Supporting Information

Construction of Ni-Co alloy/zeolite nanosheet catalysts for hydrodeoxygenation of fatty acid to alkanes

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Section 1. Materials and Methods

Tetraethylorthosilicate (TEOS, Tianjin Fuchen Chemical Reagents Company), tetrabutylammonium hydroxide solution (TBAOH, 40 wt % Aladdin), ammonia solution (25%–28%, Sinopharm Chemical Reagent Company), aluminium isopropoxide (Al(C$_3$H$_7$O)$_3$, Tianjin Fuchen Chemical Reagents Company), nickel acetate (Ni(CH$_3$COO)$_2$·4H$_2$O, Sinopharm Chemical Reagent Company), ammonium chloride (NH$_4$Cl, Sinopharm Chemical Reagent Company), cobalt acetate (Co(CH$_3$COO)$_2$·4H$_2$O, Sinopharm Chemical Reagent Company, sodium hydroxide (NaOH, Sinopharm Chemical Reagent Company), ammonium nitrate (NH$_4$NO$_3$, Sinopharm Chemical Reagent Company), stearic acid (98%, Aladdin), dodecane (98%, Aladdin), Commercial ZSM-5 zeolite (Nankai Catalyst Corporation, China). All reagents were used without further purification. Deionized (DI) water was used in all experiments.

Synthesis of self-pillared ZSM-5 zeolites. The self-pillared ZSM-5 was synthesized using tetrabutylammonium hydroxide as the structural directing agent, with the gel molar ratio of 1SiO$_2$: 0.3 TBAOH: 0.01 Al(C$_3$H$_7$O)$_3$: 0.0125 NaOH: 10 H$_2$O. Firstly, 12.4 g of TBAOH solution was mixed with 3 g of deionized water, then 122 mg of aluminum isopropoxide was added and stirred for 30 minutes. After that, 12 mg of NaOH and 12.48 g of TEOS were added and stirred for 4 hours until TEOS was completely hydrolyzed. Finally, the obtained solution was transferred into a 100 mL stainless steel autoclave and crystallized in a pre-heated oven at 80 °C for 1 day and then at 160 °C for 2 days. The as-synthesized solid product was centrifuged, washed with deionized water and ethanol several times, and then dried at 80 °C in the oven

overnight, followed by calcination at 550 °C in air for 6 hours to remove the organic template agent. Finally, the calcined zeolite was converted to the proton form via the ion exchange method. 1 g of calcined zeolite was added into 50 mL 1 M NH_4NO_3 aqueous solution with continuous stirring at 80 °C for 4 hours. The solid product was centrifuged and washed with deionized water. The process was repeated three times, and the resulted solid product was calcined in air at 550 °C for 6 hours.

Synthesis of ZSM-5@Ni-Co silicate. ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.62:0.38 was prepared through a simple hydrothermal process. Typically, 8.7 mg of $Ni(CH_3COO)_2 \cdot 4H_2O$, 4.5 mg of $Co(CH_3COO)_2 \cdot 4H_2O$, 56.1 mg of NH_4Cl, and 95.6 mg of $NH_3 \cdot H_2O$ (28%) were added under stirring in 5.25 g of deionized water. Then 10 mg of the self-pillared ZSM-5 was added to the above solution and ultrasonicated for 30 min to form a uniform suspension, then the mixture was heated to 100 °C for 3 h. The resulting solid precipitate was collected, washed several times with deionized water and ethanol and dried at 80 °C in the oven for 4 hours. The ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.75:0.25 was synthesized using a similar experimental process as the ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.62:0.38 except involving the use of 8.7 mg of $Ni(CH_3COO)_2 \cdot 4H_2O$, 2.25 mg of $Co(CH_3COO)_2 \cdot 4H_2O$, 46.75 mg of NH_4Cl, 79.63 mg of $NH_3 \cdot H_2O$, and 4.375 g of deionized water.

Synthesis of ZSM-5@Ni-Co/SiO_2. ZSM-5@Ni-Co silicate was reduced under a H_2 flow (flow

rate: 20 mL min^{-1}) at 550 $^{\circ}$C for 0.5 h with a heating rate of 5 $^{\circ}$C min^{-1}, and black power of ZSM-5@Ni-Co/SiO$_2$ was collected. The obtained catalysts were designated as ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$ and ZSM-5@Ni$_{0.75}$Co$_{0.25}$/SiO$_2$ separately.

Synthesis of commercial ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$. Commercial ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$ (C-ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$) was prepared using a similar experimental process as ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$, with the only difference being the substitution of self-pillared ZSM-5 zeolites with commercial ZSM-5 zeolites.

