A DFT study for CO_2 hydrogenation on W (111) and Ni-doped W (111) surface

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(111) surface.

Table S1 Adsorption energies (E_{ad}) of reactants on the W (111) surface with different supercells.

Species	(2 × 2) supercell E_{ad} / eV	(3 × 3) supercell E_{ad} / eV	(4 × 4) supercell E_{ad} / eV
CO_2	−2.11	-2.06	-2.21
H	−3.09	-3.09	-3.06

Table S2 The Mulliken charge, binding energy and spin of Ni on Ni_xW (111) surfaces (x=1, 3)

Ni of different configuration	Mulliken charge (|e|)	Binding Energy (eV)	Spin
Ni_1W (111) - Ni	-0.192	-6.48	+0.165
Ni_3W (111) – Ni1	-0.175	-6.11	-0.016
Ni_3W (111) – Ni2	-0.182	-6.11	+0.005
Ni_3W (111) – Ni3	-0.177	-6.11	-0.016
Ni adsorbed at W (111) surface	-0.102	-5.19	-0.041

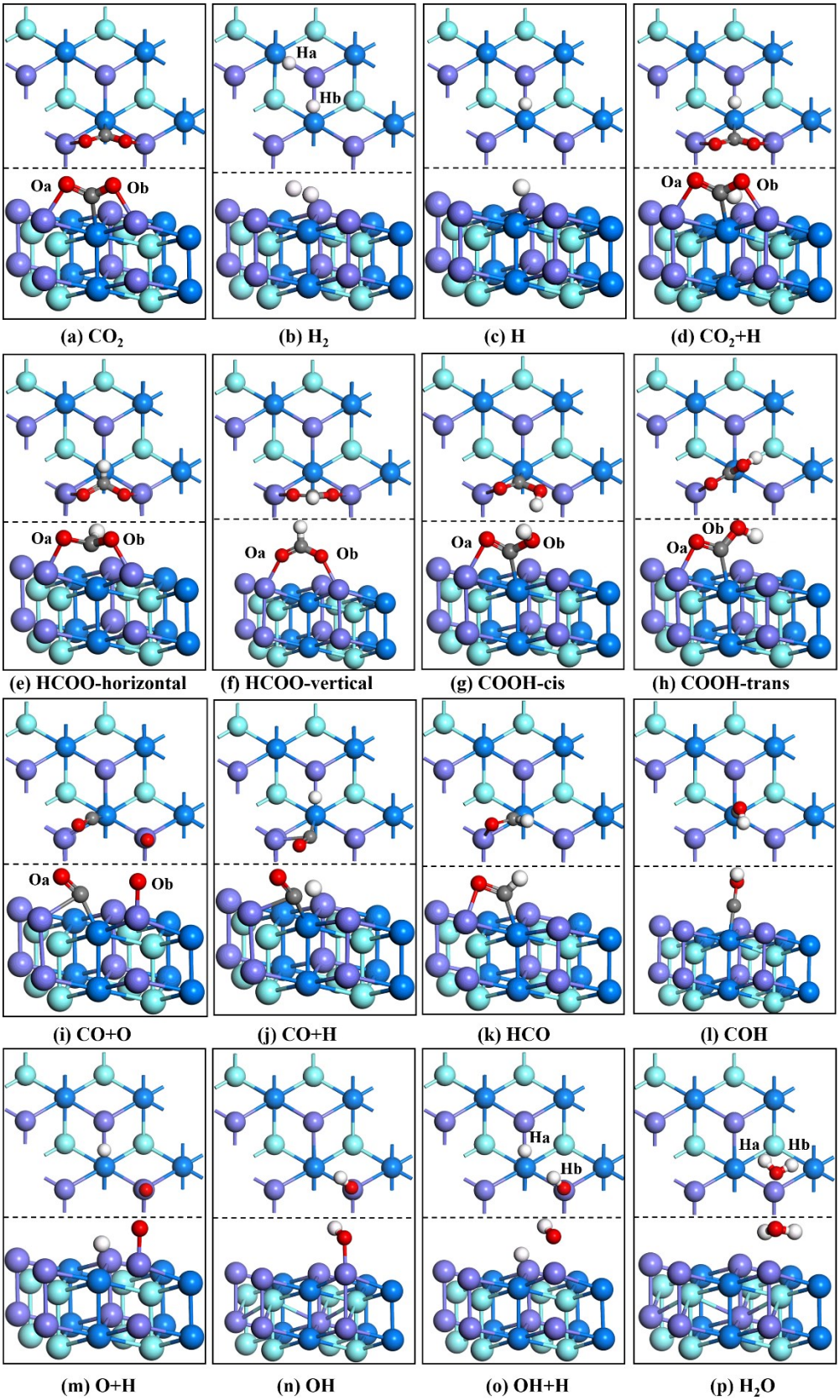


Fig. S1 The adsorption configurations of reactants and intermediates on W (111) surface; purple, the first and fourth layer of W atoms; blue, the second and fifth layer of W atoms; cyan, the third and sixth layer of W atoms; red, O atoms; gray, C atoms; white, H atoms.

