

Supporting Information

Hydrogen spillover effects in the Fischer-Tropsch reaction over carbon nanotube supported cobalt catalysts

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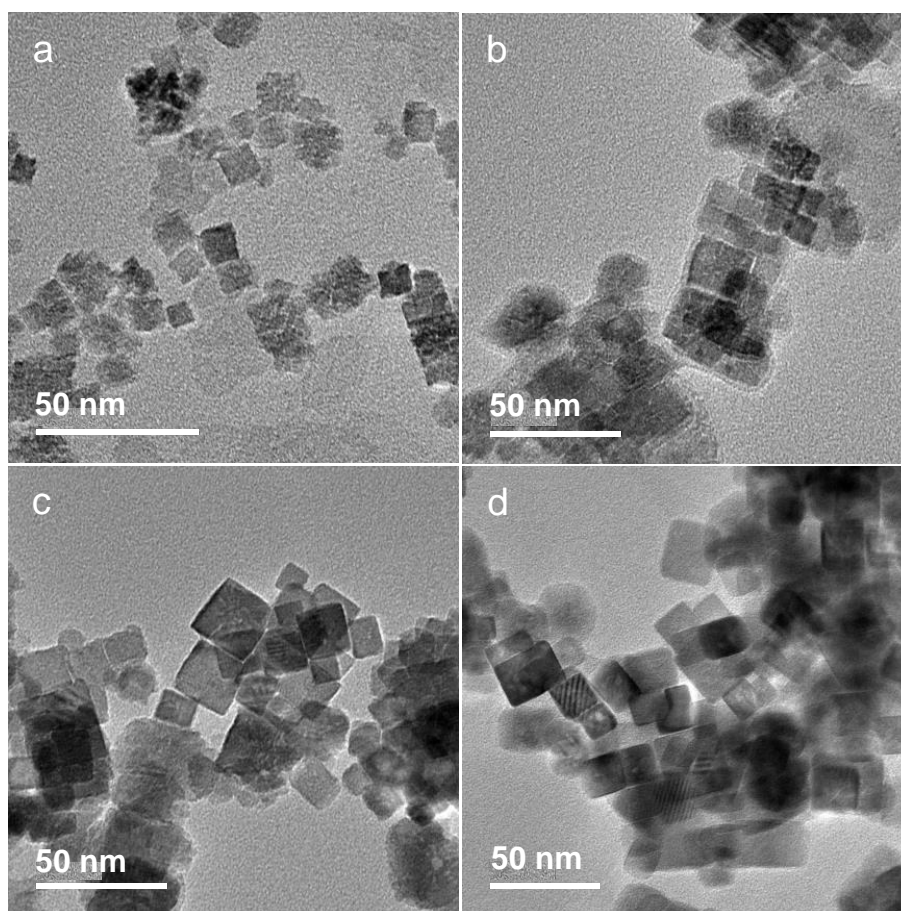


Fig. S1 TEM images of the (a) Co-100, (b) Co-125, (c) Co-175, and (d) Co-200 catalysts.

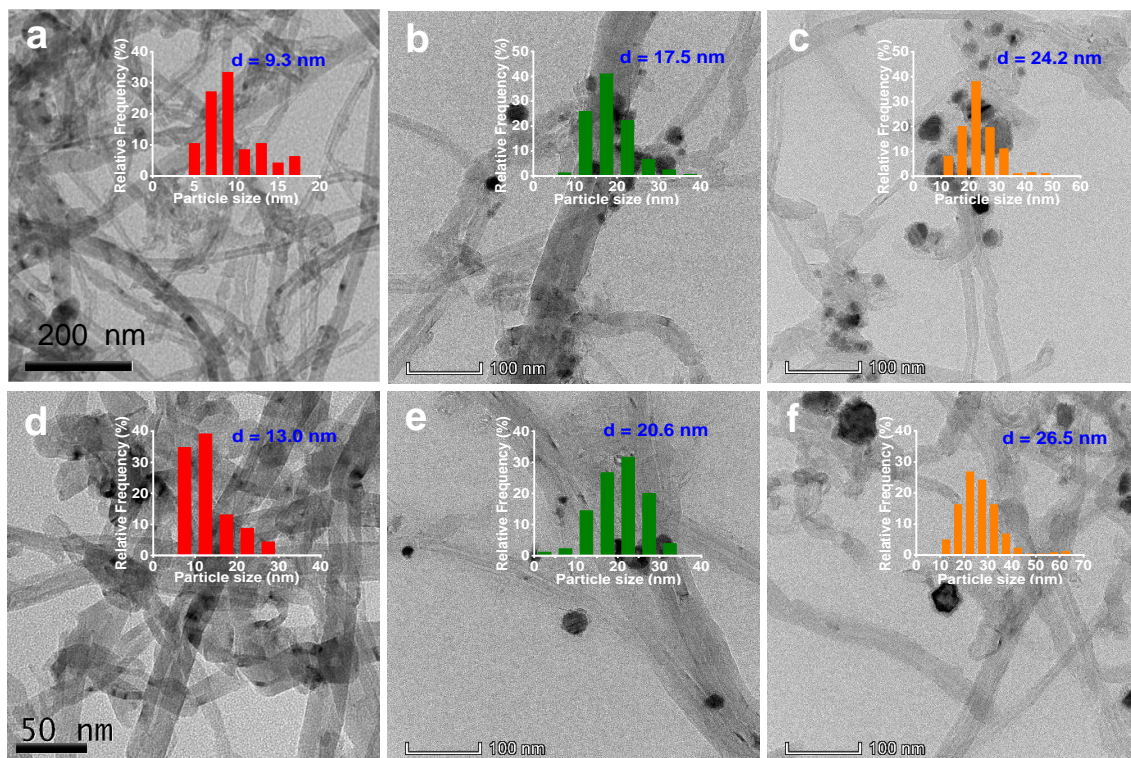


Fig. S2 TEM images and particle size of the fresh (a, d), reduced (b, e), and spent (c, f) 12Co/CNTs-IWI and 19Co/CNTs-IWI, respectively.

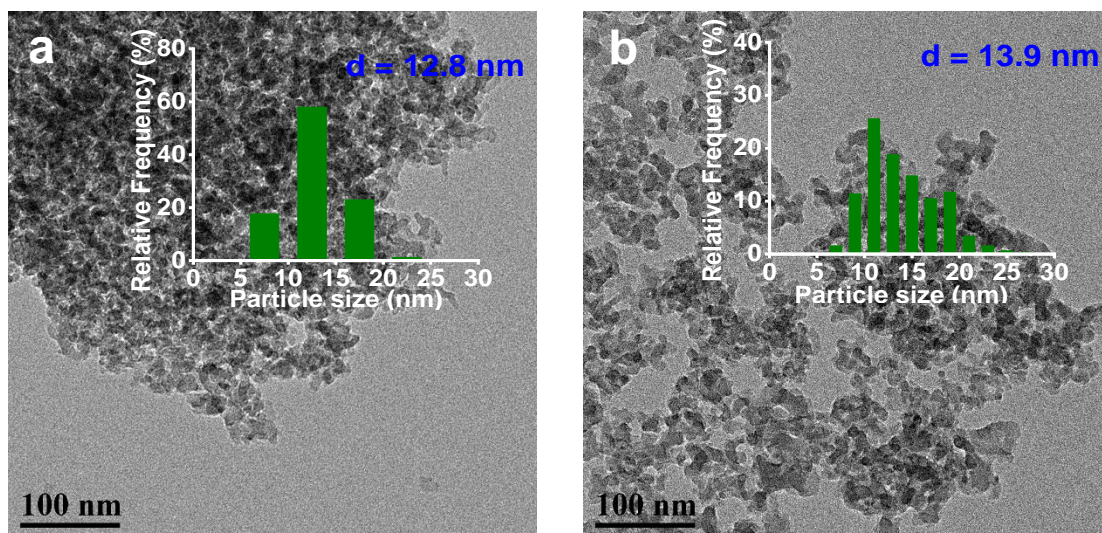


Fig. S3 TEM images and particle size of the reduced catalysts: (a) 12Co/SiO₂-IWI, and (b) 19Co/SiO₂-IWI, respectively.

