

## Supporting Information

### **Interconnected Hierarchical HUSY Zeolite-Loaded Ni Nanoparticles Probed for Hydrodeoxygenation of Fatty Acids, Fatty Esters, and Palm Oil**

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## **EXPERIMENTAL SECTION**

### **Materials**

All chemicals and reagents were received from commercial suppliers and used without further purification: stearic acid (Sinopharm Chemical Reagent Co., Ltd, AR assay), palm oil (China Grain Reserves Co.), n-dodecane (Sinopharm Chemical Reagent Co., Ltd, >98% GC assay), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sinopharm Chemical Reagent Co., Ltd, ≥98% AR assay), Urea (Sinopharm, AR), NaOH (Sinopharm Chemical Reagent Co., Ltd, ≥96% AR assay), piperidine (Aladdin, ≥99.5% AR assay), tetra-propyl-ammonium hydroxide (TPAOH, Sinopharm Chemical Reagent Co., Ltd, 25 wt%), ammonium chloride (Alfa Aesar, 98%), Methyl stearate (Aladdin, ≥99% AR assay), Ethyl palmitate (Aladdin, ≥98% AR assay), Isopropyl palmitate (Aladdin, ≥97% AR assay), Palmityl palmitate (Aladdin, ≥98% AR assay), Stearyl stearate (Sigma-Aldrich, ≥98% AR assay). Air, H<sub>2</sub>, and N<sub>2</sub> gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

### **Material preparations**

#### **Preparation of HUSY-2 by steaming**

Prior to steaming, HUSY-1 was calcined in the flowing air at 550 °C for 4 h. Then the solid was steamed (4.4 mL min<sup>-1</sup>, heating rate 5 grad min<sup>-1</sup>) at 650 °C for 2 h.

#### **Preparation of HUSY-3 or HUSY-4 by post-treatments**

HUSY-2 (4.0 g) was added into a mixed alkaline solution (133 mL, C<sub>x</sub>/C<sub>OH-1</sub> = 0.7, x stand for TPAOH or PI) which contained 20.17 g (25 wt% in water) TPAOH (HUSY-3), or 2.106 g PI (HUSY-4) and NaOH (0.425 g). Then the mixed solution was reacted at 65 °C for 190 min (HUSY-3) or 120 min (HUSY-4) with continuous stirring. Subsequently the powder was collected by centrifugation at 10 000 rpm for 10 min, dried at 80 °C, and calcined at 550 °C for 6 h. The solid product was decationized by three consecutive exchanges with a NH<sub>4</sub>NO<sub>3</sub> solution (0.1 M) and calcined in the flowing air (flow rate: 150 mL min<sup>-1</sup>) at 550 °C for 6 h.

### **Catalyst preparation**

The nickel nanoparticles were introduced into the HUSY samples by the deposition–precipitation (DP) method. In a typical synthesis,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (10.2 g, 0.035 mol) was dissolved in distilled water (250 mL), 200 mL of which was used to prepare a suspension with the HUSY zeolite (2.0 g), and the other 50 mL was mixed with urea (6.3 g), and then the mixed solution was slowly dropped into the HUSY suspension after the former was heated to 70 °C. Subsequently the mixture was reacted at 90 °C for 10 h. After cooling to ambient temperature, the suspension was filtered and washed with distilled water until the pH of the filtrate was neutral. After completing this procedure, the catalyst precursor was dried at 80 °C, calcined in air (flow rate: 150 mL min<sup>-1</sup>) at 500 °C for 6 h, and reduced in H<sub>2</sub> (flow rate: 150 mL min<sup>-1</sup>) at 500 °C for 6 h.

### **Catalyst characterization**

The amounts of Si, Al, and Ni were determined by inductively coupled plasma (ICP) atomic emission spectroscopy (AES) on a Thermo IRIS Intrepid II XSP.

Nitrogen sorption isotherms were recorded at 77 K on a BELSORP-MAX instrument after degassing the samples for 10 h under vacuum at 573 K. The t-plot method was used to discriminate between micro- and mesoporosity. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distributions were obtained from the analysis of adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) algorithm.

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer using Cu K $\alpha$  radiation at 35 kV and 25 mA in the 2 $\theta$  angle range of 5°–80° at a scanning speed of 60° min<sup>-1</sup>. The relative crystallinity was calculated by comparing the treated samples and parent sample according the SH/T 0340-92 [1]. The unit cell  $a_0$  were determined from the position of the (533) reflection, using pure silicon (99.999 wt.%) as the internal standard for angle calibration (2 h = 28.443°) according to SH/T 0339-92. The scan rate was 0.1° min<sup>-1</sup> with a step width of 0.01°.

