

Electronic Supplementary Information

The effect of the particle size on Fischer–Tropsch synthesis for ZSM-5 zeolite supported cobalt-based catalysts

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Experimental Details

Catalyst preparation

Synthesis of mesoporous ZSM-5 (Z5) zeolite: Pristine ZSM-5 zeolites were hydrothermally synthesized using n-butylamine and ethylamine as templates according to the literature.¹ Pristine H-ZSM-5 was prepared by mixing 8.0 g of as-synthesized ZSM-5 and 80 g of 0.2 M NaOH solution at 70 °C for 1 h. After being stirred for 1 h, resultant solids were collected by filtration, washing, and drying. This treatment process was repeated once. The H-form of the sample was obtained by ion-exchanging with a 1.0 M NH₄Cl solution at 70 °C for 1 h (1.0 g of zeolite in 10 mL of solution), and

the ion-exchange process was performed three times followed by calcination at 550 °C for 4 h. Z5 was prepared by treating H-ZSM-5 zeolite using 0.5 M TPAOH solutions. In a typical synthesis, 5.0 g of H-ZSM-5 and the calculated CTAB were mixed with 50 mL of 0.5 M TPAOH solution by using a sealed Teflon-lined stainless-steel autoclave. After hydrothermal treatment at 170 °C for 24 h, Z5 was obtained by filtrating, washing with deionized water, drying at 110 °C overnight, and calcining at 550 °C for 4 h.

Synthesis of Co-x/Z5 catalysts: Co-x/Z5 catalysts were prepared by an incipient wetness impregnation method. For Co-4.5/Z5, Co-9.9/Z5 and Co-14/Z5 catalysts, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved into deionized water, the cobalt loading was 4.6, 17.8 and 19.2 wt.%, respectively. Then the precursor solution was impregnated on Z5 support and mixed for about 20 min. Next, the mixture was frozen at -80 °C for 20 h and then transferred to a freeze dryer for 48 h. After that, the Co-4.5/Z5 and Co-9.9/Z5 samples were calcined in 10% NO/Ar at 250 °C for 5 h while the Co-14/Z5 samples were calcined in 10% NO/Ar at 450 °C for 5 h. For Co-18/Z5 catalyst, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was first dissolved into deionized water. Then the precursor solution was impregnated on Z5 support with cobalt loading of 18.1 wt.% and mixed for about 20 min. Next, the mixture was aged at 80 °C for 20 h in an oven. After that, the sample was calcined in N_2 at 250 °C for 5 h.

Catalyst characterization

Powder X-ray diffraction (XRD) pattern was performed on a Rigaku Ultima IV X-ray powder diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation, scanning from 5° to 90° with a scanning rate of 4° min^{-1} . The average size of the Co_3O_4 crystallite ($d(\text{Co}_3\text{O}_4)$) was calculated by the Scherrer's

equation from the Co_3O_4 peak at $2\theta = 36.9^\circ$. And the average Co size was calculated from the corresponding $d(\text{Co}_3\text{O}_4)$ by applying the molar volume correction: $d(\text{Co}^0) = 0.75d(\text{Co}_3\text{O}_4)$.

The specific surface area, pore volume, and pore size were determined by N_2 adsorption–desorption measurements using Micromeritics ASAP 2420 instrument. All $\text{Co-}x/\text{Z5}$ catalysts were degassed at 300°C for 12 h before analysis. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the pore volume was determined at a relative pressure (P/P_0) of 0.99.

Scanning electron microscopy (SEM) images were obtained by a Zeiss Supra 55 instrument with an accelerating voltage of 2.0 kV. Transmission electron microscopy (TEM) images were taken on a JEOL-JEM 2000FX electron microscope with an accelerating voltage of 200 kV. Pyridine-adsorption Fourier transform infrared (FT–IR) experiment was carried out with a Fourier transform infrared spectrometer equipped with Nicolet Nexus 4700.

Temperature programmed desorption of NH_3 (NH_3 –TPD) was performed on a Micromeritics 2920 chemisorption system. The sample was pre-treated with an Ar flow at 400°C for 1 h and then cooled down to 100°C . Next, the sample was exposed to NH_3 for 1 h and purged with Ar to remove the physically adsorbed NH_3 . Finally, the signal was recorded from 100°C to 600°C at a rate of 5°C min^{-1} .

