1. Adsorption performance

Adsorption performance of O, OH, CHO, COH, CHOH, CH_2OH, CH_3O, CH_2, CH_3, and H_2O species over Co-MoS_2 was summarized in this text. Table 1 listed adsorption energies (E_{ads}, in kcal/mol) and the geometry parameters (in Å). Fig. 1 and Fig. 2 showed the adsorption configurations of reactants and intermediates involved.

As can be seen, O atom on T_1 tends to adsorbed on Mo site instead of Co site, and OH species favors to bridge on Co-Mo site or on bare Mo site. Similarly, on T_2, both O atom and OH species prefer to bridge on adjacent Mo-Mo site rather than Co-Mo site. On T_1, CHO prefers to bridge adsorb by its carbon atom binding with Co site and its oxygen site binding with Mo site, as shown in Fig. 1. In addition, for T_2, CHO prefer to adsorb either by its carbon atom binding with Mo site and its oxygen site binding with Co site (-48.45 kcal/mol) or by its carbon atom binding with Co site and its oxygen site binding with Mo site (-45.68 kcal/mol). For COH species, the most stable adsorption configuration on T_1 termination was its carbon atom bridging on the adjacent Co-Mo site (-82.68 kcal/mol), yet on T_2 termination COH prefers to either bridge at Co-Mo site with its carbon atom (-90.14 kcal/mol) or bind at the bare Co site with its carbon atom (-90.12 kcal/mol). CHOH species on T_1 and T_2 has analogous adsorption configurations, by its carbon binding with Co site, or bridge the Co-Mo site with its carbon and oxygen atom. Likewise, CH_2OH species on T_1 and T_2 has similar adsorption configurations by bridging the Co-Mo site with its carbon and oxygen atom. CH_3O was discovered to adsorb at the bare Mo site or bare Co site with its oxygen center on T_1 termination, and bridge at the Co-Mo site with its oxygen atom on T_2 termination. On the T_1 termination, CH_2 favors to bridge the Co-Mo site (-98.40 kcal/mol) or adsorb at unsaturated Co site (-93.55 kcal/mol), while CH_3 species

tends to interact with unsaturated Co site (-50.62 kcal/mol) or unsaturated Mo site (-48.94 kcal/mol). On the T_2 termination, adjoining Mo-S site (-109.92 kcal/mol) and Co-Mo site (-101.84 kcal/mol) was both active for CH_2, while S site (-43.82 kcal/mol) was the most active adsorption site for CH_3, as can be seen in Fig. 2. H_2O species on Mo edge preferred to adsorb on the Co site, while on S edge, Mo site was prior to Co site for the adsorption of H_2O species.

Table 1 Adsorption energies (E_{ads}, in kcal/mol) and the geometry parameters (in Å) of reactants, intermediates, and products on T_1 and T_2 terminations

	T₁		T₂	
	E_{ads}	$d_{C\text{-}O/Co\text{-}C/Co\text{-}O/Co\text{-}H/Mo\text{-}C/Mo\text{-}O/Mo\text{-}H/S\text{-}H}$	E_{ads}	$d_{C\text{-}O/Co\text{-}C/Co\text{-}O/Co\text{-}H/Mo\text{-}C/Mo\text{-}O/Mo\text{-}H/S\text{-}H/S\text{-}C}$
H(a)	-55.58	-/-/-/1.48/-/-/-/-	-59.27	-/-/-/-/-/-/1.93,1.81/-/-
H(b)	-53.04	-/-/-/-/-/-/1.71/-	-52.35	-/-/-/1.78/-/-/1.77/-/-
H(c)	-44.51	-/-/-/-/-/-/-/1.36	-50.50	-/-/-/-/-/-/-/1.36/-
O(a)	-146.66	-/-/-/-/-/1.75/-/-	-157.04	-/-/-/-/-/1.84,2.15/-/-/-
O(b)	-119.68	-/-/1.68/-/-/-/-/-	-141.36	-/-/1.97/-/-/1.83/-/-/-
OH(a)	-77.94	-/-/2.10/-/-/2.20/-/-	-80.71	-/-/-/-/-/2.24,2.14/-/-/-
OH(b)	-76.79	-/-/-/-/-/2.02/-/-	-72.87	-/-/1.99/-/-/2.20/-/-/-
CO(a)	-45.43	1.15/1.77/-/-/-/-/-/-	-24.91	1.16/1.78/-/-/-/-/-/-/-
CO(b)	-26.98	1.16/-/-/-/2.06/-/-/-	-24.67	1.16/-/-/-/2.05/-/-/-/-
CHO(a)	-71.79	1.27/1.84/-/-/-/2.21/-/-	-48.45	1.25/1.87/-/-/-/2.28/-/-/-
CHO(b)	-58.98	1.25/-/1.94/-/2.25/-/-/-	-45.68	1.25/-/1.99/-/2.17/-/-/-/-

