Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Investigation of the highly tunable selectivity to linear α-olefins in Fischer-Tropsch synthesis over silica supported Co and CoMn catalysts by carburization-reduction pretreatment

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Supplementary Figures and Tables

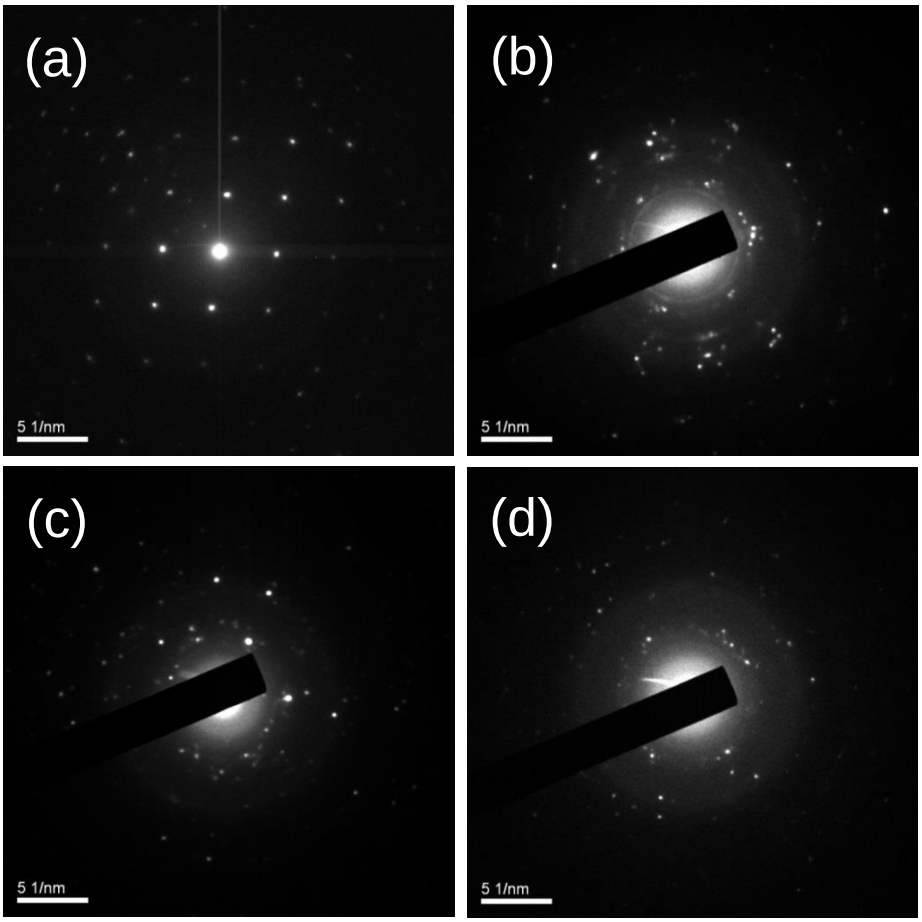

Fig. S1 Rotation electron diffraction (ED) patterns of the 15Co/SiO_2 catalysts: (a) calcined 15Co/SiO_2, (b) 15Co/SiO_2-R, (c) 15Co/SiO_2-RC, (d) 15Co/SiO_2-RCR.

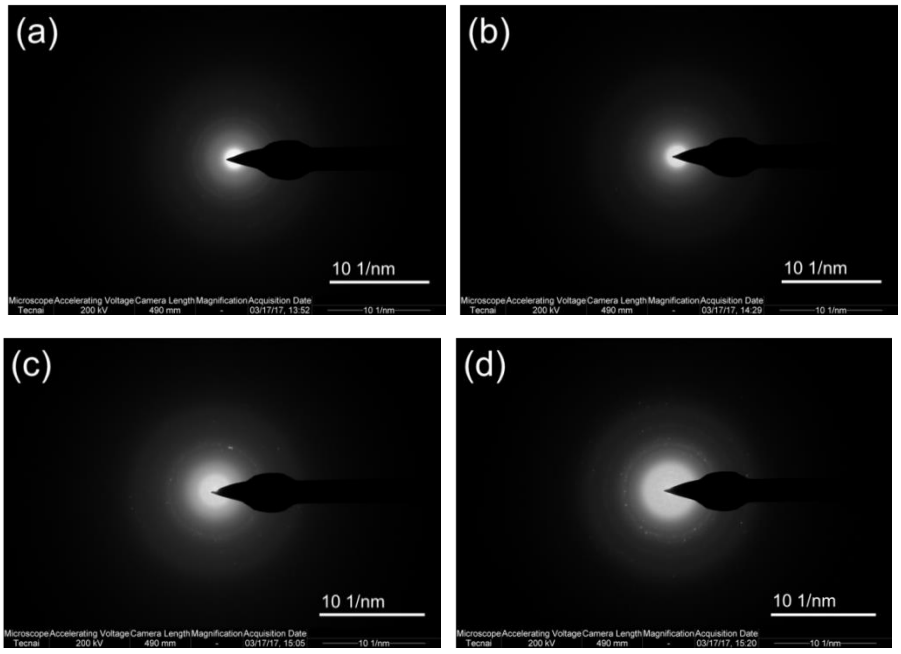

Fig. S2 Rotation electron diffraction (ED) patterns of (a) calcined 15Co3.7Mn/SiO_2, (b) 15Co3.7Mn/SiO_2-R, (c) 15Co3.7Mn/SiO_2-RC, and (d) 15Co3.7Mn/SiO_2-RCR catalysts.