Temperature programmed desorption of CO (CO –TPD) was performed on a Micromeritics 2920 chemisorption system. The sample was first reduced by a H_2 flow at 400°C for 8 h and evacuated in Ar flow for 1 h. Next, the temperature was cooled down to 50°C for CO adsorption. The sample was purged by Ar flow and then heated from 50°C to 800°C at a rate of $10^\circ\text{C min}^{-1}$.

H₂ temperature programmed reduction (H₂-TPR) was carried out with a Micromeritics 2920 chemisorption system. The sample was heated under Ar flow at 150 °C for 2 h and then cooled down to 50 °C. Then 5% H₂/Ar mixture was introduced and the temperature was raised to 800 °C at a rate of 5 °C min⁻¹.

X-ray photoelectron spectroscopy (XPS) measurements were studied on a Kratos AXIS ULTRA DLD spectrometer equipped with Al K α radiation (150 W, $h\nu = 1486.6$ eV) under ultrahigh vacuum (10⁻⁷ bar). Adventitious carbon deposit C (1s) with E_b = 284.8 eV was deemed as reference to calibrate internally the binding energies of other elements.

Co dispersion was evaluated on a Micromeritics 2920 chemisorption system. The as-prepared sample was first reduced with a H₂ flow at 400 °C for 8 h and then evacuated in an Ar flow for 1 h. Then the temperature was cooled down to 100 °C for the adsorption of H₂ for 1 h. The sample was purged by Ar flow and then heated from 100 °C to 400 °C at a rate of 10 °C min⁻¹. The dispersion was calculated according to the equation $D = 1.179X/Wf$, where X was the total H₂ uptake in micromoles per gram of catalyst, W was the weight percentage of cobalt and f was the cobalt reduction degree calculated from O₂ pulse. The O₂ pulse was injected into the sample after reduction until the peak area detected by a thermal conductivity detector (TCD) did not change. By assuming spherical metal particles with an atom density of 14.6 atom nm⁻², the particle size of metal cobalt can be calculated by: Co particle size = 0.96/dispersion.

Catalytic reaction

The FTS was performed on a fixed-bed steel reactor. Prior to the catalytic test, the calcined catalyst was ground and sieved to 60–80 meshes. Then 1.0 g of Co- x /Z5 catalyst was diluted with

silica sand and the volume ratio of catalyst and silica sand was 1:2. Before reaction, the catalyst was reduced in a pure H₂ flow (50 mL min⁻¹) at 400 °C for 8 h. After reduction, the temperature was cooled down to 200 °C and the syngas (CO/H₂ = 1/2) was introduced. The catalytic tests were performed at 240 °C, 2.0 MPa, and space velocities of 3000 mL g_{cat}⁻¹ h⁻¹. The oil and wax products of FTS were collected through cold trap (0 °C) and hot trap (120 °C), respectively, and analyzed by a flame ionization detector (FID) from Shimadzu GC2010. The tail gas passing through two traps including H₂, CO, N₂, CO₂, and C₁–C₅ hydrocarbons was analyzed by TCD and FID from Shimadzu GC2010. CO conversion was calculated by the internal standard method through the 1.5% N₂ from the feed gas. The hydrocarbon product distribution was calculated based on a molar carbon basis. All the tests keep the carbon balance in 95%–103%.

