Electronic Supplementary Material

Insight into the selective separation of CO_2 from biomass pyrolysis gas over metal-incorporated nitrogen-doped carbon materials: a first-principles study

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Content

S1 The specific applied U-J value of transition metals for DFT calculations

Table S1. The specific applied U-J value/eV of transition metals for DFT calculations

3d transition metal						4d transition metal			
Cr	Mn	Fe	Co	Ni	Cu	Mo	Ru	Rh	Pd
2.79	3.06	3.29	3.42	3.40	3.87	0.48	0.53	0.35	0.60

S2 Adsorption energies of H_2, CO, CO_2, CH_4, and C_2H_6 over M-N_3Gs (M = Cr, Mn, Fe, Co, Ni, Cu, Mo, Ru, Rh, and Pd)

Table S2. Adsorption energies/eV of H_2, CO, CO_2, CH_4, and C_2H_6 over M-N_3Gs (M = Cr, Mn, Fe, Co, Ni, Cu, Mo, Ru, Rh, and Pd)

	3d transition metals						4d transition metals			
	Cr	Mn	Fe	Co	Ni	Cu	Mo	Ru	Rh	Pd
H_2	-0.68	-0.51	-0.78	-1.54	-0.90	-1.37	-0.93	-1.01	-1.25	-1.06
CO	-1.98	-1.82	-2.15	-3.65	-2.15	-3.66	-1.48	-2.64	-2.60	-2.25
CO_2	-1.37	-1.05	-1.09	-1.74	-1.39	-1.51	-1.81	-1.14	-1.43	-0.91
CH_4	-0.38	-0.35	-0.42	-1.70	-0.35	-1.46	-0.09	-0.36	-0.58	-0.48
C_2H_6	-0.68	-0.58	-0.65	-2.05	-0.56	-2.07	-0.13	-0.18	-0.94	-0.60

