Supporting Information

Direct Synthesis of Long–Chain Primary Alcohols from Syngas over Na–driven Co_2C–Co Catalyst

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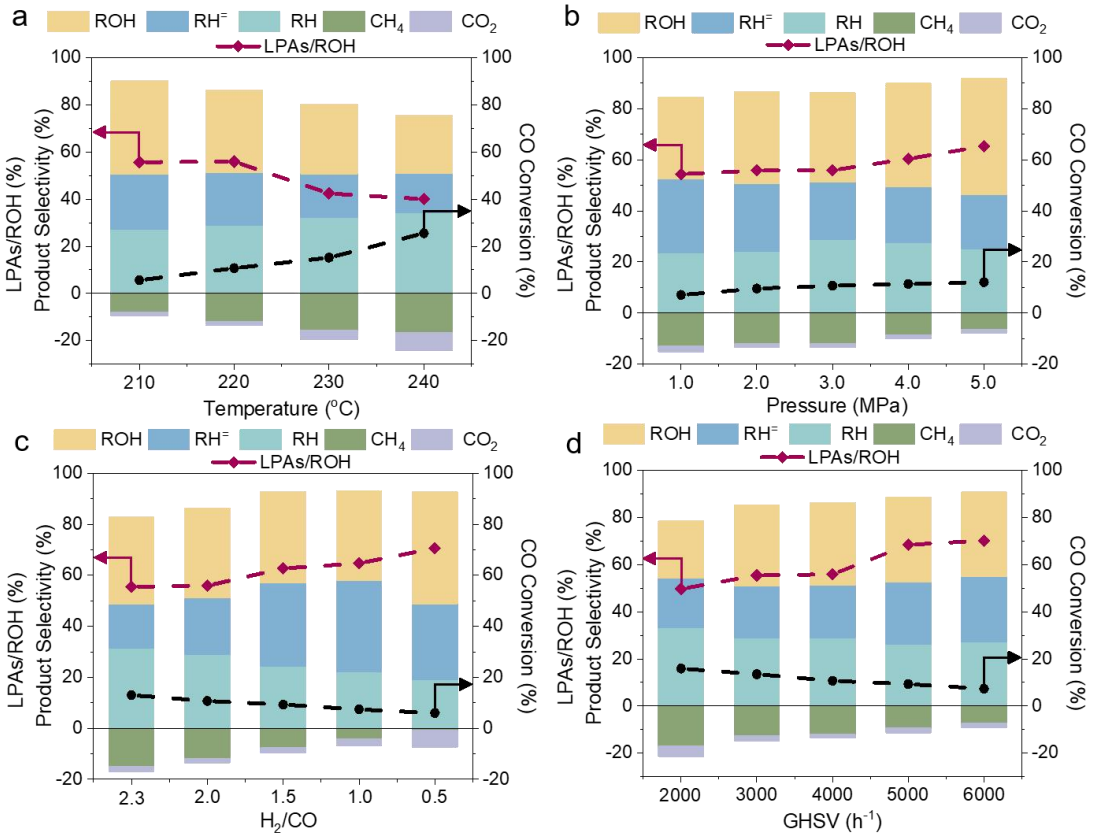

Figure S1. The effect of reaction conditions on CO conversion and product selectivity over the 0.3Na–Co/AC catalyst (Figure S1a: 3.0 MPa, 4000 h^{-1}, H_2/CO = 2.0, and reaction temperature was ranged from 210 °C to 240 °C; Figure S1b: 220 °C, 4000 h^{-1} H_2/CO = 2.0, and reaction pressure was ranged from 1.0 MPa to 5.0 MPa; Figure S1c: 220 °C, 3.0 MPa, 4000 h^{-1}, and H_2/CO ratio was ranged from 0.5 to 2.3; Figure S1d: 220 °C, 3.0 MPa, H_2/CO = 2.0, and GHSV was ranged from 2000 h^{-1} to 6000 h^{-1}).

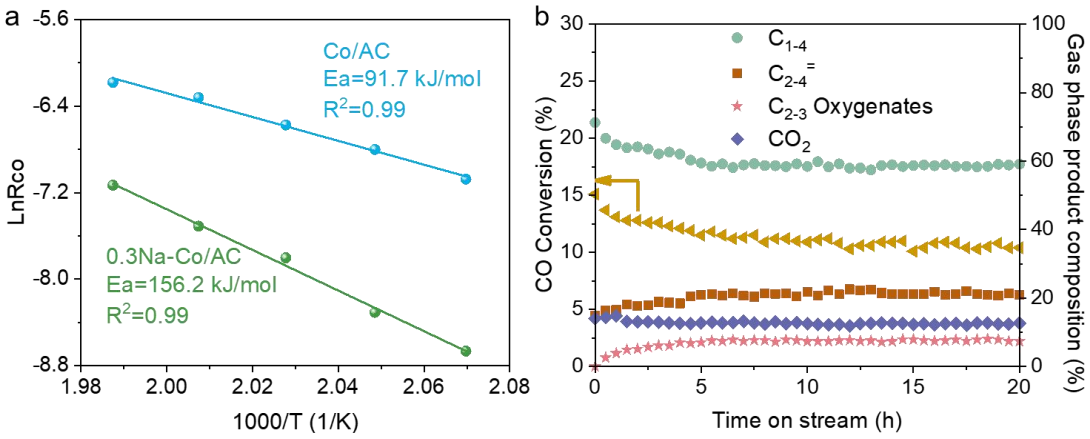

Figure S2. Arrhenius plots for the calculation of the apparent activation energy (E_a) over Co/AC and 0.3Na–Co/AC catalysts (a). CO conversion and gas phase product composition of 0.3Na–Co/AC catalyst in the initial stage of reaction (b), Reaction conditions: 220 °C, 3.0 MPa, 4000 h^{-1} and $H_2/CO = 2.0$.

