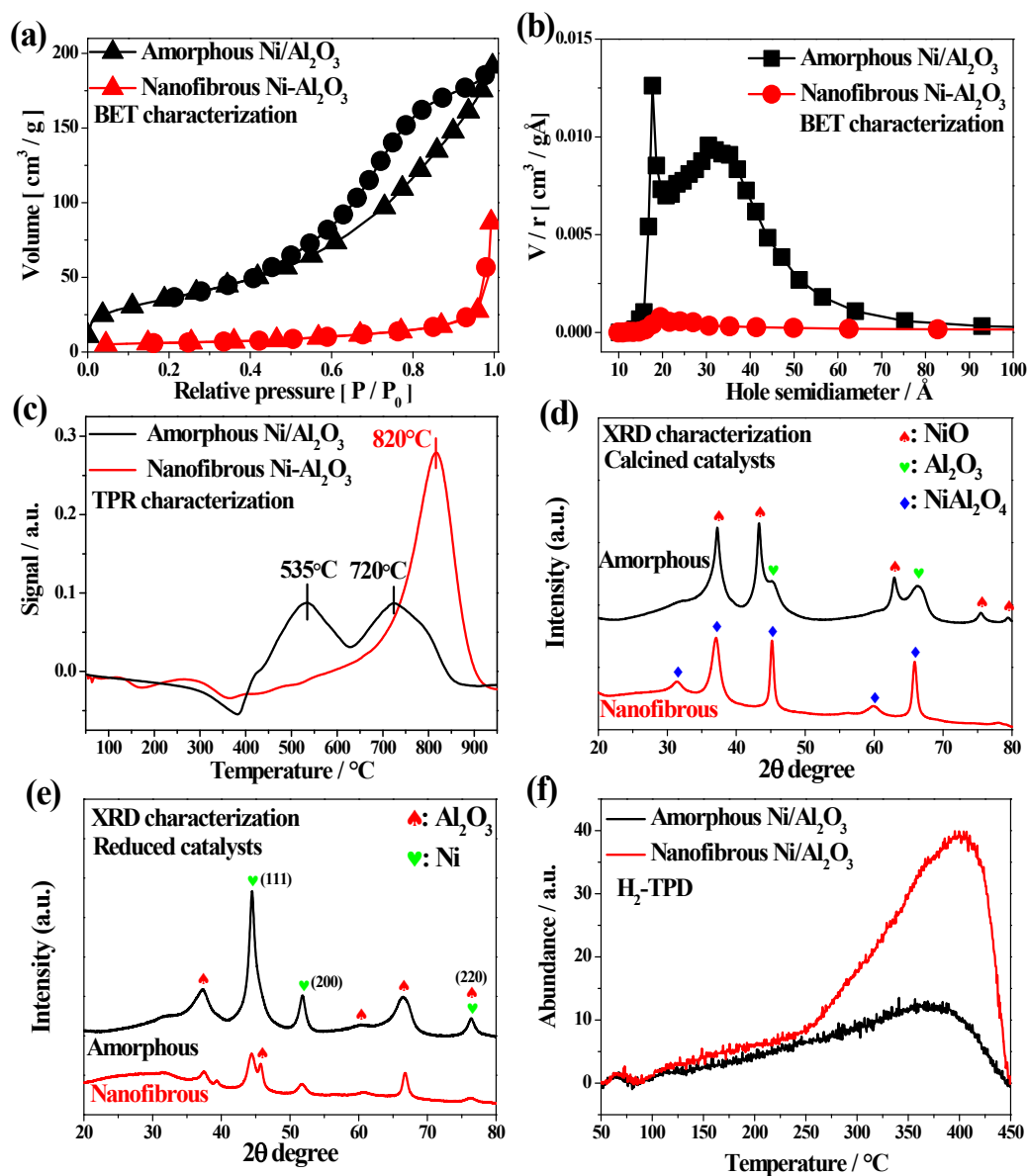
$P$ : Nitrogen partial pressure, (Pa);