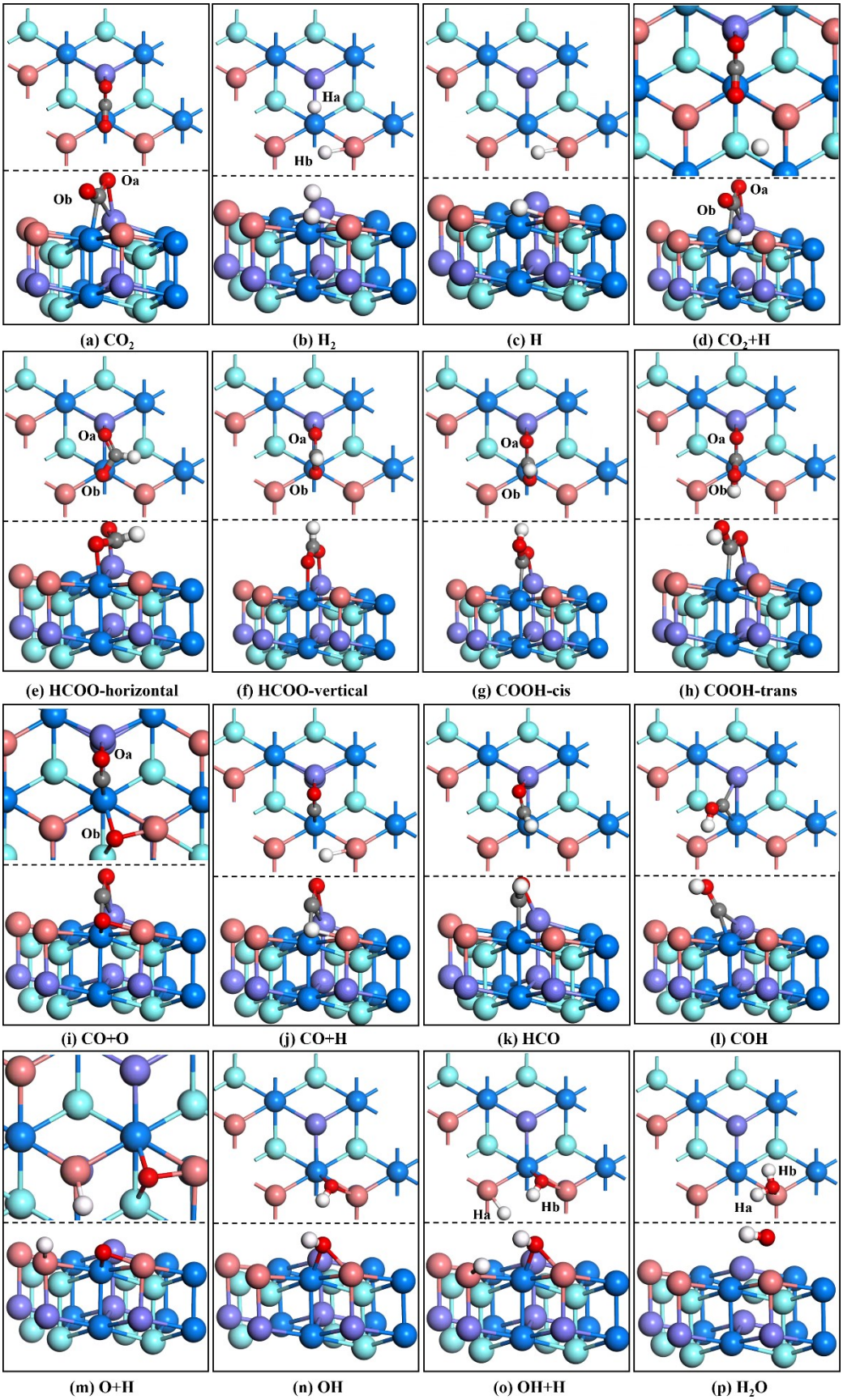
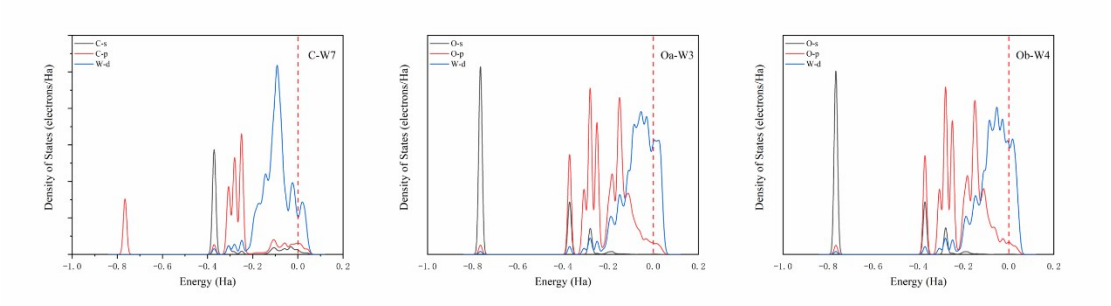
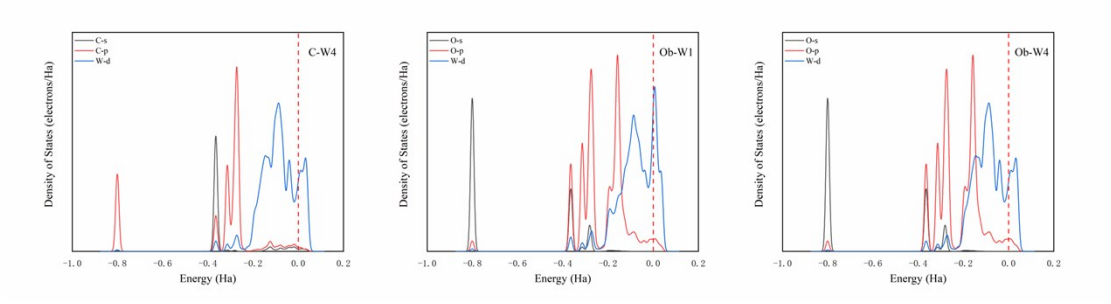