Synthesis of ZSM-5@Ni$_3$Si$_2$O$_5$(OH)$_4$. Typically, 8.7 mg of Ni(CH$_3$COO)$_2$·4H$_2$O, 37.4 mg of NH$_4$Cl, and 63.7 mg of NH$_3$·H$_2$O (28%) were added under stirring in 3.5 g of deionized water. Then 10 mg of the self-pillared ZSM-5 was added to the above solution and ultrasonicated for 30 min to form a uniform suspension, then the mixture was heated to 100 $^{\circ}$C for 3 h. The resulting solid precipitate was collected, washed several times with deionized water and ethanol and dried at 80 $^{\circ}$C in the oven for 4 hours.

Synthesis of ZSM-5@Ni/SiO$_2$. ZSM-5@Ni$_3$Si$_2$O$_5$(OH)$_4$ was reduced under a H$_2$ flow (flow rate: 20 mL min^{-1}) at 550 $^{\circ}$C for 0.5 h with a heating rate of 5 $^{\circ}$C min^{-1}, and black power of ZSM-5@Ni/SiO$_2$ was collected.

Synthesis of ZSM-5@Co$_3$Si$_2$O$_5$(OH)$_4$. ZSM-5@Co$_3$Si$_2$O$_5$(OH)$_4$ was prepared under a similar

experimental process as ZSM-5@$Ni_3Si_2O_5(OH)_4$, with the only difference being the substitution of the $Ni(CH_3COO)_2 \cdot 4H_2O$ with $Co(CH_3COO)_2 \cdot 4H_2O$.

Synthesis of ZSM-5@Co/SiO₂. ZSM-5@$Co_3Si_2O_5(OH)_4$ was reduced under a H_2 flow (flow rate: 20 mL min^{-1}) at 550 ^{o}C for 0.5 h with a heating rate of 5 ^{o}C min^{-1}, and black power of ZSM-5@Co/SiO_2 was collected.

Section 2. Characterizations

The powder X-ray diffraction measurements were performed on a Rigaku D-Max 2550 diffractometer by using Cu Kα radiation. Scanning electron microscopy images were measured with JEOL JSM-7800F. The transmission electron microscopy images and the elemental mappings were measured with a Tecnai F20 electron microscope. High resolution transmission electron microscopy (HRTEM) and energy dispersive spectrometer (EDS) mapping were performed on a JEOL JEM-2100F microscope. The H_2-TPR measurements were measured on a Micromeritics AutoChem II 2920 instrument. Chemical compositions of samples were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using iCAP 7000 Series. Nitrogen adsorption/desorption measurements were carried out on a Micromeritics ASAP 3-flex analyzer at 77 K after the samples were degassed at 350 °C under vacuum. XPS spectra of the catalysts were performed using a Thermo ESCALAB 250 spectrometer (Thermo Scientific, NY, USA). Fourier transform infrared (FTIR) spectra were recorded on a BRUKER vertex 80v; samples before testing were pelleted with KBr powder.

Section 3. Catalytic tests

The deoxygenation reaction of stearic acid (SA) was carried out in a batch autoclave (CHEMN Instrument, 100 mL). In a typical run, 0.1 g of catalysts, 1 g of SA and 40 mL of dodecane were introduced into the batch autoclave. The autoclave was sealed and firstly purged with N_2 (30 bar) three times to remove the residual air, followed by filling it with the reaction gas H_2 (40 bar) at room temperature. The reaction was performed at 260 °C at a stirring speed of 1000 rpm. The liquid products were obtained by *in-situ* sampling every 20 min and analyzed by gas chromatography (GC, Agilent 7890B) equipped with HP-innowax column (30 m × 320 μm × 25 μm) and FID detector. The methyl heptadecanoate was used as a quantitative internal standard in GC measurement. The mass balance was above 98%.

The yield, conversion, and normalized rate were calculated based on the following equations:

The conversion (%) = mass of the converted SA (g)/mass of the starting SA (g) ×100% (By GC analysis)   (Equation S1)

The selectivity (%) = mass of one product (g)/mass of all the products (g) ×100% (By GC analysis)   (Equation S2)

The yield (%) = conversion×selectivity×100%   (Equation S3)

The reaction rate (g_{SA} g_{cat}^{-1} h^{-1}) = mass of converted SA (g)/mass of catalyst (g)/reaction time (h)

