

Supporting Information

Effects of alkali metal promoters on the structure-performance relationship of CoMn catalysts for Fischer-Tropsch synthesis

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Table S1. Ionic potential of alkali metal ions.

Ion	Ionic Potential
Li ⁺	1.6641
Na ⁺	1.0404
K ⁺	0.7569
Rb ⁺	0.6724

Table S2. Elements analysis of the unpromoted and alkali metal promoted CoMn catalysts.

Sample	Alkali concentrations (wt.%) ^a	Alkali concentrations (wt.%) ^b	Co/Mn ^b
CoMn	0.0	0.006 ^c	2.02
CoMn-Li	0.4	0.39	2.08
CoMn-Na	0.4	0.37	2.09
CoMn-K	0.4	0.43	2.08
CoMn-Rb	0.4	0.50	2.12

^a Nominal loadings, ^b Atomic ratio measured with ICP, ^c Sodium concentration.

Table S3. Textural properties of the unpromoted and alkali metal promoted CoMn catalysts.

Sample	BET Surface Area (m ² /g)		Pore Volume (cm ³ /g)		Pore Diameter (nm)	
	Reduced	Spent	Reduced	Spent	Reduced	Spent
CoMn	51.1	56.5	0.19	0.18	11.7	11.3
CoMn-Li	62.1	25.9	0.21	0.14	11.4	12.1
CoMn-Na	57.8	47.7	0.20	0.17	11.6	11.0
CoMn-K	53.5	55.6	0.17	0.24	11.3	12.7
CoMn-Rb	45.3	59.1	0.18	0.23	12.5	12.2

Table S4. Catalytic performance of the unpromoted and promoted CoMn catalyst at 250 °C, 1 bar, 3000 mL/(h g_{cat}), and H₂/CO = 2 (v/v).

Catalyst	CO Conv. (C%)	CO ₂ Sele. (C%)	Product Selectivity (C%, CO ₂ -free)						O/P Ratios			
			CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₂₋₄ ⁼	C ₅₊ + Oxy	C ₂	C ₃	C ₄	C ₂₋₄
CoMn	69.2	14.9	24.9	0.3	6.3	8.5	15.1	44.3	0.1	1.0	1.9	1.0
CoMn-Li	36.7	32.8	26.9	1.4	7.5	4.5	13.4	40.1	0.1	1.0	1.9	0.7
CoMn-Na	16.4	42.0	4.1	10.5	26.5	12.0	49.0	45.2	17.8	40.4	29.1	29.5
CoMn-K	6.4	34.3	9.3	13.0	25.3	9.6	47.9	41.0	19.7	32.7	24.1	26.1
CoMn-Rb	8.1	16.6	13.1	9.5	26.6	10.5	46.5	36.6	6.5	18.1	12.4	12.3

Table S5. Catalytic performance of the unpromoted and promoted CoMn catalyst at different GHSV, 250 °C, 1 bar, and H₂/CO = 2 (v/v).

GHSV (mL/(h·g _{cat}))	CO Conv. (C%)	CO ₂ Sele. (C%)	Product Selectivity (C%, CO ₂ -free)		
			CH ₄	C ₂₋₄ ⁼	C ₅₊ + Oxy
3000	15.5	45.6	6.0	52.3	39.8
4500	13.8	44.8	6.7	55.6	34.8
6000	9.5	42.2	6.1	52.8	38.9

