Supporting information

A Nickel-Phyllosilicate Core-Echinus Catalyst via Green and Base Additive Free Hydrothermal Approach for Hydrogenation Reactions

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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 ($1\sim2\times10^5$) and fumed silica were purchased from Sigma-Aldrich Co., sodium hydroxide (Sinopharm Chemical Reagent Co., Ltd., ≥98% analytical standard), ammonium chloride (Alfa Aesar, ≥98%), aqueous ammonia solution (Sinopharm Chemical Reagent Co., Ltd., 28 wt%), $Ni(CH_3COO)_2\cdot4H_2O$ (Micxy Reagent Co., Ltd., ≥98% analytical standard), $Ni(NO_3)_2\cdot6H_2O$ (Sinopharm Chemical Reagent Co., Ltd., analytical standard), $NiCl_2\cdot6H_2O$ (Micxy Reagent Co., Ltd., ≥98% analytical standard), $Co(CH_3COO)_2\cdot4H_2O$ (Micxy Reagent Co., Ltd., ≥98% analytical standard), $Cu(CH_3COO)_2\cdot1H_2O$ (Micxy Reagent Co., Ltd., ≥98% analytical standard), stearic acid (Sinopharm Chemical Reagent Co., Ltd., analytical standard), Ethylbenzene (Sinopharm Chemical Reagent Co., Ltd., analytical standard), ndodecane (Sinopharm Chemical Reagent Co., Ltd., ≥98% GC assay). Air, H_2, and N_2 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 $NaAlO_{2,}$ 1.081 g NaOH were added into 40 g H_2O. 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 °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 °C for 5 h, the obtained powder was gained.

Catalyst preparation

Hydrothermal synthesis of Ni phyllosilicate samples

Three Ni phyllosilicate samples were prepared through the hydrothermal treatment without adding any base precipitant. Firstly, $Ni(AC)_2\cdot4H_2O$ (0.348 g) was dissolved to distilled water (140 g) to form an aqueous solution. Secondly, HBEA (0.2 g) was added to such solution, and then the mixture was ultrasonicated for 30 min to form a uniform suspension. Subsequently such suspension was transferred to a Teflon autoclave (100 mL) and heated to 120 °C for 2 h. The resulting green precipitate was washed and dried.

Before catalytic tests, the Ni phyllosilicate precursor was directly reduced under flowing H_2 in 550 °C for 6 h.

The preparation of Ni/HBEA-$Ni(NO_3)_2$ or Ni/HBEA-$NiCl_2$ sample follows a similar experimental procedure but with a different Ni salt precursor.

Catalytic tests

The conversion of stearic acid was conducted as follows: 5.0 g stearic acid and 0.2 g reduced Ni/HBEA prepared in different conditions were added into 80 ml dodecane. In the batch autoclave (Parr Instrument, 300 mL), the mixture was heated to 260 °C in the hydrogen atmosphere which was about 40 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%.

The conversion of ethylbenzene was conducted as follows: 5.0 g ethylbenzene and 0.1 g Ni/HBEA prepared in different conditions were added into 80 ml dodecane. In the batch autoclave (Parr Instrument, 300 mL), the mixture was heated to 200 °C in the hydrogen atmosphere which was about 40 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%.

Catalyst Characterization

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_α (λ = 1.5405 Å) radiation at 35 kV and 25 mA in the 2θ angle range of 5-90 ° using a step size of 0.04 ° and at a scanning speed of 30 min^{-1}. 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^{-1}, and the samples were measured in absorbance mode. Hydrogen temperature programmed reduction (TPR) experiments 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 $°\cdot min^{-1}$. For the determination of the silanol number, a special transmission FTIR setup was used. FTIR spectra were recorded at a resolution of 4 cm^{-1}, accumulating 64 scans, on a Nicolet NEXUS 670 FTIR spectrometer which was equipped with an in situ IR cell with CaF_2 windows. The silica powders were pressed into self-supported discs (2 cm^2 area, 10-15 mg). They were placed in a cell equipped with KBr windows, heated in situ up to 500 °C under 50 mL/min He, kept at this temperature for 1 h, and cooled down to 100 °C. Before the DRIFT measurements, a background spectrum was recorded at the same resolution and number of scans. Scanning electron microscopy (SEM) was measured on the Hitachi S-4800 microscope (operating at 20 kV) 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 ^{29}Si and ^{27}Al MAS NMR spectra were performed on a VARIAN VNMRS 400WB NMR spectrometer under one-pulse conditions. The ^{29}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 ($[(CH_3)_3SiO]_8SiO_{12}$). The ^{27}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. $KAl(SO_4)_2{\bullet}12H_2O$ was used as the reference for its chemical shift.