(Equation S4)
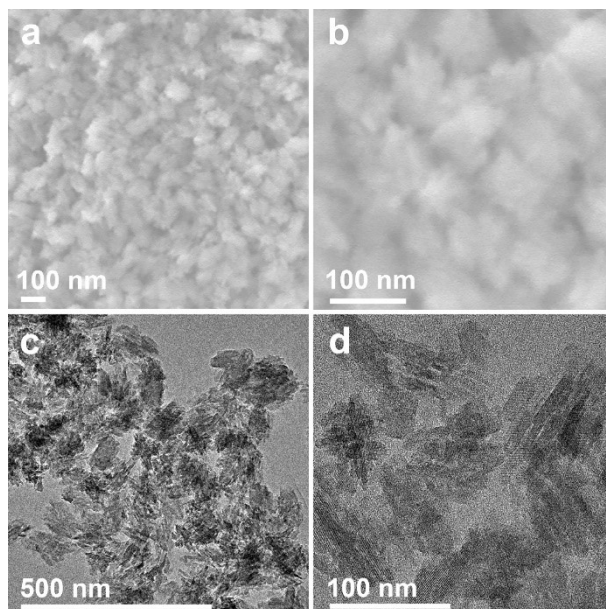
Section 4. Additional figures and tables

Fig. S1 (a, b) SEM and (c, d) TEM images of ZSM-5 zeolites with self-pillared nanosheet morphology.
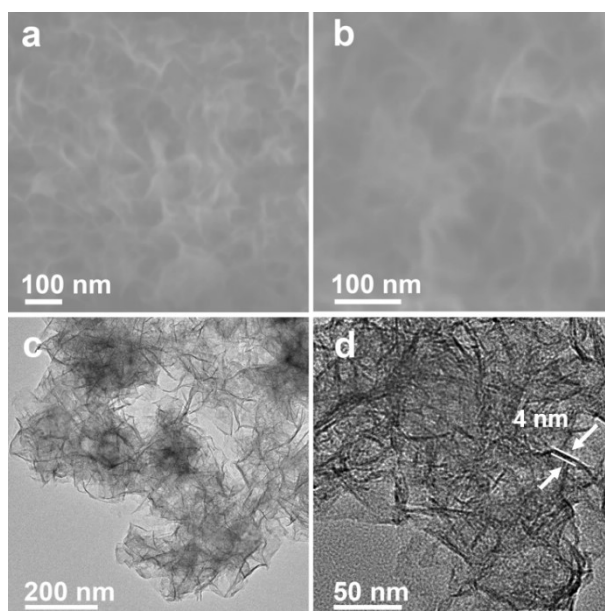

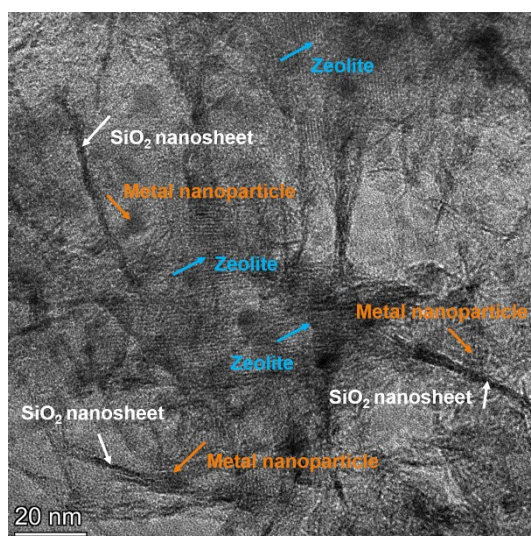**Fig. S2** (a, b) SEM and (c, d) TEM images of ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.62:0.38.

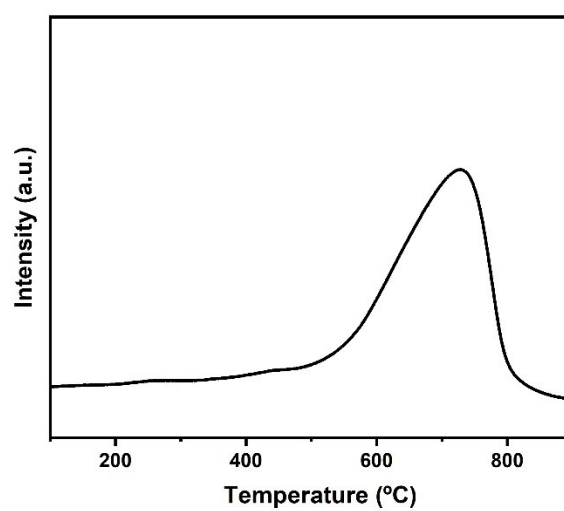**Fig. S3** TEM image of ZSM-5@$Ni_{0.62}Co_{0.38}$/SiO_2 catalysts.