Fig. S2 The adsorption configurations of reactants and intermediates on Ni_3W (111) surface



(a) (b) (c)

Fig. S3 PDOS diagrams of W and (a) C, (b) Oa, (c) Ob atoms of CO_2 adsorbed on the W (111) surfaces.



(a) (b) (c)

Fig. S4 PDOS diagrams of W and (a) C, (b-c) Ob atoms of CO_2 adsorbed on the Ni_3W (111) surfaces.

Table S3 Geometric parameters of reactants and intermediates on the Ni_xW (111) surfaces (x=0, 1, 3).

Species	W (111) surface	Ni_1W (111) surface	Ni_3W (111) surface
CO_2	d(W3-Oa) = 2.09 Å d(W4-Ob) = 2.09 Å d(W7-C) = 2.17 Å d(C-Oa) = 1.32 Å d(C-Ob) = 1.32 Å	d(W2-Oa) = 2.09 Å d(W3-Ob) = 2.09 Å d(W6-C) = 2.17 Å d(C-Oa)= 1.32 Å d(C-Ob)= 1.32 Å	d(W1-C) = 2.23 Å d(W4-C) = 2.23 Å d(W1-Oa) = 2.14 Å d(C-Oa) = 1.25 Å d(C-Ob) = 1.29 Å
H_2	d(Ha-W5) = 1.93 Å d(Ha-W1) = 1.92 Å d(Hb-W1) = 1.93 Å d(Hb-W7) = 1.92	d(Ha-Ni) = 1.72 Å d(Hb-W3) = 1.90 Å d(Hb-W6) = 1.92 Å	d(Ha-W1) = 1.90 Å d(Ha-W4) = 1.92 Å d(Hb-Ni3) = 1.77 Å
H	d(H and W1) = 1.93 Å, d(H and W7) = 1.92 Å	d(Ni-H) = 1.72 Å d(H and W6) = 1.97 Å d(H and W8) = 2.10 Å	d(Ni3-H) = 1.75 Å d(H and W4) = 1.96 Å.
CO_2+H	d(H and C) = 2.19 Å, d(W3-Oa) = 2.11 Å d(W4-Ob) = 2.11 Å d(W7-C) = 2.21 Å d(C-Oa) = 1.30 Å d(C-Ob) = 1.30 Å	d(H and C) = 2.73 Å d(W2-Oa) = 2.09 Å d(W3-Ob) = 2.10 Å d(W6-C) = 2.16 Å d(C-Oa)= 1.32 Å d(C-Ob)= 1.31 Å d(Ni-H) = 1.72 Å	d(H and C) = 3.94 Å d(W1-Oa) = 2.13 Å d(W4-C) = 2.22 Å d(W1-C) = 2.23 Å d(C-Oa)= 1.29 Å d(C-Ob)= 1.25 Å d(Ni and H) = 1.88 Å