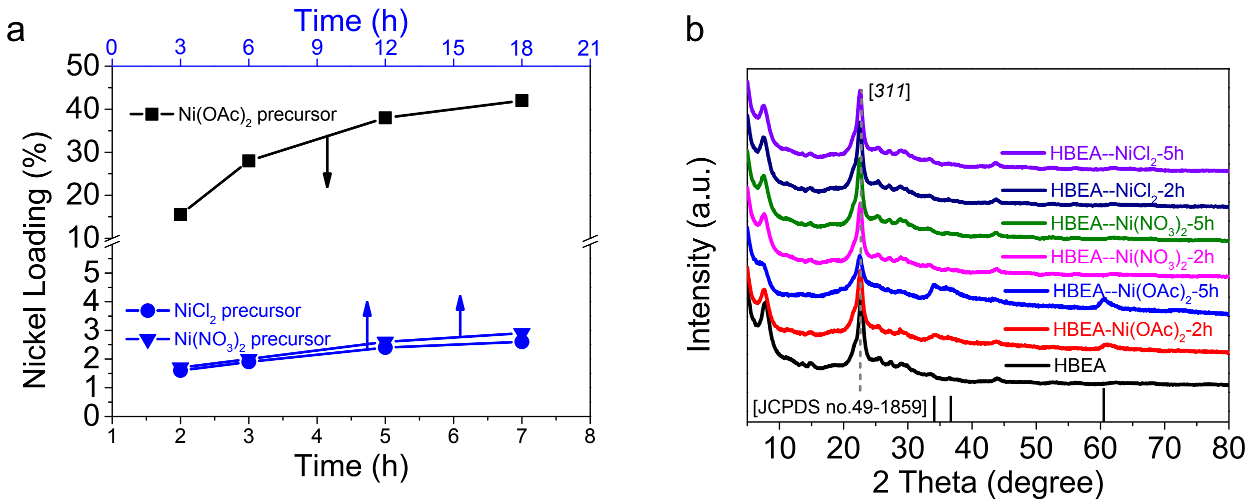

Figure S1. (a) The nickel loading as a function of different hydrothermal treatment times; (b) the XRD patterns of HBEA zeolites of reactions with Ni(OAc)$_2$, NiCl$_2$, or Ni(NO$_3$)$_2$ salts after hydrothermal treatment for 2 h and 5 h.

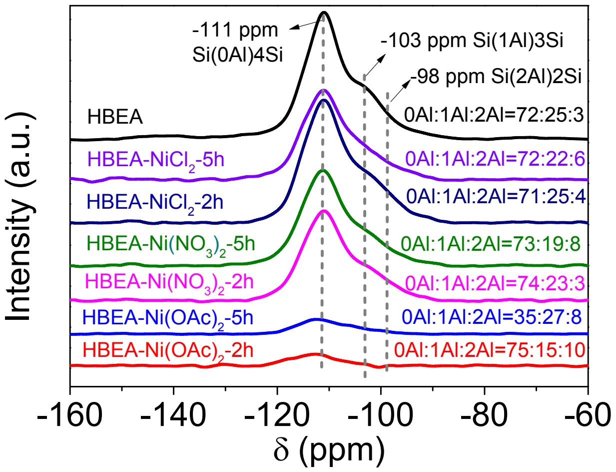

Figure S2. ^{29}Si NMR spectra of HBEA zeolites with reactions of Ni(OAc)$_2$, NiCl$_2$, or Ni(NO$_3$)$_2$ salts after hydrothermal treatment for 2 h and 5 h. Catalyst preparation condition: 0.2 g HBEA, 0.348 g Ni(OAc)$_2$, 140 mlL H_2O, 120°C.