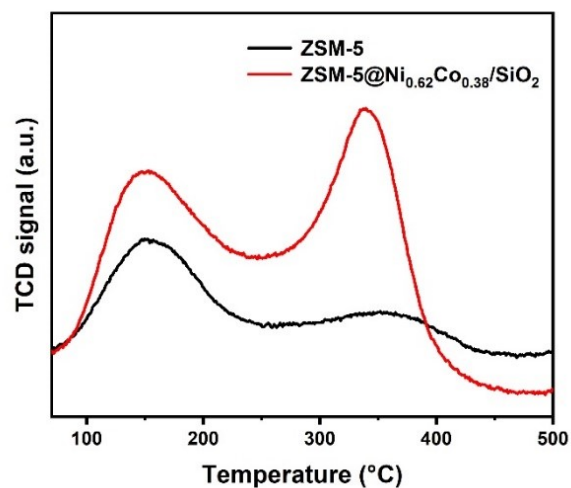**Fig. S4** H_2-TPR profile of ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.62:0.38.

Fig. S5 NH$_3$-TPD profiles of ZSM-5 and ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$.
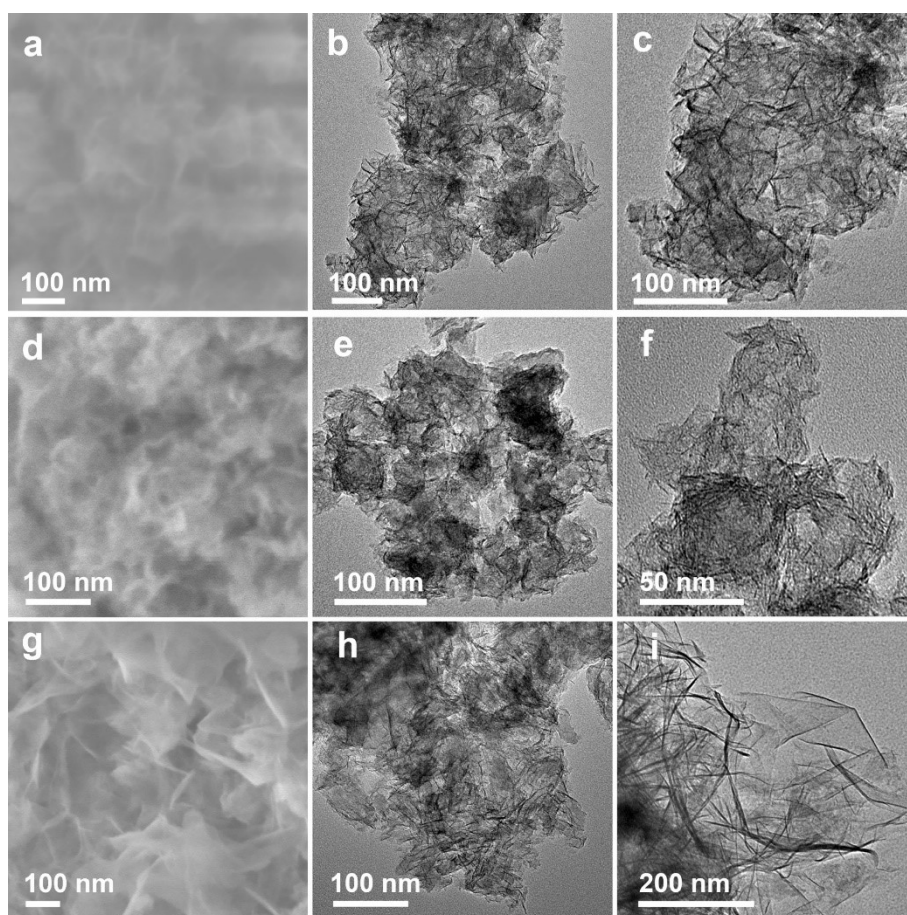
Fig. S6 (a, d, g) SEM and (b, c, e, f, h, i) TEM images of (a–c) ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.75:0.25, (d–f) ZSM-5@Ni$_3$Si$_2$O$_5$(OH)$_4$, and (g–i) ZSM-5@Co$_3$Si$_2$O$_5$(OH)$_4$.
