

Supporting Information

Ni Nanoparticles Encapsulated into Mesoporous Single-Crystalline

HBEA: Application for Drainage Oil Hydrodeoxygenation to Diesel

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Experimental Section

Materials

All chemicals were used without further purification: polydiallyldimethylammonium chloride (PDADMA) with molecular weight $1-2 \times 10^5$ (Sigma-Aldrich Co.), *n*-dodecane (Sinopharm Chemical Reagent Co., Ltd., > 98 % GC assay), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., > 98 % AR assay), NaOH (Sinopharm Chemical Reagent Co., Ltd., ≥ 96 % AR assay), urea (Sinopharm Chemical Reagent Co., Ltd., ≥ 99 % AR assay), NaAlO_2 (Sinopharm Chemical Reagent Co., Ltd., $\text{Al}_2\text{O}_3 \geq 41$ %), fumed silica (Sigma-Aldrich Co.), HBEA (Nankai University in China, Si:Al₂ = 20 and 26), Air, H₂, and N₂ gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of HBEA-MS

The HBEA-MS support was synthesized according to the method^[1], and the ratio of composition was $45\text{SiO}_2/\text{Al}_2\text{O}_3/13\text{Na}_2\text{O}/2250\text{H}_2\text{O}/7.5\text{PDADMA}$. In a typical synthesis, 1.081 g of NaOH and 0.211 g of NaAlO_2 were mixed with 40 mL of H₂O, and subsequently 6.74 g of PDADMA ($1-2 \times 10^5$, 20 wt % in water) was added into the suspension with stirring for 0.5 h. After a clear solution was formed, 3.16 g of fumed silica was added to the solution. With stirring of such suspension for 12 h, the resulted gel was transferred into an autoclave for crystallization at 180 °C for 144 h. The obtained powder was collected by filtration at ambient temperature, and then dried at 100 °C, and calcined at 550 °C for 5 h to remove the organic template.

Catalyst preparation

The Ni/HBEA catalysts were synthesized by the deposition-precipitation (DP) method. In a typical procedure: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10.2 g, 0.035 mol) was mixed with distilled water (250 mL), 200 mL of which was used to make a suspension with the HBEA zeolite (2.0 g), and the urea (6.3 g) was dissolved in other 50 mL $\text{Ni}(\text{NO}_3)_2$ solution, and then the mixed solution was added drop-wise to the HBEA suspension after the former was heated to 70 °C. Subsequently the mixture was brought up 90 °C for 10 h. The suspension was cooled to room temperature and filtered and washed with distilled water until the pH of the filtrate was neutral, and then the sample was dried at 80 °C, the catalyst precursors were calcined in the flowing air at 500 °C for 6 h and reduced in the flowing H₂ at 500 °C for 6 h.

Catalytic tests

The typical experiment with stearic acid and drainage oil conversion was carried out as follows: 5 g stearic acid, 0.2 g Ni/HBEA catalyst (or 5 g drainage oil, 0.8 g Ni/HBEA-MS), and 80 mL dodecane were loaded into a batch autoclave (Parr Instrument, 300 ml). The autoclave was firstly purged with N₂ to remove the residual air, and then the reaction gas H₂ was also introduced into the reactor at ambient temperature. The reaction was conducted at 260 °C at a stirring speed of 600 rpm. The liquid products

were collected 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 × 0.25 mm × 0.25 μm). An internal standard undecane was used to calculate the yields of liquid products. Conversion = (the weight of the converted reactant) / (the weight of the starting reactant) × 100%. Yield of liquid products = (C atoms in liquid products / C atoms in the starting reactant) × 100%. Analysis for gaseous products was performed on a GC (Techcomp 7900) equipped with a TCD and two columns (TDX-01: 30 cm × 3 mm, TDX-01: 2 m × 3 mm).

Characterization methods

Nitrogen sorption isotherms were carried out at 77 K on a BELSORP-MAX instrument, and the samples were evacuated for 10 h under vacuum at 573 K.

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu K α radiation at 35 kV and 25 mA ($\lambda = 1.5405 \text{ \AA}$) over a 2θ ranging from 10° to 70° at a scanning speed of 60° min⁻¹.

The pyridine-adsorption Infrared spectra were recorded with a Nicolet NEXUS 670 FTIR spectrometer equipped with an *in situ* IR cell. The samples were activated in a vacuum at 823 K for 1 h before equilibration with pyridine at 423 K, and then evacuated at 423 K for 1 h.

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

The crystal morphologies and sizes were determined by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were performed on a JEOL JEM-2100 microscope operating at an accelerating voltage of 200 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).

The temperature programmed reduction (TPR) analysis of calcined catalysts was performed by using Micromeritics tp5080 apparatus equipped with a thermal conductor detector (TCD), using a 3% H₂/He mixture (flowing rate: 20 mL·min⁻¹) and a heating rate of 5 K·min⁻¹.