Species				
COH(a)	-82.68	1.32/1.90/-/-/2.22/-/-/-	-90.14	1.35/1.94/-/-/2.12/-/-/-/1.83
COH(b)	-66.20	1.51/1.94/-/-/-/2.03/-/-	-90.12	1.34/1.84/-/-/-/-/-/-/-
CH_2O(a)	-30.87	1.38/2.02/-/-/-/1.98/-/-	-12.62	1.34/-/-/-/2.21/2.03/-/-/-
CH_2O(a)	-20.37	1.29/-/1.92/-/2.46/-/-/-	-11.47	1.23/-/-/-/-/2.39/-/-/-
CHOH(a)	-79.94	1.31/1.81/-/-/-/-/-/-	-72.97	1.44/-/2.09/-/2.20/-/-/-/1.81
CHOH(a)	-79.04	1.39/1.97/-/-/-/2.32/-/-	-71.53	1.44/1.95/-/-/-/2.31/-/-/1.82
CH_3O(a)	-66.02	1.34/-/-/-/-/2.17/-/-	-61.77	1.42-/2.00/-/-/2.10/-/-/-
CH_3O(b)	-62.38	1.34/-/1.94/-/-/-/-/-		
CH_2OH(a)	-64.49	1.51/1.94/-/-/-/2.18/-/-	-41.10	1.47/-/2.04/-/2.26/-/-/-/-
CH_2OH(b)	-61.51	1.49/-/2.00/-/2.24/-/-/-	-40.27	1.48/2.00/-/-/-/2.30/-/-/-
CH_3OH(a)	-27.99	1.46/-/2.04/-/-/-/-/-	-13.20	1.45/-/-/-/-/2.45/-/-/-
CH_3OH(b)	-22.28	1.45/2.57/-/-/-/2.31/-/-	-12.15	1.46/-/2.22/-/-/2.58/-/-/-
CH_2(a)	-98.40	-/2.02/-/-/2.21/-/-/-	-109.92	-/-/-/-/2.21/-/-/-/1.77
CH_2(b)	-93.55	-/1.77/-/-/-/-/-/-	-101.84	-/1.98/-/-/2.16/-/-/-/-
CH_3(a)	-50.62	-/1.99/-/-/-/-/-/-	-43.82	-/-/-/-/-/-/-/-/1.84
CH_3(b)	-48.94	-/-/-/-/2.26/-/-/-	-37.74	-/-/-/-/2.25/-/-/-/-
H_2O(a)	-25.50	-/-/2.06/-/-/-/-/-	-14.50	-/-/-/-/-/2.45/-/-/-
H_2O(b)	-24.22	-/-/2.06/-/-/-/-/-	-12.57	-/-/-/-/-/2.47/-/-/-
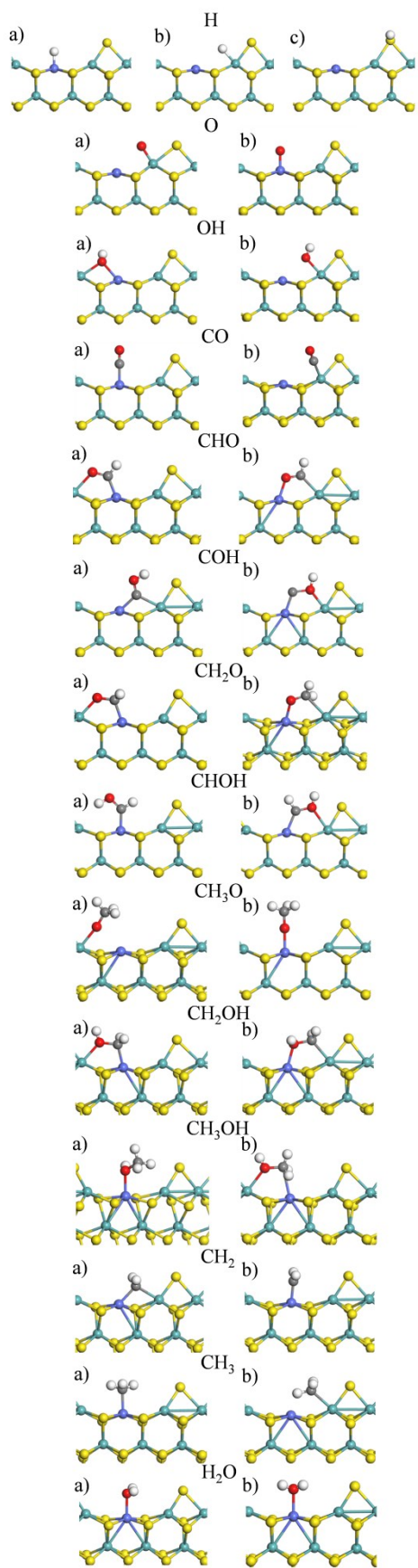
Fig. 1. Adsorption configurations of reactants and intermediates in most stable states on T_1

termination

H

a) b) c)