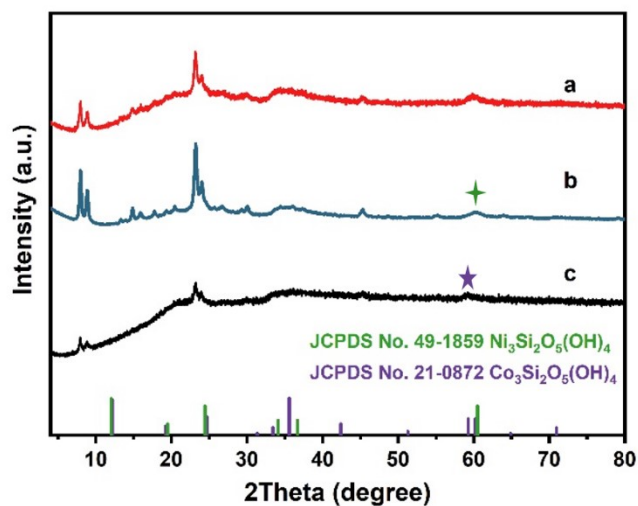
Fig. S7 XRD patterns of (a) ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.75:0.25, (b) ZSM-5@$Ni_3Si_2O_5(OH)_4$, and (c) ZSM-5@$Co_3Si_2O_5(OH)_4$.
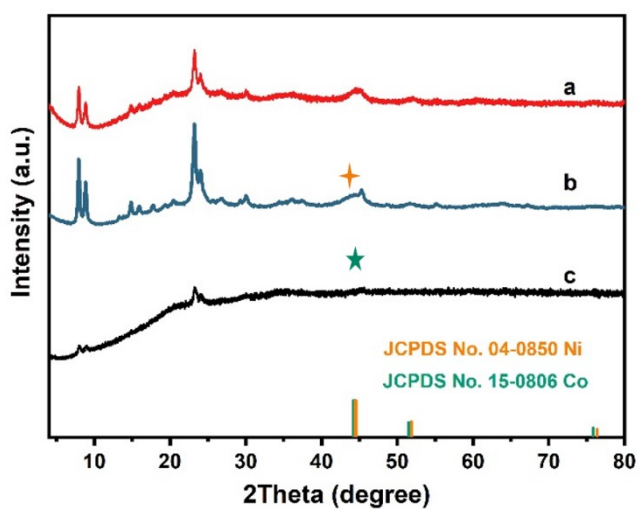
Fig. S8 XRD patterns of (a) ZSM-5@$Ni_{0.75}Co_{0.25}$/SiO_2, (b) ZSM-5@Ni/SiO_2, and (c) ZSM-5@Co/SiO_2.
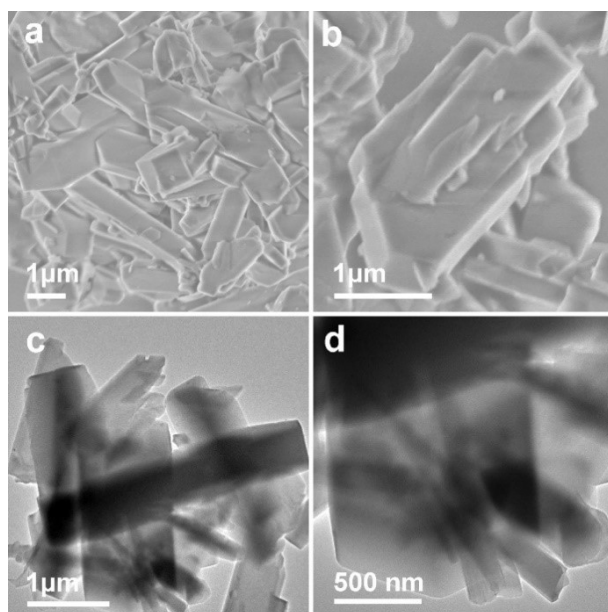
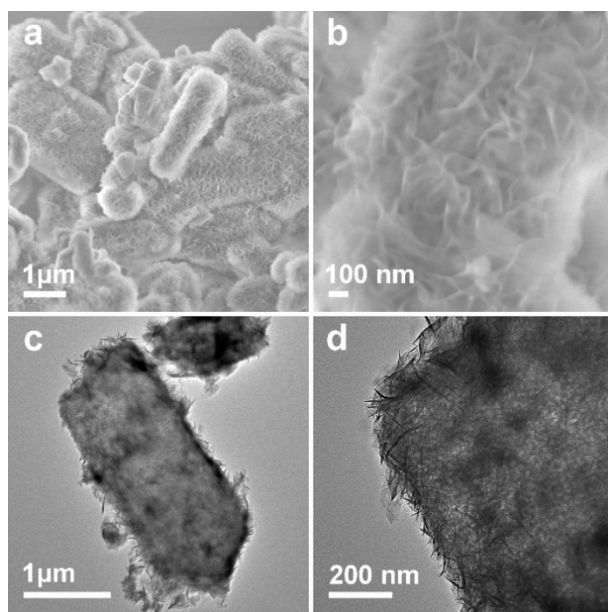**Fig. S9** (a, b) SEM and (c, d) TEM images of commercial ZSM-5 zeolites.