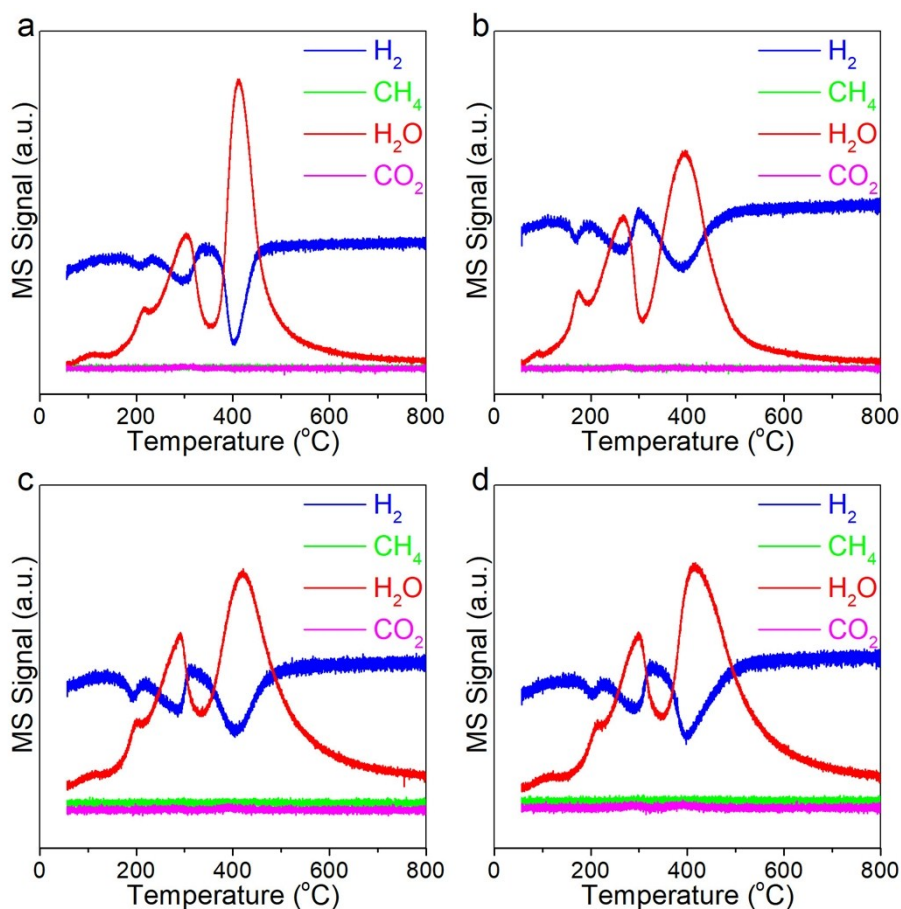


Figure S1. MS signals of the alkali metal promoted CoMn catalysts in H₂-TPR: (a) CoMn-Li; (b) CoMn-Na; (c) CoMn-K; (d) CoMn-Rb.

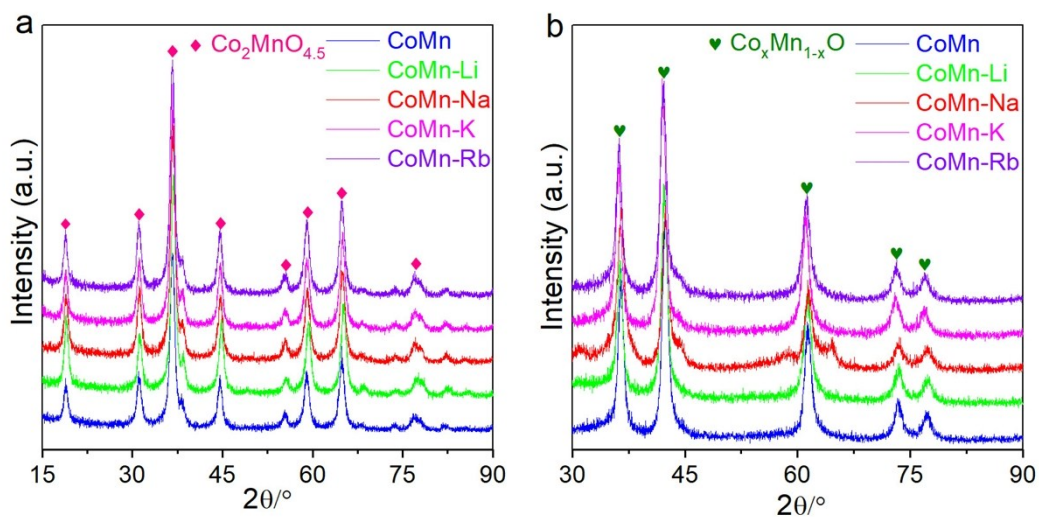


Figure S2. XRD patterns of the calcined and reduced CoMn catalysts with different alkali metal promoters: (a) the calcined catalysts; (b) the reduced catalysts.