O

a) b)

OH

a) b)

CO

a) b)

CHO

a) b)

COH

a) b)

CH$_2$O

a) b)

CHOH

a) b)

CH$_3$O

CH$_2$OH

a) b)

CH$_3$OH

a) b)

CH$_2$
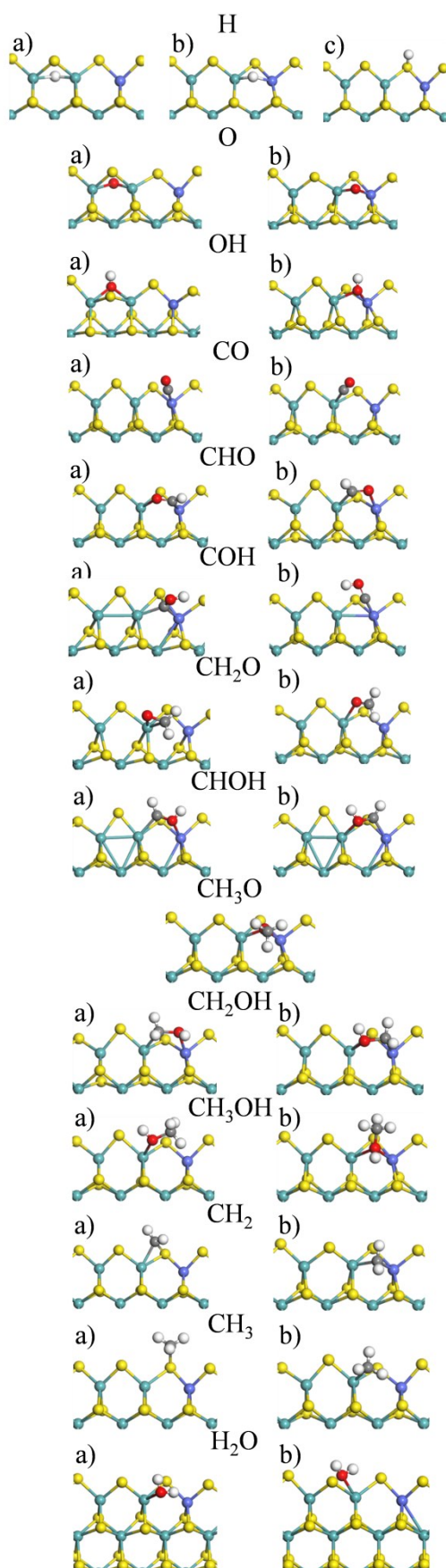
a) b)

CH$_3$

a) b)

H$_2$O

a) b)

Fig. 2. Adsorption configurations of reactants and intermediates in most stable states on T_2 termination

Structurally, for all adsorbed C1 species involved in CO methanation reaction on T_1 and T_2 terminations, the C-Mo distance ranges from 2.06 to 2.46 Å, and the C-Co bonds were from 1.77 to 2.02 Å in length, in which strong interactions between the catalysts and the adsorbed atoms lead to relative adsorbed intermediates elongation.

2. Discussions on dispersion interactions

The impact of dispersion interactions on calculation results was tested. Results of adsorption performance with or without dispersion show little difference. However, dispersion interactions were found to affect transition state configurations and reaction barriers to different degrees, which couldn't be ignored. The first elementary reaction step $CO + H \rightarrow CHO$ and the second one $CHO + H \rightarrow CH_2O$ on both edges of Co-MoS$_2$ catalysts were taken as examples, the values of reaction barrier (E_a) and reaction energy (E_{sep}) were listed below.

Table 2 Reaction barriers and reaction energies with or without dispersion interactions of reaction step CO + H → CHO on both edges of Co-MoS$_2$ catalytst, the values were given in kcal/mol.