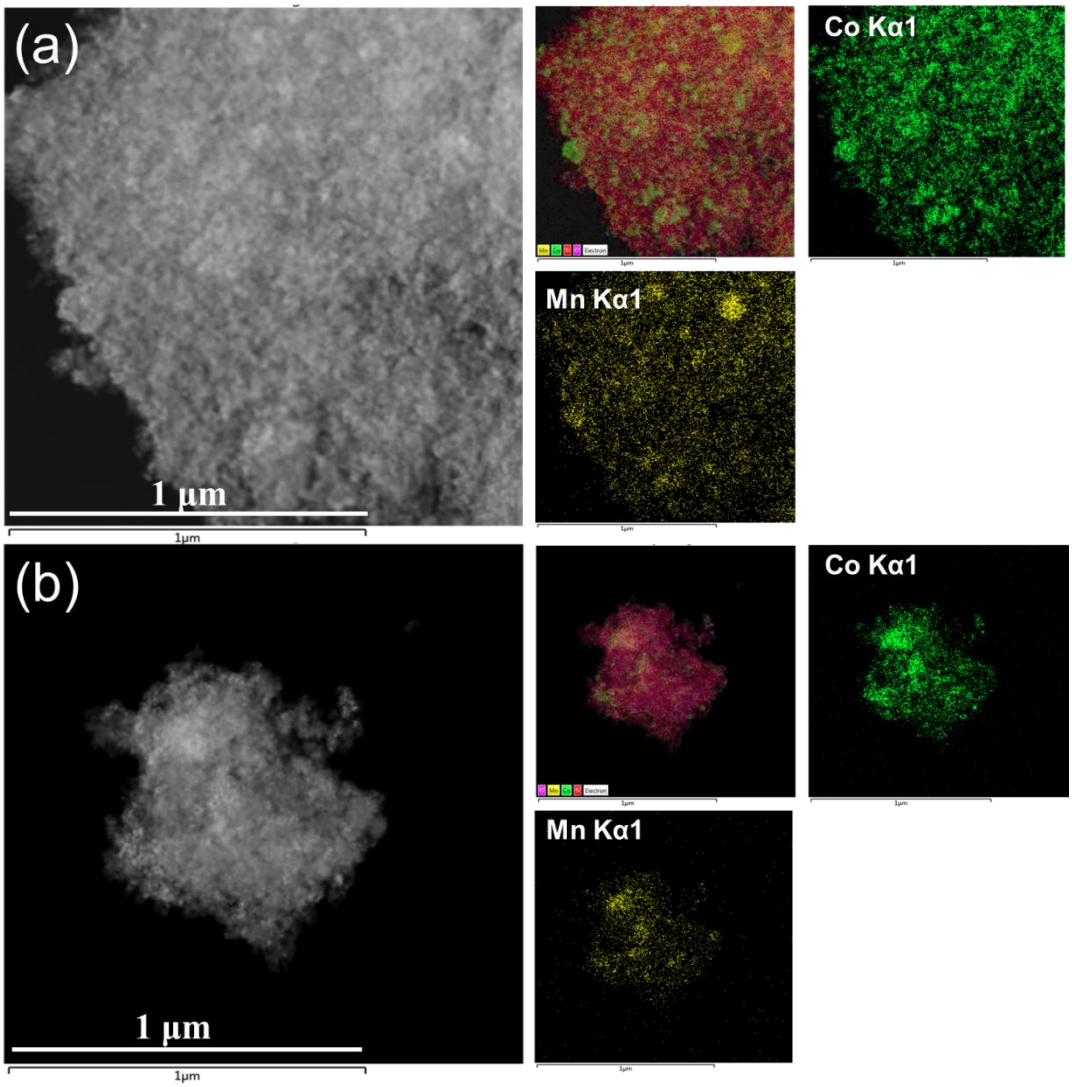

Fig. S3 EDX mapping of the calcined 15Co3.7Mn/SiO_2 (a), and 15Co3.7Mn/SiO_2-R (b).