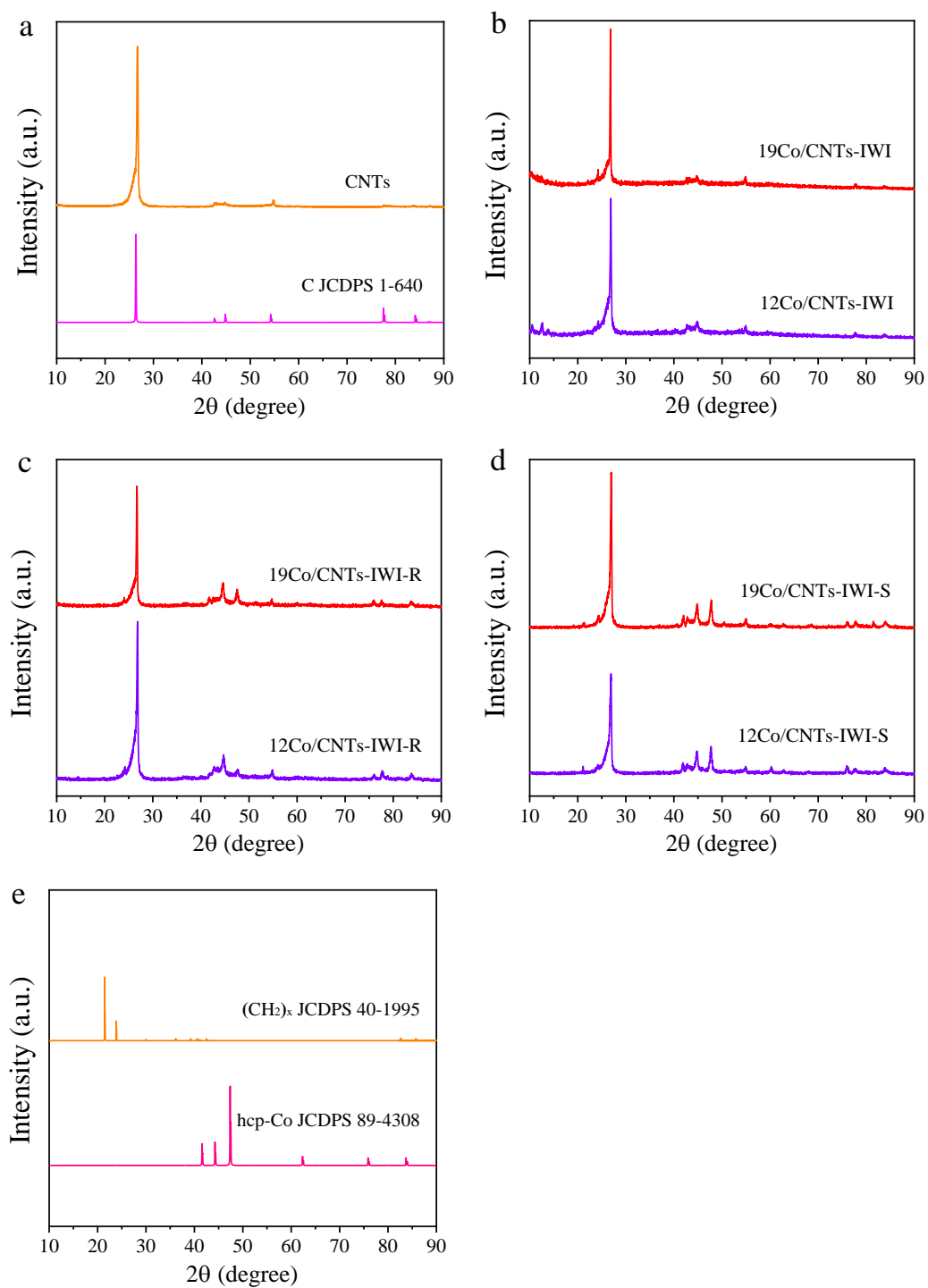


Fig. S4 XRD patterns of the CNTs support (a), fresh (b), reduced (c), spent (d) Co/CNTs-IWI catalysts, and standard references (e).

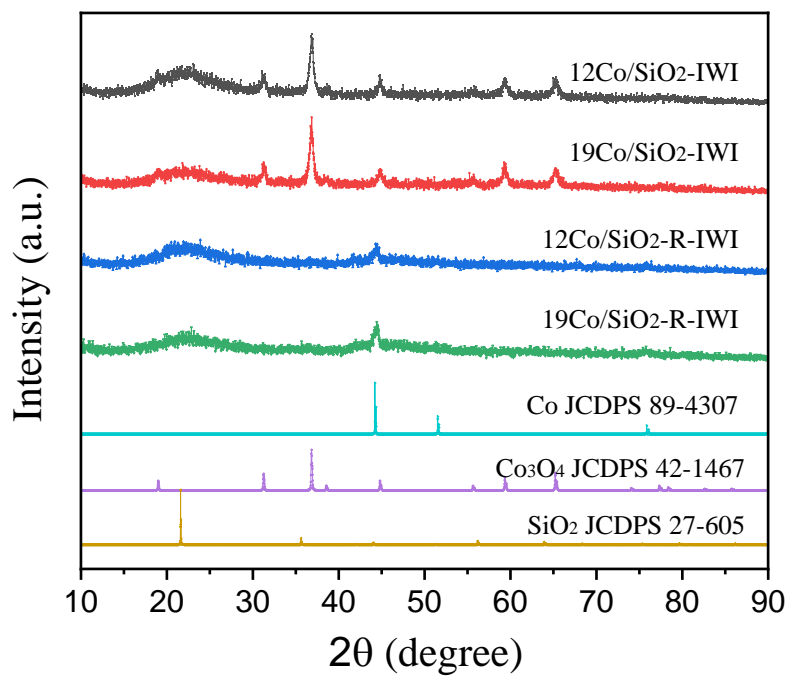


Fig. S5 XRD patterns of the fresh and reduced 12Co/SiO₂ and 19Co/SiO₂ catalysts.