$P_0$ : Saturated vapor pressure of nitrogen at adsorption temperature, (Pa);

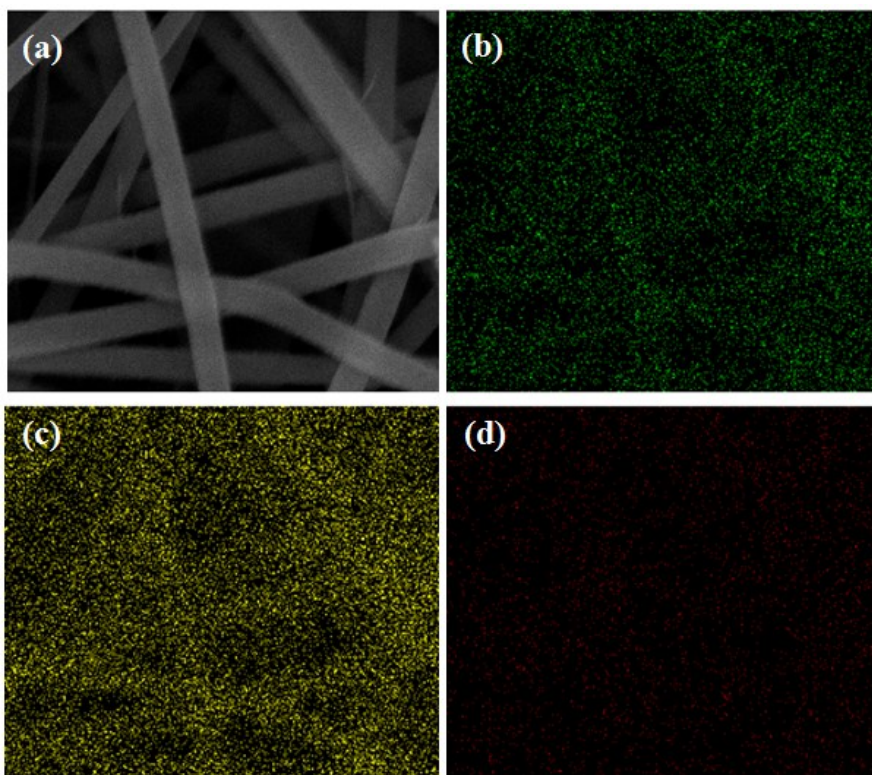
$V_m$ : The amount of gas required to form a monolayer on the sample, (mL);

$V$ : Total volume of adsorbed gas, (mL);