		Mo edge of Co-MoS$_2$	*S edge of Co-MoS$_2$*
E_a	*With dispersion*	*25.08*	*16.99*
	Without	*25.22*	*30.96*
E_{sep}	*With dispersion*	*2.60*	*5.94*
	Without	*2.76*	*6.96*

Table 3 Reaction barriers and reaction energies with or without dispersion interactions of reaction step of CHO + H → CH$_2$O on both edges of Co-MoS$_2$ catalytst, the values were given in kcal/mol.

		Mo edge of Co-MoS$_2$	S edge of Co-MoS$_2$
E_a	With dispersion	12.77	14.83
	Without	10.55	18.58
E_{sep}	With dispersion	-6.58	6.91
	Without	-6.48	6.88

As can be seen from table 2 and table 3, although dispersion interactions influenced the reaction energies slightly, this factor affected the reaction barriers obviously and it should be taken in to consideration.

3. Configurations of species

The configurations of reactants, transition states and products along feasible pathways on four edges were given in Fig. 3-8 below, with detailed information including bond lengths (in Å) and angles (in °). Fig. 3 and Fig. 4 shown the configurations involved in the optimal pathway on Mo edge and S edge of pure MoS$_2$ catalysts, respectively. Configurations involved in all feasible pathways on Mo edge of Co-MoS$_2$ was given in Fig. 5 and Fig. 6, while Fig. 7 and Fig. 8 showed the configurations on S edge of Co-MoS$_2$.

d$_{C\text{-}O}$ = 1.16
d$_{Mo\text{-}C}$ = 2.05

d$_{C\text{-}O}$ = 1.19 d$_{C\text{-}H}$ = 1.28
d$_{Mo\text{-}C}$ = 2.26
∠$_{H\text{-}C\text{-}O}$ = 120.76

d$_{C\text{-}O}$ = 1.26 d$_{C\text{-}H}$ = 1.11
d$_{Mo\text{-}C}$ = 2.19 d$_{Mo\text{-}O}$ = 2.17
∠$_{H\text{-}C\text{-}O}$ = 112.16

d$_{C\text{-}O}$ = 1.25 d$_{C\text{-}H2}$ = 1.12
d$_{Mo\text{-}C}$ = 2.17 d$_{Mo\text{-}O}$ = 2.25
∠$_{H\text{-}C\text{-}O}$ = 113.64

d$_{C\text{-}O}$ = 1.26 d$_{C\text{-}H1}$ = 1.82
d$_{C\text{-}H2}$ = 1.11 d$_{Mo\text{-}C}$ = 2.12
d$_{Mo\text{-}O}$ = 2.17 ∠$_{H2\text{-}C\text{-}O}$ = 113.45

d$_{C\text{-}O}$ = 1.38 d$_{C\text{-}H1}$ = 1.11
d$_{C\text{-}H2}$ = 1.10 d$_{Mo\text{-}C}$ = 2.23
d$_{Mo\text{-}O}$ = 1.95 ∠$_{H1\text{-}C\text{-}O}$ = 111.59
∠$_{H2\text{-}C\text{-}O}$ = 107.97

d$_{S\text{-}H1}$ = 1.36

d$_{O\text{-}H1}$ = 1.40

d$_{O\text{-}H1}$ = 0.98
∠$_{H1\text{-}O\text{-}C}$ = 111.08

d$_{C\text{-}O}$ = 1.47

d$_{C\text{-}O}$ = 2.41

d$_{C\text{-}O}$ = 2.80

d$_{S\text{-}H1}$ = 1.36

d$_{C\text{-}H1}$ = 1.77

d$_{C\text{-}H1}$ = 1.13

d$_{Mo\text{-}H1}$ = 1.69

d$_{C\text{-}H1}$ = 2.16

d$_{C\text{-}H1}$ = 1.10

Fig. 3. Configuration of reactants, transition states, and products in the optimal pathways on Mo termination of MoS$_2$ catalysts (bond distances in Å and angles in °)

$d_{C-O} = 1.17$
$d_{Mo-C} = 2.00$

$d_{C-O} = 1.17$ $d_{C-H} = 1.59$
$d_{Mo-C} = 1.98$
$\angle_{H-C-O} = 121.18$

$d_{C-O} = 1.25$ $d_{C-H} = 1.11$
$d_{Mo-C} = 2.14$ $d_{Mo-O} = 2.20$
$\angle_{H-C-O} = 114.55$

$d_{C-O} = 1.26$ $d_{C-H2} = 1.11$
$d_{Mo-C} = 2.12$ $d_{Mo-O} = 2.16$
$\angle_{H-C-O} = 112.30$

$d_{C-O} = 1.27$ $d_{C-H1} = 1.68$
$d_{C-H2} = 1.10$ $d_{Mo-C} = 2.11$
$d_{Mo-O} = 2.09$ $\angle_{H2-C-O} = 114.40$