S3 Adsorption configurations over transition metal-incorporated M-N_3Gs

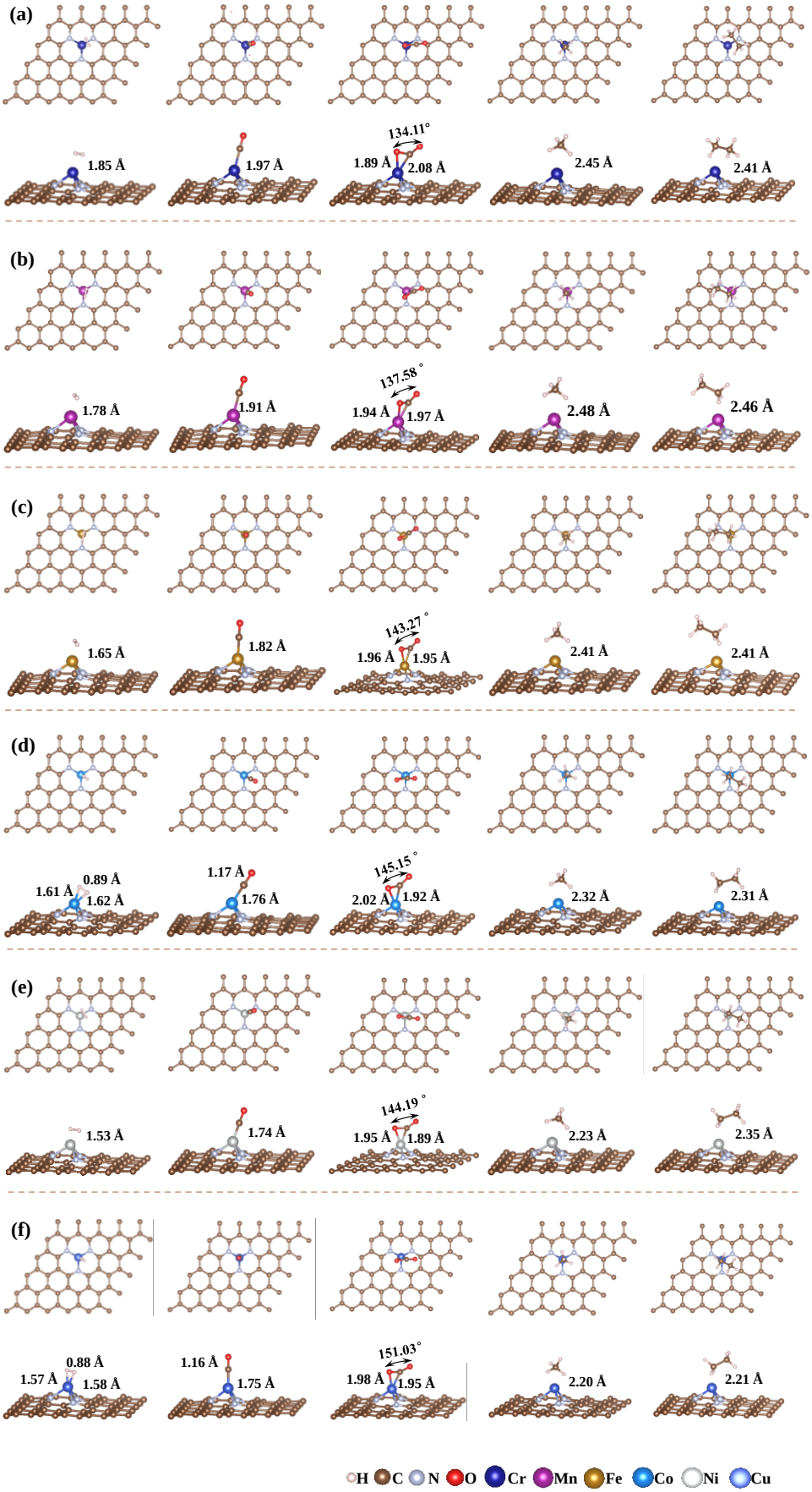

Fig. S1. Adsorption configurations of H_2, CO, CO_2, CH_4, and C_2H_6 over Cr-N_3G (a), Mn-N_3G (b), Fe-N_3G (c), Co-N_3G (d), Ni-N_3G (e), and Cu-N_3G (f)