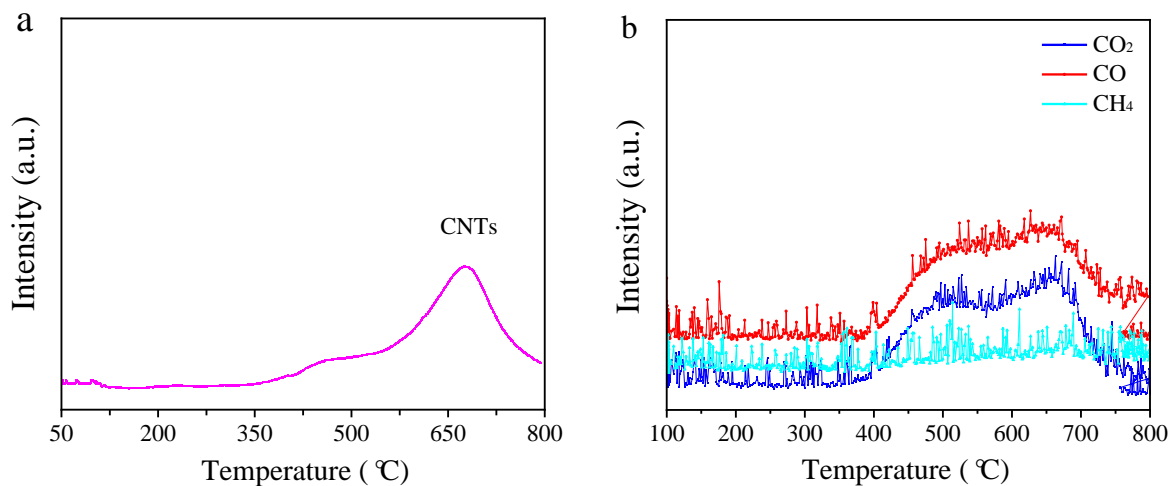


Fig. S6 H₂-TPR-MS profiles of the CNTs support: (a) H₂-TPR; (b) MS. Note that: The intensity of vertical axis in a is 1/32 of that in Figure S7. And that in b is ranged from 1×10^{-13} to 2×10^{-12} .

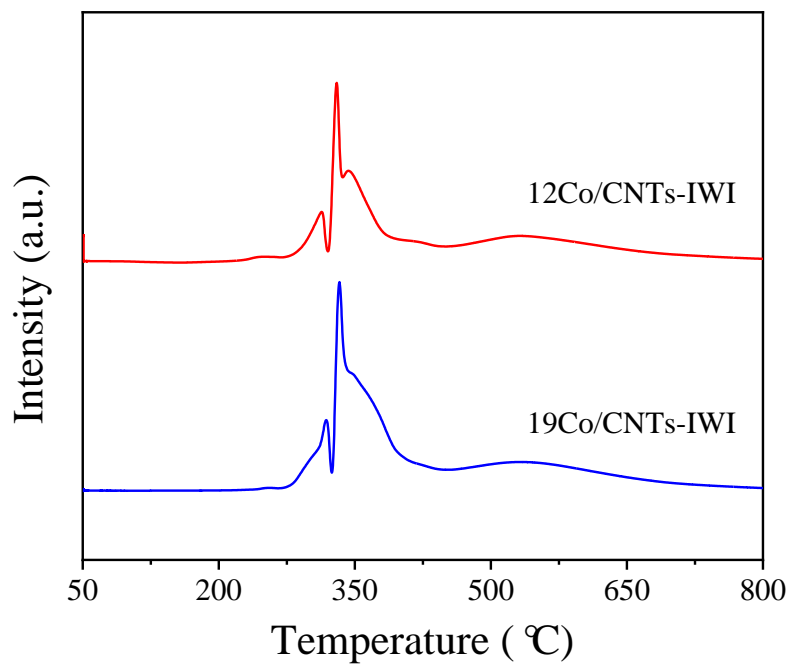


Fig. S7 H₂-TPR profiles of the fresh Co/CNTs-IWI catalysts.

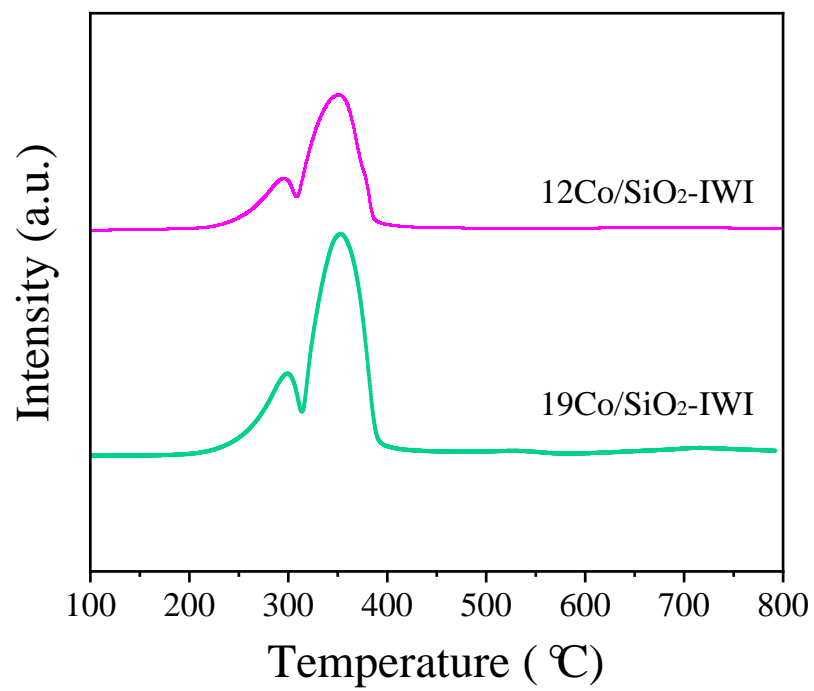


Fig. S8 H₂-TPR profiles of the fresh Co/SiO₂-IWI catalysts.

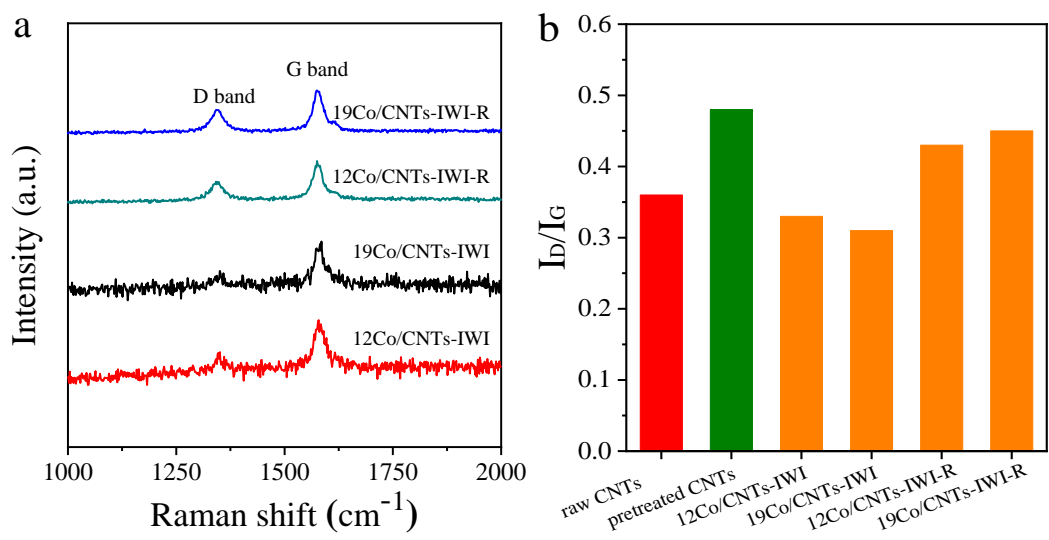


Fig. S9 Raman spectra of the fresh and reduced Co/CNTs-IWI catalysts (a), and the corresponding calculated I_D/I_G values (b).