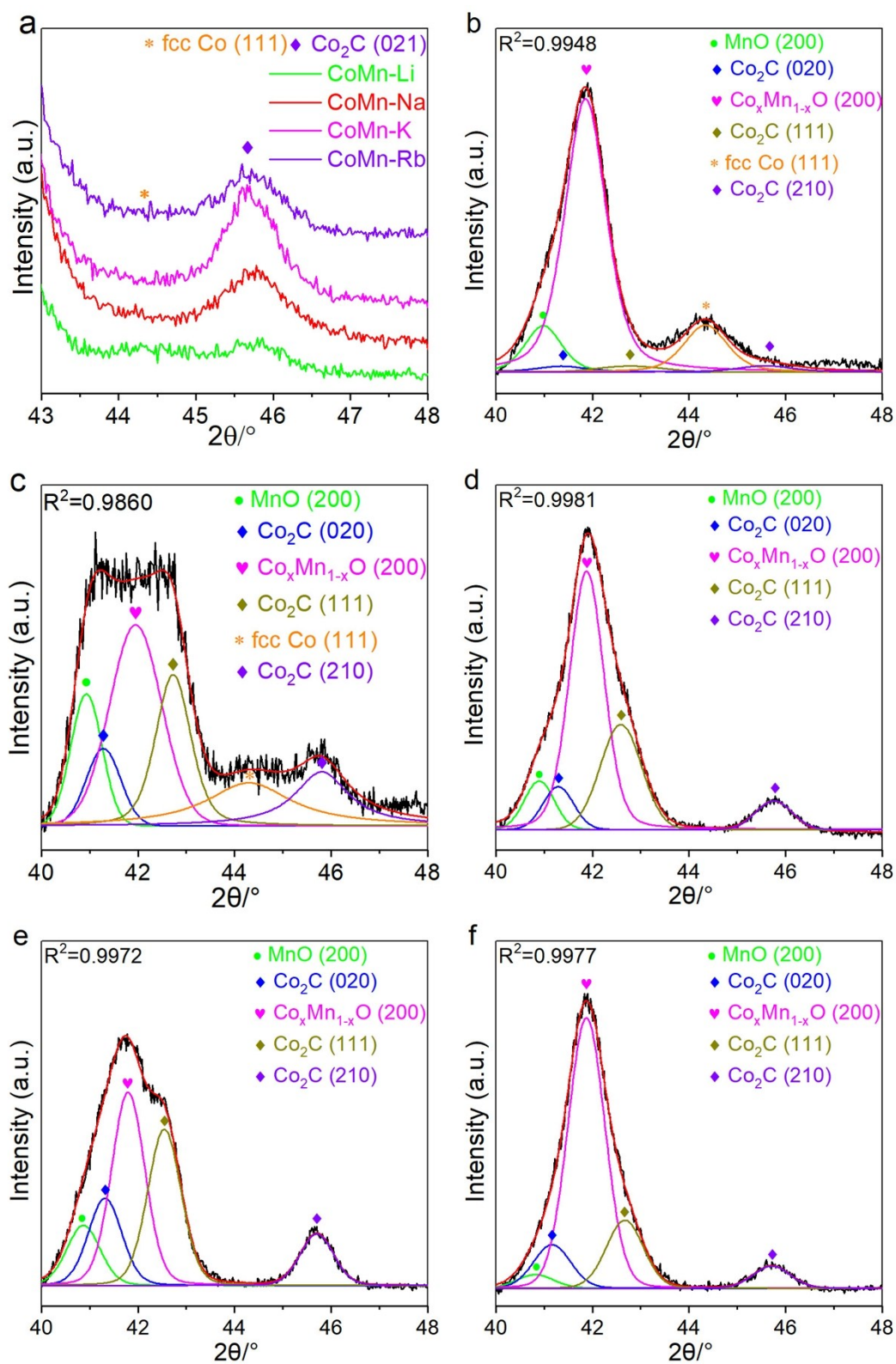


Figure S3. XRD patterns and peak fitting results of the spent CoMn catalysts with different alkali metal promoters: (a) step scanning with 2θ from 43° to 48° ; (b) CoMn; (c) CoMn-Li; (d) CoMn-Na; (e) CoMn-K; (f) CoMn-Rb. TOS = 24 h for all samples.

