

Supplementary Information

## **Cobalt Nanoparticles Confined in Silica Networks with 3D Hierarchical Porous Features for Fischer-Tropsch Synthesis**

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## Experimental Sections

### Chemicals and materials

All chemical reagents were used without further purification unless otherwise noted. Cobalt(II) acetate tetrahydrate ( $(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$ ,  $\geq 99\%$ ), ammonium hydroxide solution ( $\text{NH}_3\cdot\text{H}_2\text{O}$ , 28 wt. %) and tetraethoxysilane (TEOS,  $\geq 99.99\%$ ) were purchased from Beijing Chemical Reagent Company. Ethanol (EtOH,  $\geq 99\%$ ), methylbenzene ( $\text{C}_7\text{H}_8$ ,  $\geq 99\%$ ), n-butanol ( $\text{C}_4\text{H}_9\text{OH}$ ,  $\geq 99\%$ ), cyclohexane ( $\text{C}_6\text{H}_{12}$ ,  $\geq 99\%$ ), triethanolamine (TEA) and cetyltrimethylammonium chloride (CTAC) were purchased from Shanghai Aladdin Biochemical Technology. Distilled water was used throughout. The high-purity  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{N}_2$  and  $\text{He}$  gas are from Sichuan Tianyi Technology Co., Ltd. and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd.

### Catalyst preparation

**Synthesis of  $\text{Co}_3\text{O}_4$  nanoparticles (NPs).**  $\text{Co}_3\text{O}_4$  NPs were synthesized according to Ref. <sup>1</sup> and <sup>2</sup> with slight modifications. Briefly, 4.50 g cobalt(II) acetate tetrahydrate as a precursor for  $\text{Co}_3\text{O}_4$  NP growth was first dissolved in 8 mL of water and 400 mL ethanol solution at 45 °C. 25 mL ammonium hydroxide solution (28 wt. %) was added dropwise to the above solution with vigorous stirring. After stirring for a further 40 min, the reaction mixture was transferred into a 500 mL Teflon-lined stainless steel autoclave and kept at 160 °C for 6 h. After the autoclave was cooled to room temperature, the resulting black suspension was centrifuged in the presence of ethanol. The collected solid product was washed with acetone and dried at 100 °C for 4 h. The obtained  $\text{Co}_3\text{O}_4$  NPs were used for further catalyst preparation.

#### Synthesis of $\text{Co@H-mSiO}_2$ .

The synthesis procedure for the  $\text{Co}_3\text{O}_4@\text{mesoporous SiO}_2$  according to the previous reported method <sup>3</sup> and <sup>4</sup> with process modifications at various stages. First, the 0.80 g of  $\text{Co}_3\text{O}_4$  NPs were dispersed in 300 mL solution ( $V_{\text{EtOH}} : V_{\text{H}_2\text{O}} = 1:4$ ) by ultrasonic dispersion. After 30 min of ultrasonic treatment, 3.5 g of CTAC and 0.45 g TEA and 0.25 mL ammonium hydroxide solution (28 wt. %) was added and stirred for 30 min. Then 6.5 mL TEOS and 60 mL methylbenzene was added and stirred for another 5 h. The product was collected by centrifugation, washed with EtOH and  $\text{H}_2\text{O}$ , and dried at 60 °C under a vacuum overnight. The products were calcined at 500 °C for 6 h. The as-made samples were named as  $\text{Co@H-mSiO}_2$ .

**Synthesis of  $\text{Co@M-mSiO}_2$ .** For preparing  $\text{Co}_3\text{O}_4@$ larger-mesoporous  $\text{SiO}_2$  ( $\text{Co@M-mSiO}_2$ ) catalysts, the same procedure as the above was used by using n-butanol to replace methylbenzene.

**Synthesis of  $\text{Co@S-mSiO}_2$ .** For preparing  $\text{Co}_3\text{O}_4@$ small-mesoporous  $\text{SiO}_2$  ( $\text{Co@S-mSiO}_2$ ) catalysts, the same procedure as the above was used by using cyclohexane to replace methylbenzene.

### Catalyst Characterization

Morphology measurements of the samples were performed on a field emission scanning electron microscope (Hitachi SU-8010, Japan) at an accelerating voltage of 10 kV. The crystallinity of the materials was characterized using a D8 Advance X-ray diffractometer (Bruker, Germany) with a

Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ , 40 kV, 40 mA). The testing range for the sample was  $2\theta = 10^\circ$ - $80^\circ$ .

