## **Supporting Information**

# Controllable Hydrothermal Synthesis of Ni/H-BEA with Hierarchical Core–Shell Structure and Highly Enhanced Biomass Hydrodeoxygenation Performance

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#### **EXPERIMENTAL SECTION**

#### Materials

All chemicals and reagents were obtained from commercial suppliers and used without further purification: Poly-diallyldimethyl-ammonium chloride (PDADMA) with molecular weight  $(1~2 \times 10^5)$ and fumed silica were purchased from Sigma-Aldrich Co., sodium hydroxide (Sinopharm Chemical Reagent Co., Ltd.,  $\geq$ 98% analytical standard), ammonium chloride (Alfa Aesar,  $\geq$ 98%), aqueous ammonia solution (Sinopharm Chemical Reagent Co., Ltd., 28 wt%), Ni(CH<sub>3</sub>COO)<sub>2</sub> 4H<sub>2</sub>O (Micxy Reagent Co., Ltd.,  $\geq$ 98% analytical standard), stearic acid (Sinopharm Chemical Reagent Co., Ltd., analytical standard), ndodecane (Sinopharm Chemical Reagent Co., Ltd.,  $\geq$ 98% GC assay). Air, H<sub>2</sub>, and N<sub>2</sub> gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

#### Synthesis of HBEA-MS

HBEA–MS were synthesized by using PDADMA as the template. Typically, 0.211 g NaAlO<sub>2</sub>, 1.081 g NaOH were added into 40 g H<sub>2</sub>O. After stirring for 5 minutes, a colorless transparent solution was formed. Then 6.74 g PDADMA were added in, after stirring for 5 minutes, and light yellow gel mixture was formed. After adding in 3.16 g fumed silica, the mixture was stirred for 24 h. Then the white gel mixture was put into a Teflon autoclave (100 mL) and heated to 180  $^{\circ}$ C for 6 days. Then the resulting white gel was washed with water until pH of the filtrate reached 7.0. The zeolite powder was collected and dried, after calcination at 550  $^{\circ}$ C for 5 h, the obtained powder was gained.

#### **Catalyst preparation**

Three Ni based HBEA samples were prepared through hydrothermal treatment. Firstly, Ni(AC)<sub>2</sub> 4H<sub>2</sub>O (0.348 g), NH<sub>4</sub>Cl (1.498 g), and NH<sub>3</sub> H<sub>2</sub>O (2.548 g, 28%) were added under stirring to 140 g of distilled water. Secondly, HBEA (0.2 g) was added to such solution and ultrasonicated for 30 min to form a uniform suspension, then the mixture was transferred to a Teflon autoclave (100 mL) and heated to 120  $\degree$  for 2 h. The resulting green precipitated were washed and dried. Then the catalyst was directly reduced under flowing H<sub>2</sub> in 550  $\degree$  for 6 h. And the condition is changed only according to different precipitates.

#### Catalytic tests

The conversion of stearic acid was conducted as follows: 5.0 g stearic acid, 0.2 g Ni/HBEA prepared in different conditions were added into 80ml dodecane. In the batch autoclave (Parr Instrument, 300 mL), the mixture was heated to 260 °C in the hydrogen atmosphere which was about 4 bar. The stirring speed was at about 600 rpm, and the liquid products were collected in situ every twenty minutes. Then the product samples were analyzed by the Shimadu GC coupled with MS and then be equipped with the Rtx-5Sil MS capillary column with the size 30 nm×0.25 mm×0.25 µm. Conversion = (the weight of the converted reactant) / (the weight of the starting reactant) × 100%. Yield = Conversion × Selectivity × 100%.