The IR spectra of adsorbed CO were measured on a Nicolet Fourier transform infrared spectrometer (NEXUS 670). The samples were activated in H₂ at 773 K for 1 h, and then H₂ was removed by Vacuum pump. After the temperature was cooled to 313 K, the samples were exposed to CO until adsorption saturation. Subsequently the samples were evacuated at 313 K to remove the physically adsorbed CO. Afterwards, the IR spectra of adsorbed CO were recorded until no further changes in the spectra were observed.

For determination of the metal dispersion, pulse CO chemisorption was performed by a Micromeritics AutoChem 2910. Prior to the test, 50 mg catalyst was reduced in a flow of 100 ml min⁻¹ 10 vol% H₂ in He at 500 °C for 2 h and then flushed with He for 1 h. After cooling to ambient temperature in He, the CO gas pulses (5 vol% in He) were introduced at a flow rate of 100 ml min⁻¹. The changes in the CO gas phase concentration were tracked by TCD.

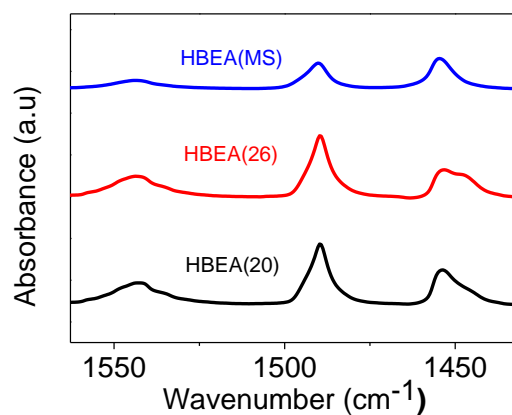


Figure S1. The IR spectra of adsorbed pyridine towards three HBEA-MS, HBEA-20 and HBEA-26 samples.

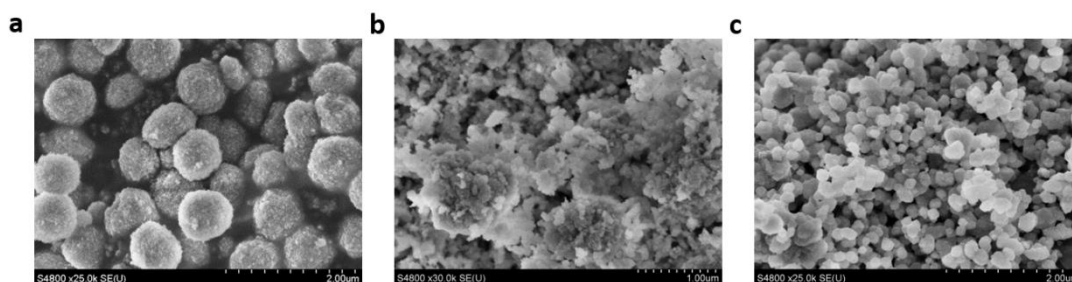


Figure S2. The SEM images of (a) HBEA-MS, (b) HBEA-20, and (c) HBEA-26.

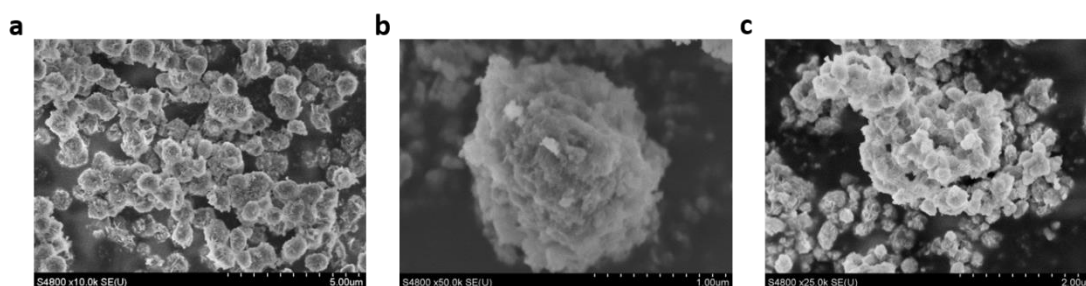


Figure S3. The SEM images of (a) Ni/HBEA-MS, (b) Ni/HBEA-20, and (c) Ni/HBEA-26.

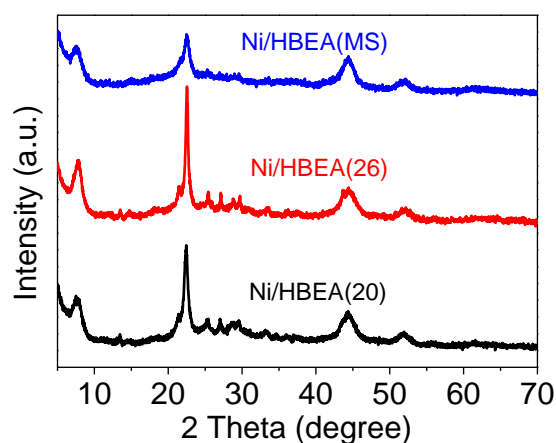


Figure S4. XRD patterns of three Ni based catalysts.