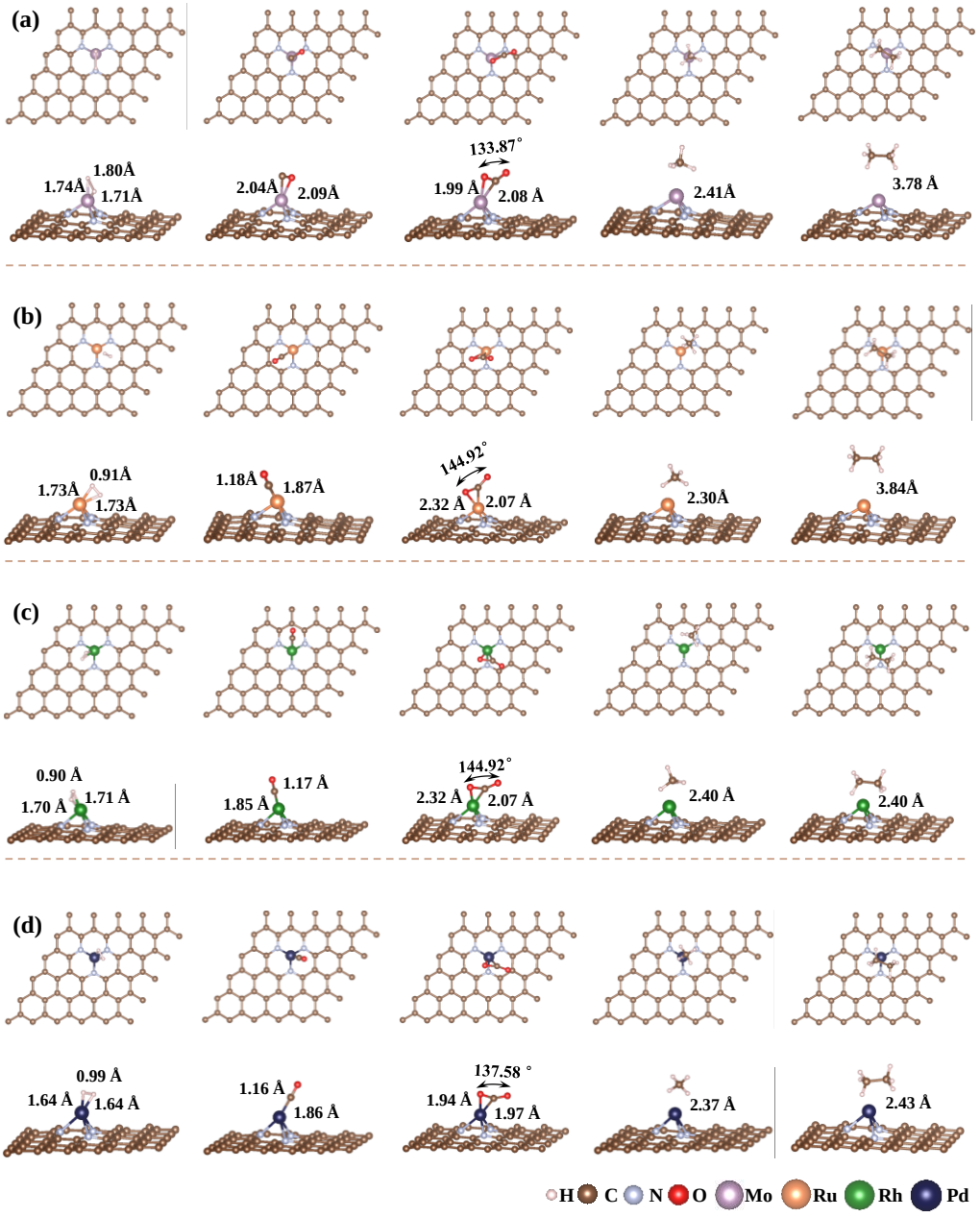

Fig. S2. Adsorption configurations of H_2, CO, CO_2, CH_4, and C_2H_6 over Mo-N_3G (a), Ru-N_3G (b), Rh-N_3G (c), Pd-N_3G (d)

Table S3. The adsorption energies and structural parameters of CO_2 over M-N_3Gs incorporated with transition metals

	ΔE_{ads}/eV	M–O distance/Å	M–C distance/Å	Angel/°
Cr-N_3G	-1.368	1.89	2.08	134.11
Mn-N_3G	-1.050	1.94	1.97	137.58
Fe-N_3G	-1.089	1.96	1.95	143.27
Co-N_3G	-1.737	2.02	1.92	145.15
Ni-N_3G	-1.394	1.95	1.89	144.19
Cu-N_3G	-1.505	1.98	1.95	151.03
Mo-N_3G	-1.809	1.99	2.08	133.87
Ru-N_3G	-1.136	2.32	2.07	144.92
Rh-N_3G	-1.430	2.32	2.07	144.92
Pd-N_3G	-0.909	1.94	1.97	137.58

S4 Scatter plot and linear fitting plot of d-band center and adsorption energies

Table S4. The d-band center/eV of each M-N_3G

	d band center
Cr-N_3G	-0.1786
Mn-N_3G	-1.3658
Fe-N_3G	-2.7651
Co-N_3G	-2.3116
Ni-N_3G	-3.7017
Cu-N_3G	-2.6923
Mo-N_3G	-0.9401
Ru-N_3G	-2.3740
Rh-N_3G	-2.3627
Pd-N_3G	-1.8240