#### **Characterization methods**

The contents of Ni, Si and Al were measured through inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid II XPS emission spectrometer. And the samples of the filtrate were measured just as after filtration, while the samples of the catalyst were measured after dissolving in the HF solution. Nitrogen sorption isotherms were conducted on a BELSORP-MAX instrument and after evacuating for 10 hours at 300 °C, the surface area and the pore size distribution could be gained according to Brunauer-Emmett-Teller method and T-plot. X-ray diffraction (XRD) patterns were measured with the Rigaku Ultima IV X-ray diffractometer using Cu K<sub>a</sub> ( $\lambda = 1.5405$  Å) radiation. Infrared spectrum (IR) was measured by Nicolet Nexus 670 FT-IR spectrometer and the samples were prepared in KBr technique. The spectral resolution was 2 cm<sup>-1</sup>, and the samples were measured in absorbance mode. Hydrogen temperature programmed reduction (TPR) were measured by TP-5080 multi-purpose automatic adsorption instrument equipped with a thermal conductor detector (TCD). And the temperatures were increased with the rate at about 10 ° min<sup>-1</sup>. Pyridine-adsorption Infrared spectra (Py-IR) was recorded with a Nicolet NEXUS 670 FTIR spectrometer which was equipped with an in situ IR cell. The temperature was increased with the rate at about 10 ° min<sup>-1</sup>. The samples were conducted under the aging process at 550 °C for 1 h and then measured at 150 °C. Scanning electron microscopy (SEM) was measured on the Hitachi S-4800 microscope while the transmission electron microscopy (TEM) was measured on the FEI Tecnai G2 F30 microscope working at 300 kV. Scanning electron microscopy equipped with energy dispersive X-ray (TEM-EDX) was measured on a Hitachi S-4800 microscope, and both TEM-mapping and line scan are conducted on the sample which had been cut into slices in 30-50 nm by the method of ultrathin section. The <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectra were performed on a VARIAN VNMRS 400WB NMR spectrometer under one-pulse conditions. The <sup>29</sup>Si spectra were gained with the frequency of 79.43 MHz, and the spinning rate is 3.0 kHz while the recycling delay is 60 s. The chemical shift was referred to Q8M8 ([(CH<sub>3</sub>)<sub>3</sub>SiO]<sub>8</sub>SiO<sub>12</sub>). The <sup>27</sup>Al NMR spectra were gained with the frequency of 104.18 MHz, and the spinning rate was 10.0 kHz, while the recycling delay was 4 s. KAl(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O was used as the reference for its chemical shift.

### Calculation of major Ni species in buffer NH<sub>4</sub>Cl/NH<sub>3</sub><sup>·</sup>H<sub>2</sub>O solution

Raw materials added:  $n (NH_3 H_2O) = 28\% \times 2.548/35 = 0.020 \text{ mol}$   $n (NH_4Cl) = 1.498/53.5 = 0.028 \text{ mol}$ Then,  $c (NH_3 H_2O) + c (NH_4Cl) = (0.020 + 0.028)/0.14 = 0.346 \text{ mol } L^{-1}$ 

As measured, pH = 9.3

In the NH<sub>4</sub>Cl/NH<sub>3</sub>·H<sub>2</sub>O buffer solution:  $pOH = PK_b - lg[c \text{ (base)}/c \text{ (salt)}]$ ;  $PK_b = 4.75$ 

Set c (base) equal to x

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4.7 = 4.75 - \log x/(0.346 - x)
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 $x=0.183\ mol\ L^{\text{-1}}$ 

Suppose when complexation results:

 $\beta = 10^{8.49}$ , so  $10^{8.49} = [Ni(NH_3)_6]^{2+}/[Ni^{2+}] [NH_3]^6$ Raw materials added:  $c [Ni^{2+}] = 0.348/248.86/0.14 = 0.01 \text{ mol } \text{L}^{-1}$ Then set  $c [Ni^{2+}]$  equal to y  $10^{8.49} = (0.01 - y)/y/(0.183)^6$  $y = 8.62 \times 10^{-7}$ 

$$Qc = [Ni^{2+}]_{true} [OH]_{true}^{2}$$
  
= 8.62 × 10<sup>-7</sup> × 10<sup>-4.7</sup> × 10<sup>-4.7</sup>  
= 3.43 × 10<sup>-16</sup>  
K<sub>sp</sub> = 2 × 10<sup>-15</sup> > Qc

In conclusion: when the  $[Ni(NH_3)_6]^{2+}$  complex is formed, hardly any Ni(OH)<sub>2</sub> will form.



**Figure S1.** Photographs of filtrates before hydrothermal treatment with (a)  $NH_4Cl/NH_3 \cdot H_2O$  buffer solution, (c)  $NH_3 \cdot H_2O$  solution, and (e)  $NH_4Cl$  solution. Photographs of filtrates after hydrothermal treatment for 120 min with (b)  $NH_4Cl/NH_3 \cdot H_2O$  buffer solution, (d)  $NH_3 \cdot H_2O$  solution, and (f)  $NH_4Cl$  solution.



**Figure S2.** Photographs of (a) solid  $Ni_xSi_yO_z/HBEA$  samples and (b) filtrate after hydrothermal synthesis times from 20 to 120 min.



Figure S3. (a)  $N_2$  adsorption and desorption isotherms, and (b) Barrett–Joyner–Halenda adsorption pore size distributions of HBEA and Ni/HBEA samples. HT represents the hydrothermal process with  $NH_4Cl/NH_3 \cdot H_2O$  buffer solution.