Table S1. The comparison of alcohol synthesis performance from syngas for representative catalysts

Catalysts	T (°C)	P (MPa)	GHSV (h^{-1})	H_2/CO ratio	X_{CO}(%)	S_{CO2}(%)	S_{CH4}(%)	S_{ROH}(%) [b]	S_{C6+OH}(%) [c]	Ref
0.3Na–Co_2C–Co/AC	220	5	4000	2	12.1	1.6	6.3	45.9	30.0	This work
CoMn–0.6Na	240	2	6000 [a]	2	11.6	31.6	8.8	19.8	9.8	[1]
CuCoMn	270	2.5	7500	2	29.7	0.4	16.6	46.2	0.65 [d]	[2]
Co/MnO_x@quasi–MOF–74	230	3	4500 [a]	2	21.4	0.8	10.0	39.0	~13.6	[3]
CuCoAl	270	2.5	7500	2	36.2	0.5	24.0	40.7	0.65 [d]	[4]
Co−Co_2C/AC1	200	3	3665 [a]	2	71.4	7.6	–	38.4	15.0	[5]
15Co5Fe/AC	220	3	4000 [a]	2	16.4	1.6	–	20.6	5.7	[6]
15Co–0.5La/AC	220	3	1500	2	21.4	5.1	23.8	38.9	13.3	[7]
Co1Mn/AC	220	3	2000	2	29.1	2.4	8.1	21.4	~8.6	[8]
Co0.5Mn1La/AC	220	3	1000	2	32.2	3.2	13.8	25.7	~5.1	[9]
15Co–0.1Ca/AC	220	3	900	2	49.0	0.7	–	30.6	16.1	[10]
CuZnAl–A	250	4.5	–	2	20.2	43.2	–	27.0	~0	[11]
CuZnFeMn	220	2	6000	2	23.5	6.9	–	38.8	~0.8	[12]
$Ca_{0.7}La_{0.3}Ti_{0.7}Co_{0.3}O_3$	270	3	3900 [a]	2	12.0	~7.0	–	42.0	~0	[13]
CoMnZn/r–TiO_2	260	4	2000 [a]	2	44.7	free	~19	43.4	~17.4 [d]	[14]

[a] WHSV: ml/g_{cat}/h. [b] ROH (total alcohols). [c] Alcohols with six or more carbon numbers. [d] Alcohols with five or more carbon numbers.

Table S2. Textural properties of various catalysts determined by N_2 physical adsorption−desorption

Catalysts	A_{BET} (m^2/g)	V_{total} (cm^3/g)	D (Å)
Co/AC	837	0.19	19.1
0.1Na–Co/AC	808	0.19	19.2
0.3Na–Co/AC	738	0.17	19.1
0.5Na–Co/AC	665	0.12	19.1