The pyridine-adsorption Infrared spectra were collected on a Nicolet NEXUS 670 FTIR spectrometer equipped with an in situ IR cell. The samples were evacuated at 823 K for 1 h

before equilibration with pyridine at 423 K, and then evacuated at 423 K for 0.5 h. The IR spectra were obtained at 523 K and 623 K.

The crystal morphologies and sizes were collected by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were performed on a TECNAI G2 F30 operating at 300 kV. The ultra-thin slicing treatment is conducted as follows: the materials were infiltrated with a mixture of acetone and Spurr's resin, and then embedded in pure Spurr's resin. Specimens were initially thick-sectioned for the presence of samples and subsequently thin-sectioned with a diamond knife on an Ultracut-E ultramicrotome (Reichert-Jung, Germany). Specifically, a series of TEM images was continuously acquired by tilting the specimen over a range from  $-70^\circ$  to  $70^\circ$  at regular intervals of  $1^\circ$ . The image series was aligned and processed to reconstruct a "volume" that could be visualized (movies S1 and S2 in the Supporting Information).

Pulse CO chemisorption was performed by a Micromeritics AutoChem 2910. Before the test, 50 mg catalyst was activated in a flow of  $100 \text{ ml min}^{-1}$  10 vol%  $\text{H}_2$  in He at  $500^\circ\text{C}$  for 2 h and then blowed with He for 1 h. After cooling to ambient temperature, the CO gas pulses (5 vol% in He) were introduced at a flow rate of  $100 \text{ ml min}^{-1}$ . The changes in the CO gas phase concentration were recorded by TCD.

The  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra were recorded on a Varian VNMRS 400WB multinuclear solid-state magnetic resonance spectrometer. The Si/Al ratio of the samples were calculated from  $^{29}\text{Si}$  MAS NMR data based on the equation 1:

$$\text{Si/Al} = \sum_n I_n = I_4 / (I_4 + 0.75I_3 + 0.5I_2 + 0.25I_1) \text{ (equation 1)}$$

The 1D and 2D  $^1\text{H}$  NMR experiments were performed on a Bruker Ascend-500 spectrometer at a resonance frequency of 500.57 MHz for  $^1\text{H}$ . The  $^1\text{H}$  MAS and  $^1\text{H}$  double quantum (DQ) NMR spectra were recorded using a 4 mm triple-resonance MAS probe at a spinning rate of 12.5 kHz. Pulse width ( $\pi/2$ ) for  $^1\text{H}$  was measured to be  $4.0 \mu\text{s}$  and a recycle delay of 5 s was used for the  $^1\text{H}$  MAS NMR experiments. For the  $^1\text{H}$  double quantum MAS NMR experiments, DQ coherences were excited and reconverted with a POST-C7 pulse sequence [2] following the general scheme of two-dimensional (2D) multiple-quantum spectroscopy. The increment interval in the indirect dimension was set to  $80 \mu\text{s}$ . Typically, 300 scans were acquired for each  $t_1$  increment, and two-dimensional data sets consisted of

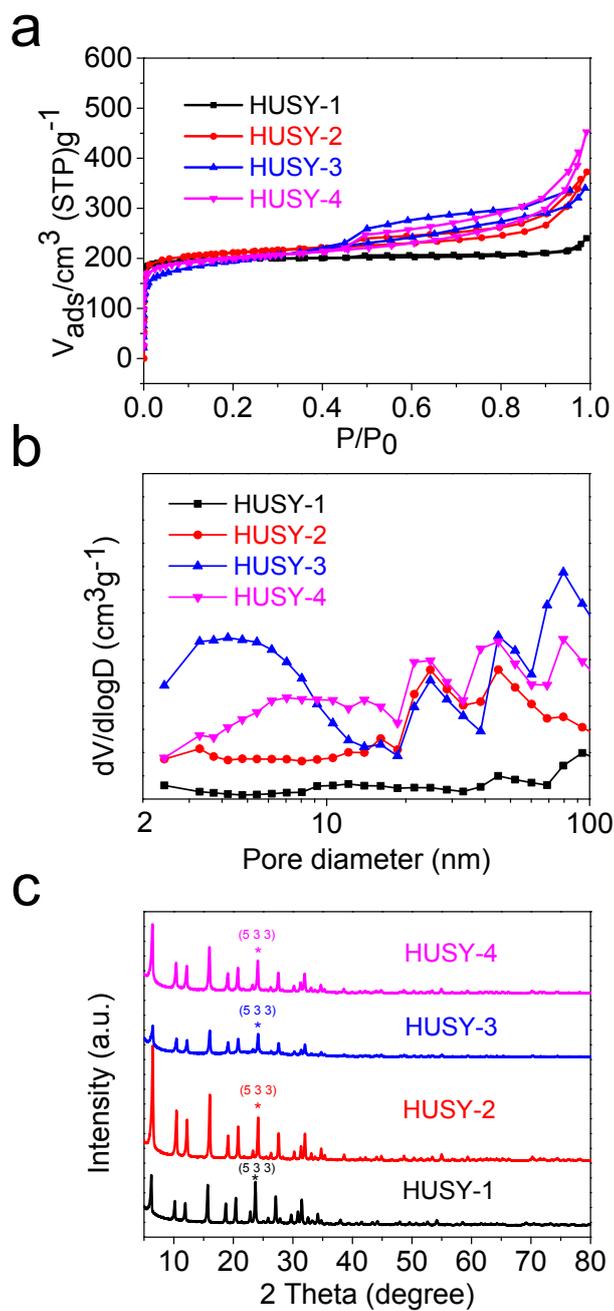
300  $t_1 \times 96 t_2$ . The chemical shift of  $^1\text{H}$  was externally referenced to adamantane. Prior to the NMR experiments, the dealuminated H-USY sample was placed in a glass tube and connected to a vacuum line for dehydration. The temperature was gradually increased at a rate of 1 K/min, and the sample was kept at a final temperature of 673 K under a pressure below  $10^{-3}$  Pa over a period of 10 h and was then flame-sealed. Subsequently, the sealed sample was transferred into a  $\text{ZrO}_2$  rotor (tightly sealed by a Kel-F cap) under a dry nitrogen atmosphere in a glove box.