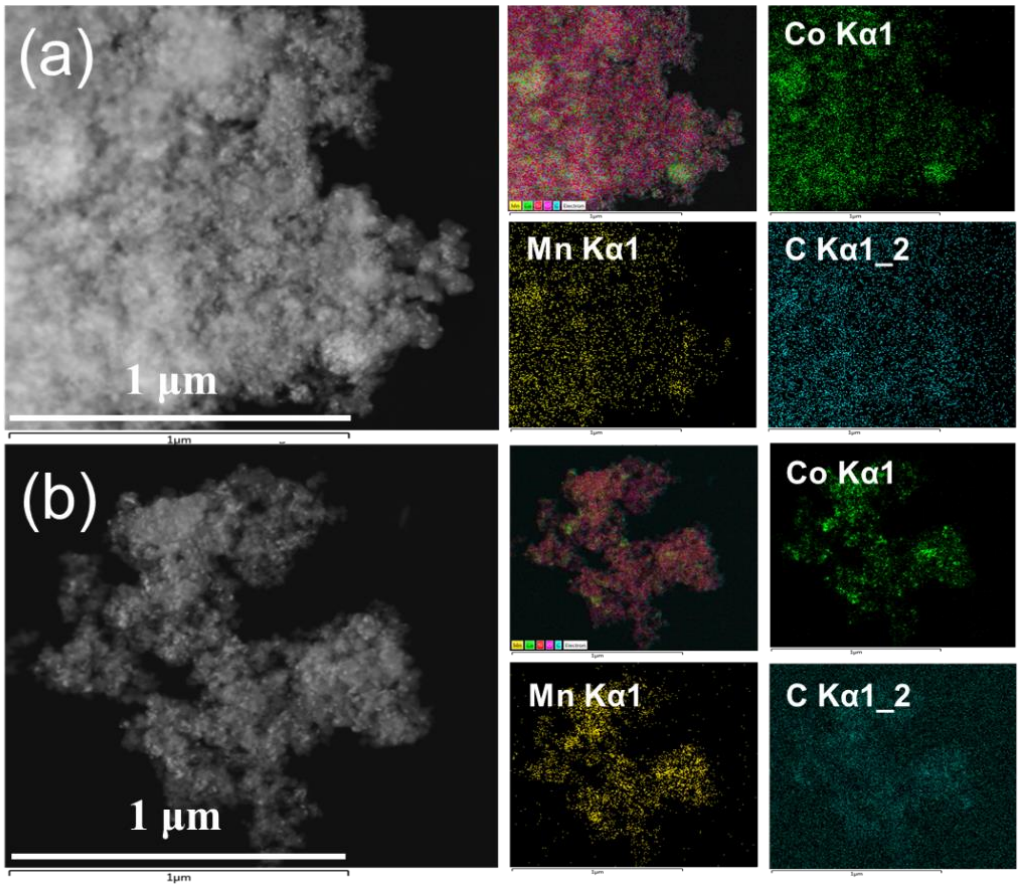

Fig. S4 EDX mapping of (a) 15Co3.7Mn/SiO_2-RC, and (b) 15Co3.7Mn/SiO_2-RCR catalysts.

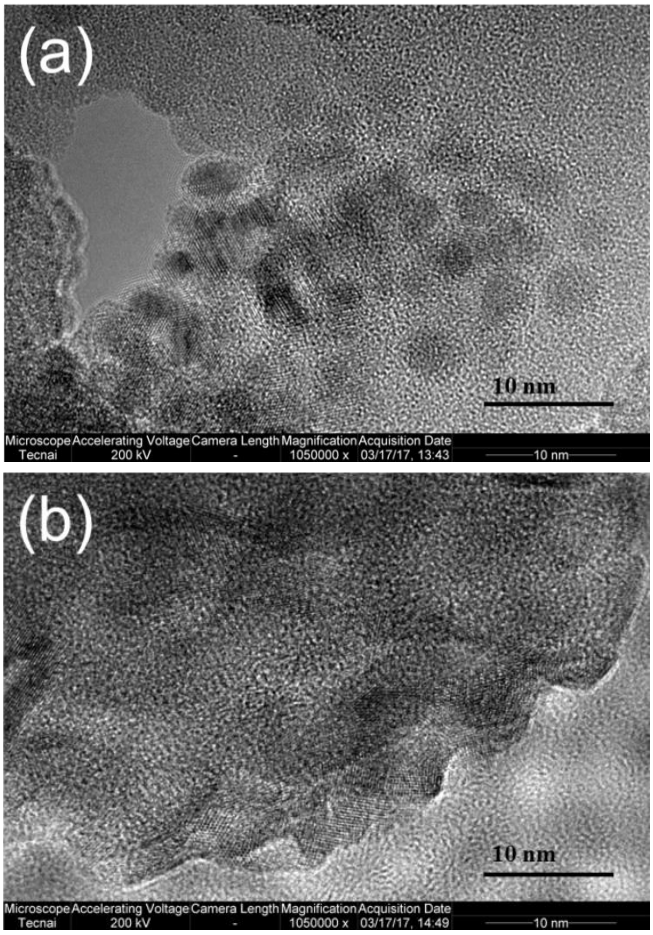

Fig. S5 High resolution TEM images of (a) calcined 15Co3.7Mn/SiO_2 and (b) 15Co3.7Mn/SiO_2-RC catalysts.