HCOO-horizontal	d(W3-Oa) = 1.97 Å d(W4-Ob) = 1.98 Å d(C-Oa) = 1.40 Å d(C-Ob) = 1.40 Å d(C-H) = 1.11 Å	d(W2-Oa) = 1.98 Å d(W3-Ob) = 1.98 Å d(C-Oa) = 1.40 Å d(C-Ob) = 1.40 Å d(C-H) = 1.12 Å	d(W1-Oa) = 1.97 Å d(W4-Ob) = 2.06 Å d(C-Oa) = 1.37 Å d(C-Ob) = 1.35 Å d(C-H) = 1.10 Å
HCOO-vertical	d(W3-Oa) = 2.13 Å d(W4-Ob) = 2.13 Å d(C-Oa) = 1.28 Å d(C-Ob) = 1.28 Å d(C-H) = 1.10 Å	d(W2-Oa) = 2.14 Å d(W3-Ob) = 2.14 Å d(C-Oa) = 1.28 Å d(C-Ob) = 1.28 Å d(C-H) = 1.10 Å	d(W1-Oa) = 2.08 Å d(W4-Ob) = 2.20 Å d(C-Oa) = 1.29 Å d(C-Ob) = 1.26 Å d(C-H) = 1.10 Å
COOH-cis	d(W3-Oa) = 2.13 Å d(C-W7) = 2.12 Å d(C-Oa) = 1.30 Å d(C-Ob) = 1.46 Å d(Ob-H) = 0.98 Å d(Ob and W4) = 2.33 Å	d(W2-Oa) = 2.14 Å d(C-W6) = 2.13 Å d(C-Oa) = 1.29 Å d(C-Ob) = 1.44 Å d(Ob-H) = 0.99 Å	d(W1-Oa) = 2.08 Å d(C-W4) = 2.19 Å d(C-Oa) = 1.31 Å d(C-Ob) = 1.34 Å d(Ob-H) = 0.98 Å
COOH-trans	d(W3-Oa) = 2.09 Å d(C-W7) = 2.18 Å d(C-Oa) = 1.30 Å d(C-Ob) = 1.36 Å d(Ob-H) = 0.98 Å d(Ob and W4) = 3.88 Å	d(W2-Oa) = 2.08 Å d(C-W6) = 2.20 Å d(C-Oa) = 1.30 Å d(C-Ob) = 1.35 Å d(Ob-H) = 0.99 Å	d(W1-Oa) = 2.07 Å d(C-W4) = 2.19 Å d(C-Oa) = 1.30 Å d(C-Ob) = 1.34 Å d(Ob-H) = 0.98 Å
CO+O	d(C-Oa) = 1.24 Å d(C-W3) = 2.27 Å d(C-W7) = 2.00 Å d(Ob-W4) = 1.74 Å d(Ob and C) = 3.51 Å	d(W2-Oa) = 2.22 Å d(C-W6) = 2.00 Å d(C-Oa) = 1.24 Å d(Ob-W3) = 1.74 Å d(C and Ob) = 3.38 Å	d(W1-C) = 2.18 Å d(W4-C) = 1.99 Å d(W1-Oa) = 2.18 Å d(C-Oa) = 1.25 Å d(C and Ob) = 2.91 Å, d(Ob-W4) = 2.02 Å d(Ob-Ni3) = 1.96 Å
CO+H	d(C-O) = 1.24 Å d(C-W3) = 2.24 Å d(C-W7) = 2.03 Å d(H and W1) = 1.88 Å d(H and W7) = 1.89 Å d(H and C) = 2.32 Å	d(W2-O) = 2.26 Å d(C-W6) = 2.01 Å d(C-O) = 1.24 Å d(H-W6) = 1.94 Å d(H-W8) = 2.12 Å d(C and H) = 2.49 Å	d(W1-C) = 2.21 Å d(W4-C) = 1.99 Å d(W1-O) = 2.20 Å d(C-O) = 1.24 Å d(Ni3-H) = 1.76 Å d(C and H) = 2.78 Å
HCO	d(C-O) = 1.35 Å d(C-H) = 1.11 Å d(C-W7) = 2.13 Å d(O-W3) = 2.01 Å	d(W2-O) = 2.02 Å d(C-W6) = 1.34 Å d(C-H) = 1.11 Å d(C-W6) = 2.11 Å	d(W1-O) = 2.03 Å d(W4-C) = 2.11 Å d(C-O) = 1.34 Å d(C-H) = 1.11 Å
COH	d(C-O) = 1.33 Å d(O-H) = 0.98 Å d(C-W7) = 1.92 Å	d(W2-C) = 2.03 Å d(C-W6) = 2.15 Å d(C-O) = 1.35 Å d(O-H) = 0.98 Å	d(W1-C) = 2.06 Å d(W4-C) = 2.10 Å d(C-O) = 1.35 Å d(O-H) = 0.98 Å
O+H	d(H-W1) = 1.92 Å	d(H-Ni) = 1.71 Å	d(H-Ni2) = 1.68 Å