### **Catalytic reactions**

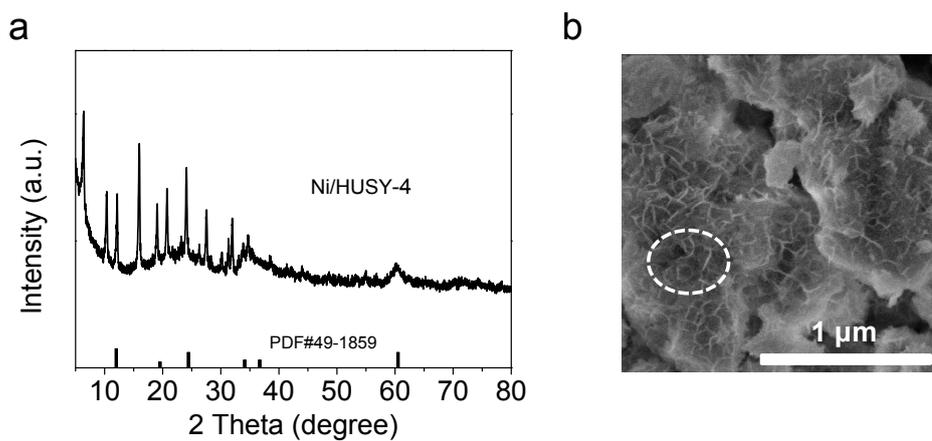
In a typical experiment with stearic acid, fatty acid monoglyceride and palm oil conversion was carried out as follows: 5 g substrate, 0.2 g Ni/HUSY catalyst (or 5 g palm oil, 0.4 g Ni/HUSY-4), and 80 mL dodecane were introduced into a batch autoclave (Parr Instrument, 300 ml). The autoclave was firstly filled with  $\text{N}_2$  to remove the residual air, and then the reaction gas  $\text{H}_2$  was also introduced into the reactor at ambient temperature. The reaction was performed at 260 °C at a stirring speed of 600 rpm. The liquid products were obtained by in situ sampling every 20 min., and then analyzed by a Shimadzu GC coupled with GC-MS and equipped with a Rtx-5Sil MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). Undecane acted as an internal standard was used to calculate the yields of liquid products. Conversion = (the weight of the converted reactant) / (the weight of the starting reactant)  $\times$  100%. Yield of liquid products = (C atoms in liquid products / C atoms in the starting reactant)  $\times$  100%.

**Table S1.** Comparison of Brønsted and Lewis acid sites determined by IR of adsorbed pyridine on the four catalysts at different desorption temperatures.