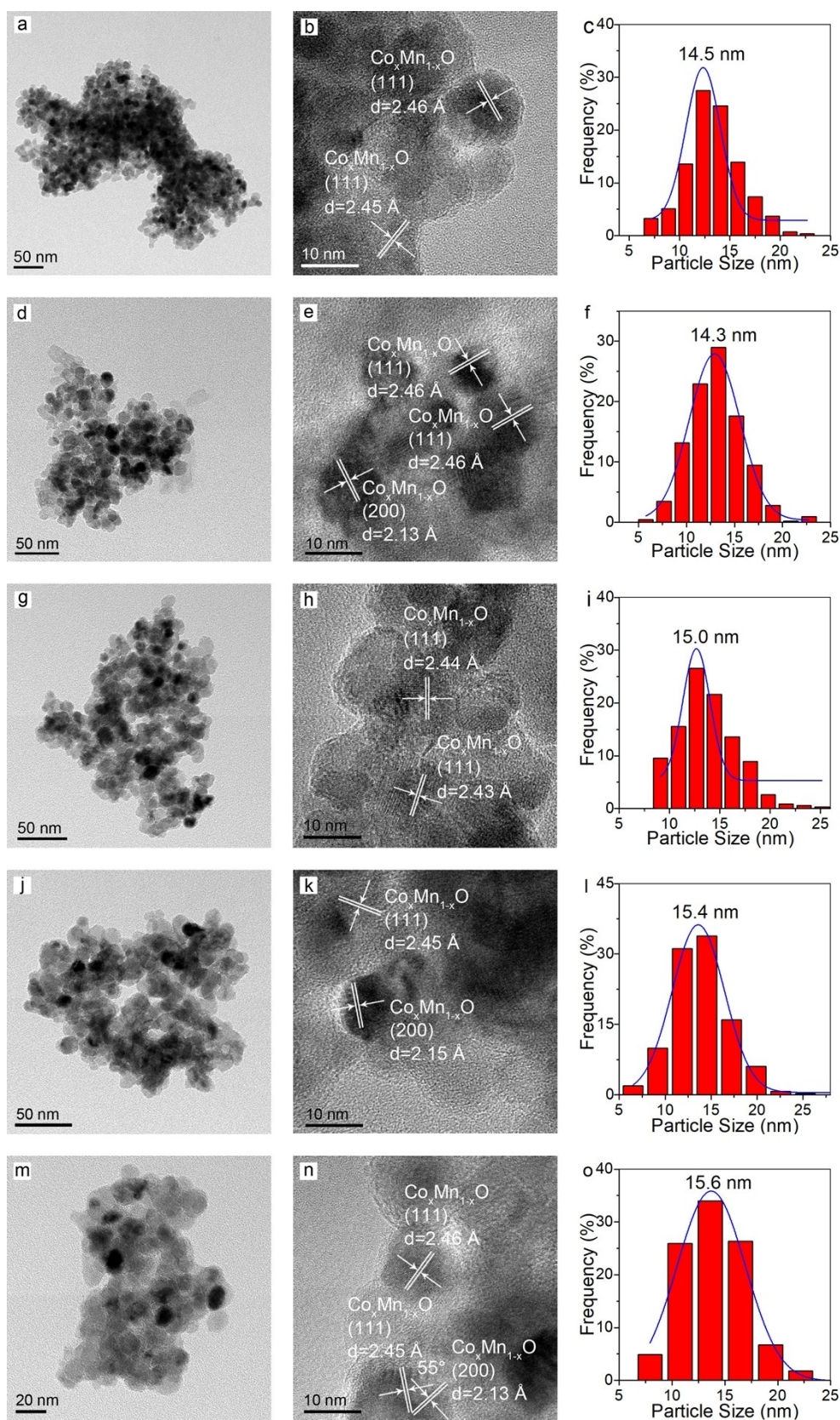


Figure S4. TEM images of the reduced CoMn catalysts with different alkali metal promoters: (a-c) CoMn; (d-f) CoMn-Li; (g-i) CoMn-Na; (j-l) CoMn-K; (m-o) CoMn-Rb.