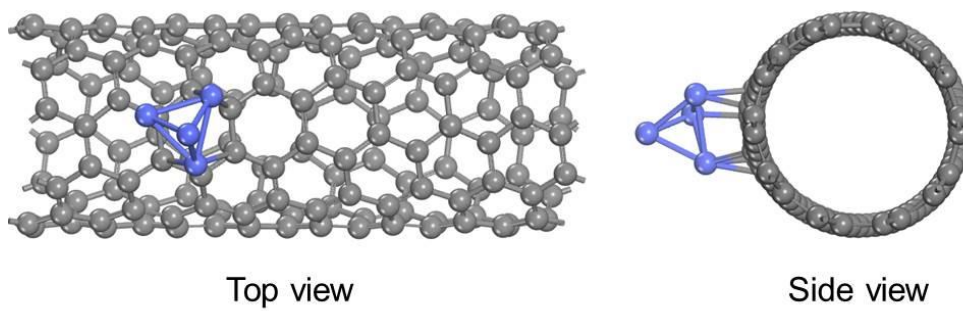


Fig. S10 Structural model for Co_4 cluster absorbed on outside surface of CNT.

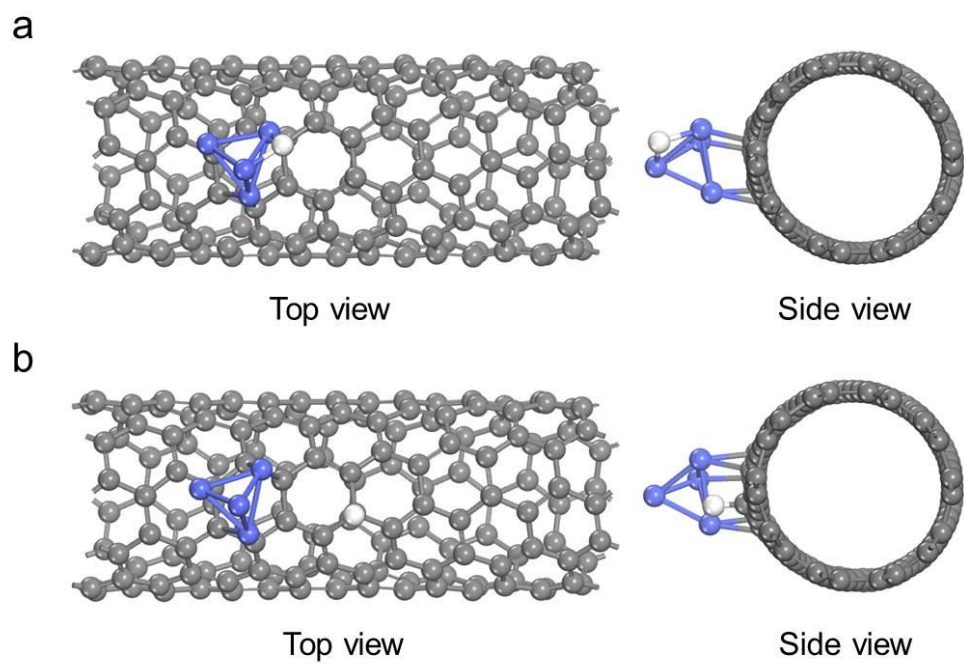


Fig. S11 Structural models for hydrogen spillover from (a) Co_4 cluster to (b) pristine CNT.

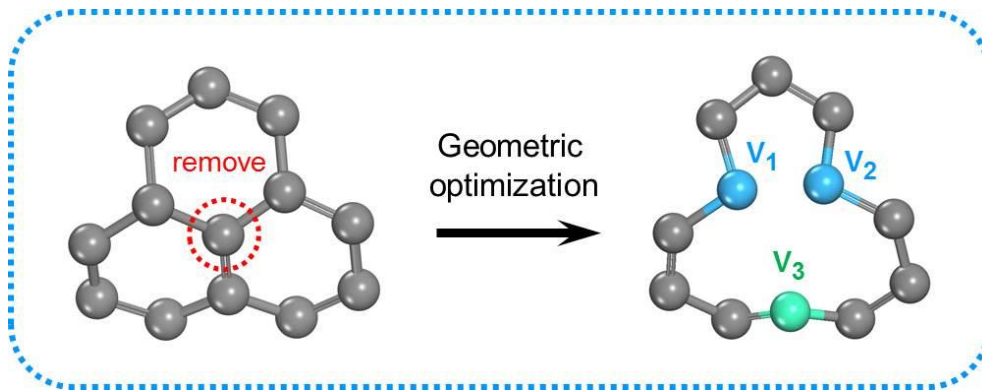


Fig. S12 The illustration of defect carbon sites in CNT.

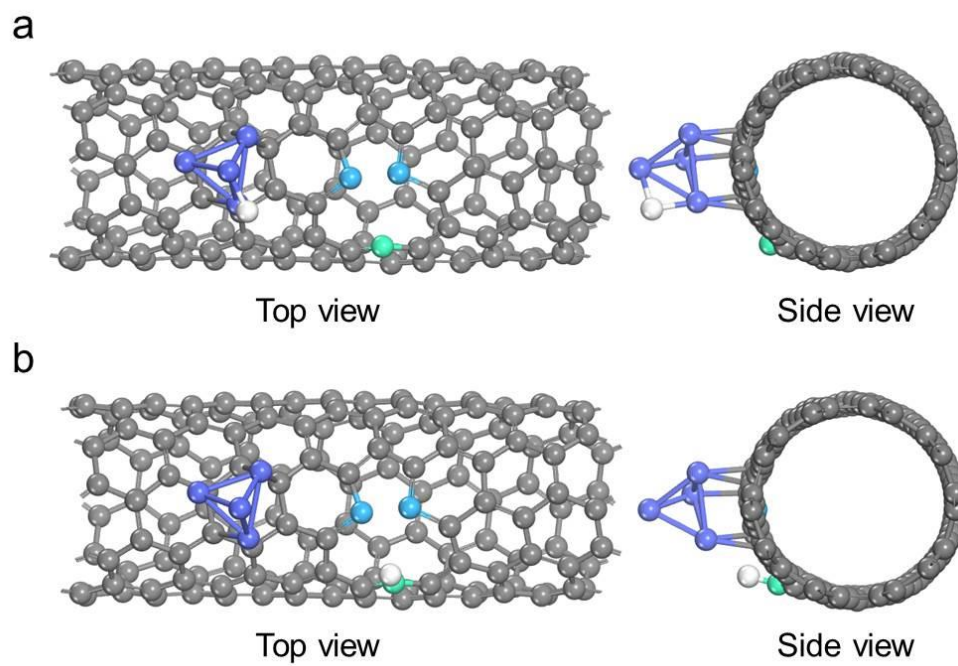
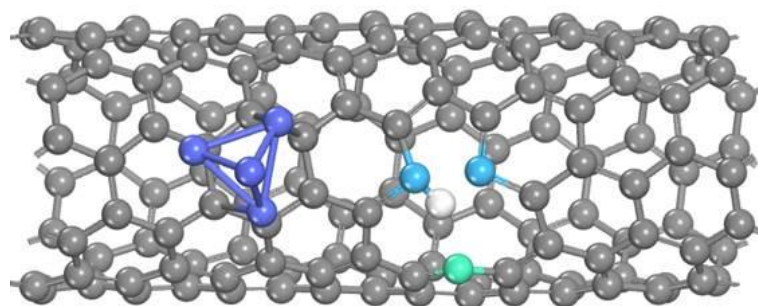
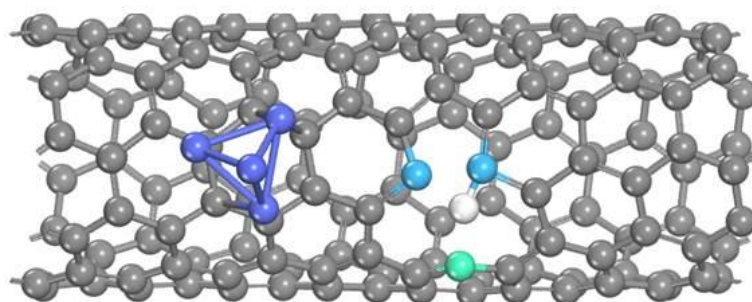


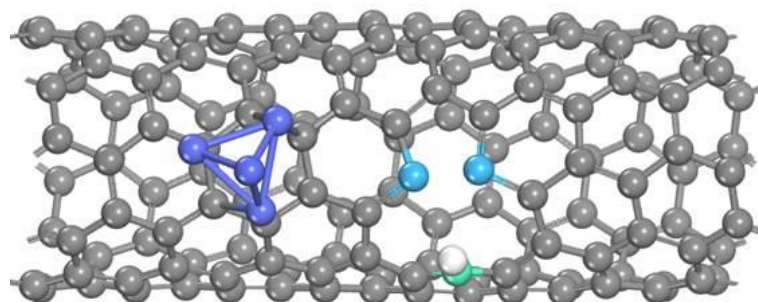
Fig. S13 Structural models for hydrogen spillover from (a) Co₄ cluster to (b) V₃ defect site.