The textural properties of the samples were measured using a Micromeritics ASAP 2020M N<sub>2</sub> adsorption-desorption system. Prior to each test, the sample was degassed at 200°C under vacuum for 6 hours. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Pore size distributions were measured using the Barrett-Joyner-Halenda (BJH) model from the N<sub>2</sub> desorption branch. Pore volume was calculated by analyzing the amount of nitrogen adsorbed at a relative pressure of 0.995. The microstructure of the samples was obtained using an FEI Talos F200X field emission transmission electron microscope (FE-TEM) with energy dispersive X-ray spectroscopy (EDX). Elemental mapping was performed at an accelerating voltage of 200 kV. For TEM studies, the sample suspension was dropped onto micro Cu grids with carbon filaments. The cobalt content of the catalysts was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a PerkinElmer 7300 DV instrument. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) over the fresh catalysts was performed on a Zeton Altamira AMI-200 unit. Prior to measurement, the catalyst sample was purged with high purity argon at 150 °C for 1 hour to remove impurities. During TPR, the temperature ramp is from 50 °C to 800 at a rate of 10 °C · min<sup>-1</sup> in a flow of 10 vol% H<sub>2</sub> in Ar (30 mL · min<sup>-1</sup>).

## Catalyst evaluation

FTS Catalytic studies was conducted in a fixed-bed reactor (internal diameter of 12 mm). 0.5 g catalyst (140-200 mesh) diluted with 5.0 g quartzite (40-100 mesh) was packed in the reactor. The catalyst was reduced at 450 °C using pure H<sub>2</sub> (35 mL · min<sup>-1</sup>) for 8 hours at atmospheric pressure. The catalytic performances were carried out under reaction conditions of GHSV = 6000 mL · g<sub>cat</sub><sup>-1</sup> · h<sup>-1</sup>, 220 °C, 1.0 MPa, H<sub>2</sub>/CO = 2/1. The wax, oil and water products were collected in hot trap (100 °C) and cold trap (0 °C). The gases products were detected by an online gas chromatograph (Agilent Micro GC 3000A). The wax, oil and water were separated from mixed solution and analyzed in offline Agilent GC 7890A GC, 6890 N and Agilent 4890 instrument, respectively. Catalyst activity and product selectivity were calculated as follows:

$$CO \text{ conversion (\%)} = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100\%$$

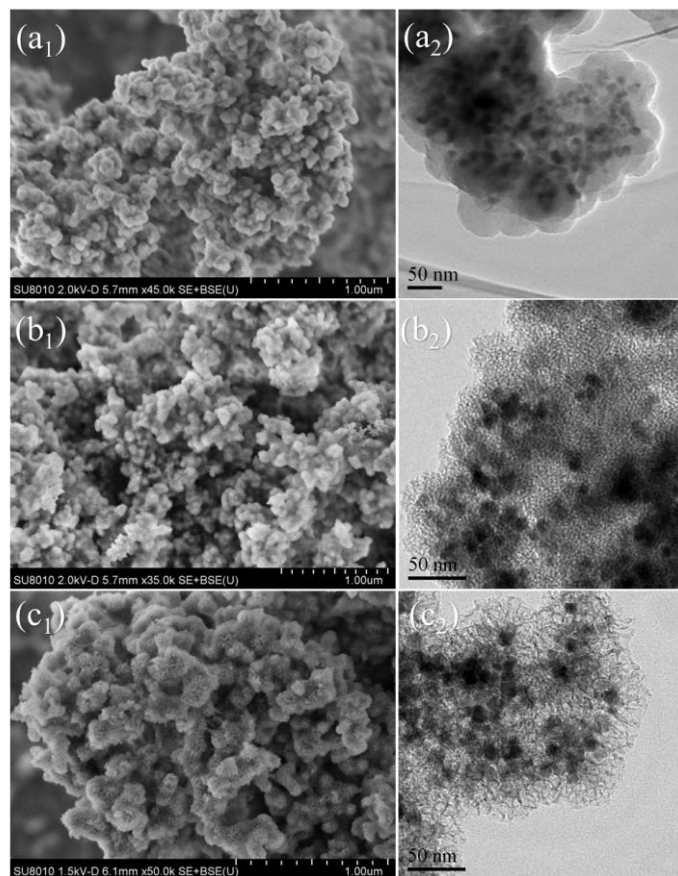
$$CO_2 \text{ selectivity (\%)} = \frac{CO_{2 \text{ out}}}{CO_{in} - CO_{out}} \times 100\%$$

$$C_i \text{ hydrocarbon selectivity (mol\%)} = \frac{\text{mol of } C_i \text{ hydrocarbon} \times i}{\sum_i \text{mol of } C_i \text{ hydrocarbon} \times i} \times 100\%$$