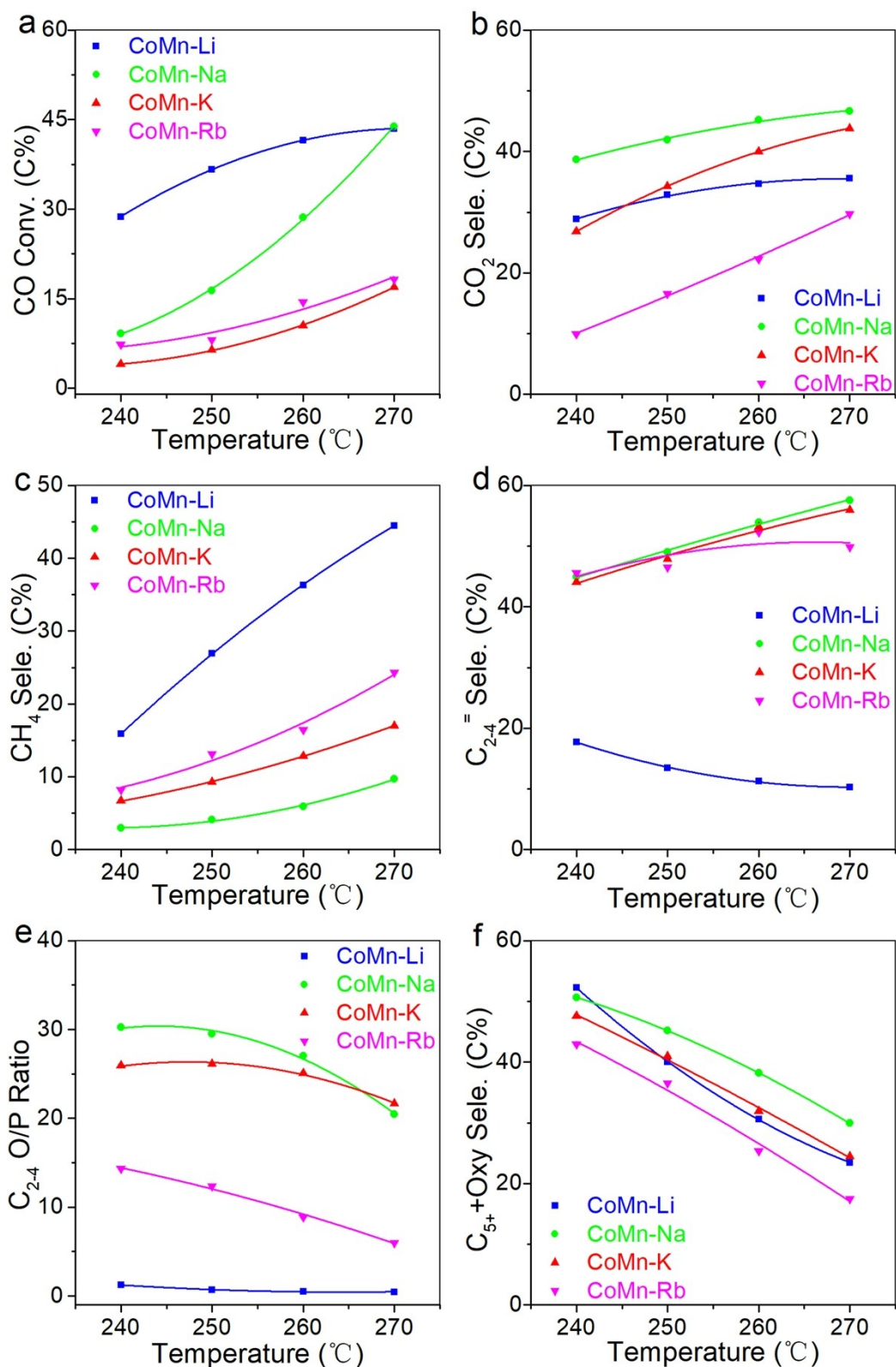


Figure S5. Catalytic performance of the CoMn catalysts with different alkali metal promoters at different temperatures, 1 bar, 3000 ml/(h·g_{cat}), H₂/CO=2: (a) CO conversion; (b) CO₂ selectivity; (c) CH₄ selectivity; (d) Lower olefin selectivity; (e) O/P ratios of C₂₋₄; (f) C₅₊ + Oxy selectivity.