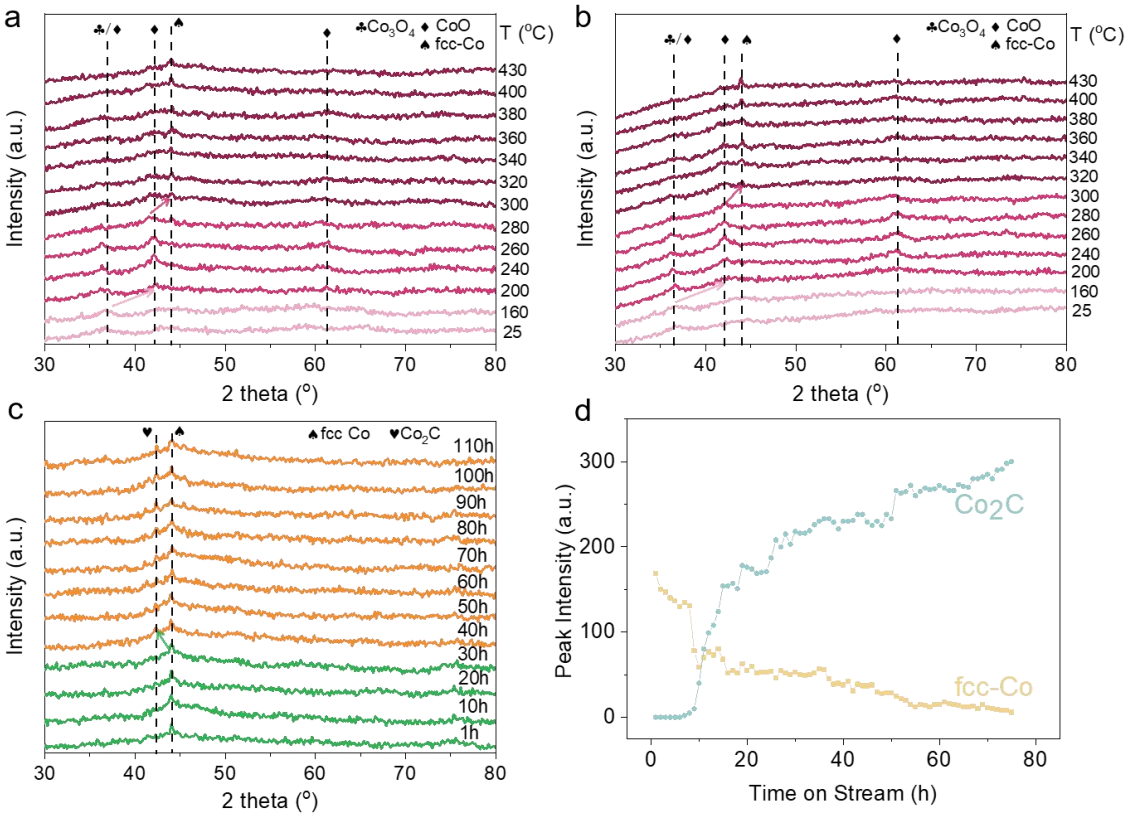

Figure S3. Temperature–programmed reduction of Co/AC (a) and 0.3Na–Co/AC (b) catalysts in a H_2 atmosphere, as well as temperature–programmed reactions of Co/AC catalysts in a syngas (H_2/CO=2.0) atmosphere characterized by *in situ* XRD (c). Reaction–induced formation of Co_2C promoted by Na as a function of time characterized by *in situ* XRD (d).

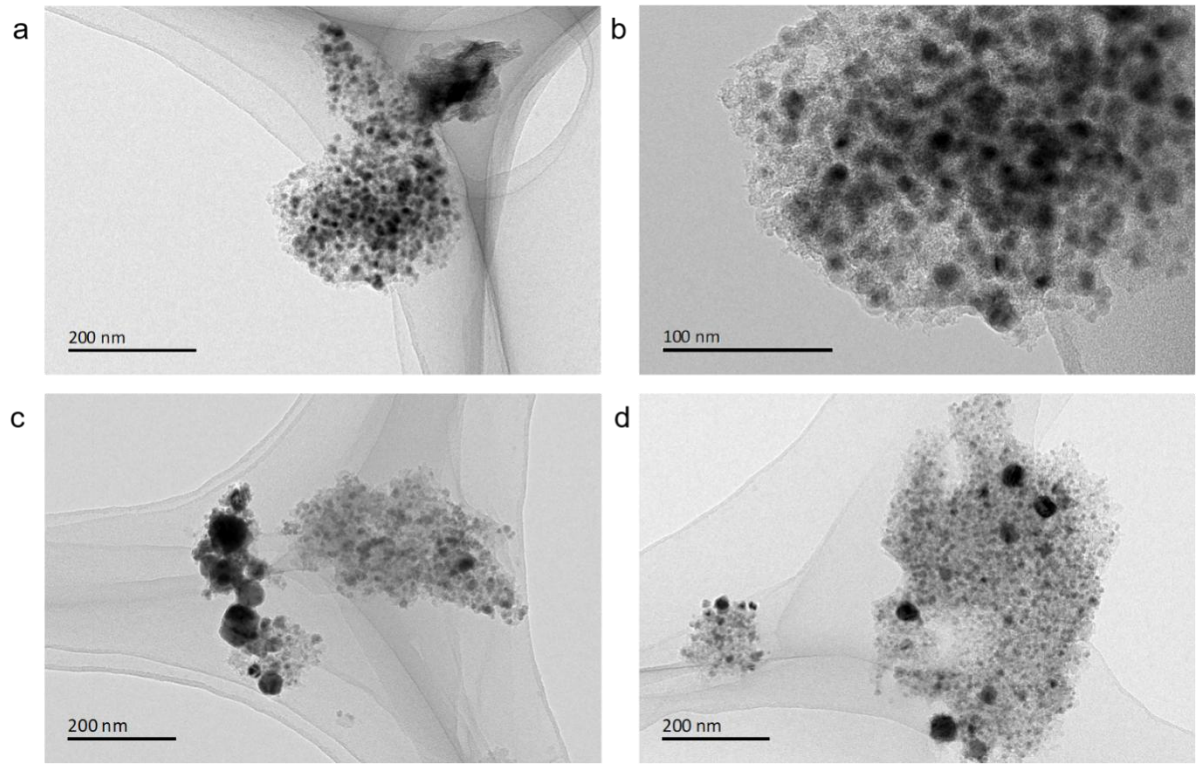

Figure S4. HRTEM images for spent 0.3Na–Co_2C–Co/AC (a and b) and Co/AC (c and d) catalysts.