Supplementary tables and figures

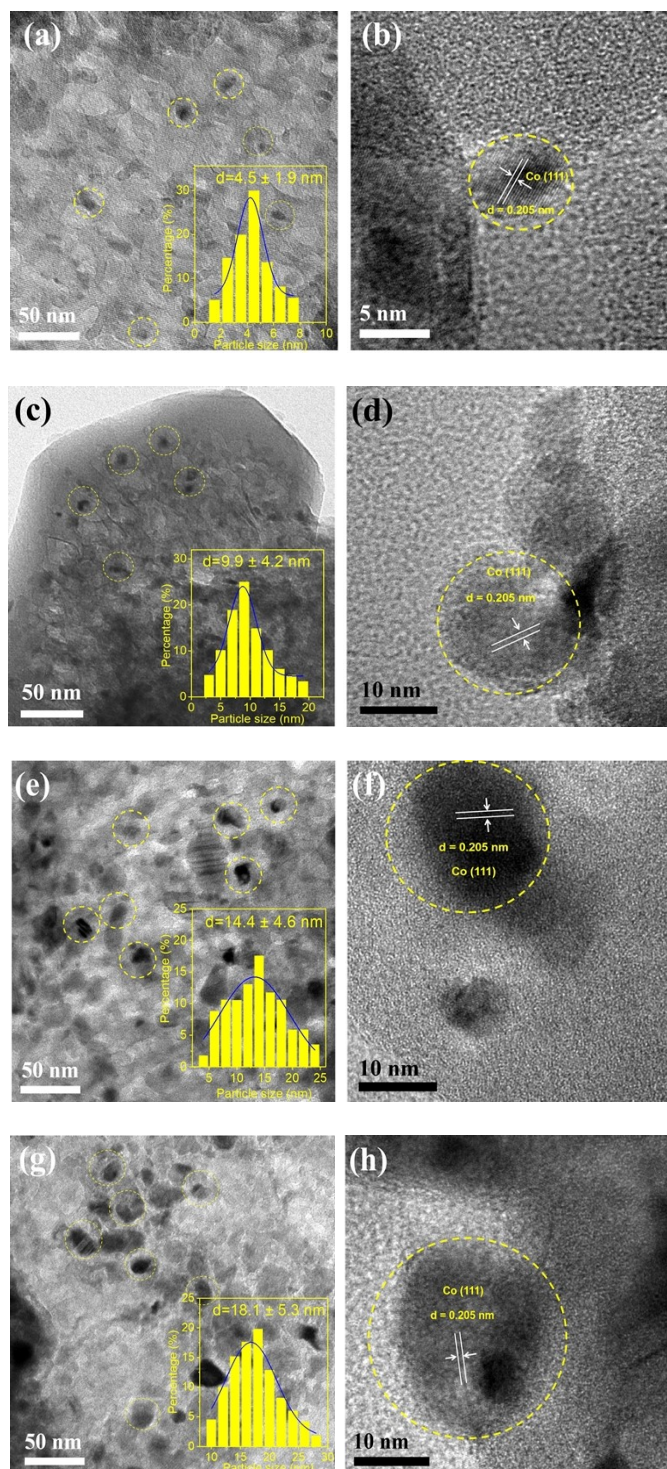


Fig. S1 (a,c,e,g) TEM and (b,d,f,h) HRTEM images of reduced (a,b) Co-4.5/Z5, (c,d) Co-9.9/Z5, (e,f) Co-14/Z5 and (g,h) Co-18/Z5 catalysts and the inset in TEM images is the corresponding cobalt particle size distribution.

