Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table S1 Tested results of cutoff energy, smearing width and *k*-point mesh by using CO at the top site of Co(0001)

Test of cutoff energy by RPBE functional	
Cutoff energy	**Eads**
350	**-1.36**
400	**-1.37**
450	**-1.37**
Test of k points by RPBE functional	
k-point mesh	**Eads**
3×3×1	**-1.32**
5×5×1	**-1.37**
7×7×1	**-1.36**
Test of smearing width by RPBE functional	
0.05	**-1.37**
0.1	**-1.37**
0.2	**-1.35**

Table S2 Comparison of adsorption energies (eV) and geometric parameters of CO on the one-side and two-side model by RPBE functional

Configurations	Two-side model		One-side model	
	E_{ads}	$d_{C\text{-}O}$	E_{ads}	$d_{C\text{-}O}$
top	-1.36	1.173	-1.37	1.173
fcc	-1.29	1.198	-1.27	1.199
hcp	-1.27	1.200	-1.27	1.201
bridge	-1.23	1.192	-1.23	1.194

Table S3 $\triangle H_{cal}$ (eV) of alkane, alkene and alkanol formation reactions calculated by 6-311+G(d,p) and cc-pVTZ basis sets, as well as phonon calculation using VASP code

	$\triangle H_{cal}$ 6-311+G(d,p)	$\triangle H_{cal}$ cc-pVTZ	$\triangle H_{cal}$ vasp	$\triangle H_{exp}$
CH_4	-2.17	-2.12	-2.12	-2.14
C_2H_6	-3.60	-3.49	-3.42	-3.59
C_3H_8	-5.10	-4.96	-5.02	-5.16
C_6H_{14}	-9.58	-9.25	-9.46	-9.90
$C_{10}H_{22}$	-15.56	-15.03	-15.35	-16.19
C_2H_4	-2.21	-2.11	-2.21	-2.18
C_3H_6	-3.87	-3.74	-3.87	-3.87
C_6H_{12}	-8.35	-8.02	-8.25	-8.60
$C_{10}H_{20}$	-14.33	-13.78	-14.09	-14.90
CH_3OH	-0.99	-0.94	-0.97	-0.94
C_2H_5OH	-2.65	-2.59	-2.60	-2.65
C_3H_7OH	-4.14	-4.05	-4.07	-4.40
$C_6H_{13}OH$	-8.62	-8.34	-8.50	-8.93
$C_{10}H_{21}OH$	-14.60	-14.09	-14.40	-15.11

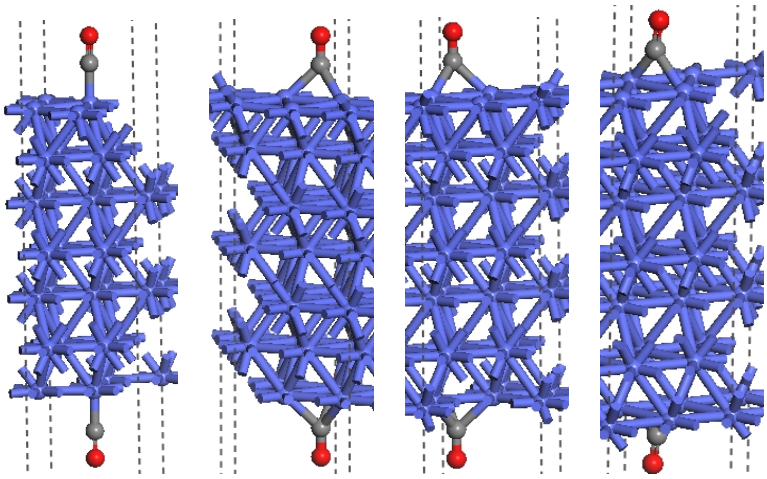

Fig. S1 CO adsorbed at the top, fcc, hcp and bridge sites of Co(0001)

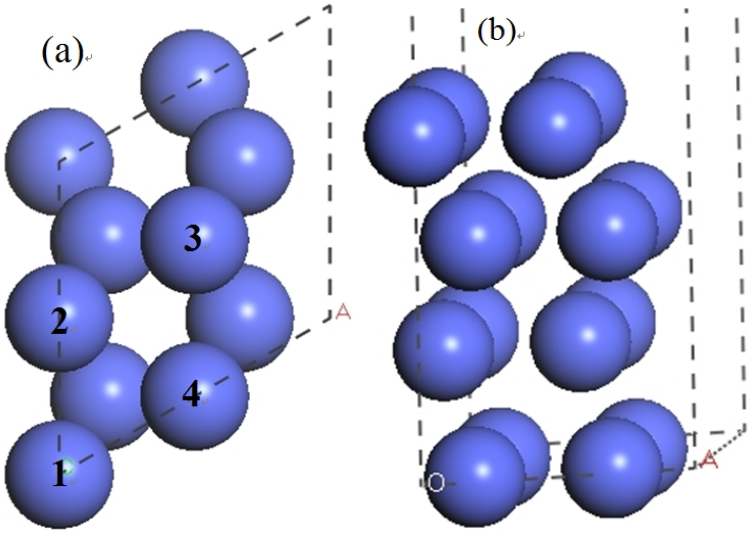

Fig. S2 Co(0001) slab model. (a) Topview, (b) Sideview