POSCAR1



POSCAR2



CONTCAR

Fig. S14 Geometric optimization for hydrogen absorbed on V_1 and V_2 defect sites.

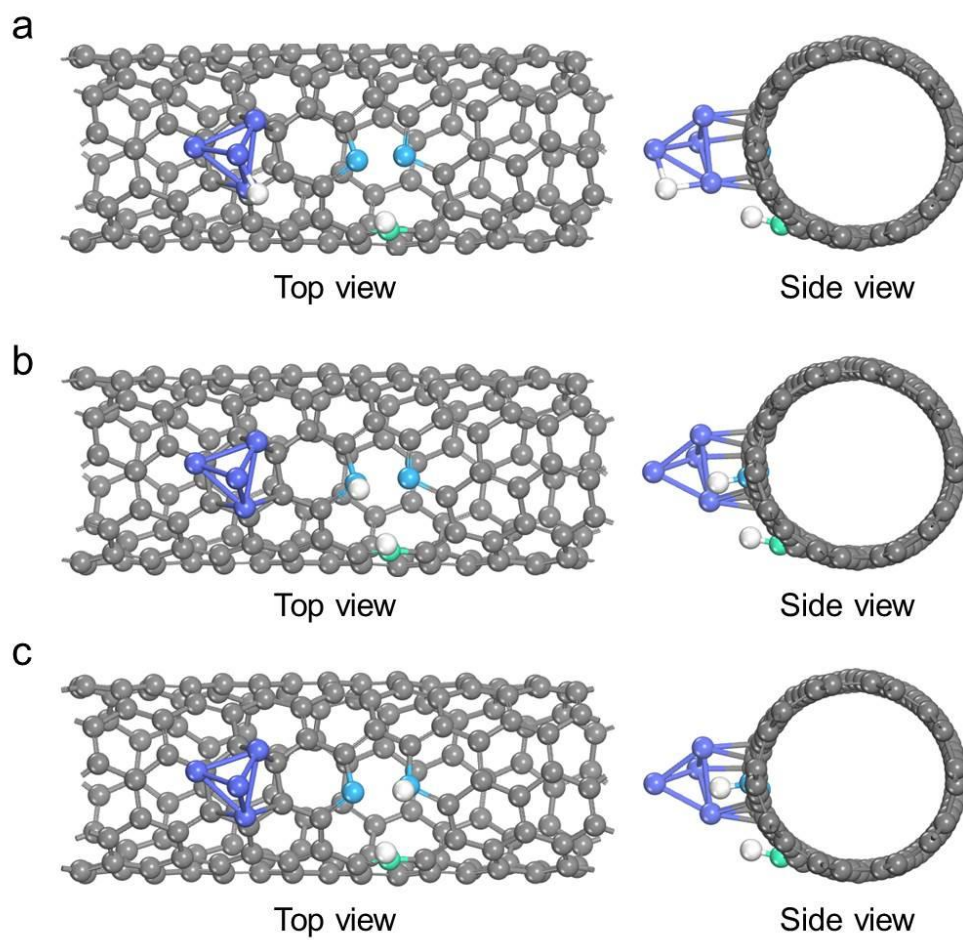


Fig. S15 Structural models for hydrogen spillover from (a) Co₄ cluster to (b) V₁ and (c) V₂ defect sites.

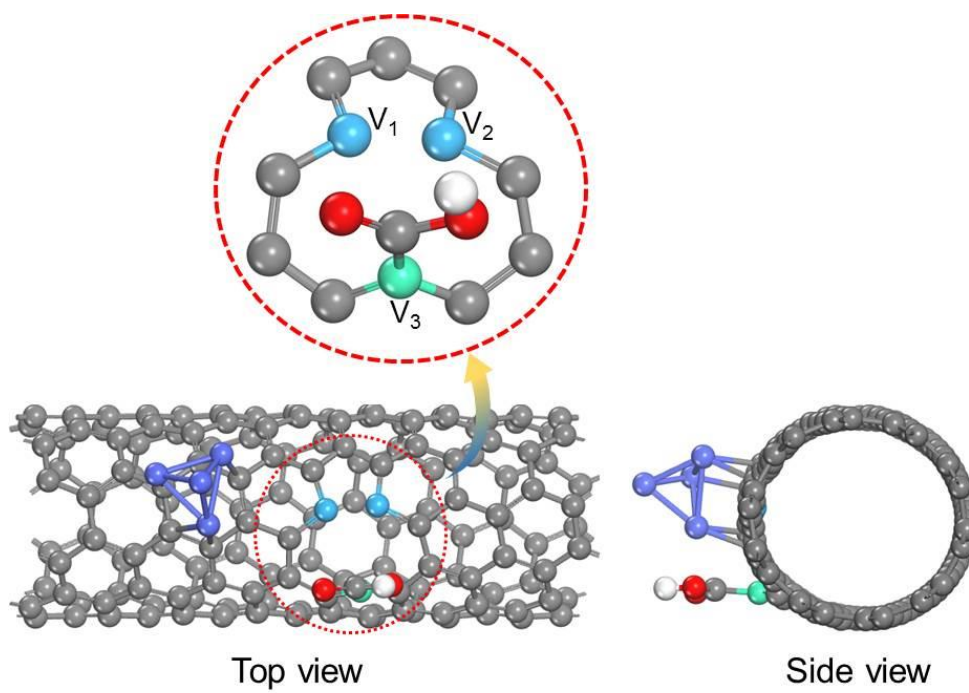


Fig. S16 Structural model for Co_4 cluster adsorbed on outside surface of CNT with COOH group.