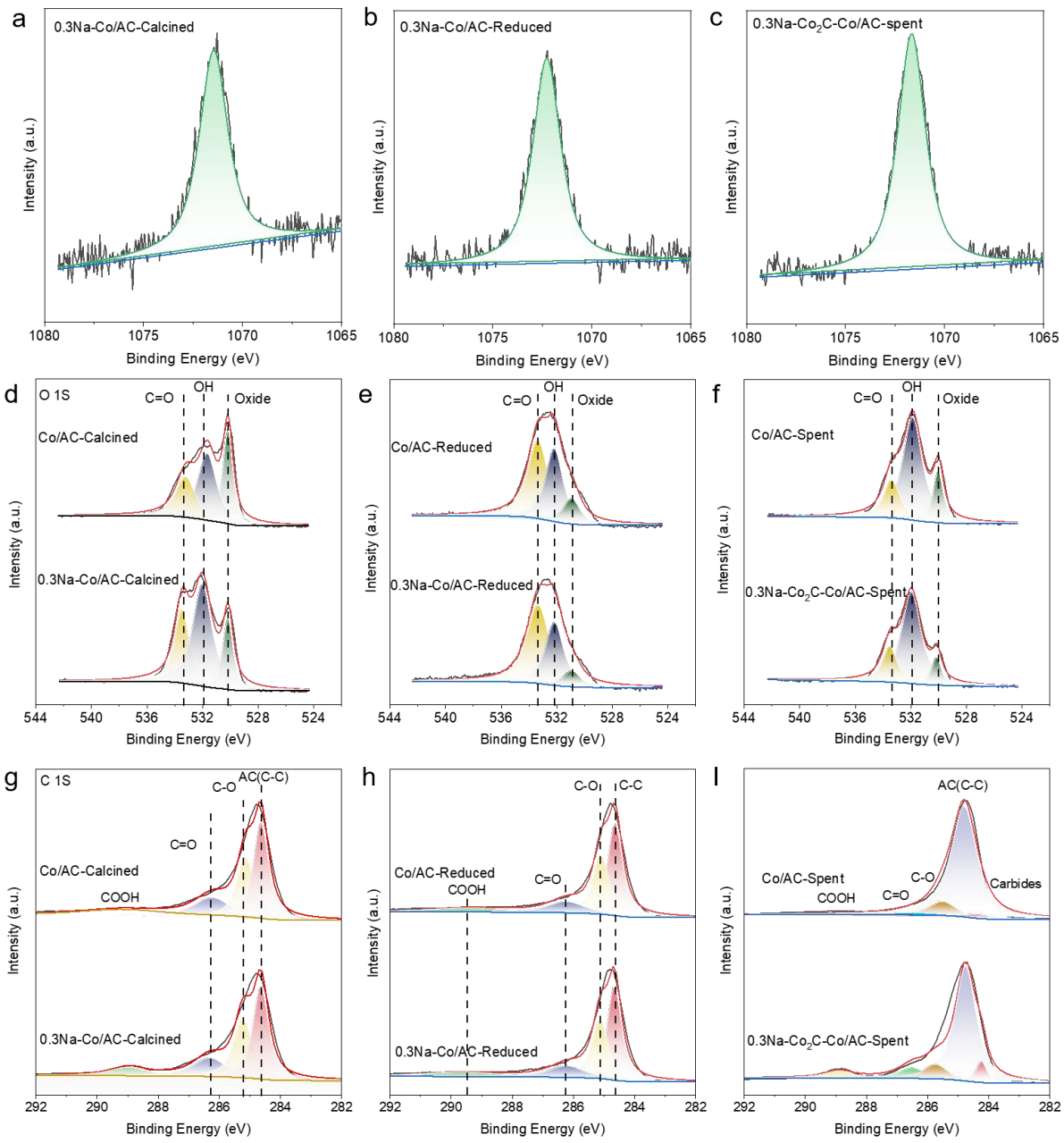

Figure S5. XPS spectra of Co/AC and 0.3Na–Co/AC catalysts under varying treatment conditions. Na 1s spectra: (a) Calcined at 350 °C in Ar atmosphere; (b) *In situ* reduced at 430 °C under H_2 for 4 h; (c) Spent after 48 h time on stream, at the condition of 220 °C, 3.0 MPa, GHSV = 4000 h^{-1}, H_2/CO = 2.0. O 1s spectra: (d) Calcined at 350 °C in Ar atmosphere; (e) *In situ* reduced at 430°C under H_2 for 4 h; (f) Spent after 48 h time on stream, at the condition of 220 °C, 3.0 MPa, GHSV = 4000 h^{-1}, H_2/CO = 2.0. C 1s spectra: (g) Calcined at 350 °C in Ar atmosphere; (h) *In situ* reduced at 430°C under H_2 for 4 h; (i) Spent after 48 h time on stream, at the condition of 220°C, 3.0 MPa, GHSV = 4000 h^{-1}, H_2/CO = 2.0.

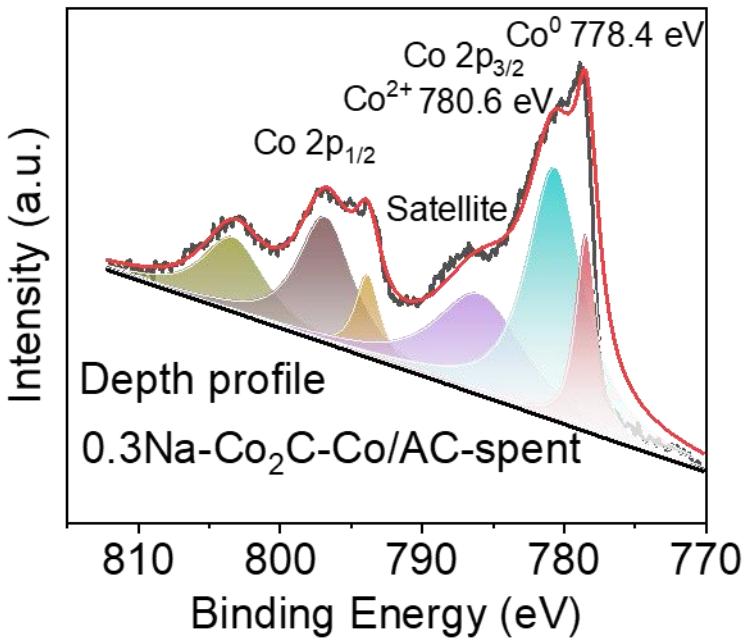

Figure S6. Depth–profiling Co 2p XPS spectra of 0.3Na–Co_2C–Co/AC–spent catalysts.