Fig. S10 (a, b) SEM and (c, d) TEM images of C-ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.62:0.38.
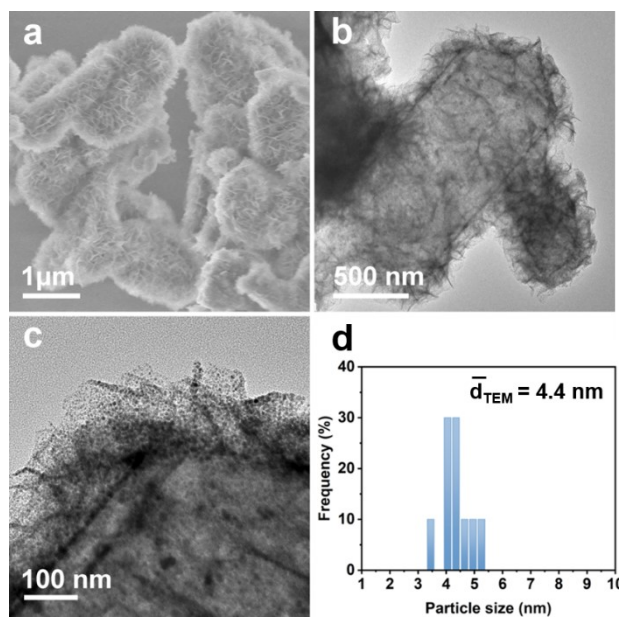
Fig. S11 (a) SEM image, (b, c) TEM images of C-ZSM-5@$Ni_{0.62}Co_{0.38}$/SiO$_2$, and (d) the corresponding size distribution of Ni-Co alloy nanoparticles.
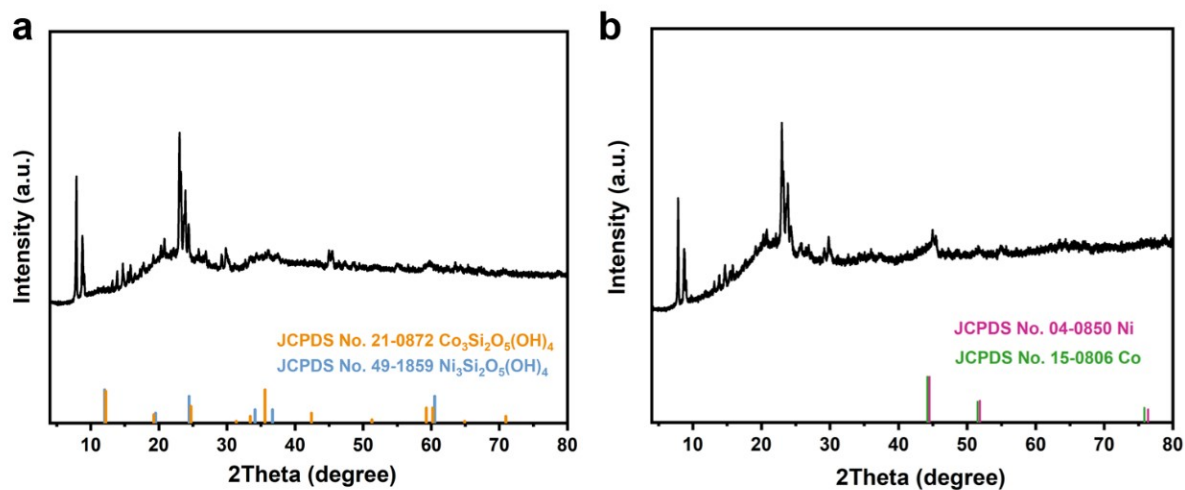

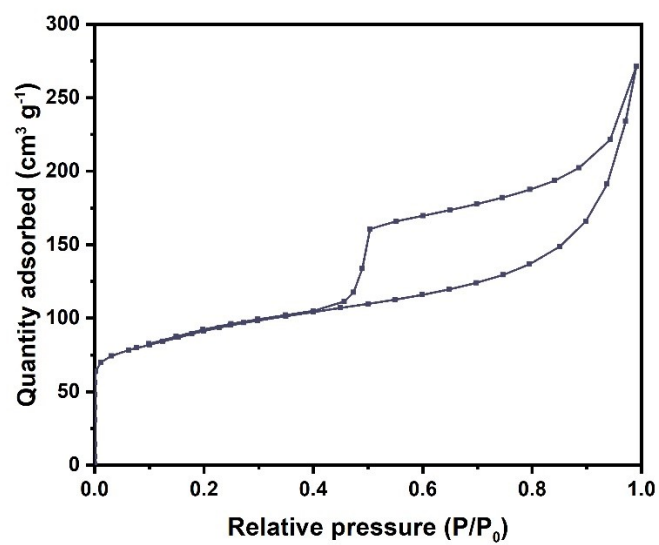**Fig. S12** XRD patterns of (a) C-ZSM-5@Ni-Co silicate with the Ni/Co ratio of 0.62:0.38 and (b) C-ZSM-5@$Ni_{0.62}Co_{0.38}$/SiO$_2$.