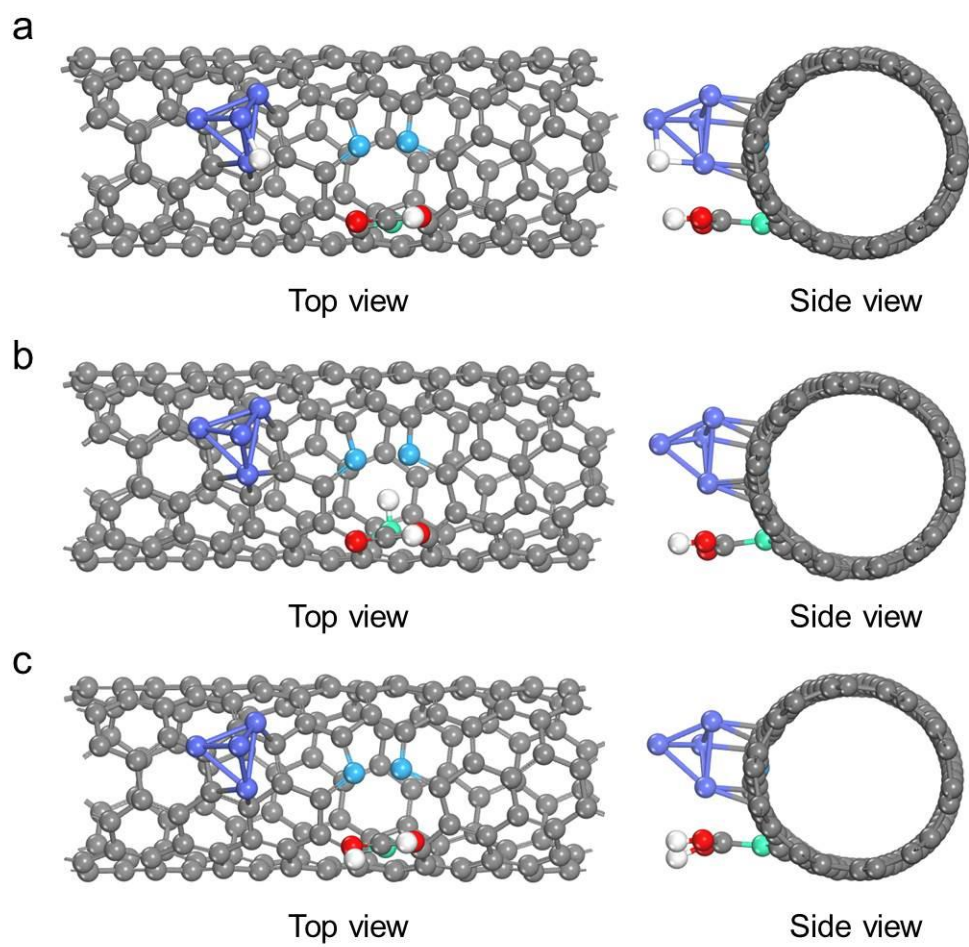


Fig. S17 Structural models for hydrogen spillover from (a) Co₄ cluster to (b) V₃ defect site and (c) O site.

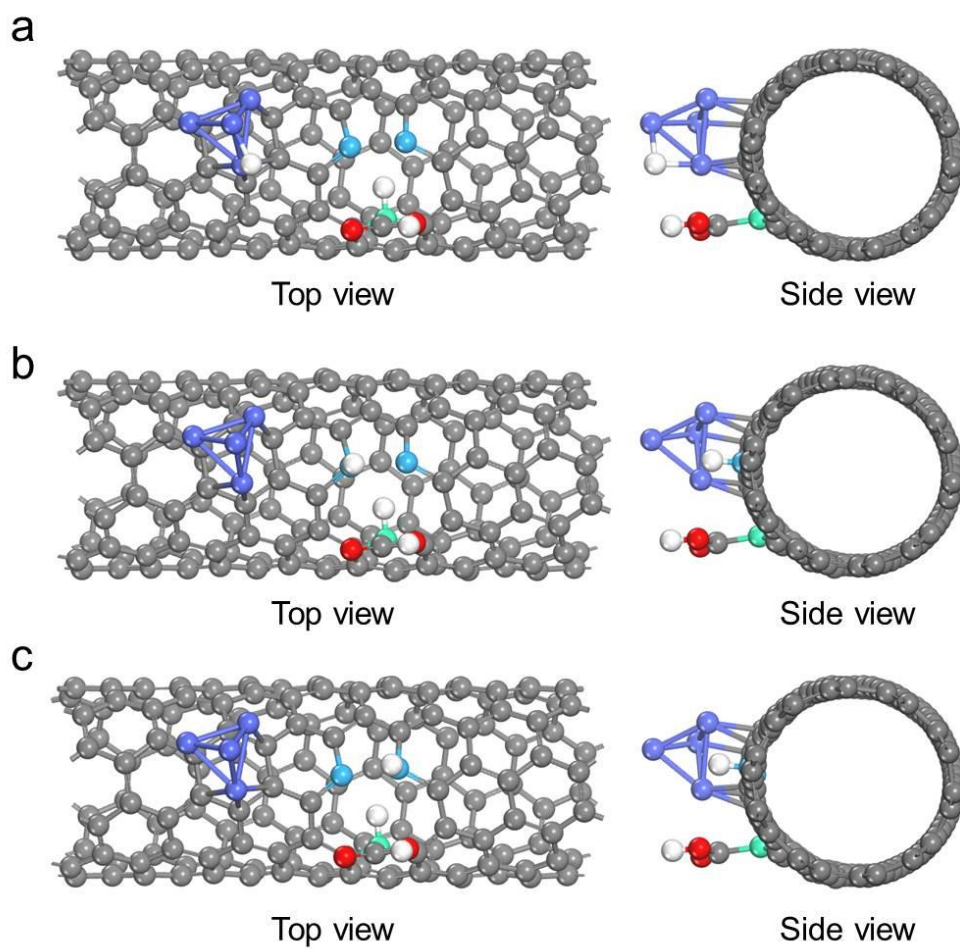


Fig. S18 Structural models for hydrogen spillover from (a) Co₄ cluster to (b) V₁ and (c) V₂ defect sites.

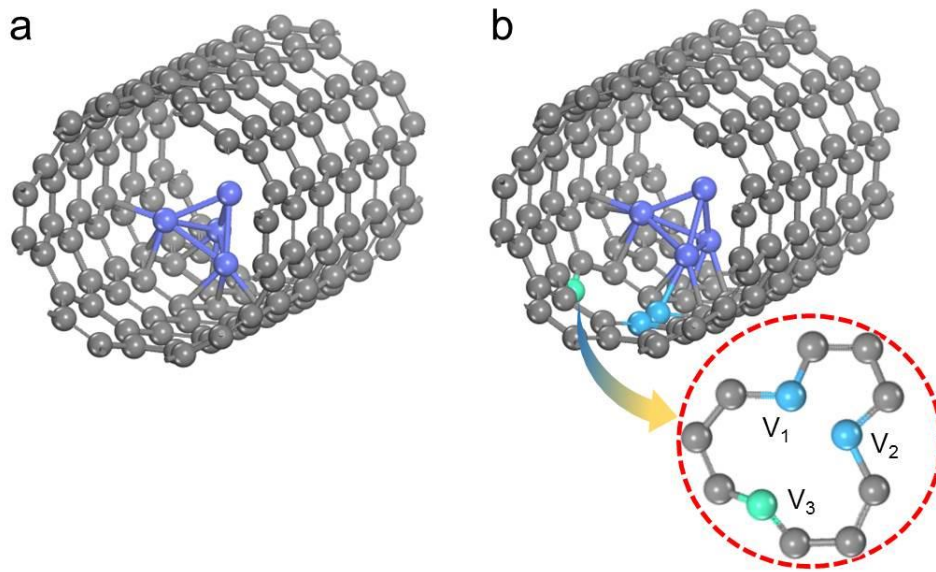


Fig. S19 Structural models for Co_4 cluster loaded inside (a) pristine CNT and (b) defect CNT.