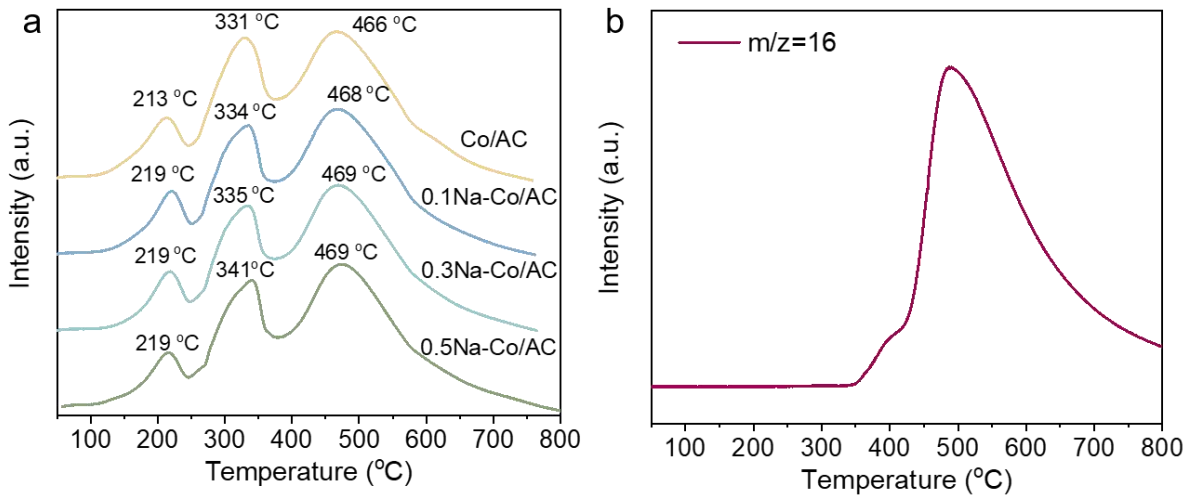

Figure S7. H_2–TPR profiles of the xNa–Co/AC catalysts (a) and H_2–TPR–MS (m/z=16) profiles of the 0.3Na–Co/AC catalysts (b).