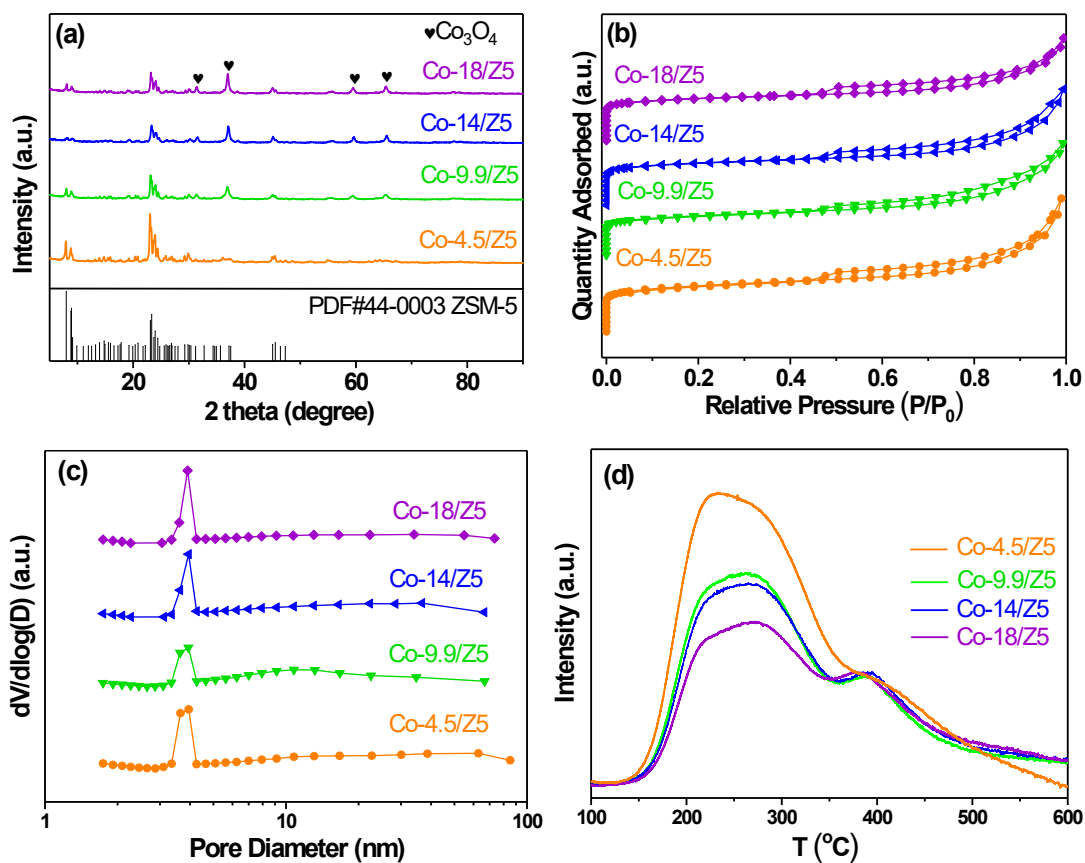


Fig. S2 (a) XRD patterns, (b) N₂ adsorption–desorption curves, (c) the pore distribution and (d) NH₃–TPD of Co-*x*/Z5 catalysts.

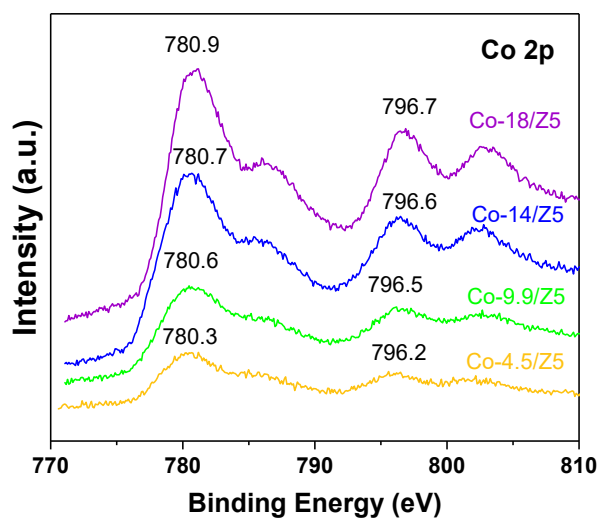


Fig. S3 The Co 2p XPS spectra of Co-*x*/Z5 catalysts.

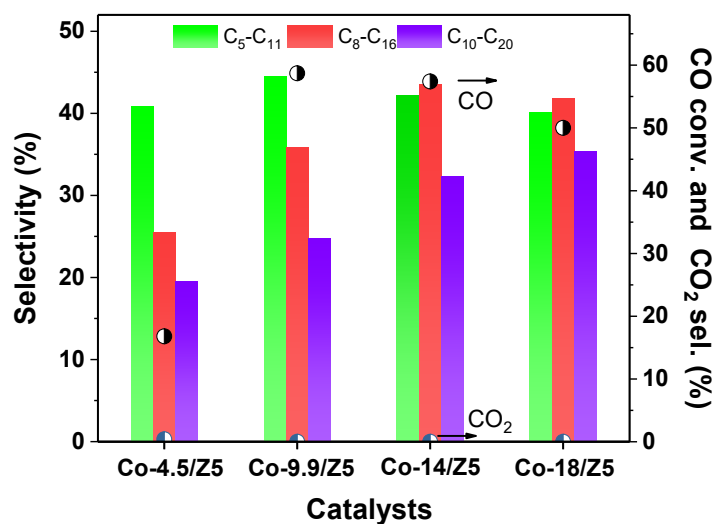


Fig. S4 The Fischer-Tropsch performance over Co-*x*/Z5 catalysts. Reaction conditions: T = 240 °C, P = 2.0 MPa, H₂/CO = 2, WHSV = 3000 mL g_{cat}⁻¹ h⁻¹ and time-on-stream of 48 h.