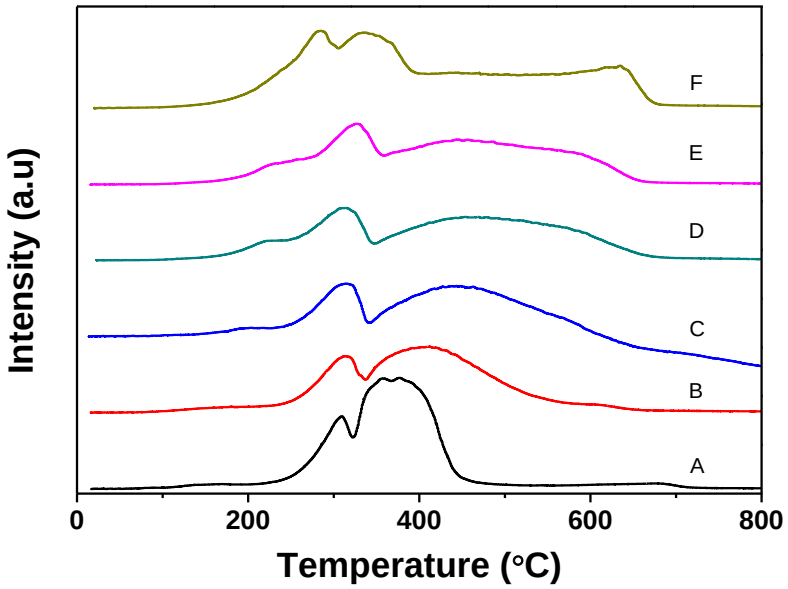

Fig. S6 H_2-TPR profiles for the Mn-promoted $15Co/SiO_2$ catalysts: (A) $15Co/SiO_2$, (B) $15Co0.8Mn/SiO_2$, (C) $15Co1.7Mn/SiO_2$, (D) $15Co3.7Mn/SiO_2$, (E) $15Co5Mn/SiO_2$, (F) $15Co15Mn/SiO_2$.

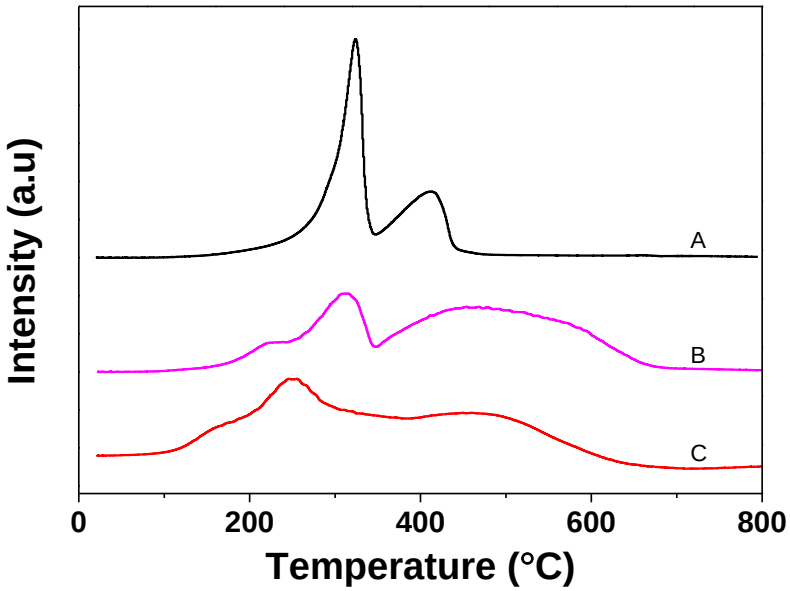

Fig. S7 H_2-TPR profiles for (A) calcined $15Mn/SiO_2$, (B) calcined $15Co3.7Mn/SiO_2$, and (C) $15Co3.7Mn/SiO_2$-RC catalysts.