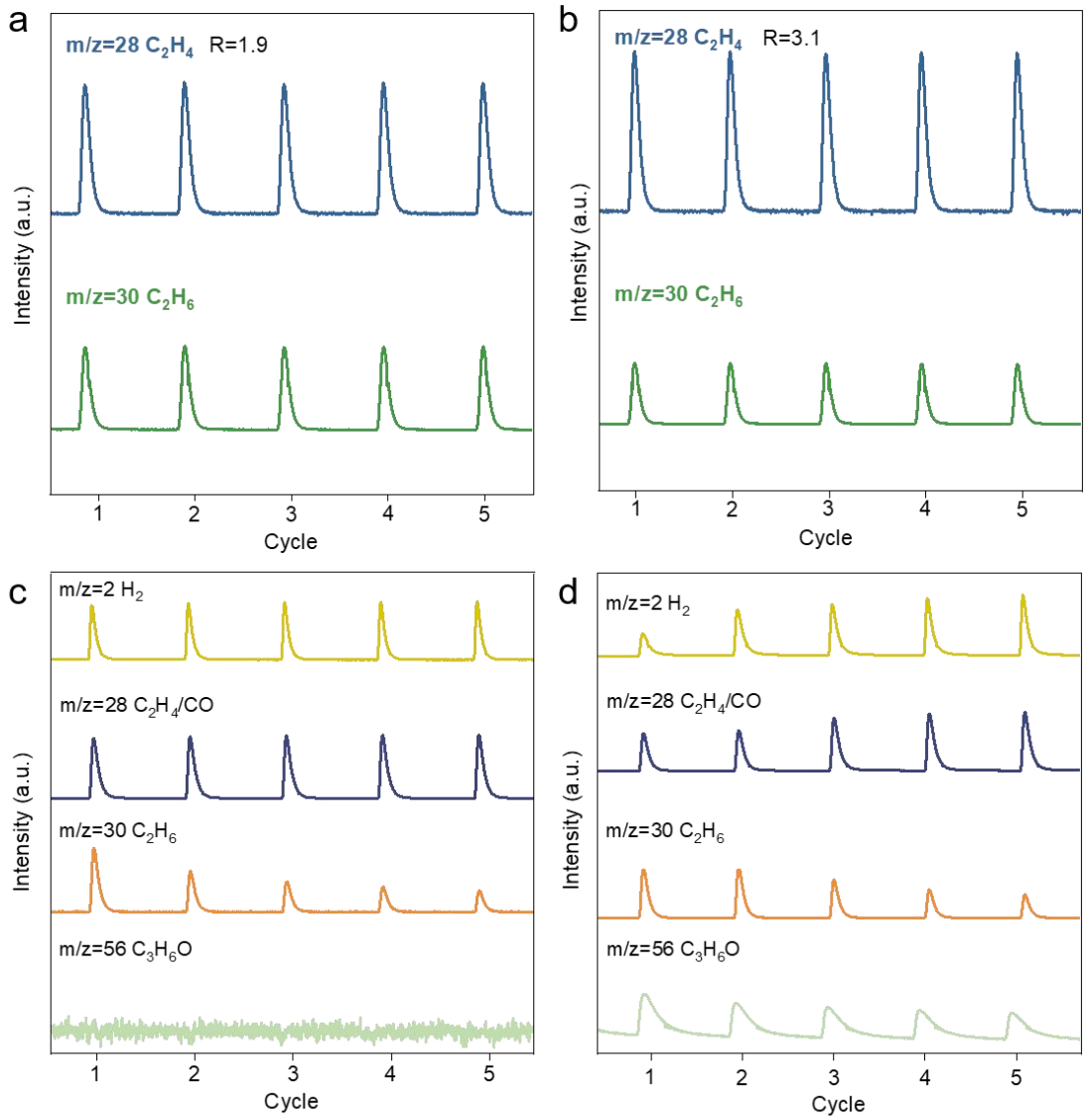

Figure S8. Transient response curves of ethylene hydrogenation pulse experiments at 220 °C over Co/AC (a) and 0.3Na–Co_2C–Co/AC (b). Transient response curves from ethylene, carbon monoxide and hydrogen pulse experiments at 220 °C for Co/AC (c) and 0.3Na–Co_2C–Co/AC (d).

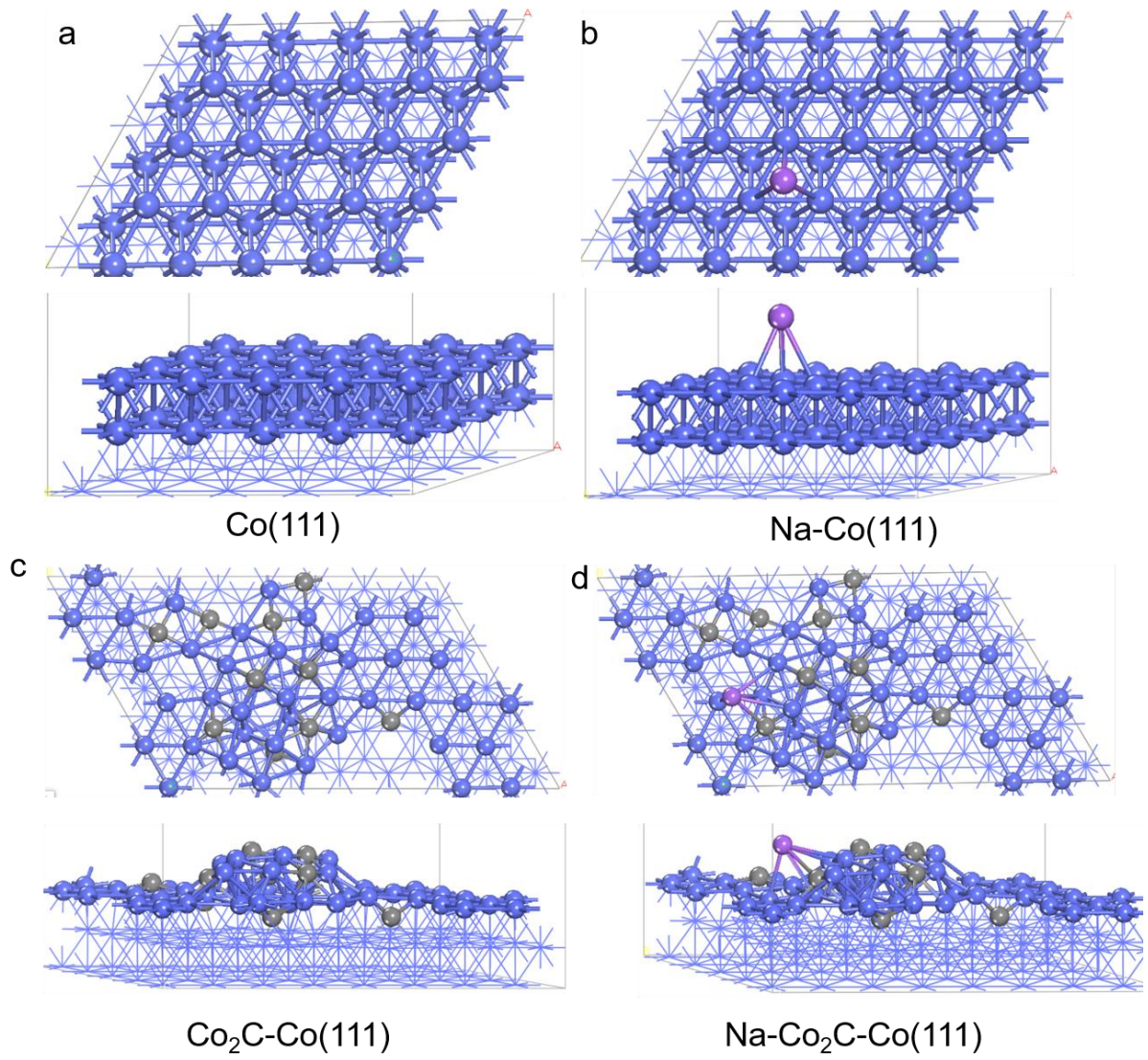

Figure S9. Illustrations of the top and side views of the surface of (a) Co (111), (b) Na–Co (111), (c) Co_2C–Co (111) and Na–Co_2C–Co (111). Color code: Co, blue; C, black; and Na, purple.