$d_{C-O} = 1.36$ $d_{C-H1} = 1.10$
$d_{C-H2} = 1.10$ $d_{Mo-C} = 2.23$
$d_{Mo-O} = 1.99$ $\angle_{H1-C-O} = 113.63$
$\angle_{H2-C-O} = 117.13$

$d_{S-H1} = 1.36$

$d_{O-H1} = 1.30$

$d_{O-H1} = 0.98$
$\angle_{H1-O-C} = 108.57$

$d_{C-O} = 1.43$

$d_{C-O} = 1.91$

$d_{C-O} = 3.12$

$d_{S-H1} = 1.36$

$d_{C-H1} = 1.84$

$d_{C-H1} = 1.10$

$d_{S-H1} = 1.36$

$d_{C-H1} = 1.55$

$d_{C-H1} = 1.10$

Fig. 4. Configuration of reactants, transition states, and products in the optimal pathways on S termination of MoS_2 catalysts (bond distances in Å and angles in °)

d_{C-O} = 1.15
d_{Co-C} = 1.77
d_{Mo-H} = 1.69

d_{C-O} = 1.18 d_{C-H} = 1.43
d_{Co-C} = 1.86
∠H-C-O = 121.79

d_{C-O} = 1.27 d_{C-H} = 1.11
d_{Co-C} = 1.84 d_{Mo-O} = 2.21
∠H-C-O = 113.44

d_{C-O} = 1.26 d_{C-H2} = 1.11
d_{Co-C} = 1.83 d_{Mo-O} = 2.23
d_{Mo-H1} = 1.70
∠H2-C-O = 115.19

d_{C-O} = 1.26 d_{C-H1} = 2.04
d_{C-H2} = 1.11 d_{Co-C} = 1.88
d_{Mo-O} = 2.20
∠H2-C-O = 113.32

d_{C-O} = 1.38 d_{C-H1} = 1.10
d_{C-H2} = 1.10 d_{Co-C} = 2.02
d_{Mo-O} = 1.98 ∠H1-C-O = 110.66
∠H2-C-O = 110.66