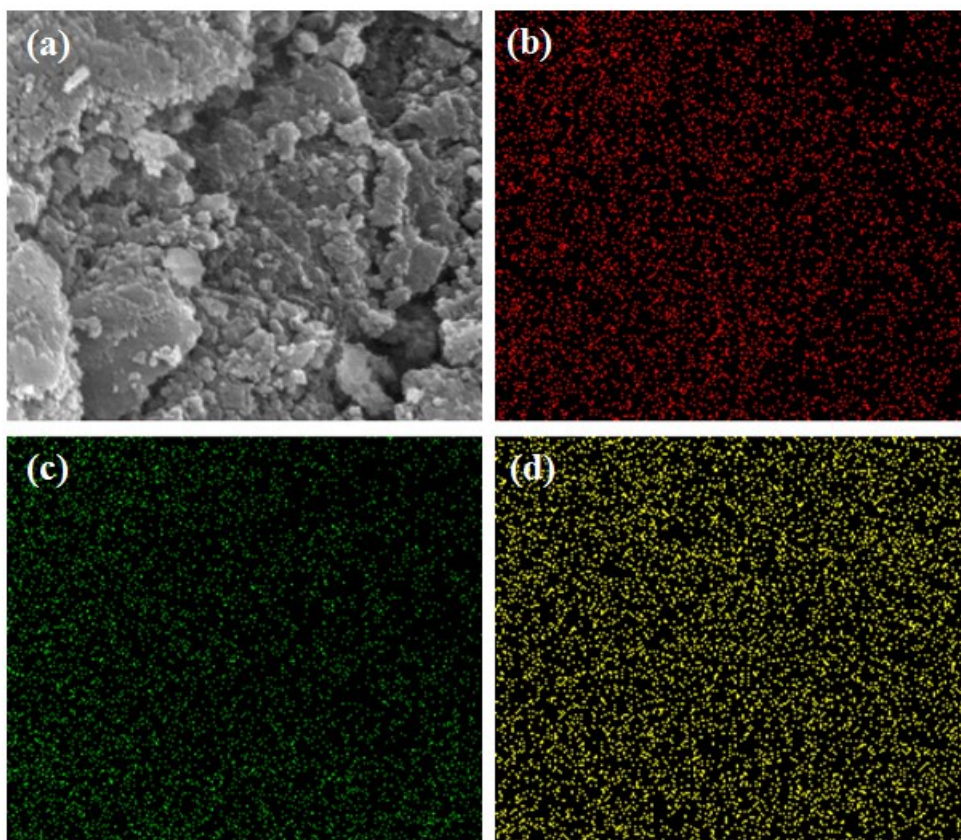
High Resolution Transmission Electron Microscope (HRTEM) characterization was conducted to analyse the structural and composition through high resolution image and energy spectrum analysis. The powder sample after reduction (about 2 mg) was ultrasonically dispersed in absolute ethanol before measurement. After that, the homogeneous solution was added dropwise to the copper grid and evaporated at room temperature.



**Fig. S1** The properties of the two forms over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. (a): The isothermal curves; (b): Pore size distribution diagram of BJH desorption hole; (c): TPR test; (d) and (e): XRD test; (f): H<sub>2</sub>-TPD test.

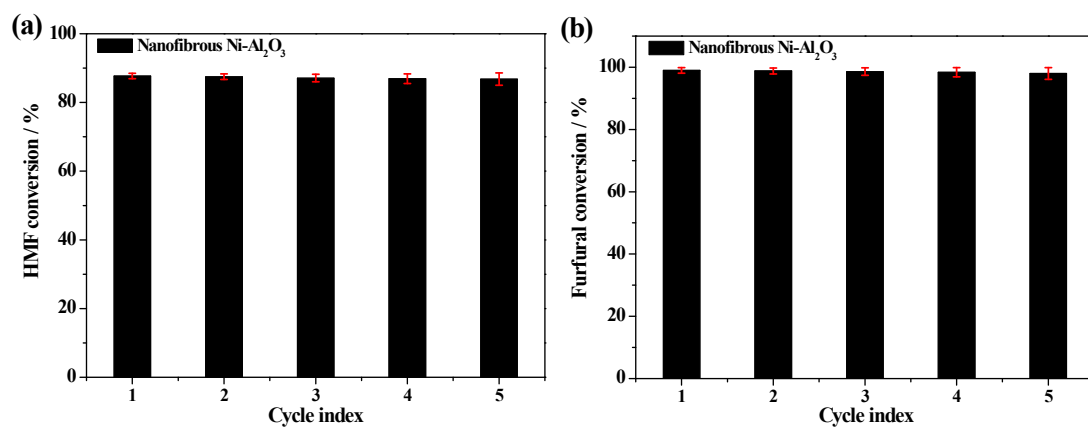


**Fig. S2** The mapping of the reduced nanofibrous Ni-Al<sub>2</sub>O<sub>3</sub> catalyst. (a): SEM image; (b): O; (c): Al; (d): Ni.



**Fig. S3** The mapping of the reduced amorphous Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. (a): SEM image; (b): O; (c): Al; (d): Ni.





**Fig. S4** The recycle tests of hydrogenation of furfural and HMF. Reaction condition: T = 25°C; time of each test = 120 min; number of recycle tests = 5; P = 3 Mpa; Catalyst loading = 15 mg.