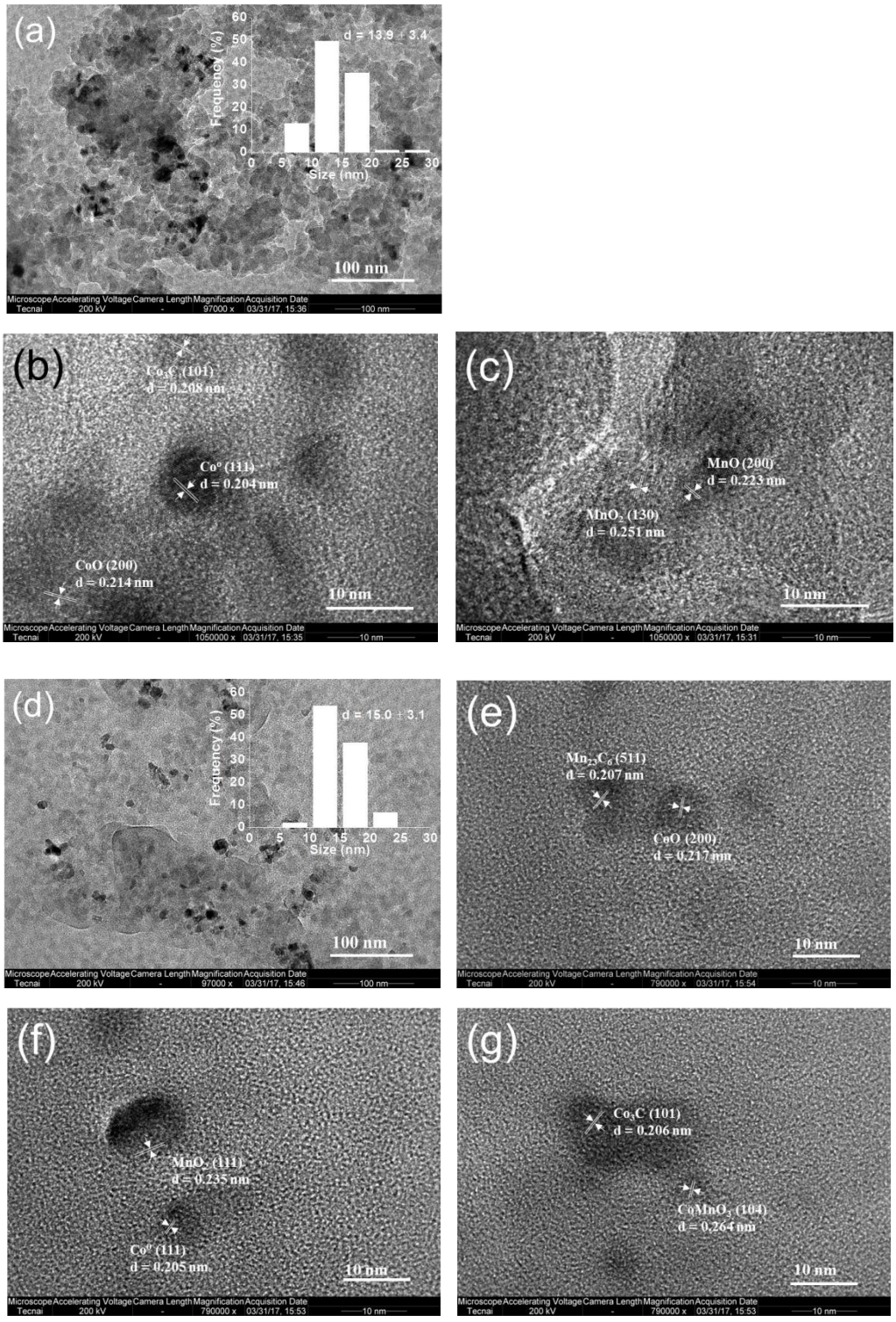

Fig. S8 Low and high resolution TEM images for the spent 15Co3.7Mn/SiO_2 catalyst with TOS under the reaction conditions of T = 230 ℃, P =10 bar, H_2/CO =2, and GHSV = 4.5 L g_{cat}^{-1} h^{-1}: (a-c) t = 2 h; (d-g) t = 20 h.