d_{S-H1} = 1.36

d_{O-H1} = 1.42

d_{O-H1} = 0.98
∠H1-O-C = 112.50

d_{Mo-H1} = 1.70

d_{C-H1} = 2.27

d_{C-H1} = 1.12
∠H1-C-O = 106.86

d_{C-O} = 1.45

d_{C-O} = 1.95

d_{C-O} = 3.07

d_{Mo-H1} = 1.70

d_{C-H1} = 2.22

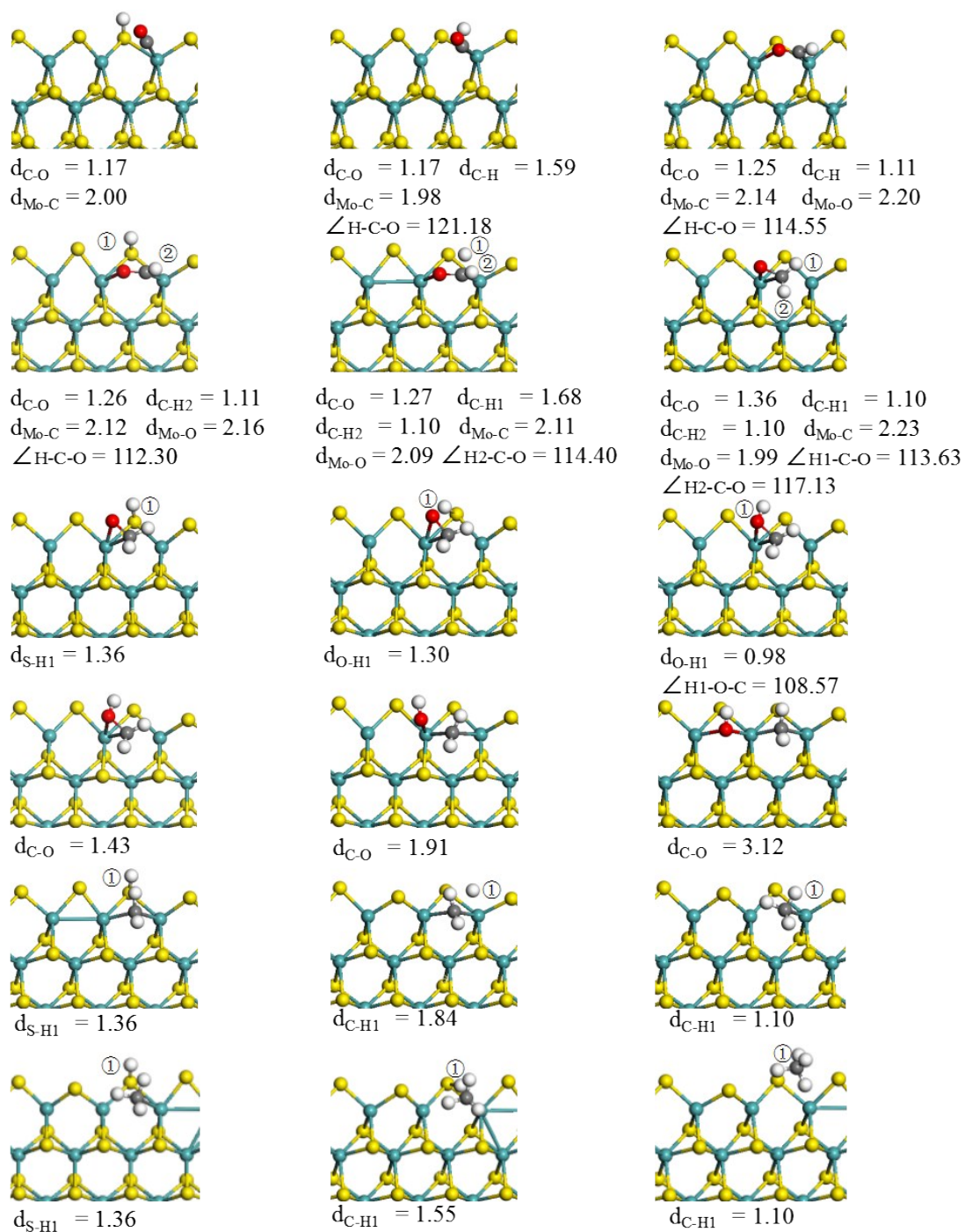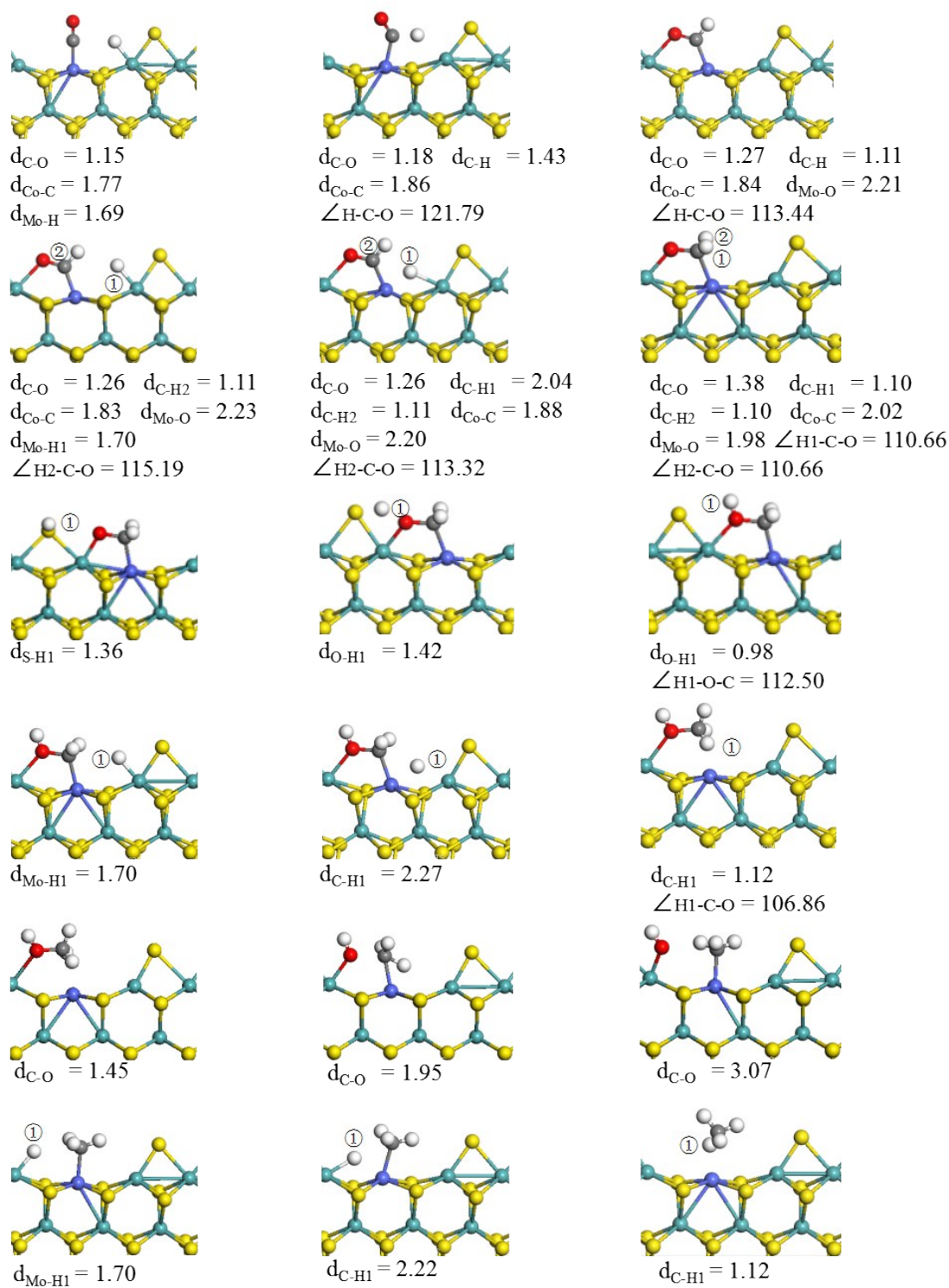d_{C-H1} = 1.12