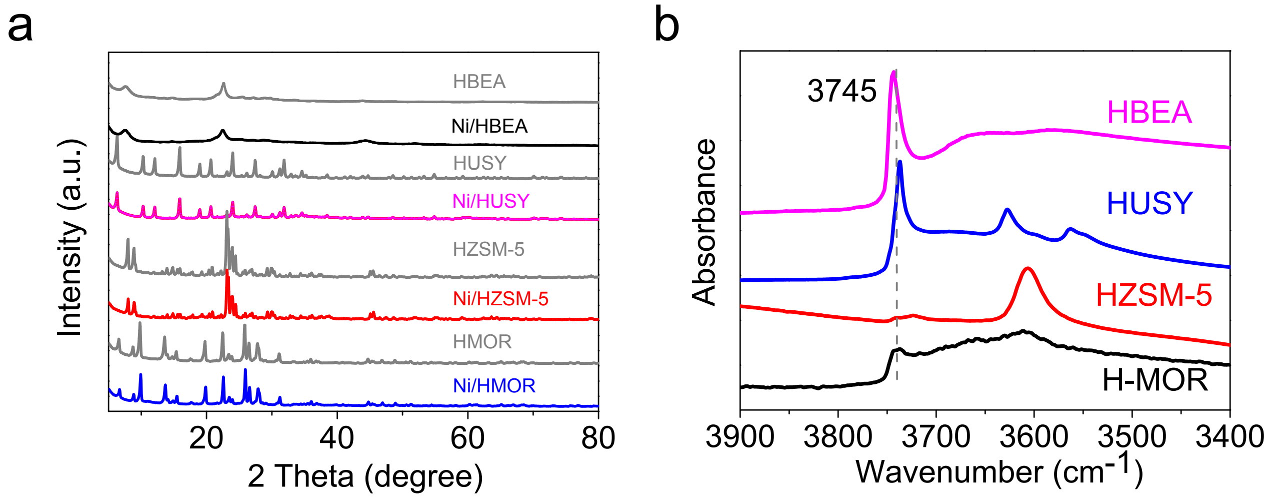

Figure S3. (a) The XRD patterns of zeolites and catalysts, (b) FTIR spectra of four zeolites (HZSM-5, HMOR, HUSY, and HBEA).

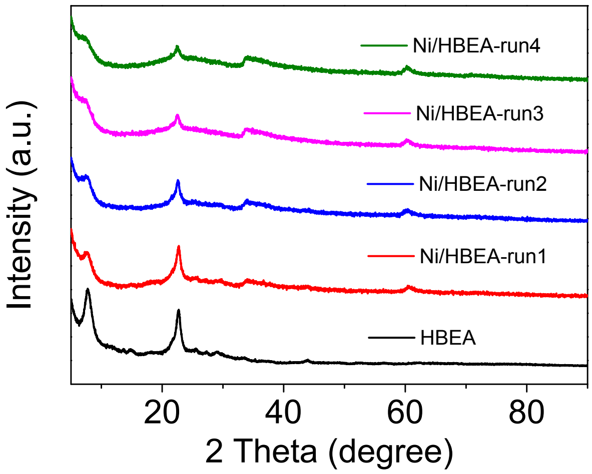

Figure S4. The XRD patterns of Ni/HBEA after the four hydrothermal synthesis cycles.

Catalyst preparation condition: 0.2 g HBEA, 0.348 g $Ni(OAc)_2$, 140 mL H_2O, 120°C, hydrothermal synthesis time: 2 h.