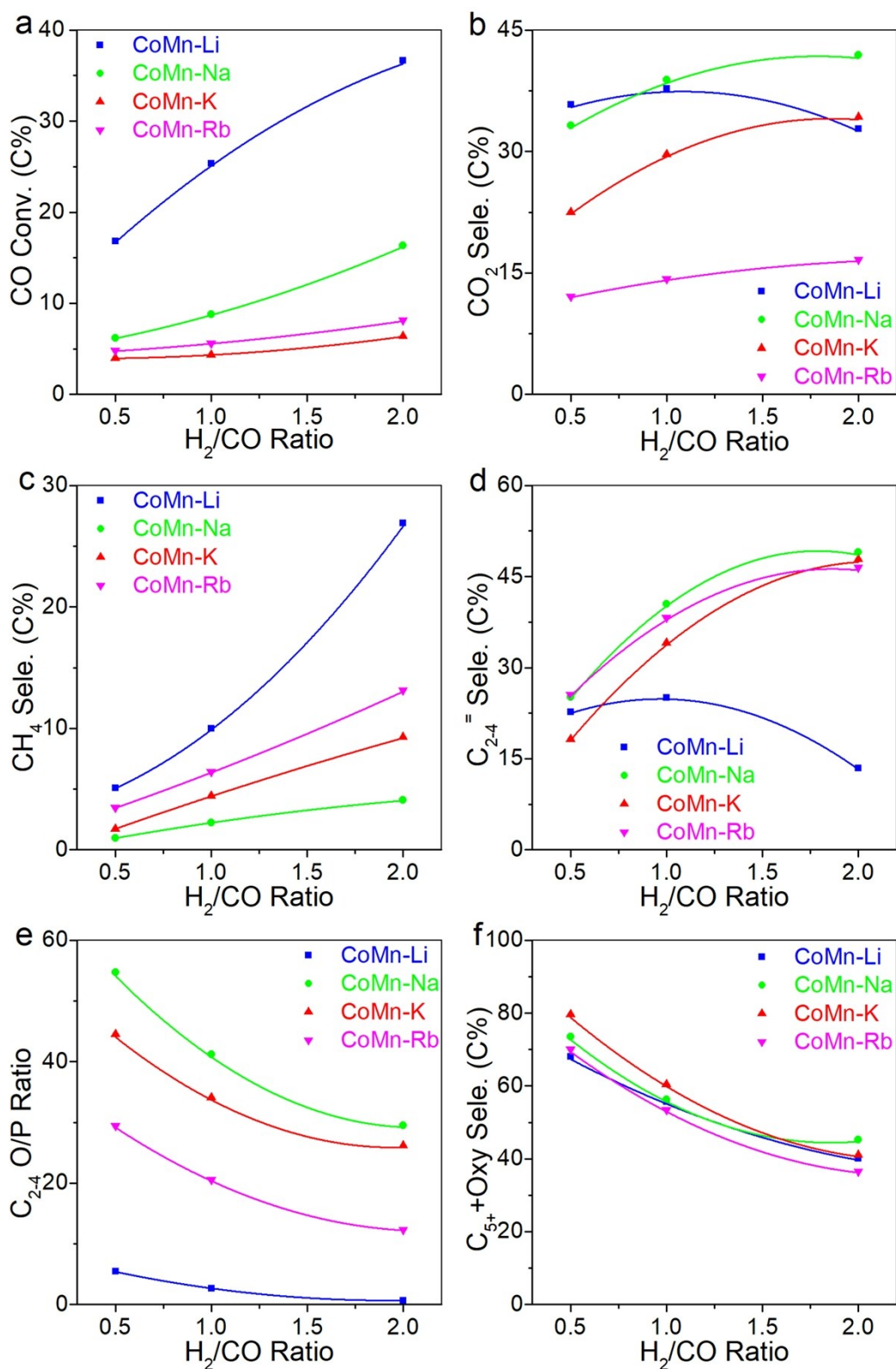


Figure S6. Catalytic performance of the CoMn catalysts with different alkali metal promoters at different H₂/CO ratios, 250 °C, 1 bar, 3000 ml/(h·g_{cat}): (a) CO conversion; (b) CO₂ selectivity; (c) CH₄ selectivity; (d) Lower olefin selectivity; (e) O/P ratios of C₂₋₄; (f) C₅₊ + Oxy selectivity.