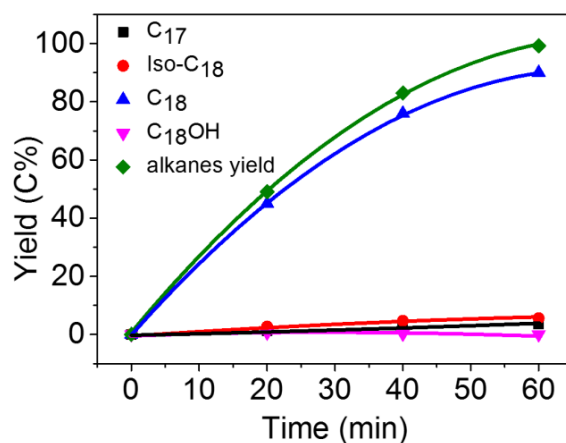


Figure S5. Product distributions on stearic acid conversion over Ni/HBEA-MS as a function of time. Reaction conditions: stearic acid (5.0 g), catalyst (0.2 g), dodecane (80 mL), 40 bar H_2 , at a stirring speed of 600 rpm.

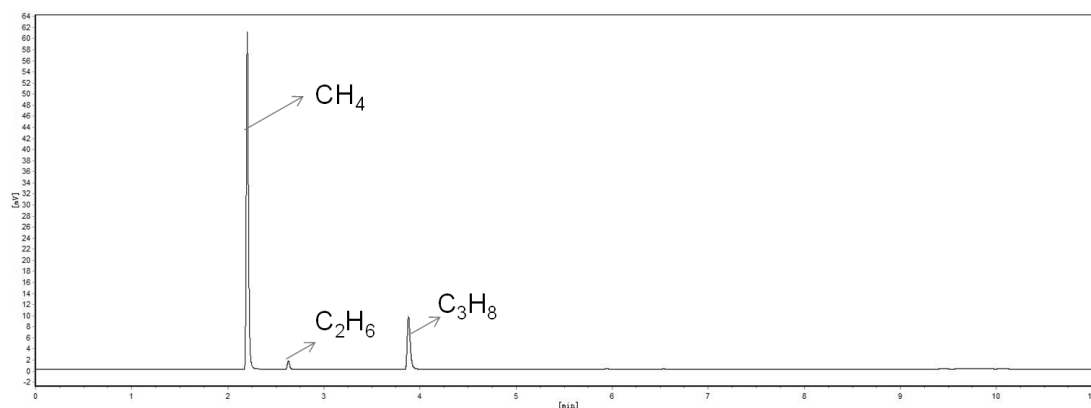


Figure S6. GC spectrum of gaseous products from drainage oil hydrodeoxygenation.

Table S1. The N₂ adsorption and desorption data for HBEA and Ni/HBEA samples.

Sample	S _{meso} B [m ² ·g ⁻¹] ^a	S _{meso} Ni/B [m ² ·g ⁻¹] ^a	V _{meso} B [cm ³ ·g ⁻¹] ^a	V _{meso} Ni/B [cm ³ ·g ⁻¹] ^a
B-MS	371	285	0.53	0.49
B-20	161	163	0.36	0.33
B-26	42	111	0.08	0.18

^a. Specific surface areas and pore volumes are determined by N₂ sorption at 77 K at the pore size distribution of 2-60 nm.

Table S2. Comparison of stearic acid conversion over three Ni/HBEA catalysts.

Catalyst	Conv. (%)	Rate [g·g ⁻¹ ·h ⁻¹]	Selectivity C ₁₈ (%)	Yield (C %)				
				<i>iso</i> -C ₁₇	C ₁₇	<i>iso</i> -C ₁₈	C ₁₈	C ₁₈ OH
Ni/HBEA (MS)	100	38	96		3.6	5.6	90	
Ni/HBEA (20)	53	13	57	1.8	7.3	3.7	26	13
Ni/HBEA (26)	44	11	63	1.4	5.2	3.8	24	

Reaction conditions: stearic acid (5.0 g), catalyst (0.2 g), dodecane (80 mL), 40 bar H₂, at a stirring speed of 600 rpm.

Table S3. Fatty acid compositions of the used waste oil.

C _{9:0} ^a	C _{12:0}	C _{14:0}	C _{15:0}	C _{16:1}	C _{16:0}	C _{17:0}	C _{18:2}	C _{18:1}	C _{18:0}	C _{20:1}	C _{20:0}	C _{22:0}
0.06	0.13	0.58	0.12	1.06	18.76	0.35	39.32	32.58	5.83	0.63	0.41	0.18

^a The nomenclature shows the number of carbon atoms and the number of C=C double bonds: for example the alkyl chain of the present fatty acid contains 9 carbon atoms and no double bonds

References

- 1 J. Zhu, Y. Zhu, L. Zhu, M. Rigutto, A. van der Made, C. Yang, et al. *J. Am. Chem. Soc.*, 2014, **136**, 2503–2510.