Fig. S13 N_2 adsorption-desorption isotherms of C-ZSM-5@$Ni_{0.62}Co_{0.38}$/SiO_2.
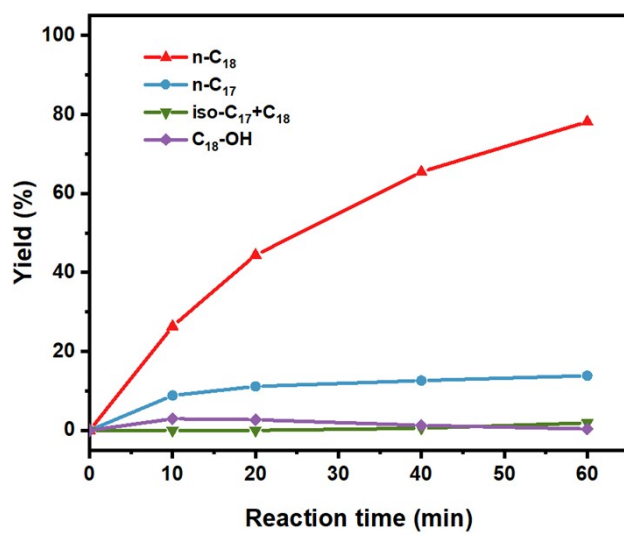

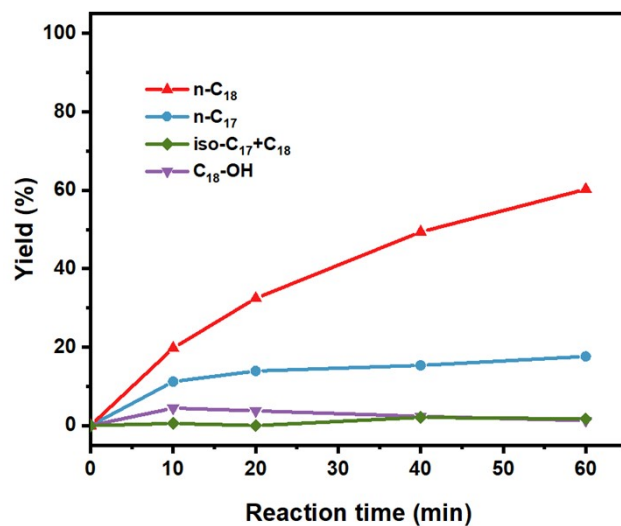**Fig. S14** Time-dependent product yields with ZSM-5@$Ni_{0.75}Co_{0.25}$/SiO_2 catalysts.

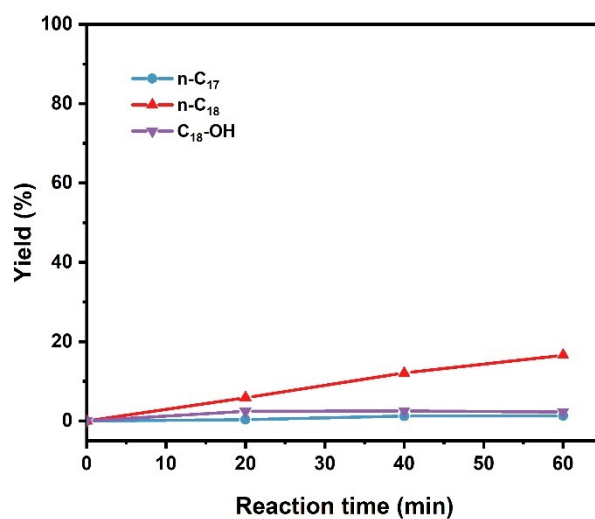**Fig. S15** Time-dependent product yields with ZSM-5@Ni/SiO$_2$ catalysts.