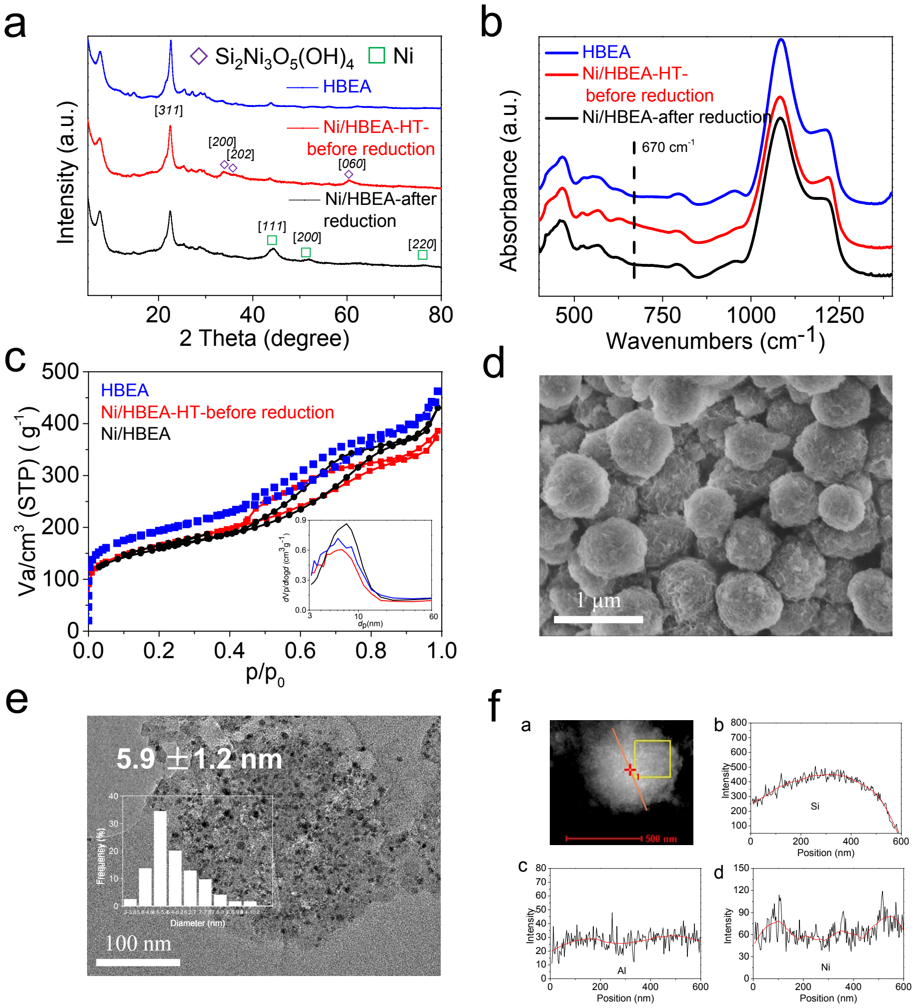

Figure S5. (a) XRD, (b) IR, and (c) N_2 adsorption and desorption isotherms with HBEA and Ni/HBEA (before and after hydrogen reduction) samples; (d) SEM, (e) TEM image (cut in 30-50 nm slices), and (f) corresponding EDX line profiles of elemental (g) Ni, (h) Si, and (i) Al.

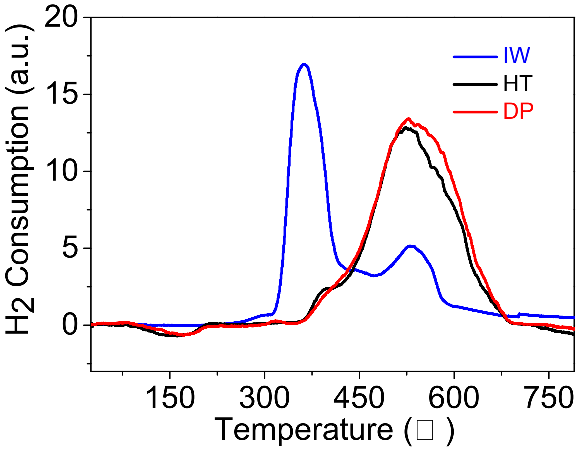

Figure S6. The profile of temperature programmed reduction of H_2 towards the three Ni/HBeta catalysts. (blue line: prepared by the incipient wetness impregnation (IW); black line: prepared by hydrothermal treatment (HT); red line: prepared by deposition-precipitation (DP))