	d(H-W7) = 1.90 Å d(O-W4) = 1.74 Å d(H and O) = 3.46 Å	d(O-W3) = 1.74 Å d(H and O) = 3.50 Å	d(O-Ni3) = 1.95 Å d(O-W4) = 1.97 Å d(H and O) = 2.80 Å
OH	d(O-W4) = 1.92 Å d(O-H) = 0.97 Å	d(O-W3) = 1.91 Å d(O-H) = 0.97 Å	d(O-Ni3) = 2.03 Å d(O-W4) = 2.08 Å d(O-H) = 0.97 Å
OH+H	d(Ha-W1) = 1.93 Å d(Ha-W7) = 1.92 Å d(O-W4) = 1.91 Å d(O-Hb) = 0.97 Å d(Ha and O) = 3.29 Å	d(Ha-Ni) = 1.70 Å d(O-W3) = 1.91 Å d(O-Hb) = 0.97 Å d(Ha and O) = 3.41 Å	d(Ha-Ni2) = 1.72 Å d(O-W4) = 2.08 Å d(O-Ni3) = 2.03 Å d(O-Hb) = 0.98 Å d(Ha and O) = 2.92 Å
H_2O	d(Ha-O) = 0.99 Å d(Hb-O) = 0.99 Å d(O-W4) = 2.31 Å	d(Ha-O) = 0.99 Å d(Hb-O) = 0.99 Å d(O-W4) = 2.32 Å	d(Ha-O) = 0.98 Å d(Hb-O) = 0.98 Å d(O-W4) = 2.15 Å