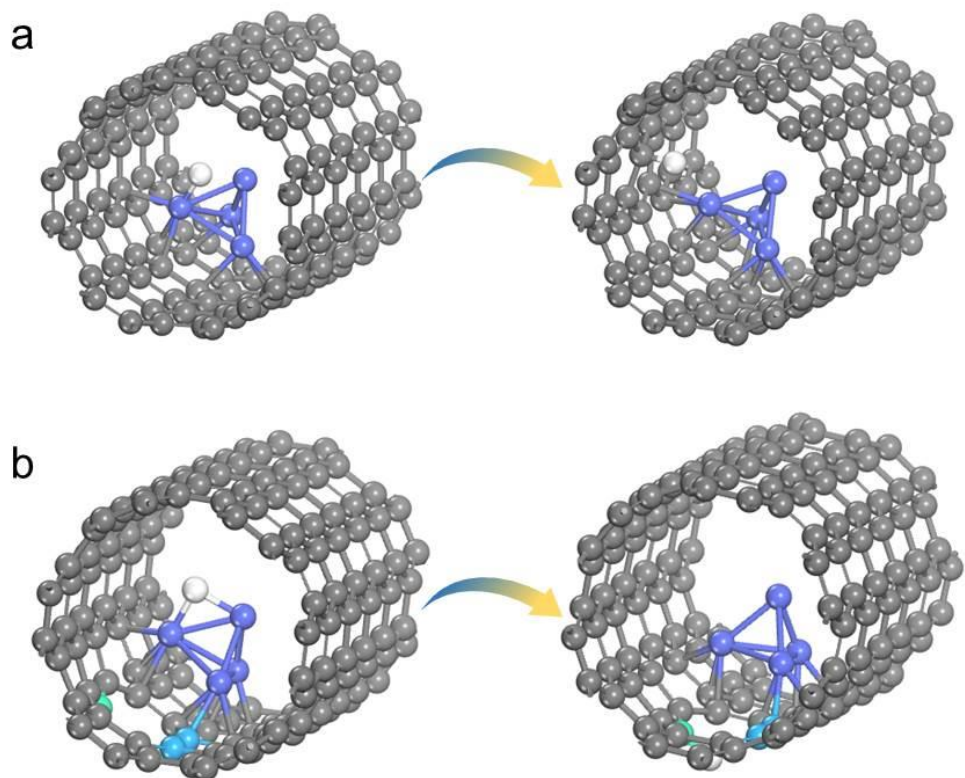


Fig. S20 Structural models for hydrogen spillover from Co_4 cluster to (a) pristine CNT and (b) V_3 defect site.

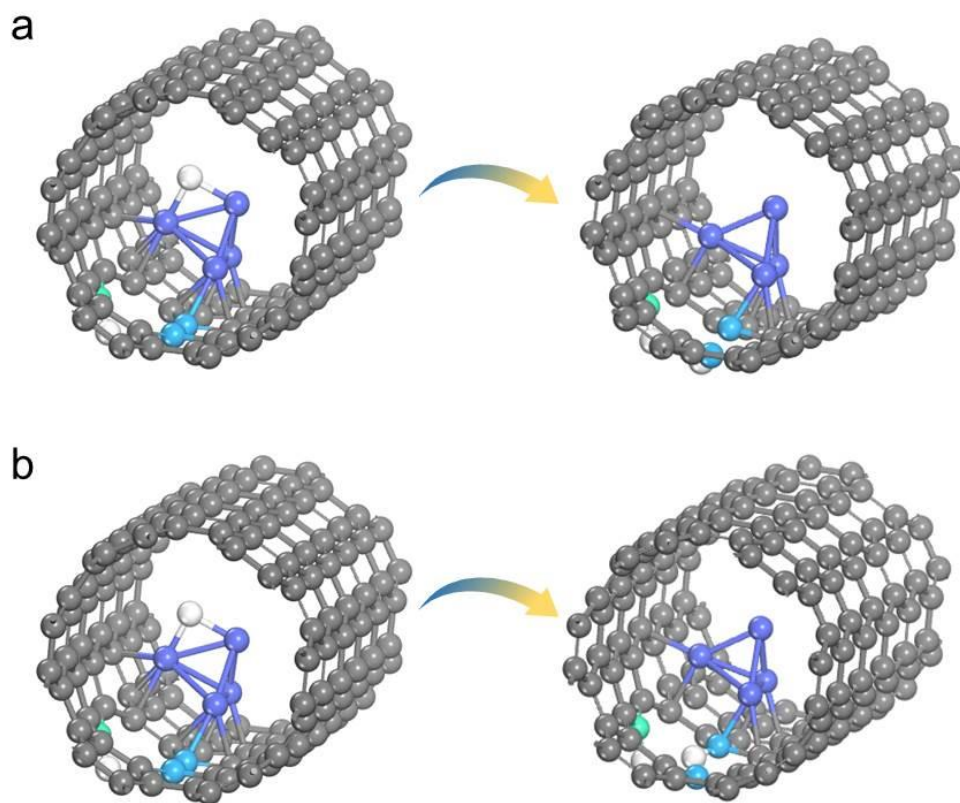


Fig. S21 Structural models for hydrogen spillover from Co_4 cluster to (a) V_1 and (b) V_2 defect sites.

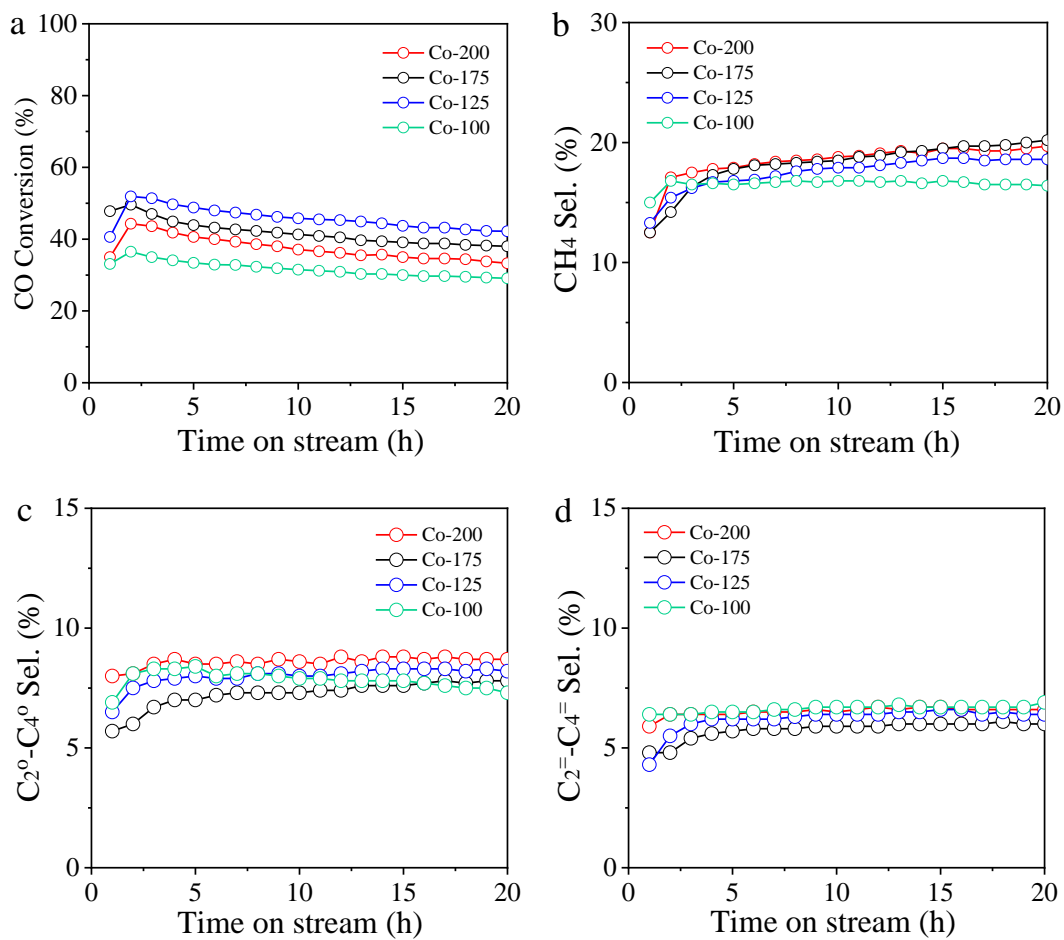


Fig. S22 Catalytic performance of the FTS reaction over unsupported cobalt catalysts: (a) CO conversion; (b) CH₄ selectivity; (c) Selectivity to C₂-C₄ paraffins; (d) Selectivity to C₂-C₄ olefins. Reaction conditions: 0.5 g of catalyst, T = 240 °C, P = 1 MPa, the molar ratio of H₂/CO/N₂ = 63.3/31.7/5, and GHSV = 4.5 L g_{cat}⁻¹h⁻¹.