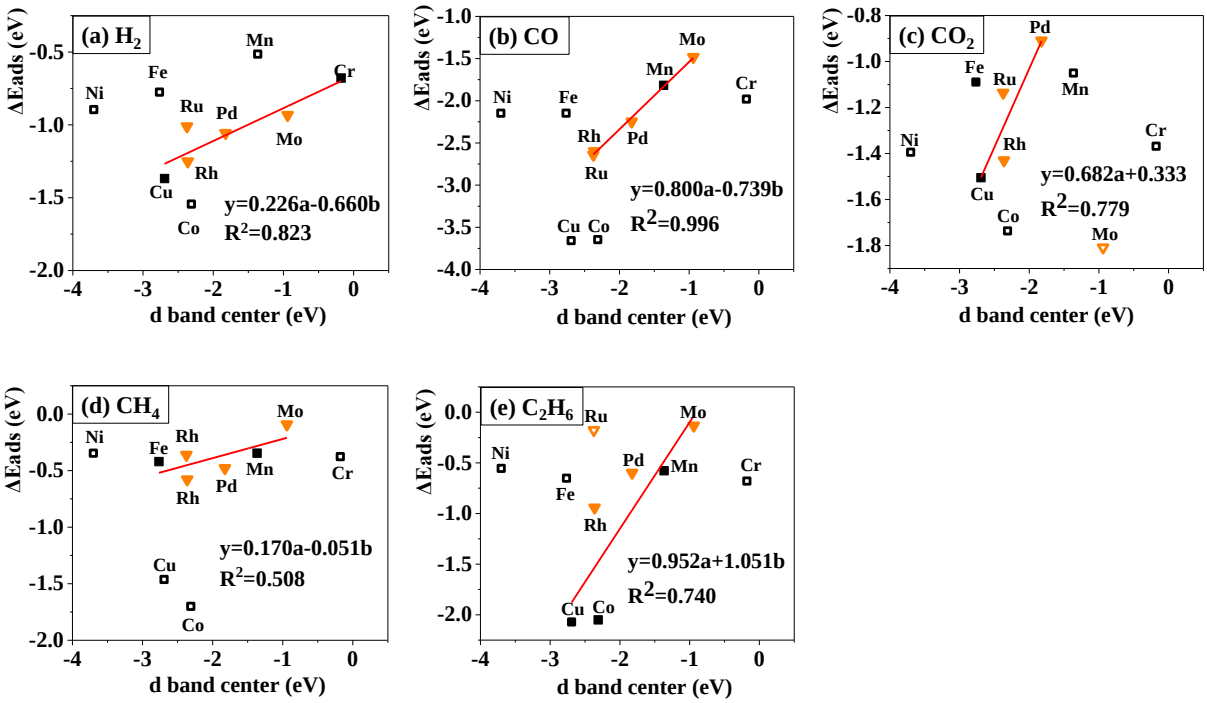

Fig. S3. Scatter and linear fitting plot of d-band center and adsorption energy for H_2 (a), CO (b), CO_2 (c), CH_4 (d), and C_2H_6 (e). The fitting is based on the solid points, the black points are 3d transition metals and the orange points are 4d transition metals.

S5 Adsorption energies of H_2, CO, CO_2, CH_4, and C_2H_6 over M-N_3Gs (M = Na, K, Rb, Mg, Ca, and Sr)

Table S5. Adsorption energies/eV of H_2, CO, CO_2, CH_4, and C_2H_6 over M-N_3Gs (M = Na, K, Rb, Mg, Ca, and Sr)

	Alkali metal			Alkaline earth metals		
	Na	K	Rb	Mg	Ca	Sr
H_2	-0.08	-0.04	-0.03	-0.11	-0.11	-0.09
CO	-0.24	-0.10	-0.09	-1.06	-0.36	-0.38
CO_2	-0.27	-0.17	-0.03	-0.84	-0.46	-0.38
CH_4	-0.15	-0.08	-0.07	-0.34	-0.22	-0.17
C_2H_6	-0.32	-0.24	-0.23	-0.24	-0.43	-0.32

S6 Adsorption configurations over alkali and alkaline earth metal-incorporated M-N_3Gs