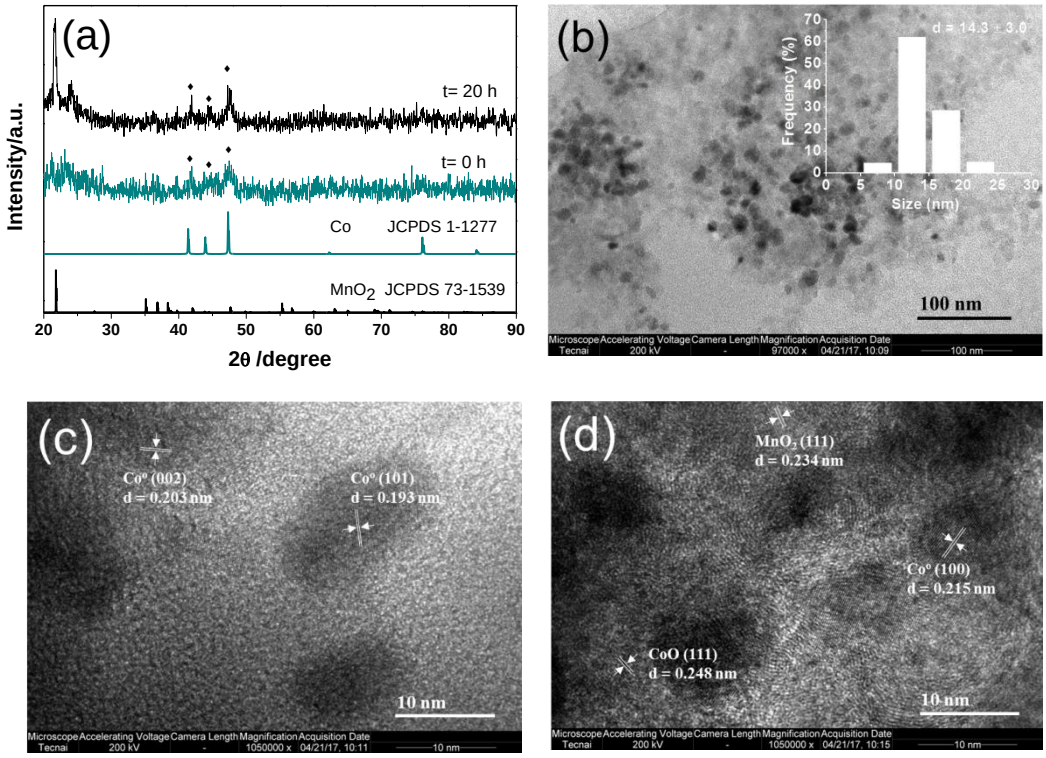

Fig. S9 XRD diffraction patterns (a, t = 0, 20 h) and low and high resolution TEM images (b-d, t = 20 h) of the 15Co3.7Mn/SiO_2-RCR catalyst with TOS under the reaction conditions of T = 230 ℃, P =10 bar, GHSV = 4.5 L g_{cat}^{-1} h^{-1}, and H_2/CO = 2.

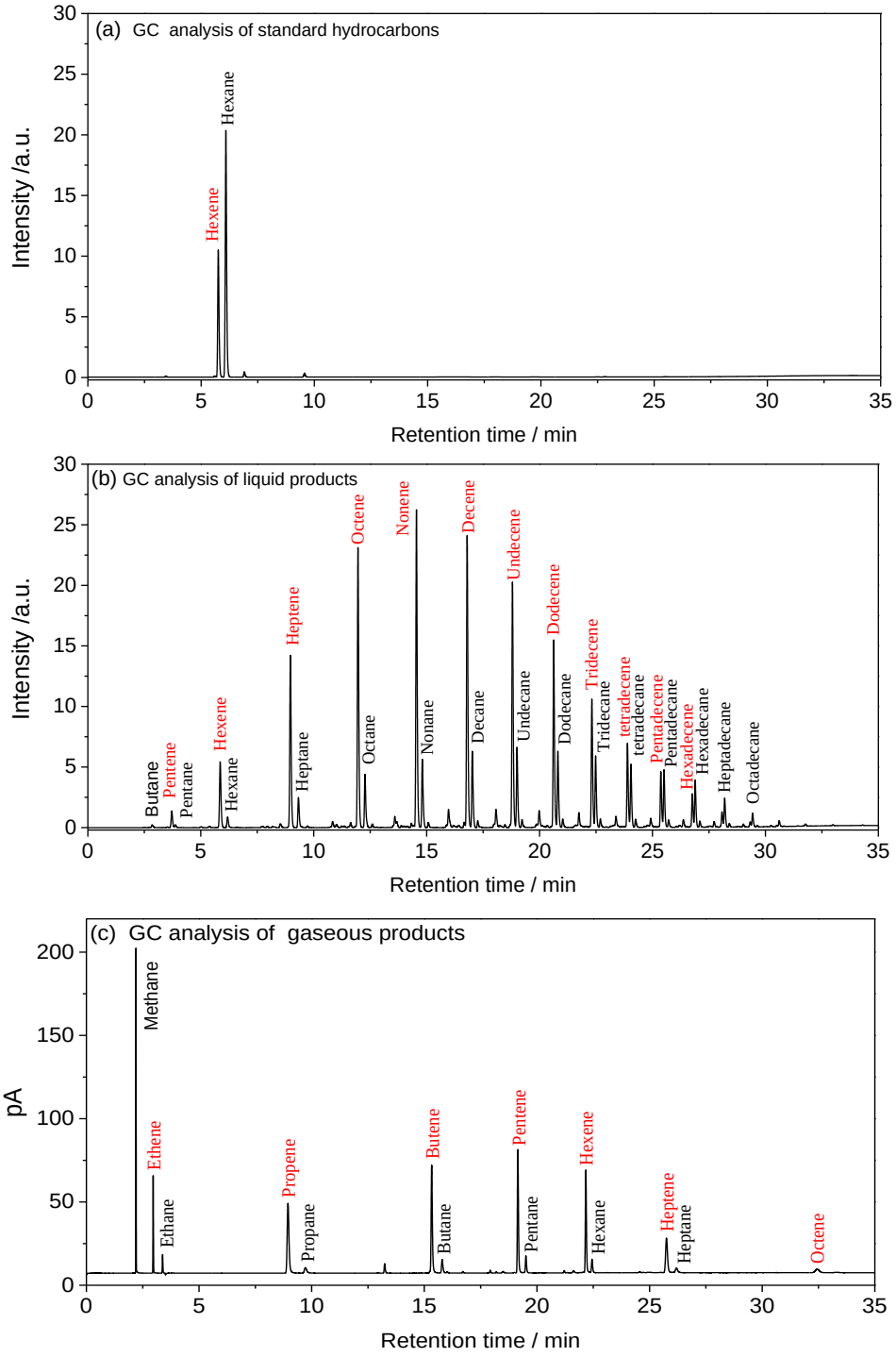

Fig. S10 GC chart of (a) the standard hydrocarbons, (b) the FT liquid products, and (c) the FT gaseous products obtained from the FTS reaction over the 15Co3.7Mn/SiO_2 catalyst under the conditions of 240 ℃, 10 bar, and H_2/CO = 0.5.

