Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information for

Carbon induced selective regulation of cobalt-based Fischer-Tropsch catalysts by ethylene treatment

Characterizations

Inductively coupled plasma atomic emission spectrometry (ICP) measurements were performed to determine the cobalt loading using a PROFILE SPEC. All of the catalysts were dissolved by nitric acid at 90 ˚C for 12 hours.

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-PC 2500 powder X-ray diffractometer, using Cu Kα radiation with scanning angle (2Θ) from 20 ˚ to 70 ˚. The accelerating voltage and current were 40 kV and 100 mA, respectively. The phases of components were identified based on the JCPDS standard cards.

Transmission electron microscopy (TEM) measurements were operated on a Fei Tecnai F30 electron microscope with 200 kV accelerating voltage. Cobalt particle size distribution was obtained by counting 150 particles.

The thermal behavior of the catalysts was studied by thermo gravimeter and differential scanning calorimeter (TG/DSC) on Q600SDT. Measurement was performed with alumina crucible at a heating ramp of 10 ˚C min^{-1} under air flow (100 ml min^{-1}) from 30 ˚C to 800 ˚C.

Raman analysis was derived on ARAMIS Raman spectrometer equipped with a CCD detector and a laser source of 532 nm. The samples were scanned from 900 to 2500 cm^{-1} to obtain the microstructure of carbon and carbonates.

Computational Methods

Periodic spin-polarized density functional theory (DFT) calculations have been conducted to study the CO activation, methanation and C_{2+} formation on pure and carbon-decorated Co (111) surfaces. All the DFT calculations were performed by using the Vienna ab into package (VASP)[1, 2] code, under the generalized gradient approximation (GGA)[3] with the Perdew-Burke-Ernzerhof (PBE)[4] functional and the projector augmented wave (PAW)[5, 6]. The p(2×3) slab model adapted here has four-metal-layers. The top two Co layers and adsorbates were allowed to fully relax and the bottom two metal layers were fixed. Monkhorst-Pack mesh of 4×6×1 was used. Periodically repeated slabs were separated by a 15 Å thick vacuum layer, which was sufficient for avoiding the interaction between the neighboring two slabs. The convergence energy and cutoff energy were set to 1×10^{-4} eV and 400 eV, respectively. All the structures were fully optimized until residual forces were smaller than 0.02 eV/ Å. Transition states (TSs) were determined by using the improved force reversed method,[7] and some of the TSs are verified by climbing-image nudged elastic band (CI-NEB) methods.[8, 9] The calculated lattice constant of bulk Co with face-centered cubic structure is a=b=c=3.52 Å, which is consistent with experimental value of 3.55 Å.[10]

Table S1 The EXAFS fitting results of Co/Al_2O_3 catalysts.

Sample	$R_{Co\text{-}O}$	$N_{Co\text{-}O}$	$R_{Co\text{-}Co}$	$N_{Co\text{-}Co}$	Co content	CoO content
Co-H	2.015±0.018	3.52±0.42	2.502±0.008	4.02±0.58	0.20	0.83
Co-H-C1	1.959±0.045	1.75±0.57	2.475±0.002	3.38±0.91	0.34	0.69
Co-M	1.976±0.027	1.63±0.53	2.482±0.006	5.87±0.63	0.48	0.55