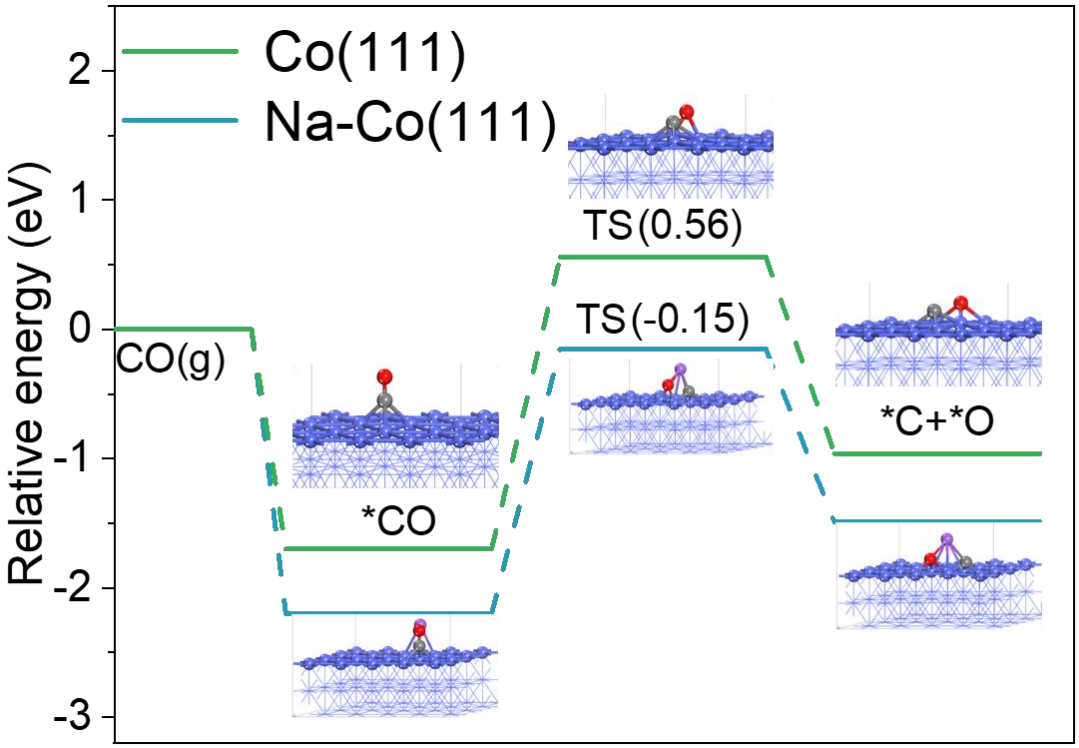

Figure S10. Schematic representation of the mechanisms for CO dissociation pathways on Co (111) and Na–Co (111) surfaces.