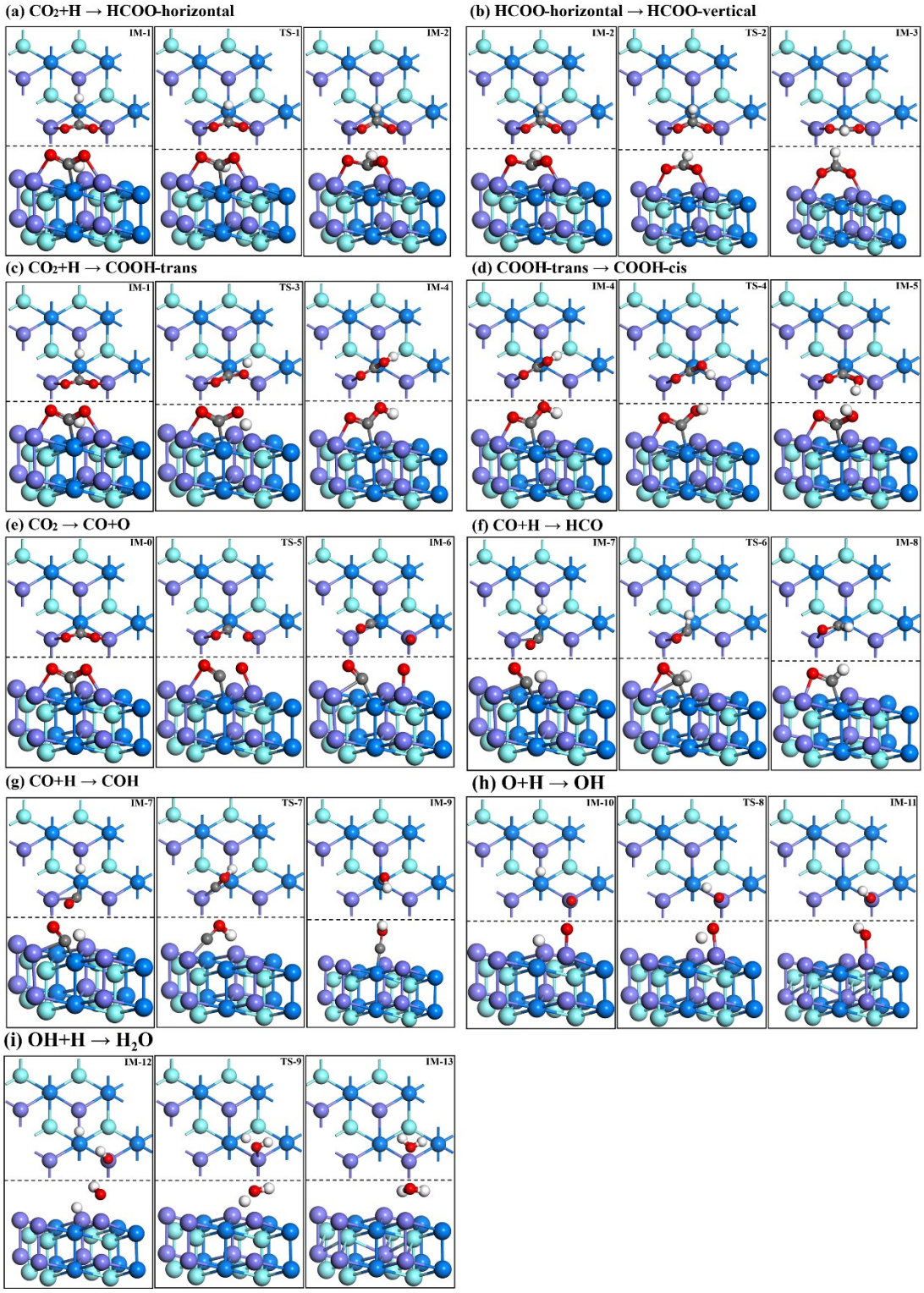


Fig. S5 The initial, transition and final states of the elementary reaction step of CO_2 hydrogenation on W (111) surface.