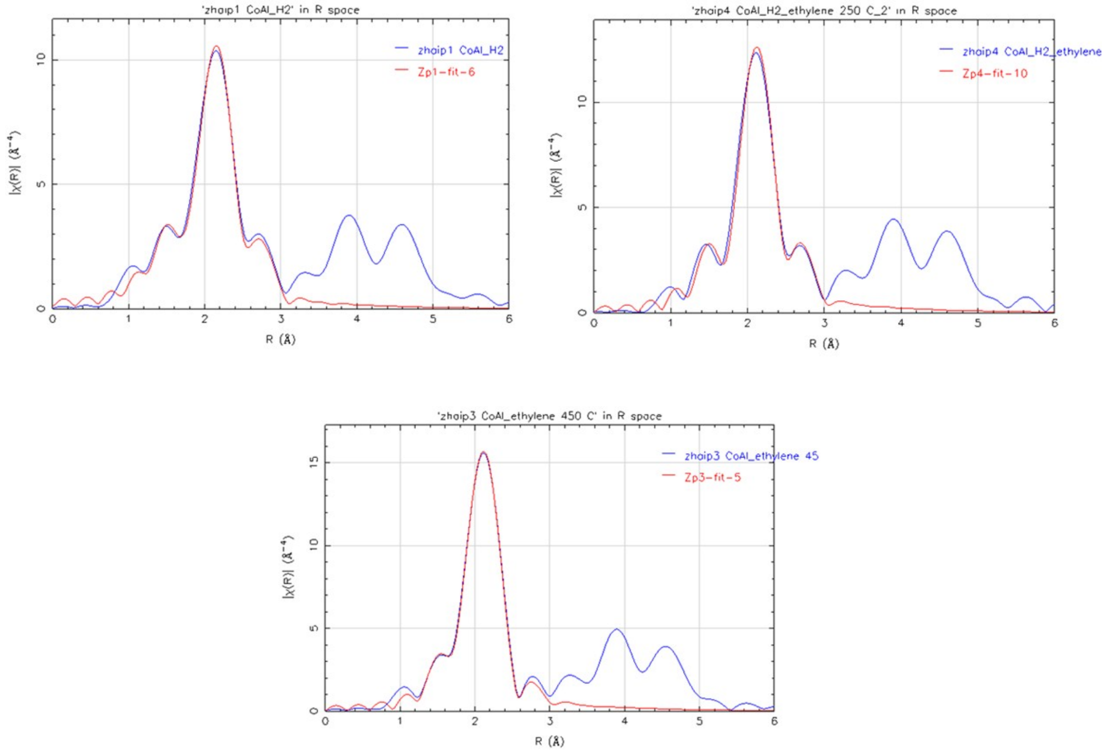

Fig S1 Fitting R space of Co k-edge EXAFS spectra. Co-H, Co-H-C1 and Co-M in order.

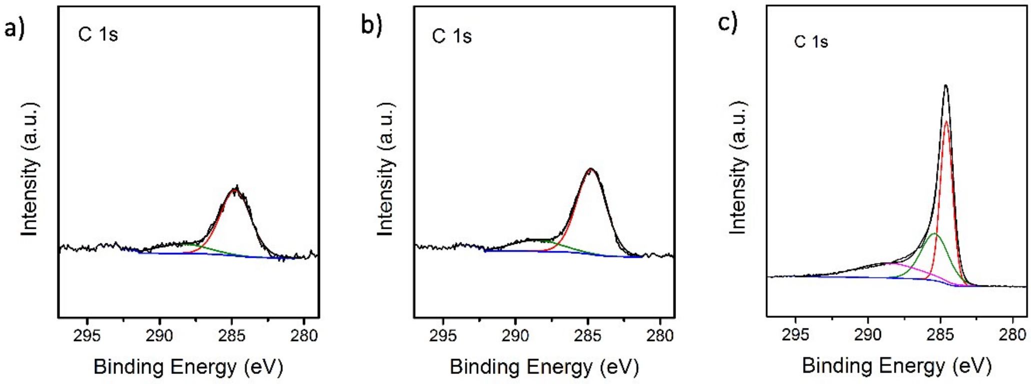

Fig. S2 C 1s XPS spectra for Co/Al_2O_3 catalysts: a) Co-H b) Co-H-C1 c) Co-M.

Table S2 Catalysts performance of Co/Al_2O_3 in Fischer-Tropsch reaction.

Catalysts	CO conv.(%)	CO_2 Sel.(%C)	Organic Compounds Selectivity(%C)					o/p[a]	α
			CH_4	C_2-C_4	C_5-C_{11}	C_{12+}	ROH		
Co-H	28.0	0.4	12.5	13.3	31.6	40.8	1.3	1.1	0.82
Co-H-C1	21.3	0.5	17.7	17.4	35.7	23.1	3.0	1.5	0.80
Co-H-C3	23.6	0.7	20.2	21.9	43.7	12.0	1.4	1.5	0.74
Co-M	17.5	3.6	54.9	16.9	19.9	3.3	0.4	0.07	0.71
Co-M-H	31.8	0.6	17.2	14.5	32.3	34.1	1.5	1.0	0.80

0.2 g catalyst mixed with 1.0 g SiC, in situ pre-treated under various conditions. Reaction conditions: 230 °C, 3.0 MPa, $H_2/CO=2$, WHSV=6000 mL $gcat.^{-1}$ h^{-1}, data was defined at the 40th hour. The selectivity was calculated on all the carbon-containing products. a: o/p defined the ratio of paraffins and olefins in the C2-C4 hydrocarbon products.