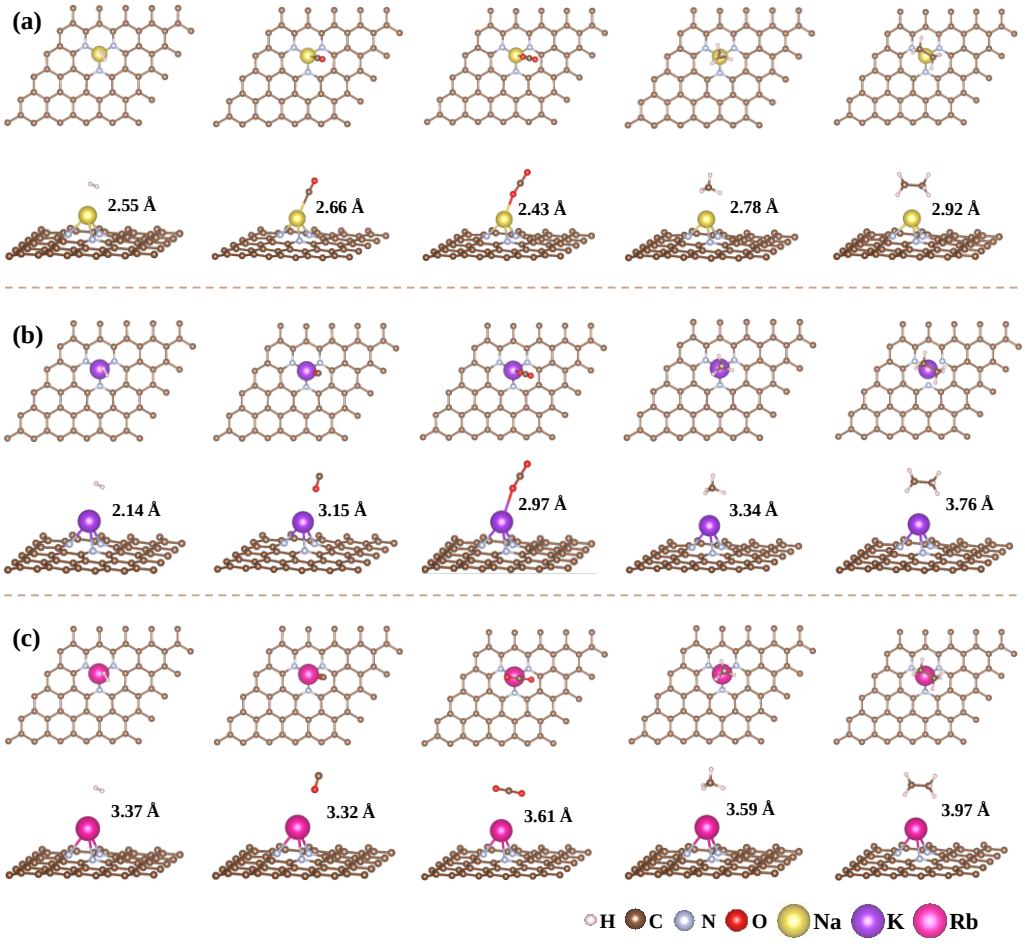

Fig. S4. Adsorption configurations of H_2, CO, CO_2, CH_4, and C_2H_6 over Na-N_3G (a), K-N_3G (b), Rb-N_3G (c)