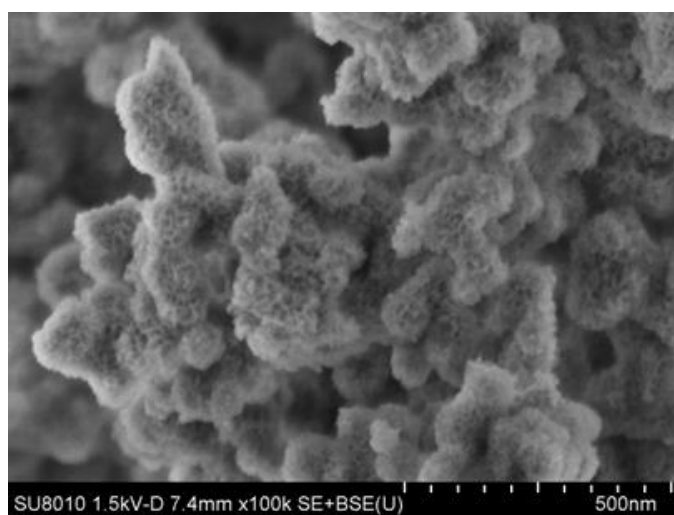
$$C_i \text{ hydrocarbon selectivity (mass\%)} = \frac{\text{mass of } C_i \text{ hydrocarbon}}{\sum_i \text{mass of } C_i \text{ hydrocarbon}} \times 100\%$$

Where the  $\text{CO}_{\text{in}}$  and  $\text{CO}_{\text{out}}$  represent the moles of CO in the inlet and outlet, and  $\text{CO}_2_{\text{out}}$  represents the mole of  $\text{CO}_2$  in the outlet, respectively.

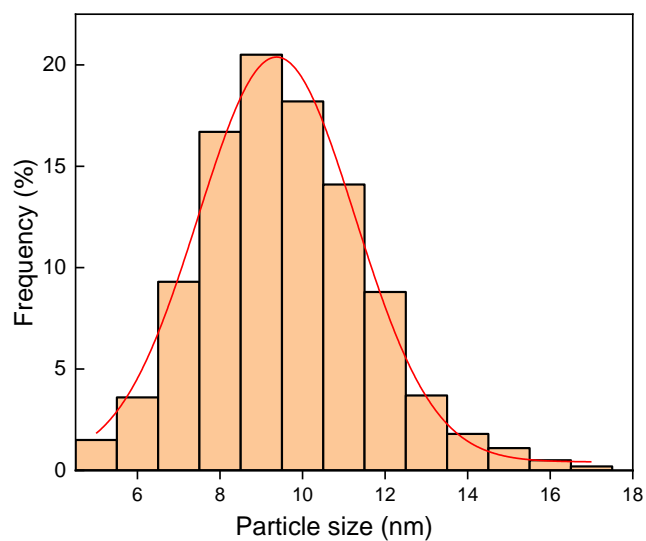
## Figures



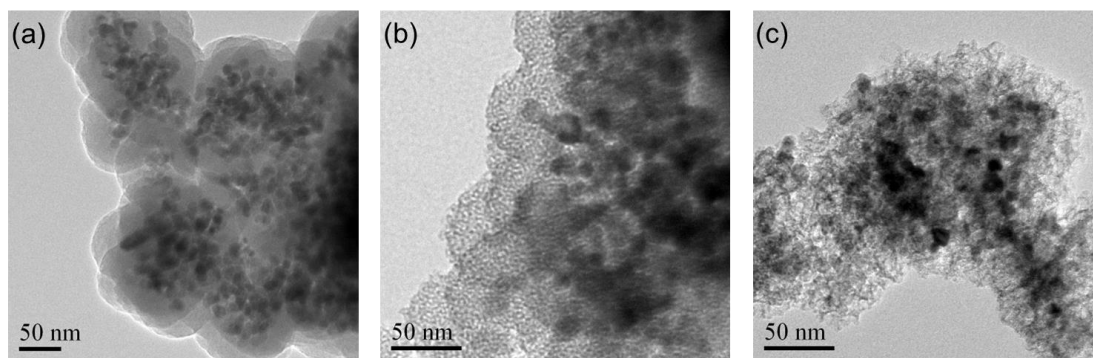
**Fig. S1.** SEM and TEM images of the fresh Co@X-mSiO<sub>2</sub> catalysts: Co@S-mSiO<sub>2</sub> (a<sub>1</sub>, a<sub>2</sub>), Co@M-mSiO<sub>2</sub> (b<sub>1</sub>, b<sub>2</sub>) and Co@H-mSiO<sub>2</sub> (c<sub>1</sub>, c<sub>2</sub>)