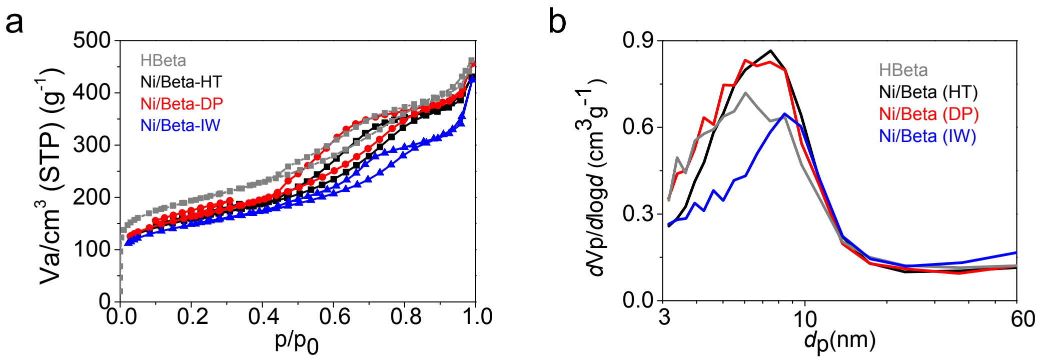

Figure S7. (a) The N_2 adsorption and desorption isotherms and (b) the BJH adsorption pore size distributions of HBeta and three Ni/HBeta.

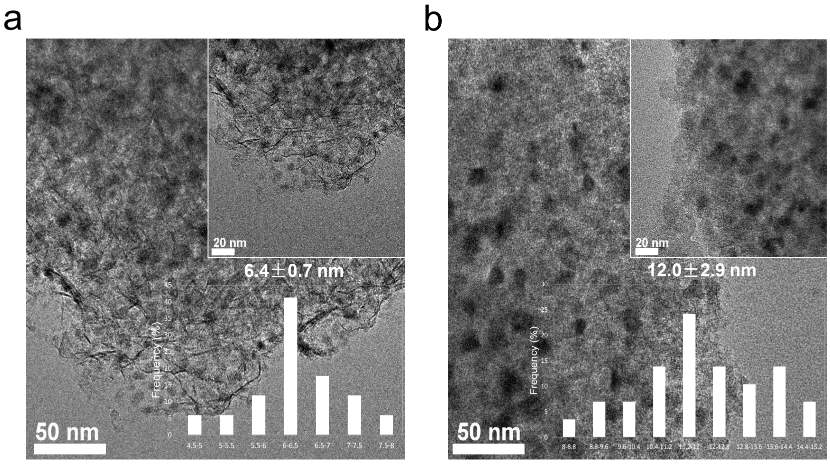

Figure S8. The TEM images of Ni/HBEA –DP (a), Ni/HBEA –IW (b).

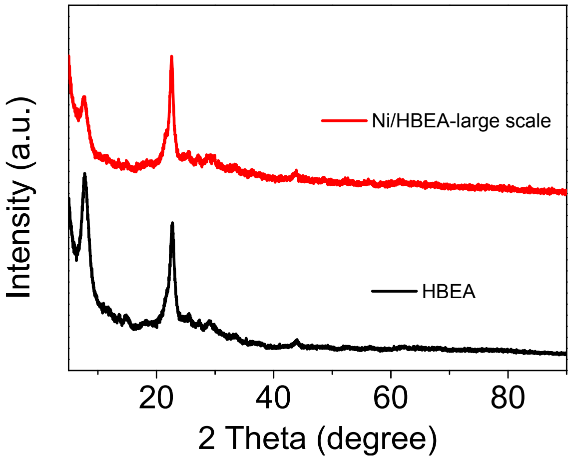

Figure S9. The XRD patterns of different as-made samples (black line: HBEA zeolite; red line: Ni/HBEA prepared in a large scale). [a]

[a] Catalyst preparation condition: 5 g HBEA, 0.348 g $Ni(OAc)_2$, 140 mL H_2O, 120°C, hydrothermal treatment of 2 h in a Parr Instrument (300 mL).