It is clearly shown in the GC chart that, in the case of the tested Co-based catalysts, the FT products mostly consist of the n-paraffins and α-olefins, including very small amount of the iso-hydrocarbons and almost no internal olefins.

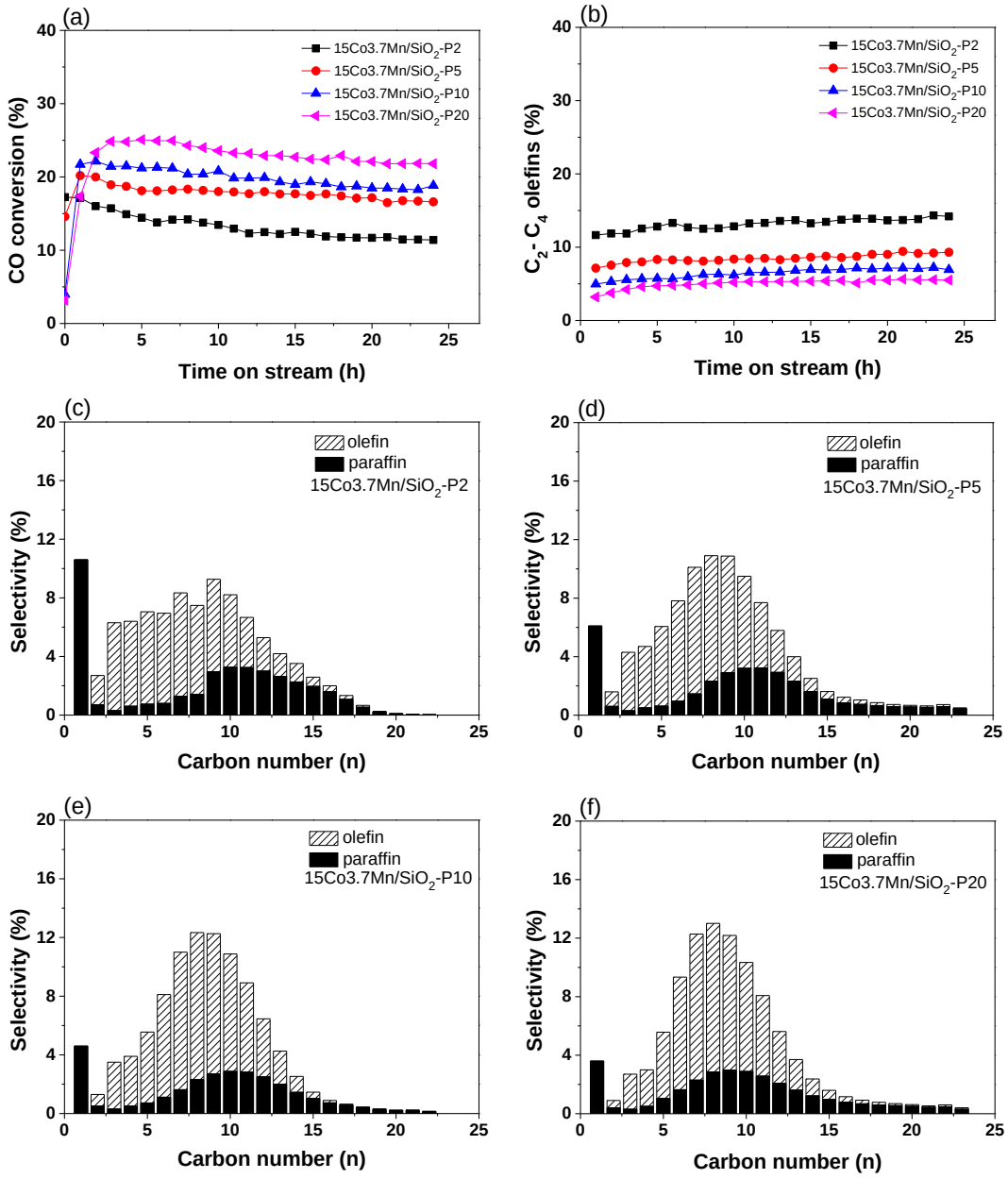

Fig. S11 Influence of the reaction pressure on the CO conversion (a) and $C_2^=$-$C_4^=$ selectivity (b) with time on stream, and products distribution (c-f) for the 15Co3.7Mn/SiO_2 catalyst.

Table S1 Textural properties of the support and prepared cobalt catalysts.

Sample	S_{BET} (m^2/g)	D_{pore} (nm)	V_{pore} (cm^3/g)
Q-15	186.8	25.1	1.17
15Co/SiO_2	153.5	25.2	0.90
15Co/SiO_2-R	153.8	22.0	0.83
15Co3.7Mn/SiO_2	158.3	21.8	0.83
15Co3.7Mn/SiO_2-R	154.7	21.5	0.81

Table S2 The influence of pretreatment on the crystal facet and phase state of cobalt over the 15Co/SiO_2 catalyst.