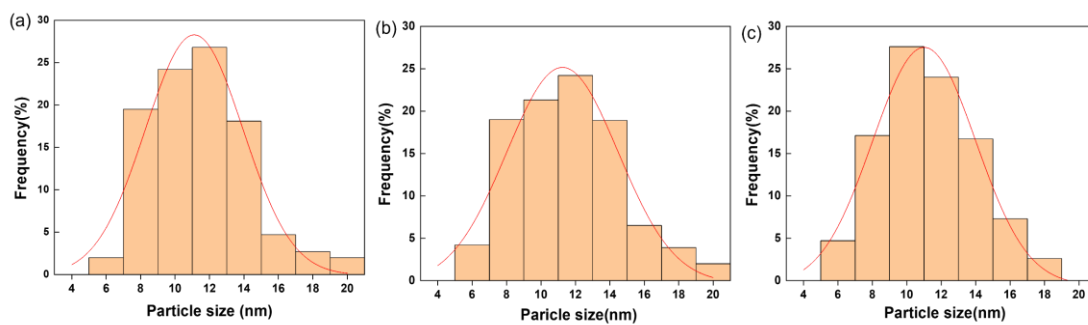
**Fig. S2.** SEM image of the fresh Co@H-mSiO<sub>2</sub> catalysts.



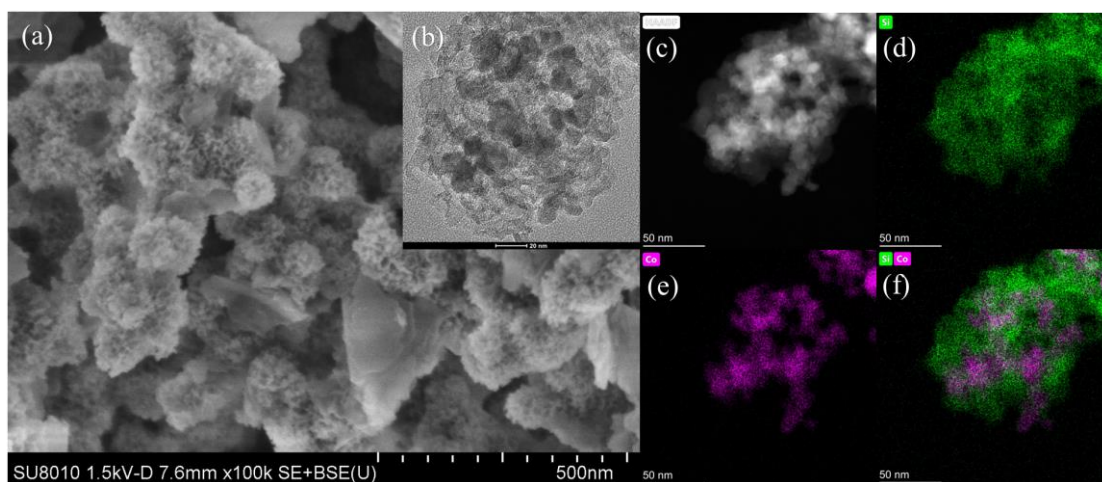
**Fig. S3.** Cobalt particle size distribution of the fresh Co@H-mSiO<sub>2</sub> catalysts.



**Fig. S4.** TEM images of the spent Co@X-mSiO<sub>2</sub> catalysts: (a) Co@S-mSiO<sub>2</sub>, (b) Co@M-mSiO<sub>2</sub> and (c) Co@H-mSiO<sub>2</sub>.



**Fig. S5.** Cobalt particle size distribution of spent Co@X-mSiO<sub>2</sub> catalysts: (a) Co@S-mSiO<sub>2</sub>, (b) Co@M-mSiO<sub>2</sub> and (c) Co@H-mSiO<sub>2</sub>.



**Fig. S6.** SEM image (a), High-magnification TEM image (b), HAADF-STEM image (c) and EDX elemental mapping images (d-f) of the spent Co@H-mSiO<sub>2</sub> catalysts.