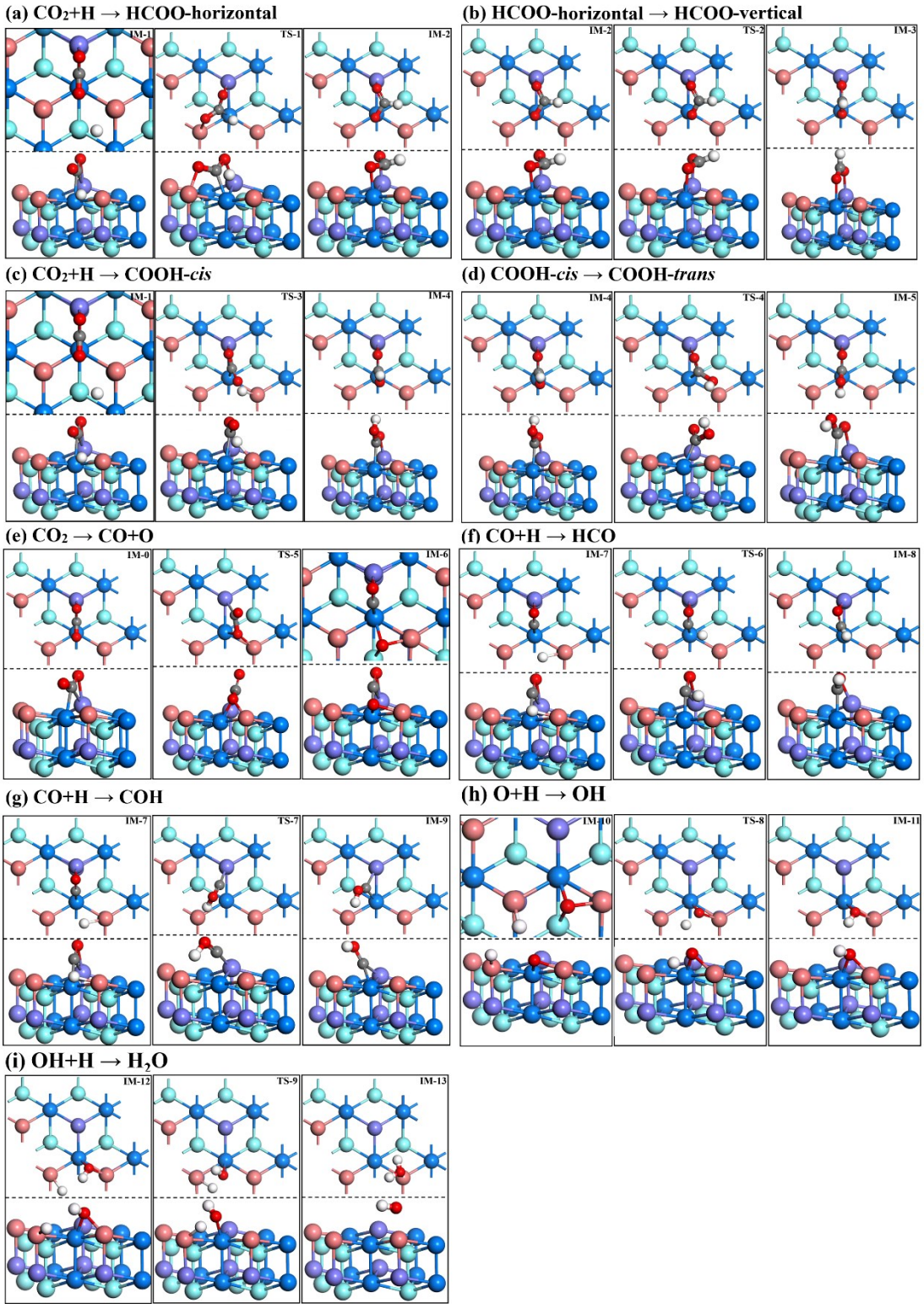


Fig. S6 The initial, transition and final states of the elementary reaction step of CO_2 hydrogenation on Ni_3W (111) surface.