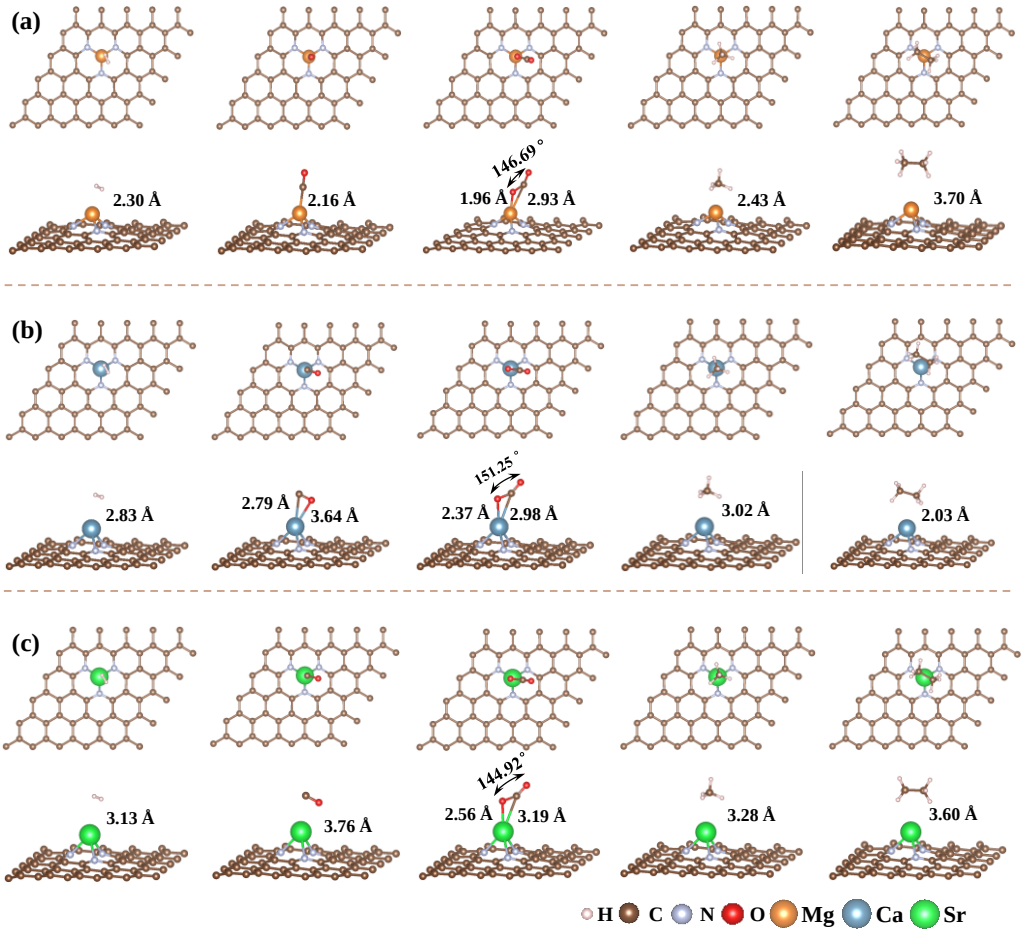

Fig. S5. Adsorption configurations of H_2, CO, CO_2, CH_4, and C_2H_6 over Mg-N_3G (a), Ca-N_3G (b), Sr-N_3G (c)