Fig. 5. Configuration of reactants, transition states, and products in the optimal pathways on Mo termination of Co-MoS$_2$ catalysts (bond distances in Å and angles in °)
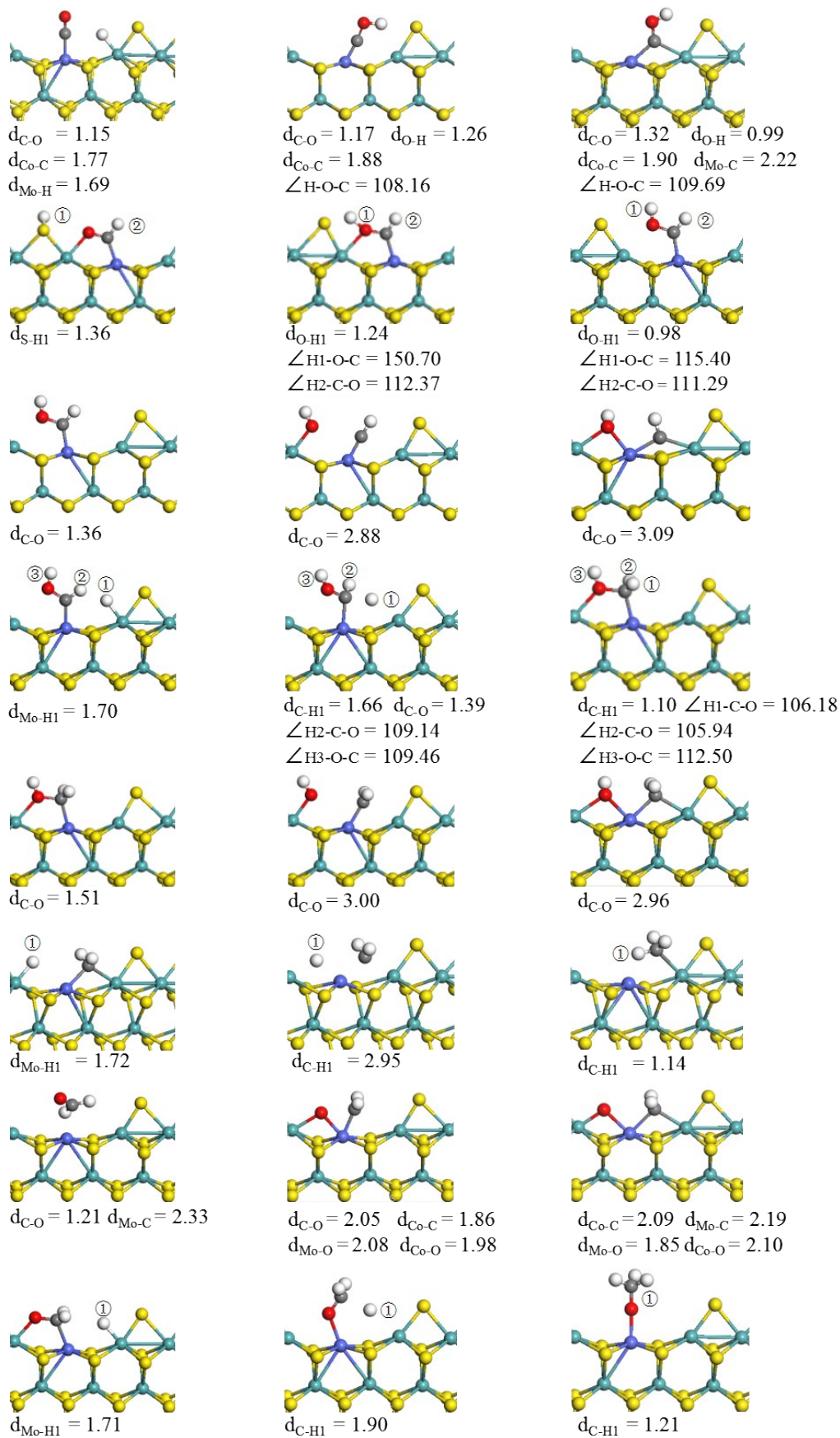
$d_{C-O} = 1.15$
$d_{Co-C} = 1.77$
$d_{Mo-H} = 1.69$