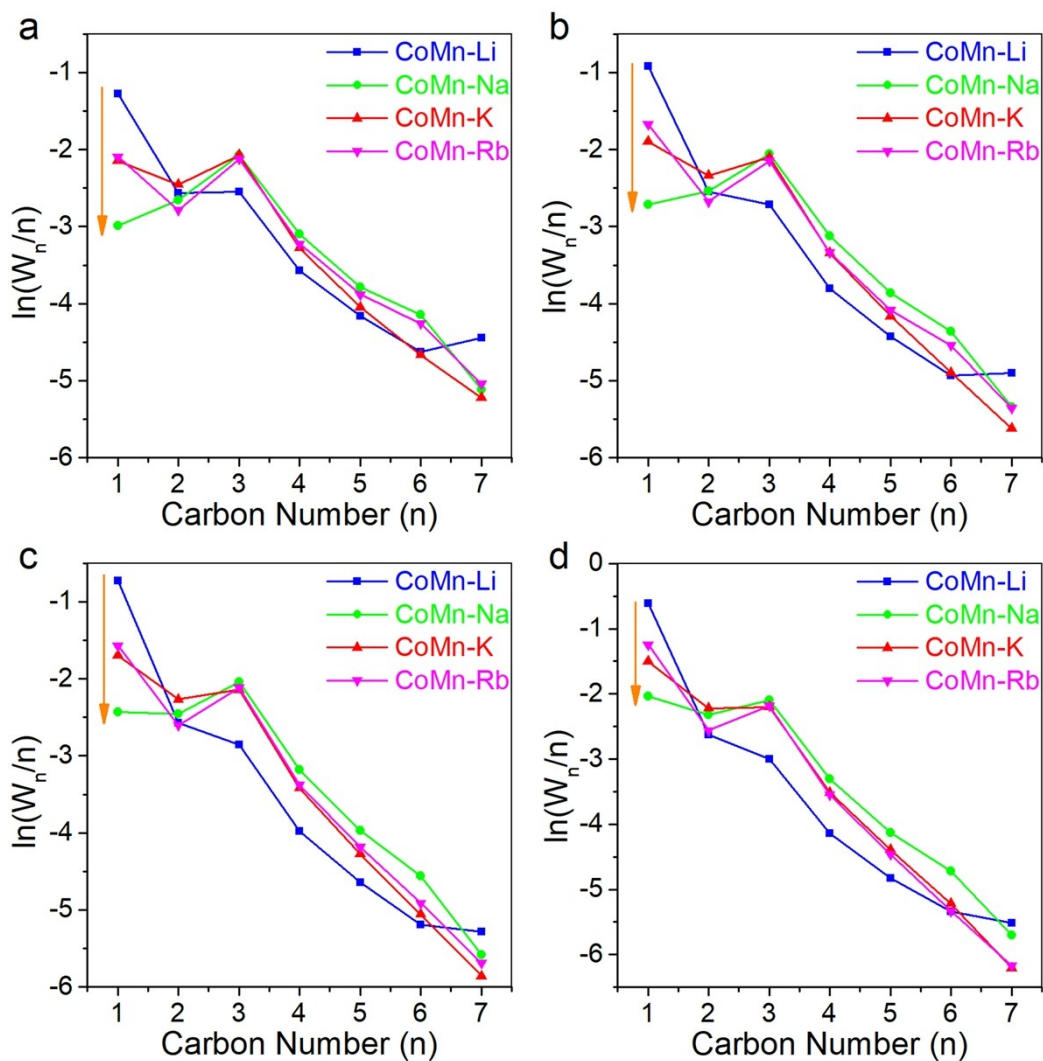


Figure S7. Product distributions of the CoMn catalysts with different alkali metal promoters at different temperatures, 1 bar, 3000 ml/(h·g_{cat}), H₂/CO=2: (a) 240 °C; (b) 250 °C; (c) 260 °C; (d) 270 °C.

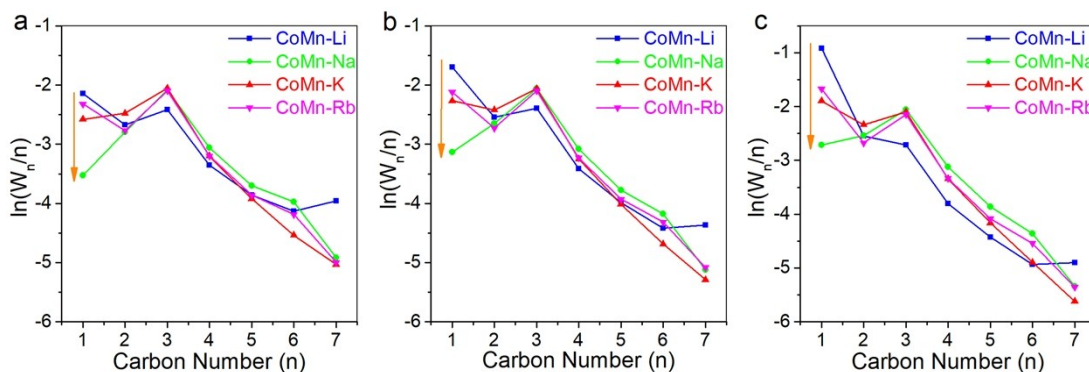


Figure S8. Product distributions of the CoMn catalysts with different alkali metal promoters at different H₂/CO ratios, 250 °C, 1 bar, 3000 ml/(h·g_{cat}): (a) H₂/CO=0.5; (b) H₂/CO=1; (c) H₂/CO=2.