S7 COHP diagrams of H_2, CO, CO_2, CH_4, and C_2H_6 adsorption over Ca-N_3G

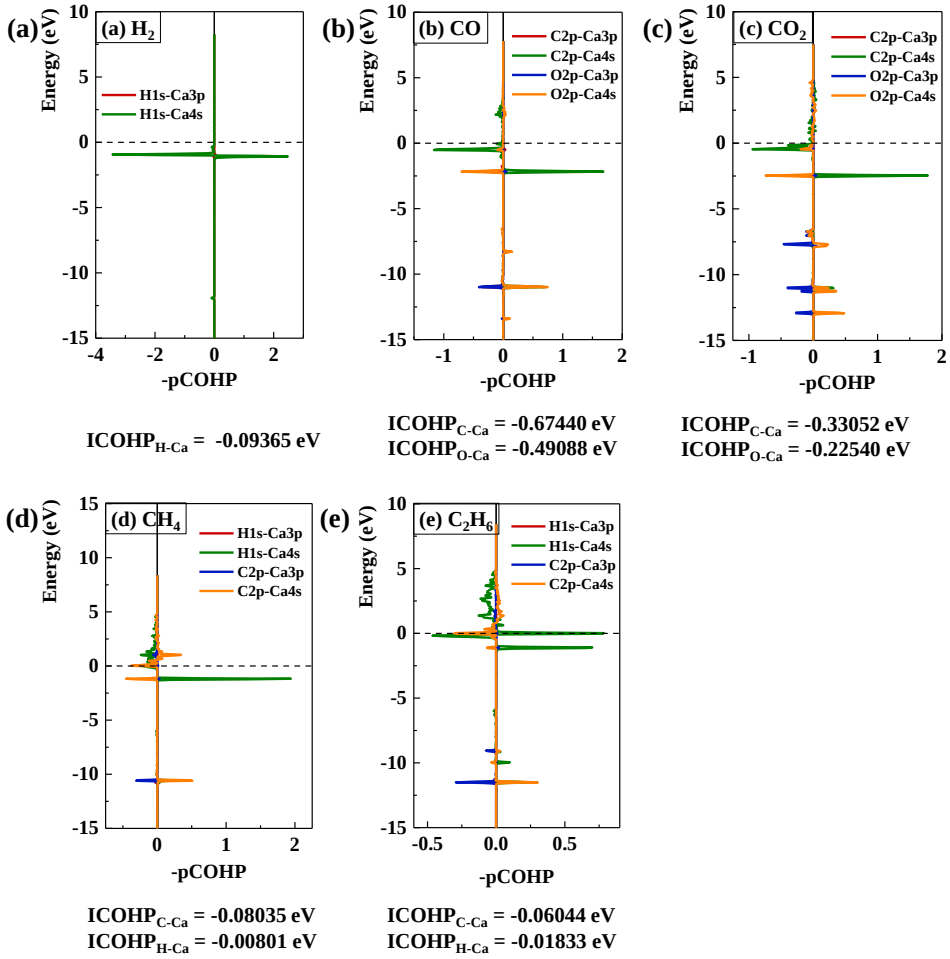

Fig. S6. COHP diagrams of H_2 (a), CO (b), CO_2 (c), CH_4 (d), and C_2H_6 (e) adsorption over Ca-N_3G

S8 Geometric configurations and electronic structures of CO_2 and CO co-adsorbed over Mg-N_3G and Ca-N_3G

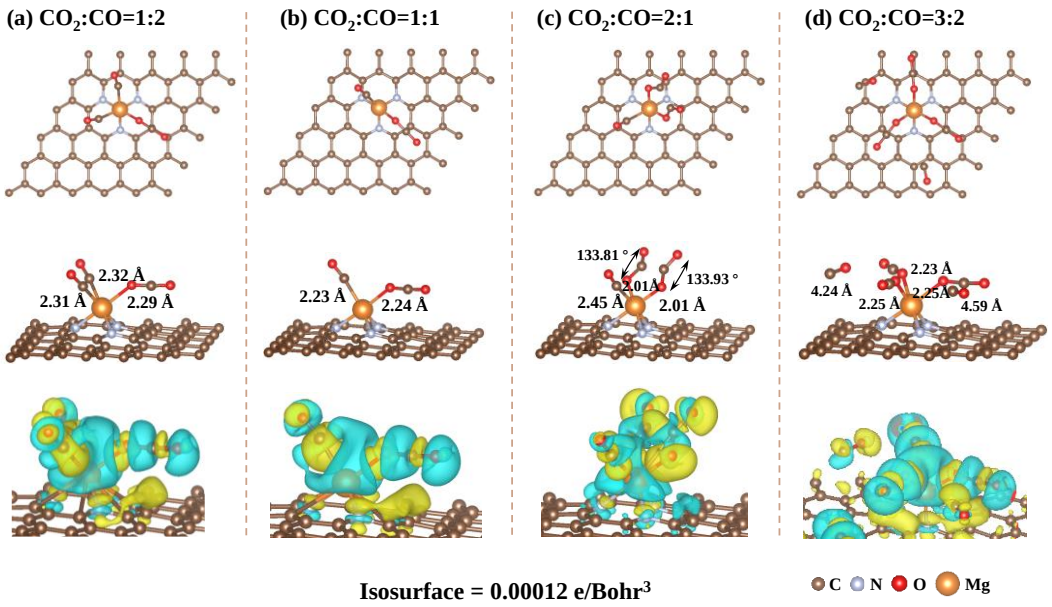

Fig. S7. The geometric configurations and CDD diagrams of CO_2 and CO molecules co-adsorbed over Mg-N_3G