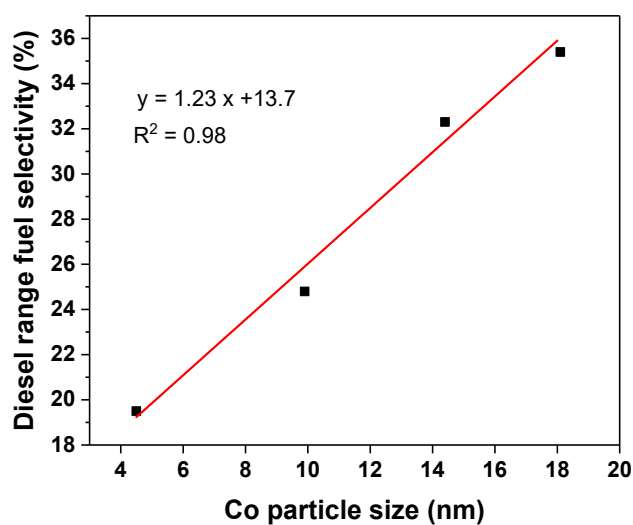


Fig. S5 The relationship between the diesel range fuel (C₁₀-C₂₀ hydrocarbons) selectivity and the Co particle size.

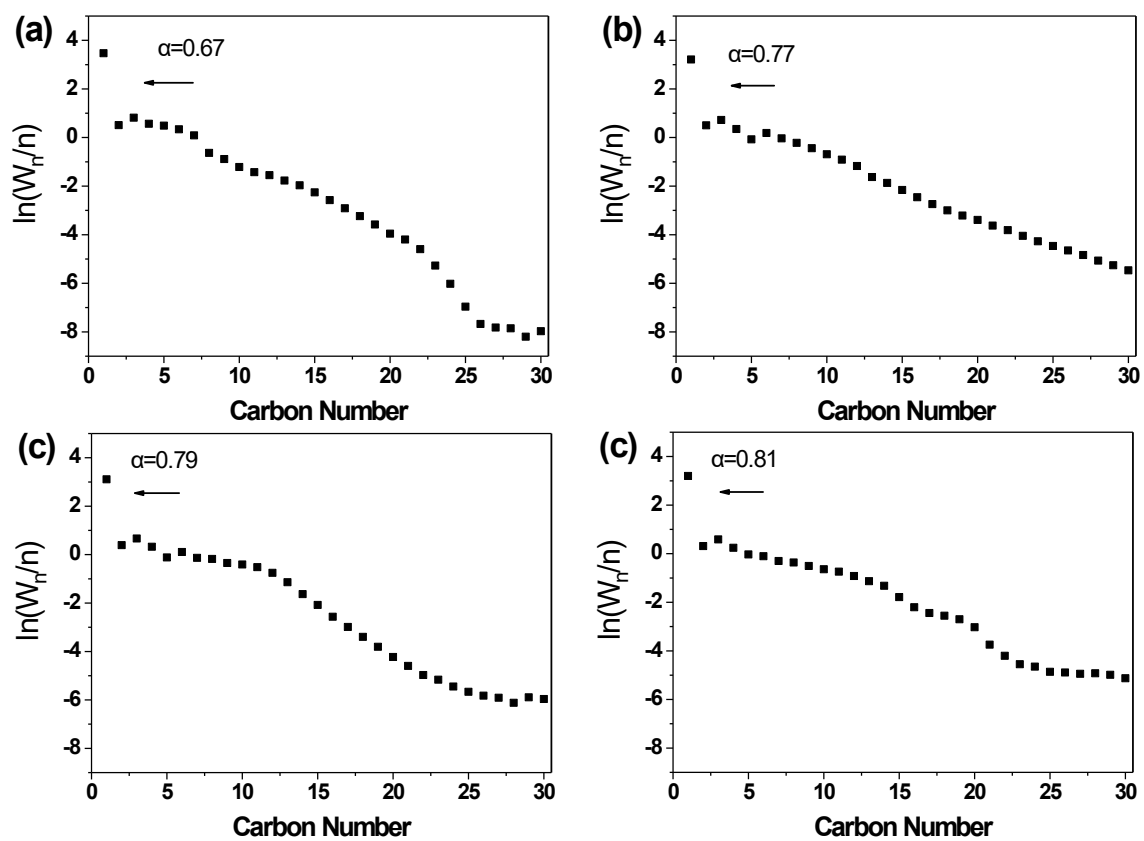


Fig. S6 The ASF distribution and α value of (a) Co-4.5/Z5, (b) Co-9.9/Z5, (c) Co-14/Z5 and (d) Co-18/Z5 catalysts.

Table S1 Physicochemical properties of the Co-*x*/Z5 catalysts.

Catalysts	$S_{\text{BET}}^{\text{a}}$	$V_{\text{pore}}^{\text{a}}$	$V_{\text{meso}}^{\text{a}}$	$V_{\text{micro}}^{\text{a}}$	$d_{\text{pore}}^{\text{a}}$	d_{Co}^{b}	d_{Co}^{c}	d_{Co}^{d}	Reducibility ^d	Co dispersion ^d
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(nm)	(nm)	(nm)	(nm)		
Co-4.5/Z5	312	0.36	0.29	0.07	4.7	-	4.5	4.8	55.2	19.8
Co-9.9/Z5	273	0.30	0.24	0.06	4.6	10.2	9.9	10.4	92.0	9.2
Co-14/Z5	295	0.30	0.24	0.06	4.4	14.7	14.4	14.7	88.6	6.5
Co-18/Z5	297	0.28	0.21	0.07	4.2	18.4	18.1	18.5	91.3	5.2

^a Determined by N₂ adsorption. ^b Calculated by the Scherrer formula based on XRD and the formula as follow: $d_{\text{Co}} = 0.75 d_{\text{Co}_3\text{O}_4}$. ^c Calculated by the TEM. ^d Calculated from H₂-TPD and O₂ titration.