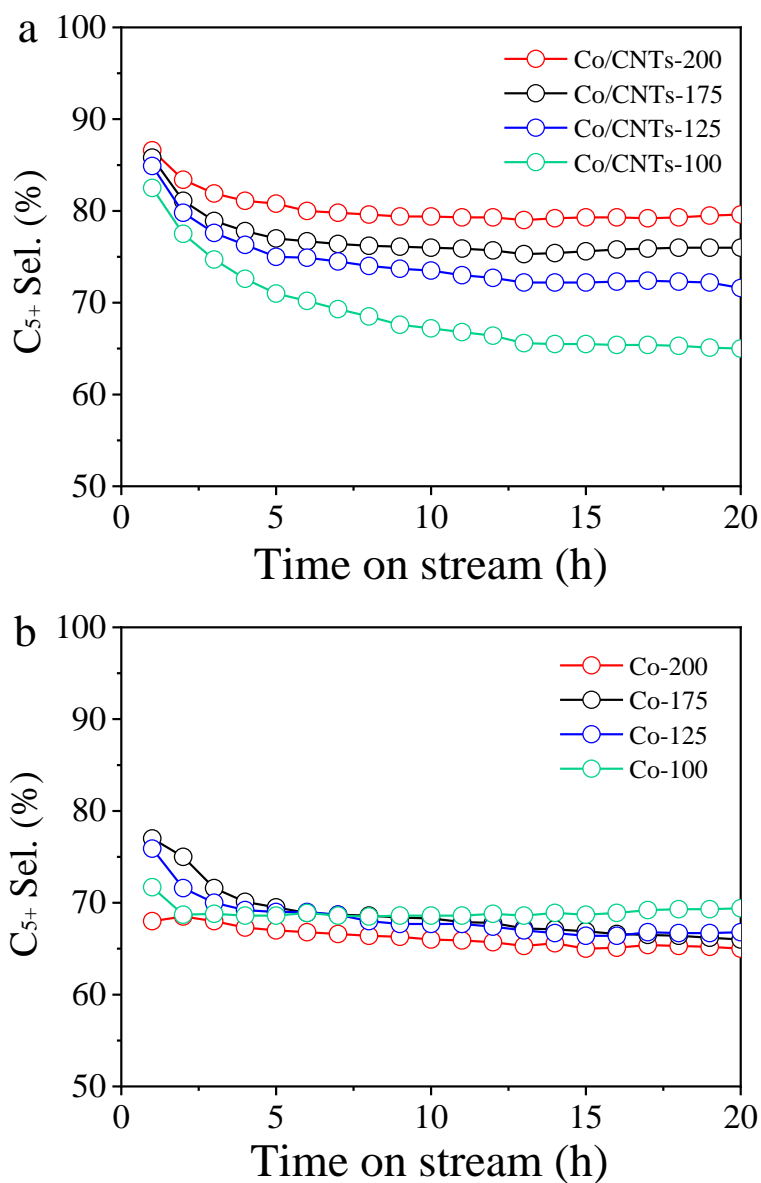


Fig. S23 Selectivity to C₅₊ in the FTS reaction over unsupported and CNT supported cobalt catalysts. Reaction conditions: T = 240 °C, P = 1 MPa, and the molar ratio of H₂/CO/N₂ = 63.3/31.7/5; (a) 1g of catalyst, GHSV=2.22 L g_{cat}⁻¹h⁻¹; (b) 0.5 g of catalyst, GHSV=4.5 L g_{cat}⁻¹h⁻¹.

Table S1 Textural properties of catalysts.

Catalysts	Surface areas (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Particle size (nm) ^a	Metallic Co (wt%) ^b
Co-100	141.6	0.17	3.8	8.4	57.3
Co-125	116.9	0.24	3.8	10.2	64.5
Co-175	49.6	0.33	30.8	16.9	69.1
Co-200	44.1	0.34	31.1	18.4	70.2
Co-100-R	8.6	0.04	3.4	---	---
Co-125-R	7.4	0.02	3.1	---	---
Co-175-R	6.5	0.03	3.8	---	---
Co-200-R	5.2	0.02	3.1	---	---
Co/CNTs-100-S	45.5	0.66	3.9	20	---
Co/CNTs-125-S	23.5	0.40	3.7	31	---
Co/CNTs-175-S	13.4	0.19	3.8	46	---
Co/CNTs-200-S	6.1	0.19	3.1	48	---

^aFrom TEM images. ^bFrom ICP-OES.

Table S2 Catalytic performance of unsupported cobalt catalysts in the FTS reactions.

Catalysts	X _{CO} (%)	S _{CO2} (%)	Hydrocarbon selectivity (%)				O/O+P (%)	TOF (10 ⁻² s ⁻¹)
			CH ₄	C ₂ ⁼ -C ₄ ⁼	C ₂ ^o -C ₄ ^o	C ₅₊		
Co-200	34.2	0.7	19.4	6.6	8.8	65.1	65.1	---
Co-175	38.4	0.6	19.9	6.0	7.7	66.3	66.3	---
Co-125	42.7	0.7	18.6	6.5	8.2	66.7	66.3	---
Co-100	29.5	0.6	16.5	6.7	7.5	69.2	69.2	---

Reaction conditions: 0.5 g of catalyst, 240 °C, 1 MPa, H₂/CO/N₂ = 63.3/31.7/5 (molar ratio), GHSV = 4.5 L g_{cat}⁻¹h⁻¹. The values for catalytic activity and selectivity were obtained by averaging the tested results in last 5 h.

Table S3 Summary of the elementary reaction steps on [10 $\bar{1}$ 0], [0002] and [10 $\bar{1}$ 1] crystal planes for CO dissociation, methane formation, and carbon-carbon coupling.

Reactions	10 $\bar{1}$ 0(ΔE /eV)	0002(ΔE /eV)	10 $\bar{1}$ 1(ΔE /eV)
CO → CO*	-1.80 (3f)	-1.62(1f)/-1.60(2f)/-1.64(3f)	-1.86(3f)/-1.92(4f)
CO* → C* + O*	0.88	0.97	-0.55
CHO* → CH* + O*	-0.64	-0.44	-1.41
CH ₂ O* → CH ₂ * + O*	-0.50	-0.61	-0.90
CH ₃ O* → CH ₃ * + O*	-0.34	-0.24	-0.38
CH ₂ * + H → CH ₃ *	-0.55	-0.23	0.30
CH ₃ * + H → CH ₄ *	0.08	0.07	0.00
CH ₂ * + CH ₂ * → C ₂ H ₄ *	-0.88	-0.55	-0.38