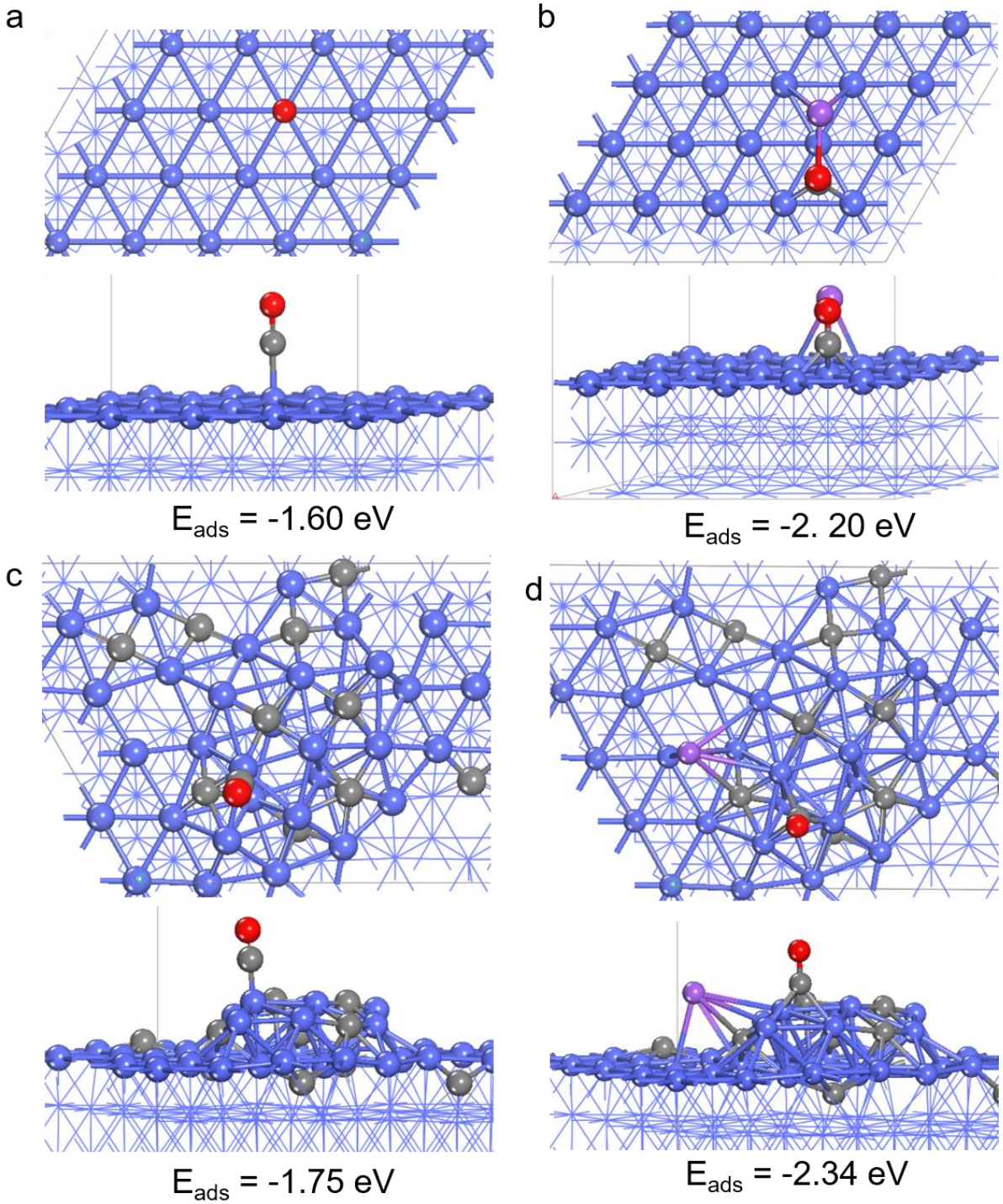

Figure S11. Illustrations of different configurations of CO* adsorptions and their associated adsorption energy values on the (a) Co (111), (b) Na–Co (111), (c) Co_2C–Co (111) and (d) Na–Co_2C–Co (111) surfaces. Color code: Co, blue; C, black; O, red; and Na, purple.

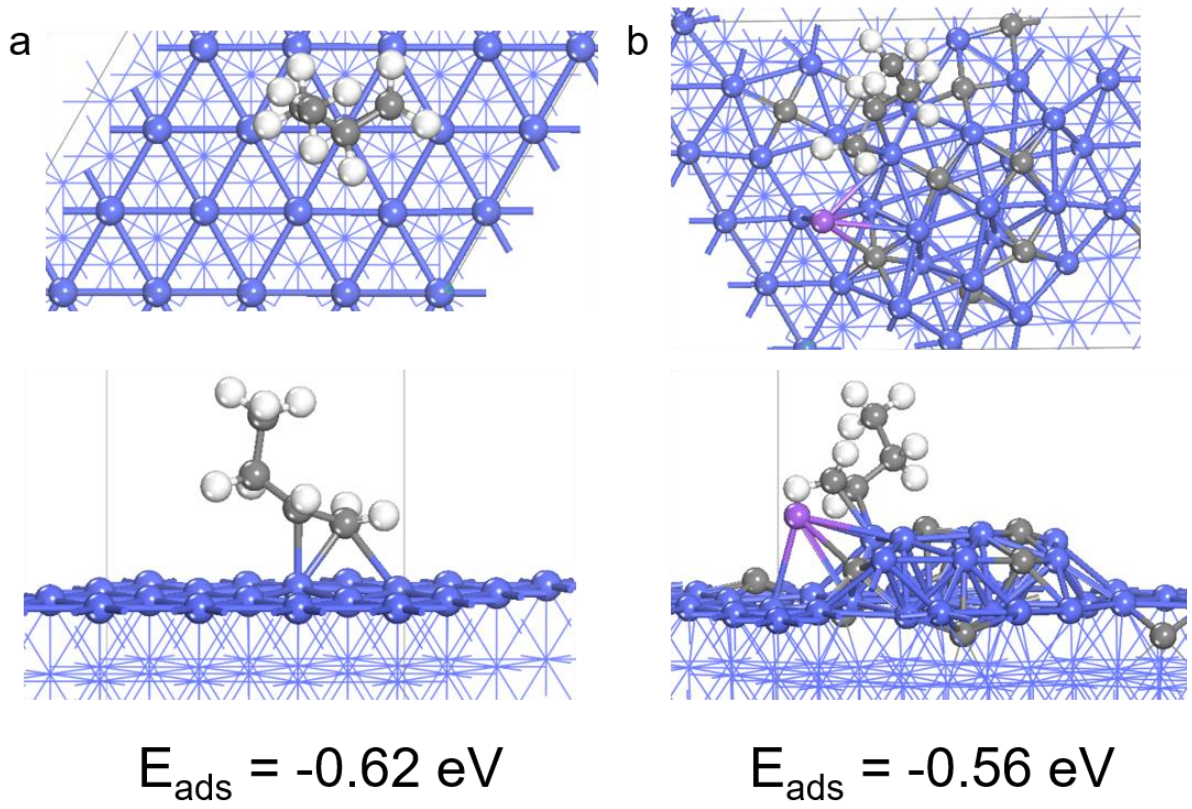

Figure S12. Illustrations of different configurations of *C_4H_8 adsorptions and their associated adsorption energy values on the (a) Co (111) and (b) Na–Co_2C–Co (111) surfaces. Color code: Co, blue; C, black; H, white; and Na, purple.

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