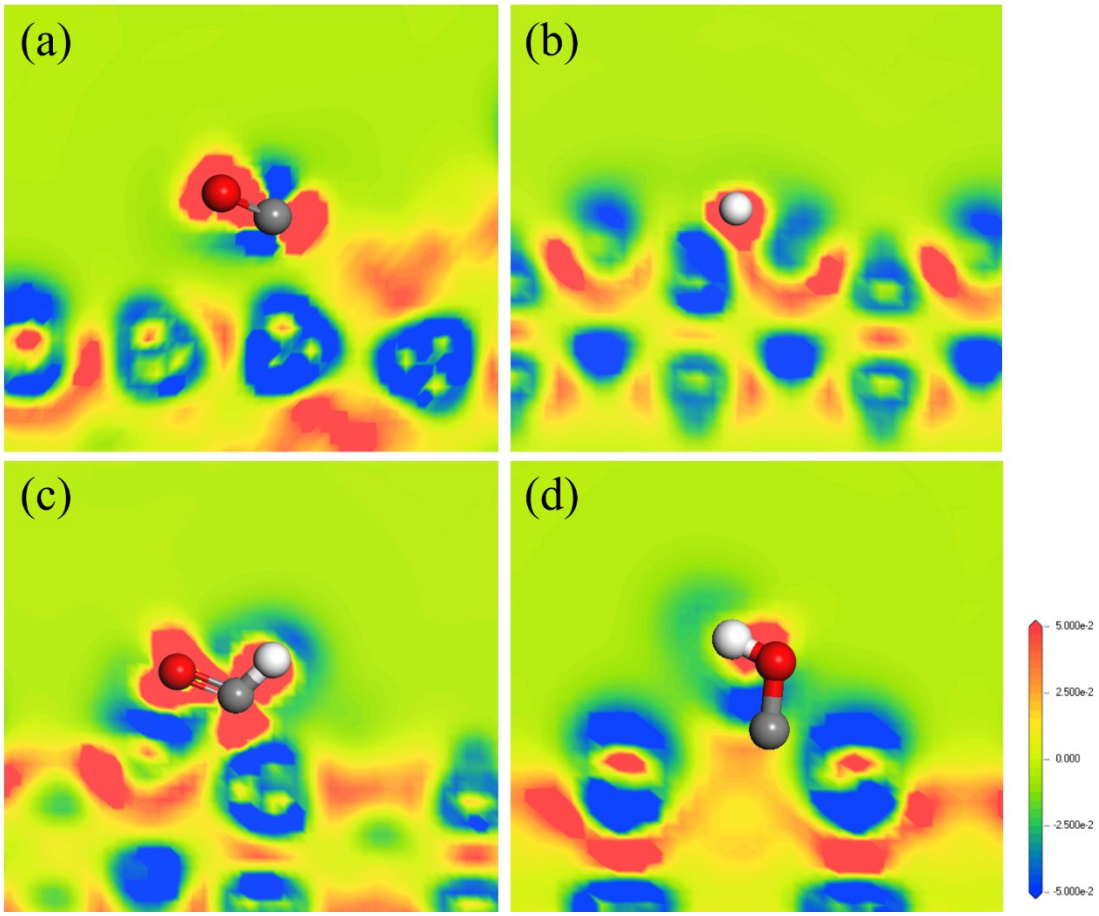


Fig. S7 Deformation charge density of (a) CO, (b) H, (c) HCO and (d) COH adsorbed on W (111) surface. Red represent accumulation of electronic density; blue represent depletion of electronic density.

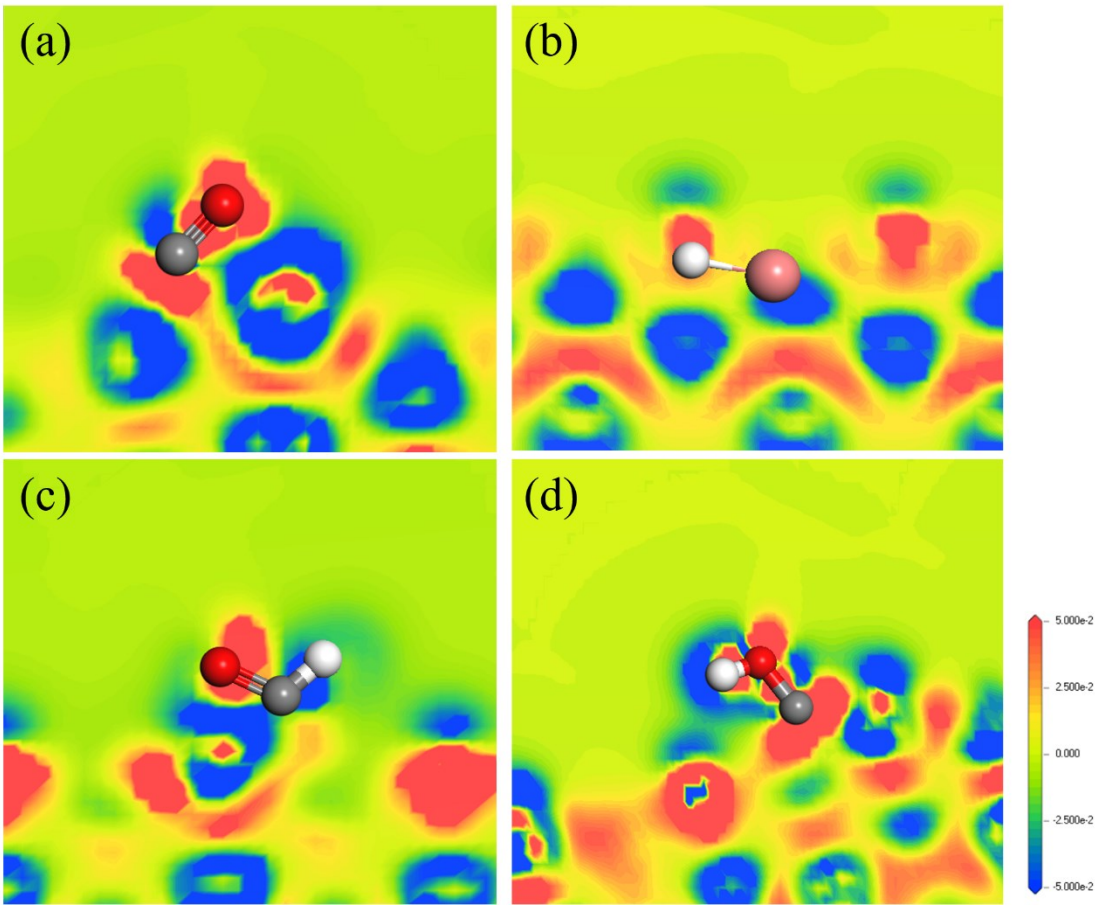


Fig. S8 Deformation charge density of (a) CO, (b) H, (c) HCO and (d) COH adsorbed on Ni_3W (111) surface.