**Figure S4.** (a, b, d) TEM images of Ni/HBEA (cut in 30-50 nm slices prepared in  $NH_3 H_2O/NH_4Cl$  buffer solution, and (c) corresponding HAADF-STEM image of (d) image.



**Figure S5.** Recorded variations in (a) XRD patterns, (b) filtrate pH, (c) Si/Al molar ratios analysed by ICP, and (d) Ni loadings in Ni/HBEA samples during hydrothermal treatment of Ni salt in  $NH_3 H_2O$  solution within 120 min.



**Figure S6.** Filtrate photographs after hydrothermal treatment for 20 min with (a) NH<sub>3</sub>·H<sub>2</sub>O solution and (b) NH<sub>4</sub>Cl/NH<sub>3</sub>·H<sub>2</sub>O buffer solution.



**Figure S7.** Comparison of three Ni-based HBEA samples prepared in NH<sub>4</sub>Cl/NH<sub>3</sub> H<sub>2</sub>O buffer solution, NH<sub>3</sub> H<sub>2</sub>O alkali solution, and acidic NH<sub>4</sub>Cl solution with Ni salt, as measured by (a) TPR-H<sub>2</sub> profiles, (b) XRD patterns (before reduction in hydrogen), and (c) XRD patterns (after reduction in hydrogen).



**Figure S8**. TEM images and the Ni particles size distributions of Ni/HBEA samples prepared with Ni salt in (a)  $NH_4Cl$  acidic solution, (b) in  $NH_4Cl/NH_3$  H<sub>2</sub>O buffer solution, and (c)  $NH_3$  H<sub>2</sub>O alkali solution.



**Figure S9.** (a)  $N_2$  adsorption and desorption isotherms, and (b) Barret–Joyner–Halenda adsorption pore size distributions of three HBEA samples prepared under different conditions.

Sample	S <sub>BET</sub>	S <sub>meso</sub>	S <sub>micro</sub>	V <sub>total</sub>	V <sub>meso</sub>	V <sub>micro</sub>
	$[m^2 \cdot g^{-1}]$	$[m^2 \cdot g^{-1}]$	$[m^2 \cdot g^{-1}]$	$[\mathrm{cm}^3 \cdot \mathrm{g}^{-1}]$	$[\mathrm{cm}^3 \cdot \mathrm{g}^{-1}]$	$[\mathrm{cm}^3 \cdot \mathrm{g}^{-1}]$
HBEA	681	399	282	0.75	0.62	0.13
Ni <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> /HBEA	417	291	126	0.50	0.44	0.06
Ni/HBEA	411	272	139	0.48	0.41	0.07

Table S1. The surface and pore properties of three HBEA based samples.<sup>a</sup>

<sup>a.</sup> Specific surface areas and pore volumes are determined by N<sub>2</sub> sorption.

Catalysts	Time [min.]	Yield (C%)					Hydrocarb	Stearic acid	Rate
		iso-C <sub>17</sub>	C <sub>17</sub>	iso-C <sub>18</sub>	C <sub>18</sub>	C <sub>18</sub> OH	- on Yield [%]	conversion [%]	$[g g^{-1} h^{-1}]$
With NH <sub>4</sub> Cl/ NH <sub>3</sub> •H <sub>2</sub> O buffer Solution	20	0.4	5.4	3.5	62.7	2.7	72.0	74.7	54
	40	0.1	6.0	4.8	84.9	0.4	95.8	96.2	
	60	0	6.3	5.1	88.5	0	100	100	
With NH <sub>3</sub> •H <sub>2</sub> O Solution	20	0	0.7	0	1.3	6.0	2.0	8	3.3
	40	0	2.2	0.4	5.4	15.3	8.0	31.3	
	60	0	4.0	0.9	11.1	19	16	51	
With NH <sub>4</sub> Cl Solution	20	0	0	0	0	0	0	0	0
	40	0	0	0	0	0	0	0	
	60	0	0	0	0	0	0	0	
HBEA zeolite	20	0	0	0	0	0	0	0	0
	40	0	0	0	0	0	0	0	
	60	0	0	0	0	0	0	0	

**Table S2.** The conversion from stearic acid to hydrocarbons using three Ni/HBEA catalysts prepared at different conditions.<sup>a</sup>

<sup>a</sup> Reaction condition: 5.0 g stearic acid, 0.2 g Ni/HBEA, 80 mL *n*-dodecane, 260 °C, 4 MPa H<sub>2</sub>, stirring at 600 rpm.