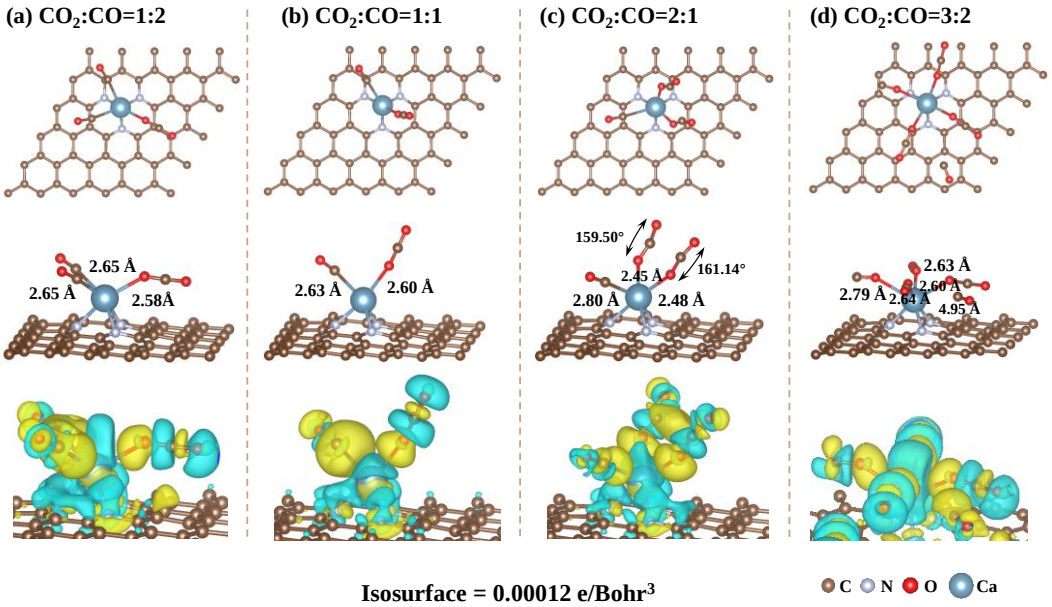

Fig. S8. The geometric configurations and CDD diagrams of CO_2 and CO molecules co-adsorbed over Ca-N_3G

S9 ICOHP of CO_2 and CO co-adsorbed over Mg-N_3G and Ca-N_3G

Table S6. ICOHP/eV of CO_2 and CO co-adsorbed over Mg-N_3G and Ca-N_3G with the mixing ratio of 1:2, 1:1, 2:1, and 3:2

CO_2:CO=1:2		CO_2:CO=1:1		CO_2:CO=2:1		CO_2:CO=3:2	
Mg-N_3G							
CO_2	$ICOHP_{O–Mg}$= -0.68197 $ICOHP_{C–Mg}$= -0.00057	CO_2	$ICOHP_{O–Mg}$= -0.68715 $ICOHP_{C–Mg}$= -0.00094	CO_2 (2.01Å)	$ICOHP_{O–Mg}$= -0.98371 $ICOHP_{C–Mg}$= -0.00127	CO_2 (2.23Å) CO_2 (2.25Å)	$ICOHP_{C–Mg}$= -0.74065 $ICOHP_{C–Mg}$= -0.00150
CO (2.31Å) CO (2.32Å)	$ICOHP_{C–Mg}$= -0.00173 $ICOHP_{C–Mg}$= 0.00003	CO	$ICOHP_{C–Mg}$= -0.00174 $ICOHP_{O–Mg}$= -0.00087	CO_2 (2.01Å) CO	$ICOHP_{O–Mg}$= -0.00141 $ICOHP_{C–Mg}$= -0.00023 $ICOHP_{C–Mg}$= -0.00041	CO_2 (2.25Å) CO (4.24Å) CO (4.59Å)	$ICOHP_{C–Mg}$= 0.00017 $ICOHP_{C–Mg}$= -0.00004 $ICOHP_{C–Mg}$= -0.00105
Ca-N_3G							
CO_2	$ICOHP_{O–Ca}$= -0.55266 $ICOHP_{C–Ca}$= -0.35535	CO_2	$ICOHP_{O–Ca}$= 0.00357 $ICOHP_{C–Ca}$= 0.00326	CO_2 (2.45Å)	$ICOHP_{O–Ca}$= -0.00439 $ICOHP_{C–Ca}$= 0.00110	CO_2 (2.60Å) CO_2 (2.63Å)	$ICOHP_{C–Ca}$= -0.17141 $ICOHP_{C–Ca}$= -0.26204
CO (2.65Å)	$ICOHP_{C–Ca}$= 0.00152 $ICOHP_{C–Ca}$= -0.00002	CO	$ICOHP_{C–Ca}$= -0.00176 $ICOHP_{O–Ca}$= -0.00011	CO_2 (2.48Å) CO	$ICOHP_{O–Ca}$= -0.00129 $ICOHP_{C–Ca}$= -0.00099 $ICOHP_{C–Ca}$= -0.00073	CO_2 (2.64Å) CO (2.79Å) CO (4.95Å)	$ICOHP_{C–Ca}$= -0.00118 $ICOHP_{C–Ca}$= 0.00056 $ICOHP_{C–Ca}$= -0.00002

* The value in the bracket is the distance between molecules and metal atoms to distinguish the adsorbates.