Table S3 The bulk and surface concentration of cobalt and carbon of Co/Al_2O_3 catalysts.

Sample	Cobalt concentration (%)				Carbon concentration (%)	
	Bulk (ICP)	Surface (XPS)	Co(0)	Co(II)	Bulk (TG)	Surface (XPS)
Co-H	6.45	0.21	38	62	1.5	3.0
Co-H-C1	6.44	0.22	21	79	2.2	3.5
Co-M	6.01	0.05	10	90	21.4	59.7
Co-M-H	6.22	0.16	52	48	19.0	68.0

The concentration of Co(0) and Co(II) was determined by Co $2p_{3/2}$ XPS spectra.

Table S4 The adsorption energies (ΔE_{ads}, in eV) of various intermediates on Co surface and C/Co surface, respectively.

Intermediates	Co	C/Co
CO	-1.67	-1.44
C	-6.82	-6.36
O	-5.62	-5.03
H	-0.53	-0.39
CH	-6.30	-6.08
CH_2	-3.94	-3.73
CH_3	-1.94	-1.42
CH_4	-0.01	-0.02

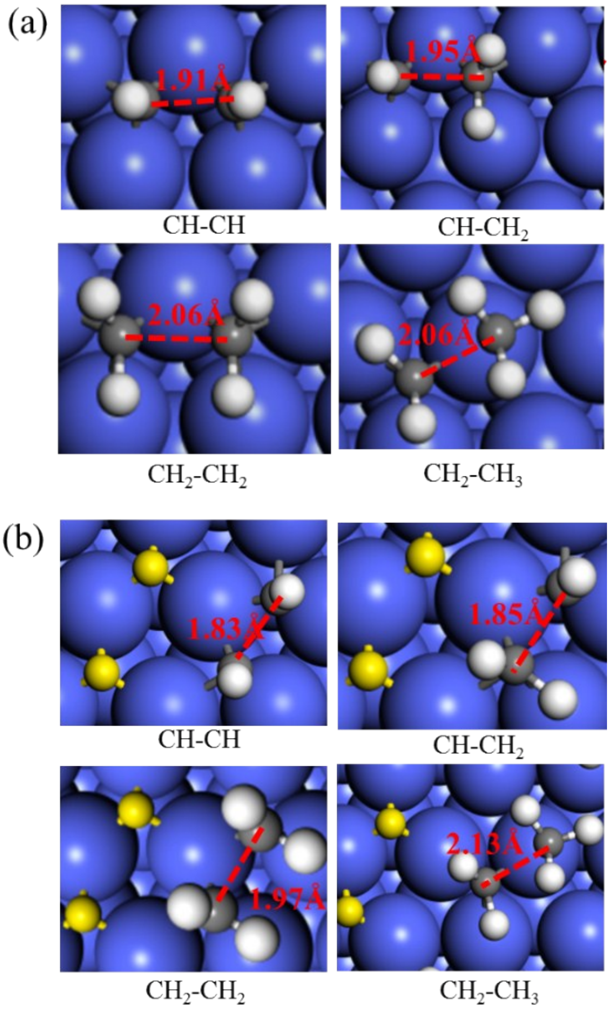

Fig. S3 Transition state (TS) structures for important C-C coupling on Co catalyst (a) and C/Co catalysts (b), and the distance of forming C-C bond at TS are indicated. Blue, yellow, grey and white balls represent Co, pre-adsorbed C, normal C, and H atoms, respectively.

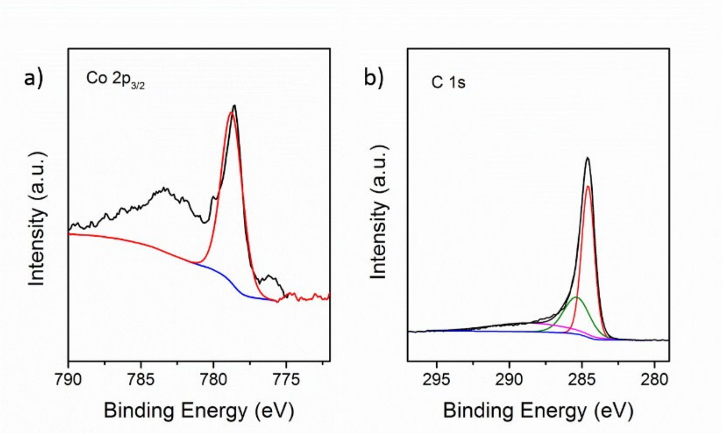

Fig. S4 Co 2p and C 1s XPS spectra of Co-M-H.