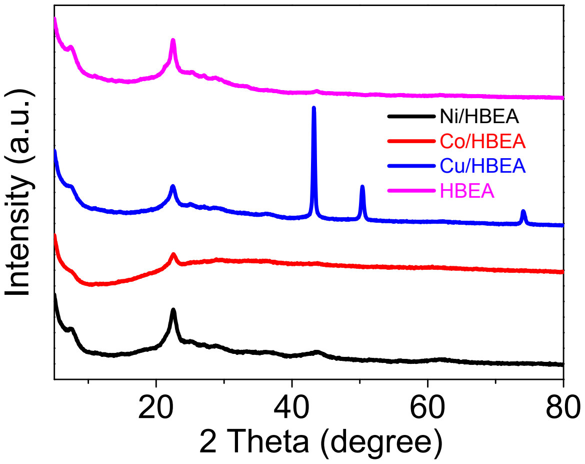

Figure S10. The XRD patterns of HBEA and Ni (Co, Cu)/HBEA samples.

Table S1. Physicochemical properties of parent and treated HBEA samples with different nickel salts

Samples	^{27}Al-NMR Relative content of various Al species [%] [a]		Relative crystallinity [%] [b]	Relative content of various H species [%] [c]		Frame-work Si/Al [d]	Bulk Si/Al [e]	Ni loading [%] [e]	Conc. of Ni (ppm) [e]	Conc. of Si (ppm) [e]	Conc. of Al (ppm) [e]
	$KAl(SO_4)_2 \cdot 12H_2O$	FAl		Si-OH	SiOHAl						
HBEA	-	-	100	28.4	71.6	13.3	12.7	-			
HBEA-$Ni(OAc)_2$-2h	91.8	8.2	74.2	69.8	30.2	11.4	9.6	16.0	466	116	0
HBEA-$Ni(OAc)_2$-5h	94.2	5.8	55.5	76.9	23.1	9.4	7.8	39.0	305	186	0
HBEA-$Ni(NO_3)_2$-2h	90.5	9.5	83.9	42.8	57.2	13.4	11.7	1.6	502	40	1.632
HBEA-$Ni(NO_3)_2$-5h	87.1	12.9	90.9	32.4	67.6	11.5	10.5	1.8	623	116	2.415
HBEA-$NiCl_2$-2h	90.5	9.5	93.2	32.2	67.8	12.4	12.4	1.5	567	44	2.525
HBEA-$NiCl_2$-5h	88.8	11.2	93.4	33.9	66.1	11.9	10.4	1.7	582	116	2.601

[a] Determined by ^{27}Al MAS NMR spectra. [b] Calculated from XRD patterns.

[c] Determined by ^{1}H MAS NMR spectra. [d] Calculated from ^{29}Si MAS NMR data.

[e] Determined by ICP.

Table S2. The nickel loading and composition of the filtrate for the catalysts prepared with HBEA after hydrothermal treatment in different nickel salt solution; and pH for the filtrates.[a]

Hydrothermal time	The pH of solution		Nickel loading (wt%)	The composition of the filtrate		
	Before reaction	After reaction		Ni *conc.* (ppm)	Si *conc.* (ppm)	Al *conc.* (ppm)
2	7.2	5.2	16	466.5	116.0	0
3		4.8	28	340.0	147.5	0
5		4.6	38	305.0	186.0	0
7		4.5	42	247.9	180.3	0

[a] Catalyst preparation condition: HBEA with a nickel acetate solution in a hydrothermal treatment at 120°C.

Table S3. Relative crystallinity, the nickel loading and Si/Al ratios for the catalysts prepared with different zeolites in nickel acetate solution after hydrothermal treatment for 2 h. [a]

Catalysts	Relative Crystallinity [wt%]	Nickel Loading [wt%]	Si/Al ratio[a]
Ni/HBEA	74.2	16	12.7
Ni/HZSM-5	78.8	5	20.5
Ni/HMOR	82.8	6	7.3
Ni/HUSY	66.2	25	17.7

[a] The Si/Al ratio of parent zeolite HBEA is 12.7, HZSM-5 is 20.5, HMOR is 7.5 and HUSY is 21.2.

Table S4. Ni, Si, and Al concentrations in filtrates by ICP measurement for catalysts prepared with different zeolites in nickel acetate solution after hydrothermal treatment for 2 h.

Catalysts	Conc. of Ni (ppm)	Conc. of Si (ppm)	Conc. of Al (ppm)
Ni/HBEA	466.5	116	0.0
Ni/HZSM-5	534.7	11.4	0.0
Ni/HMOR	523.7	29.1	0.0
Ni/HUSY	413.4	136.6	0.0

Table S5. The Ni, Si, and Al concentrations in filtrates by ICP measurement and the pH of filtrate after each cycle hydrothermal treatment, and the nickel loading of Ni/HBEA catalysts.