Table S2 The acidity and the H₂ uptake of Co-*x*/Z5 catalysts.

Catalysts	Acidity (μmol g ⁻¹) ^a		H ₂ uptake (μmol g ⁻¹) ^b
	C _B	C _L	
Co-4.5/Z5	141.5	443.7	22.6
Co-9.9/Z5	112.6	372.1	124.9
Co-14/Z5	88.6	336.5	80.2
Co-18/Z5	80.1	316.9	77.9

^a Determined by Py-FTIR. ^b Calculated from H₂-TPD.

Table S3 The catalytic activity and selectivity of the Co-*x*/Z5 catalysts.

Catalyst	CO	CO ₂	Hydrocarbon Selectivity (%)								α
	Conv. (%)	Sel. (%)	CH ₄	C ₂ -C ₄	C ₅ -C ₇	C ₈ -C ₁₆	C ₅ -C ₁₁	C ₁₀ -C ₂₀	C ₁₇₊	C ₂₁₊	
Co-4.5/Z5	16.8	0.4	28.3	15.2	26.8	25.5	41.8	19.5	4.2	1.4	0.67
Co-9.9/Z5	58.7	-	21.9	13.4	19.9	35.8	44.5	24.8	9.0	2.0	0.77
Co-14/Z5	57.4	-	20.9	13.4	17.9	43.5	42.2	32.3	4.3	4.3	0.79
Co-18/Z5	50.0	-	21.0	11.4	17.0	41.8	40.1	35.4	8.8	3.5	0.81

Reaction conditions: T = 240 °C, P = 2.0 MPa, H₂/CO = 2, WHSV = 3000 mL g_{cat}⁻¹ h⁻¹ and time-on-stream of 48 h.

Reference

1. C. Yang, M. Qiu, S. Hu, X. Chen, G Zeng, Z. Liu and Y Sun, *Micropor. Mesopor. Mat.* **2016**, 231, 110–116.