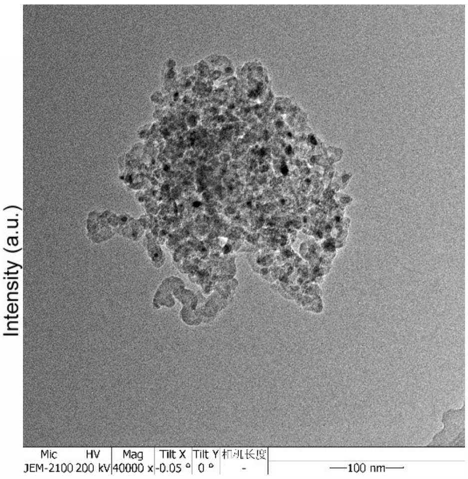

Fig. S5 TEM picture of Co-M-H.

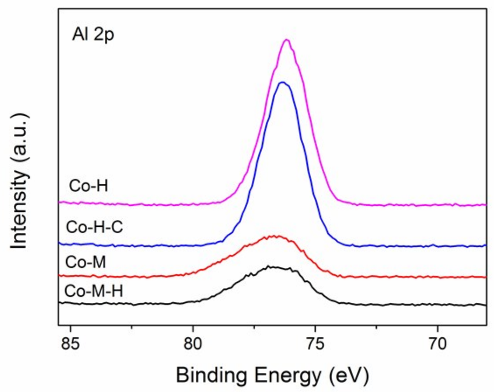

Fig. S6 Al 2p XPS spectra of Co/Al_2O_3 catalysts.

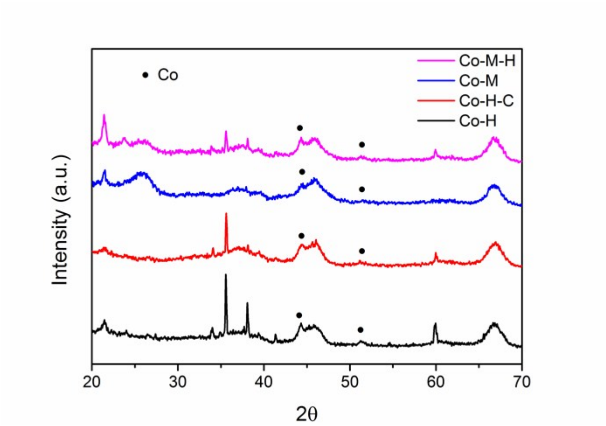

Fig. S7 XRD patterns of Co/Al_2O_3 catalysts after FTS reaction.

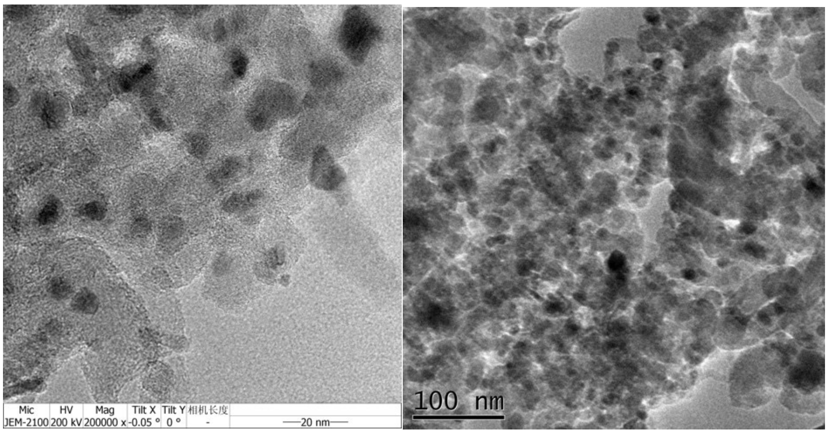

Fig. S8 TEM pictures of spent Co/Al_2O_3 catalysts, left: Co-H-spent, right: Co-M-spent.

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