Treatment/element	Run1	Run2	Run3	Run4
Conc. of Si (ppm)	116.0	175.1	179.6	181.3
Conc. of Ni (ppm)	466.5	403.0	680.8	821.2
Conc. of Al (ppm)	0	0	0	0
Nickel loading (%)	17	15	14	15
The pH of filtrate after reaction	5.20	5.07	4.67	4.52

Table S6. Physicochemical and metallic on parent HBEA, $Ni_3Si_2O_5(OH)_4$, and Ni/HBEA.

Catalyst	Specific surface area $[m^2 \cdot g^{-1}]$ [a]			Pore volume $[cm^3 \cdot g^{-1}]$ [a]			Nickel loading [wt%]	$d_{Ni\text{-}TEM}$ [nm]
	S_{BET}	S_{meso}	S_{micro}	V_{total}	V_{meso}	V_{micro}		
HBEA	638	418	220	0.72	0.60	0.12	-	-
Ni/HBEA-HT-before reduction	562	377	175	0.60	0.51	0.09	-	-
Ni/HBEA-HT-after reduction	534	336	198	0.67	0.57	0.10	17	6.0

[a] Determined by N_2 sorption.

Table S7. Physicochemical on the three Ni/HBEA catalysts.

Catalyst	Specific surface area $[m^2 \cdot g^{-1}]$ [a]			Pore volume $[cm^3 \cdot g^{-1}]$ [a]			Nickel Loading [wt%]
	S_{BET}	S_{meso}	S_{micro}	V_{total}	V_{meso}	V_{micro}	
HBEA	638	418	220	0.72	0.60	0.12	-
Ni/HBEA (HT)	534	336	198	0.67	0.57	0.10	17
Ni/HBEA (DP)	643	387	156	0.70	0.62	0.08	17
Ni/HBEA (IW)	490	299	191	0.66	0.56	0.10	17

[a] Determined by N_2 sorption.

Table S8. The conversion from stearic acid to hydrocarbons using three Ni/HBeta catalysts prepared through HT, DP and IW methods.[a]

Catalysts	Time [min.]	Conversion [%]	Selectivity [%]	C_{17} alkane Yield [%]	C_{18} alkane Yield [%]	Rate [$g \cdot g^{-1} \cdot h^{-1}$]
Ni/HBEA (HT)	20	15.6	95.3	2.8	12.1	11.2
	40	41.7	99.6	8.2	33	
	60	65.9	99.6	15.1	50.5	
Ni/HBEA (DP)	20	10.4	98.0	1.3	8.9	7.6
	40	20.4	96.1	2.4	17.2	
	60	47.9	97.7	6.1	40.8	
Ni/HBEA (IW)	20	7.8	88.0	1.2	5.7	5.2
	40	15.5	97.7	2.4	12.7	
	60	27.0	99.5	3.9	23.2	

[a] Reaction condition: 5.0 g stearic acid, 0.2 g Ni/HBEA, 80 mL *n*-dodecane, 260 °C, 4 MPa H_2, stirring at 600 rpm.

Table S9. The conversion from ethylbenzene to ethylcyclohexane using three Ni/HBeta catalysts prepared through HT, DP and IW methods.[a]

Catalysts	Time [min.]	Conversion [%]	Selectivity [%]	Hydrocarbon Yield [%]	Rate [g·g^{-1}·h^{-1}]
Ni/HBEA (HT)	20	60.7	100	60.7	120
	40	80.6	100	80.6	
	60	99.7	100	98.8	
Ni/HBEA (DP)	20	37.5	100	37.5	56.2
	40	56.5	100	56.5	
	60	80.8	100	80.8	
Ni/HBEA (IW)	20	0.7	100	0.7	1.0
	40	2.0	100	2.0	
	60	3.8	100	3.8	

[a] Reaction condition: : 5.0 g ethylbenzene, 0.1 g Ni/HBEA, 80 mL *n*-dodecane, 200 °C, 4 MPa H_2, stirring at 600 rpm.