Fig. S16 Time-dependent product yields with ZSM-5@Co/SiO$_2$ catalysts.
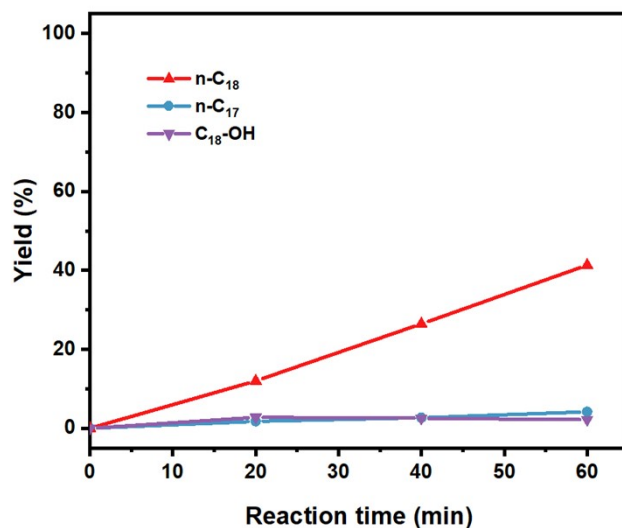
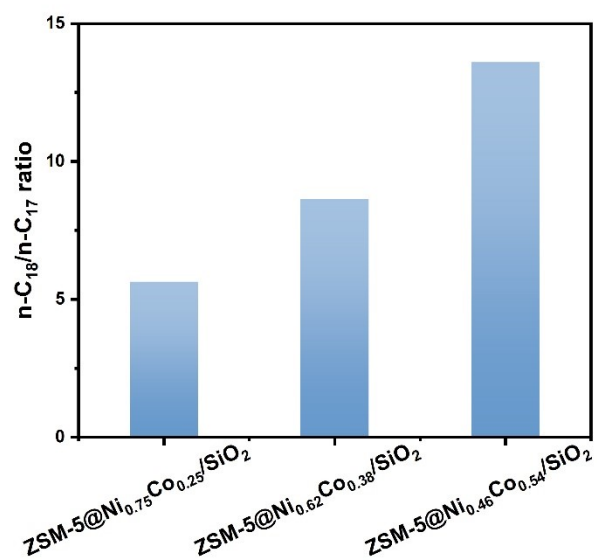**Fig. S17** Time-dependent product yields with C-ZSM-5@$Ni_{0.62}Co_{0.38}$/SiO_2 catalysts.

Fig. S18 The ratio of n-C_{18}/n-C_{17} in the product over different ZSM-5@Ni-Co alloy/SiO_2 catalysts.

Table S1. The textural properties of the various samples.

Sample	S_{BET}[a] (m²/g)	S_{micro}[b] (m²/g)	S_{ext}[b] (m²/g)	V_{micro}[b] (cm³/g)	V_{total}[c] (cm³/g)	V_{meso}[d] (cm³/g)
ZSM-5	464	359	105	0.14	0.72	0.58
ZSM-5@Ni-Co silicate	477	175	302	0.07	0.67	0.60
ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$	448	162	286	0.07	0.66	0.59
C-ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$	323	214	109	0.10	0.42	0.32

[a] Specific surface area calculated from the nitrogen adsorption isotherm using the BET method. [b] S_{micro} (micropore area), S_{ext} (external surface area), and V_{micro} (micropore volume) calculated using the t-plot method. [c] Total pore volume at $P/P_0 = 0.99$. [d] $V_{meso} = V_{total} - V_{micro}$.

Table S2. Comparisons of catalytic activities for hydrodeoxygenation of fatty acids over literature reported catalysts with this work.

Catalyst	Metal loading (wt%)	Reaction composition[a]	Reaction conditions	Time (min)	Con. (%)	Rate $(g\ g_{cat}^{-1}\ h^{-1})$	HDO/DCO$_x$[b]	Ref.
ZSM-5@Ni$_{0.62}$Co$_{0.38}$/SiO$_2$	22.6	10/1	T=260 °C P=4.0 MPa H$_2$	50	100	12	8.63	This work
Ni/Co-S	4	3/5	T=290 °C P=4.0 MPa H$_2$	180	99.0	0.20	12.3	1
Co$_x$Ni$_{1-x}$P/SiO$_2$	10	50/3	T=320 °C P=2.0 MPa H$_2$	240	96.9	4.0	0.06	2
NiCo/SiO$_2$	20	5/3	T=280 °C P=1.0 MPa H$_2$	180	83.0	0.46	mainly DCO	3
NiCo/C–Na	20	5/3	T=280 °C P=1.0 MPa H$_2$	180	100	0.55	mainly DCO	4

[a] The reaction composition refers to the mass ratio of the substrate to the catalyst in the reaction slurry.

[b] HDO/DCO$_x$ was calculated based on (selectivity of hydrodeoxygenation (HDO) products)/(selectivity of decarboxylation (DCO) or decarbonylation (DCO$_2$) products).

Reference

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3. H. Lin, Y. Chu, M. Xie, L. Yang and G. Ouyang, NiCo/SiO$_2$ nanospheres for efficient synergetic decarboxylation of fatty acids and upgrading of municipal sludge HTL bio-crude to biofuels, *J. Environ. Chem. Eng.*, 2023, **11**, 110825.

4. H. Lin, F. Liao, Y. Chu, M. Xie, L. Pan, Y. Wang, L. Leng, D. Xu, L. Yang and G. Ouyang, Hierarchical porous honeycomb NiCo/C catalyst for decarboxylation of fatty acids and upgrading of sludge bio-crude, *Chem. Eng. Sci.*, 2024, **284**, 119439.