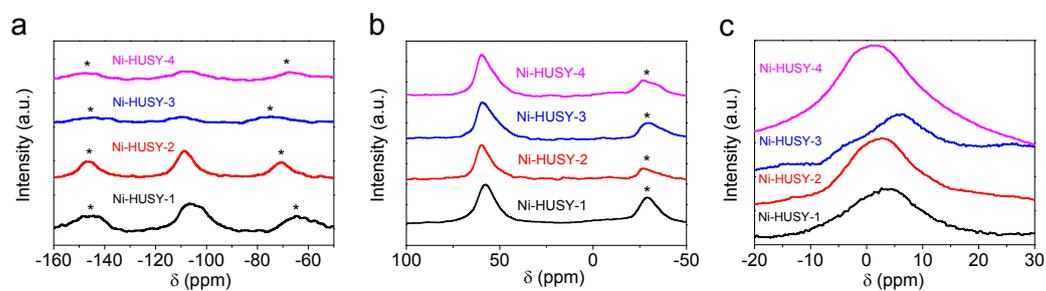
Catalyst	Desorption temperature					
	150 °C		250 °C		350 °C	
	BAS [mmol·g <sup>-1</sup> ]	LAS [mmol·g <sup>-1</sup> ]	BAS [mmol·g <sup>-1</sup> ]	LAS [mmol·g <sup>-1</sup> ]	BAS [mmol·g <sup>-1</sup> ]	LAS [mmol·g <sup>-1</sup> ]
Ni/HUSY-1	0.058	0.242	0.057	0.222	0.027	0.140
Ni/HUSY-2	0.016	0.140	0.010	0.092	0.009	0.034
Ni/HUSY-3	0.012	0.265	0.012	0.173	0.010	0.046
Ni/HUSY-4	0.013	0.267	0.013	0.164	0.012	0.054



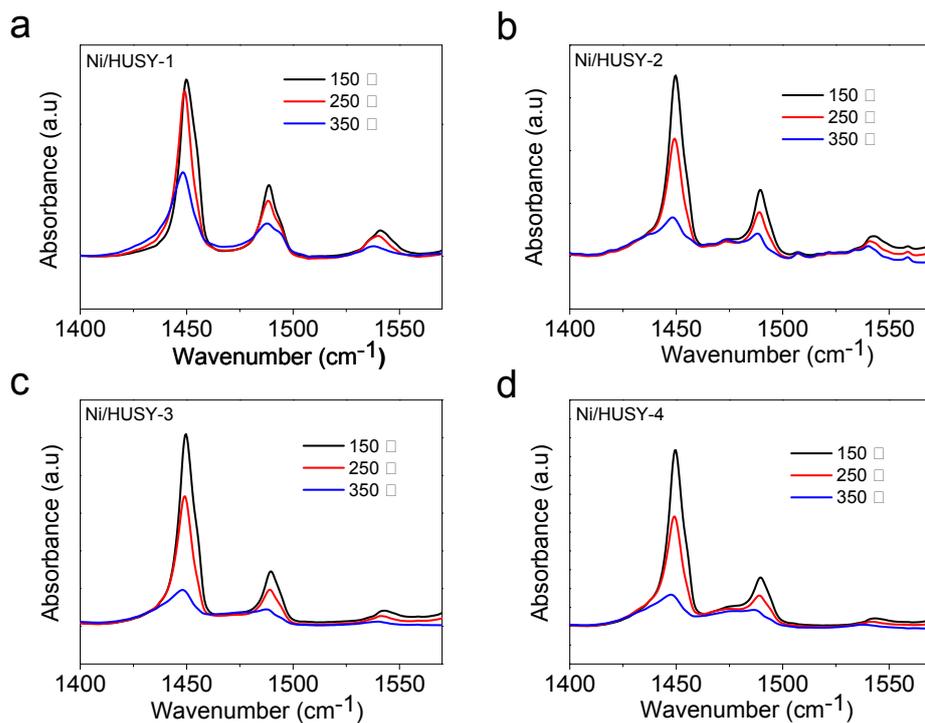
**Figure S1.** (a) N<sub>2</sub> adsorption and desorption isotherms, (b) BJH adsorption pore size distributions, (c) XRD patterns. Parent HY: HUSY-1, HY-steaming: HUSY-2, HY-steaming-TPAOH/NaOH: HUSY-3, HY-steaming-PI/NaOH: HUSY-4.



**Figure S2.** (a) The XRD pattern and (b) SEM image of the sample after Ni was incorporated into HUSY-4 support by the DP synthesis.



**Figure S3.** (a)  $^{29}\text{Si}$  MAS NMR spectra, (b)  $^{27}\text{Al}$  MAS NMR spectra, (c)  $^1\text{H}$  MAS NMR. Asterisks denote spinning sidebands



**Figure S4.** IR spectra of adsorbed pyridine on the four catalysts at different desorption temperatures.

## References

- [1] Z. Qin, B. Shen, X. Gao, F. Lin, B. Wang and C. Xu, *J. Catal.*, 2011, **278**, 266-275.
- [2] S. P. Brown and H. W. Spiess, *Chem. Rev.* 2001, **101**, 4125-4155.