**Table S1.** Textural properties, Co<sub>3</sub>O<sub>4</sub> nanocrystal sizes and Co loading of Co@X-mSiO<sub>2</sub> catalysts.

sample	S <sub>BET</sub> <sup>a</sup> /m <sup>2</sup> ·g <sup>-1</sup>	V <sub>pore</sub> <sup>b</sup> /cm <sup>3</sup> ·g <sup>-1</sup>	D <sub>pore</sub> <sup>c</sup> /nm	Co <sub>3</sub> O <sub>4</sub> <sup>d</sup> size (nm)	Co loading <sup>e</sup> (wt %)
Co@S-mSiO <sub>2</sub>	19.0	0.20	-	10.8	26.5
Co@M-mSiO <sub>2</sub>	218.5	0.46	4.9	11.3	25.6
Co@H-mSiO <sub>2</sub>	243.4	0.49	4.0-21.5	10.7	25.3

<sup>a</sup> S<sub>BET</sub>: specific surface area calculated by the BET method. <sup>b</sup> V<sub>pore</sub>: total pore volume. <sup>c</sup> D<sub>pore</sub>: maximum of pore size distribution. <sup>d</sup> Co<sub>3</sub>O<sub>4</sub> size: determined by Sherrer equation using XRD results. <sup>e</sup> Co loading: Co content was determined by ICP analysis.

Table S2. Comparison of the catalytic performance of Co catalysts under comparable reaction conditions for FTS in literatures reported recently.

Catalysts	Reaction conditions	CO Conv. (%)	CH <sub>4</sub> Select. (%)	C <sub>5+</sub> Select. (%)	CTY value (10 <sup>-5</sup> molCO · gCo <sup>-1</sup> · s <sup>-1</sup> )	Ref.
Ru/Co/Al <sub>2</sub> O <sub>3</sub>	210 °C, H <sub>2</sub> /CO=2, 20 bar, 2 L·g <sup>-1</sup> ·h <sup>-1</sup> .	37.3	13.2	79.4	---	<i>Chem. Eng. J.</i> 2024,488, 150837
Co/CF-500	240 °C, H <sub>2</sub> /CO=1, 20 bar, 8 L·g <sup>-1</sup> ·h <sup>-1</sup> .	9.9	21.2	57.3	7.93	<i>Appl. Catal. B Environ.</i> 2023,321,122078
Ru <sub>1</sub> Zr <sub>1</sub> /Co	200 °C, H <sub>2</sub> /CO=2.3, 30 bar, 2 L·g <sup>-1</sup> ·h <sup>-1</sup> .	---	8.6	80.7	3.28	<i>J. Am. Chem. Soc.</i> 2023, 145 (13), 7113.
Ir-Co/CNT	200 °C, H <sub>2</sub> /CO=1, 20 bar, 24 L·g <sup>-1</sup> ·h <sup>-1</sup> .	9.6	3.6	92	9.1	<i>Chem,</i> 2022, 8 (4), 1050.
Co@SiO <sub>2</sub> -3	210 °C, H <sub>2</sub> /CO=2, 2.0 MPa, 17.5 L·g <sup>-1</sup> ·h <sup>-1</sup> .	98.3	7.0	89.9	6.8	<i>Fuel</i> 2022, 323, 124377.
Co-9.9/Z5	240 °C, H <sub>2</sub> /CO=2, 2.0 MPa, 2 L·g <sup>-1</sup> ·h <sup>-1</sup> .	58.7	21.9	64.7	---	<i>Chem. Commun.</i> 2021, 57, 13522.
Cat-12h	220 °C, H <sub>2</sub> /CO=2, 2.0 MPa, 4.4 L·g <sup>-1</sup> ·h <sup>-1</sup> .	80.6	8.7	80.0	10.5	<i>Nat. Commun.</i> 2018, 9, 3250.
Co@SiO <sub>2</sub> - 873	210 °C, H <sub>2</sub> /CO=1, 20 bar, 11.2 L·g <sup>-1</sup> ·h <sup>-1</sup> .	15.8	5.3	90.5	4.4	<i>Nat. Commun.</i> 2017, 8, 1680.
Co@H- mSiO <sub>2</sub>	220 °C, H <sub>2</sub> /CO=2, 1.0 MPa, 6 L·g <sup>-1</sup> ·h <sup>-1</sup> .	50.6	11.0	77.2	5.0	This work

## References

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