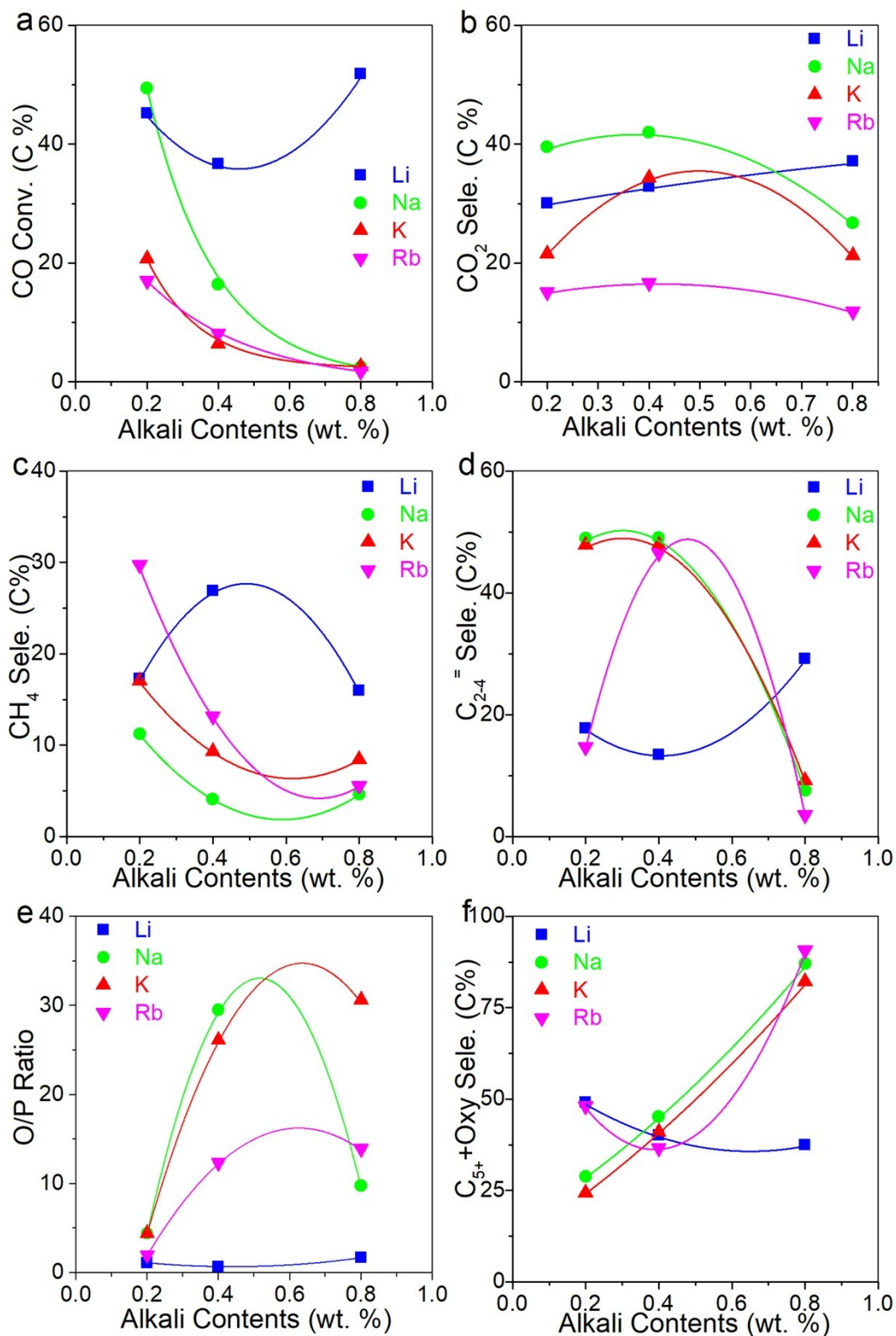


Figure S9. Catalytic performance of the alkali metal promoted CoMn catalysts with different loadings, 250 °C, 1 bar, 3000 ml/(h·g_{cat}), H₂/CO=2: (a) CO conversion; (b) CO₂ selectivity; (c) CH₄ selectivity; (d) Lower olefin selectivity; (e) O/P ratios of C₂₋₄; (f) C₅₊ + Oxy selectivity.

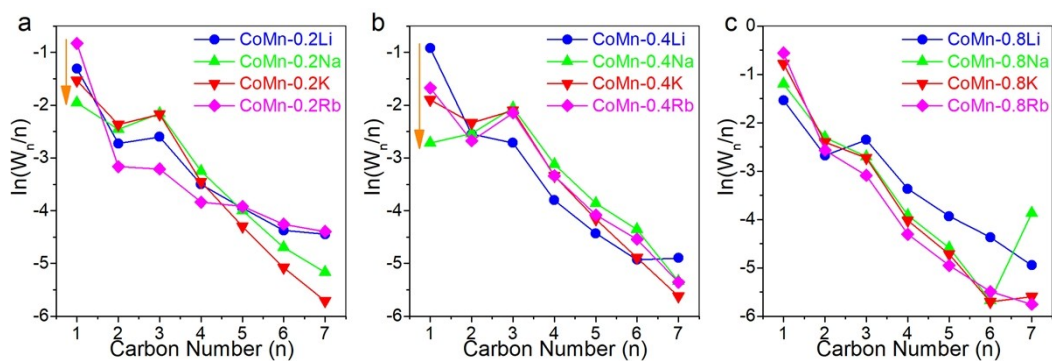


Figure S10. Product distributions of the alkali metal promoted CoMn catalysts with different loadings, 250 °C, 1 bar, 3000 ml/(h·g_{cat}), H₂/CO=2: (a) 0.2 wt.%; (b) 0.4 wt.%; (c) 0.8 wt.%.