Sample	Nanoparticle	Crystal facet	Lattice distance (nm)		
			From XRD[a]	From HRTEM[b]	From ED[c]
15Co/SiO_2	Co_3O_4	(311)	0.243	0.252	0.244
15Co/SiO_2-R	Co	(111)	0.205	0.207	0.212
15Co/SiO_2-RC	Co_2C	(111)	0.212	0.205	0.220
15Co/SiO_2-RCR	Co	(101)	0.192	0.189	0.185
	Co	(002)	0.203	0.204	0.203

[a] corresponding to Figure 1; [b] corresponding to Figure 3; [c] corresponding to Figure S1.

Table S3 Cobalt particle size calculated from XRD patterns and TEM images of the pretreated 15Co/SiO_2 catalysts.

Sample	Nanoparticle	Particle size (nm)	
		By XRD	By TEM
15Co/SiO_2	Co_3O_4	17.5 (13.1)[a]	16.1±5.0 (12.1±5.0)[a]
15Co/SiO_2-R	Co	15.0	15.5±3.4
15Co/SiO_2-RC	Co_2C	17.1	17.8±4.6
15Co/SiO_2-RCR	Co	19.7	20.3±6.4

[a] Calculated from Co_3O_4 particle, $d(Co) = 0.75 \times d(Co_3O_4)$

Table S4 Cobalt particle size calculated from XRD patterns and TEM images of the pretreated 15Co3.7Mn/SiO_2 catalysts.

Sample	Nanoparticle	Particle size (nm)	
		By XRD	By TEM
15Co3.7Mn/SiO_2	Co_3O_4	13.0 (9.8)[a]	10.0±2.3 (7.5±2.3)[a]
15Co3.7Mn/SiO_2-R	Co	14.6	13.2±2.5
15Co3.7Mn/SiO_2-RC	Co_2C	13.9	12.7±2.9
15Co3.7Mn/SiO_2-RCR	Co	11.8	12.4±2.6

[a] Calculated from Co_3O_4 particle, $d(Co) = 0.75 \times d(Co_3O_4)$

Table S5 The influence of pretreatment on the crystal facet and phase state of cobalt over the 15Co3.7Mn/SiO_2 catalyst.

Sample	Nanoparticle	Crystal facet	Lattice distance (nm)		
			From XRD[a]	From HRTEM[b]	From ED[c]
15Co3.7Mn/SiO_2	Co_3O_4	(311)	0.243	0.246	0.248
15Co3.7Mn/SiO_2-R	Co	(111)	0.205	0.209	0.197
	CoO	(200)	0.213	0.214	---
15Co3.7Mn/SiO_2-RC	Co_2C	(111)	0.212	0.212	0.227
15Co3.7Mn/SiO_2-RCR	Co	(101)	0.192	0.190	0.172
	Co	(002)	0.206	0.204	---
	Co	(100)	0.218	0.216	---

[a]corresponding to Figure 2; [b]corresponding to Figure 4; [c]corresponding to Figure S2.

Table S6 H_2 uptake and calculated cobalt reducibility over the Mn-promoted 15Co/SiO_2 catalysts.

Sample	Co (wt%)	Mn (wt%)	H_2 uptake (mmol) [a]	Reducibility (%) [b]
15Mn/SiO_2	0	15	0.064	46.7[c]
15Co/SiO_2	15	0	0.099	58.5
15Co0.8Mn/SiO_2	15	0.8	0.074	43.7[d]
15Co1.7Mn/SiO_2	15	1.7	0.058	34.3[e]
15Co3.7Mn/SiO_2	15	3.7	0.057	---
15Co5Mn/SiO_2	15	5	0.063	---
15Co15Mn/SiO_2	15	15	0.093	---

[a]50 mg sample; [b]cobalt reducibility; [c]calculated from the MnO_2 to MnO; [d,e]regardless of the reduction of MnO_2.

Table S7 The evolution of crystal facet and phase state of Co (Mn) over the 15Co3.7Mn/SiO_2 catalyst with TOS.

Reaction time (h)	Nanoparticle	Crystal facet	Lattice distance (nm)	
			From XRD data [a]	From HRTEM [b]
Reduced sample (t = 0)	Co	(111) major	0.205	0.209
	CoO	(200)	0.213	0.214
Spent sample (t= 2)	Co	(111) major	0.205	0.204
	Co_3C	(101) minor	0.205	0.208
	CoO	(200)	0.213	0.214
	MnO	(200)	0.222	0.223
	MnO_2	(130)	0.255	0.251
Spent sample (t= 20)	Co	(111) minor	0.205	0.205
	Co_3C	(101) major	0.205	0.206
	CoO	(200)	0.213	0.217
	MnO	(200)	0.222	0.223
	MnO_2	(111)	0.234	0.235
	$Mn_{23}C_6$	(511)	0.204	0.207
	$CoMnO_3$	(104)	0.267	0.264

Reaction conditions: T = 230 ℃, P =10 bar, H_2/CO = 2, GHSV = 4.5 L g_{cat}^{-1} h^{-1}. [a]corresponding to Figure 7 (a); [b]corresponding to Figure 4 (c, d) and Figure S8 (a-g).