$d_{C-O} = 1.17 \quad d_{O-H} = 1.26$
$d_{Co-C} = 1.88$
$\angle_{H-O-C} = 108.16$

$d_{C-O} = 1.32 \quad d_{O-H} = 0.99$
$d_{Co-C} = 1.90 \quad d_{Mo-C} = 2.22$
$\angle_{H-O-C} = 109.69$

$d_{S-H1} = 1.36$

$d_{O-H1} = 1.24$
$\angle_{H1-O-C} = 150.70$
$\angle_{H2-C-O} = 112.37$

$d_{O-H1} = 0.98$
$\angle_{H1-O-C} = 115.40$
$\angle_{H2-C-O} = 111.29$

$d_{C-O} = 1.36$

$d_{C-O} = 2.88$

$d_{C-O} = 3.09$

$d_{Mo-H1} = 1.70$

$d_{C-H1} = 1.66 \quad d_{C-O} = 1.39$
$\angle_{H2-C-O} = 109.14$
$\angle_{H3-O-C} = 109.46$

$d_{C-H1} = 1.10 \quad \angle_{H1-C-O} = 106.18$
$\angle_{H2-C-O} = 105.94$
$\angle_{H3-O-C} = 112.50$

$d_{C-O} = 1.51$

$d_{C-O} = 3.00$

$d_{C-O} = 2.96$

$d_{Mo-H1} = 1.72$

$d_{C-H1} = 2.95$

$d_{C-H1} = 1.14$

$d_{C-O} = 1.21 \quad d_{Mo-C} = 2.33$

$d_{C-O} = 2.05 \quad d_{Co-C} = 1.86$
$d_{Mo-O} = 2.08 \quad d_{Co-O} = 1.98$

$d_{Co-C} = 2.09 \quad d_{Mo-C} = 2.19$
$d_{Mo-O} = 1.85 \quad d_{Co-O} = 2.10$

$d_{Mo-H1} = 1.71$

$d_{C-H1} = 1.90$

$d_{C-H1} = 1.21$

Fig. 6. Configuration in the other feasible pathways on Mo edge of Co-MoS$_2$ catalysts (distances in Å and angles in °)

$d_{C-O} = 1.15$
$d_{Co-C} = 1.77$
$d_{S-H} = 1.69$

$d_{C-O} = 1.18$ $d_{C-H} = 1.43$
$d_{Co-C} = 1.86$
$\angle_{H-C-O} = 121.79$

$d_{C-O} = 1.25$ $d_{C-H} = 1.11$
$d_{Co-C} = 1.87$ $d_{Mo-O} = 2.28$
$\angle_{H-C-O} = 115.68$

$d_{C-O} = 1.26$ $d_{C-H2} = 1.11$
$d_{Co-C} = 1.87$ $d_{Mo-O} = 2.21$
$d_{S-H1} = 1.36$
$\angle_{H2-C-O} = 114.51$

$d_{C-O} = 1.23$ $d_{C-H1} = 1.25$
$d_{C-H2} = 1.08$ $d_{Mo-O} = 2.35$
$\angle_{H1-C-O} = 120.87$
$\angle_{H2-C-O} = 118.69$

$d_{C-O} = 1.23$ $d_{C-H1} = 1.11$
$d_{C-H2} = 1.11$ $d_{Mo-O} = 2.39$
$\angle_{H1-C-O} = 122.07$
$\angle_{H2-C-O} = 119.07$

$d_{S-H1} = 1.36$

$d_{O-H1} = 1.33$
$\angle_{H1-O-C} = 100.47$

$d_{O-H1} = 0.98$
$\angle_{H1-O-C} = 109.14$

$d_{C-O} = 1.48$

$d_{Mo-O} = 2.01$ $d_{Mo-C} = 2.17$

$d_{Mo-O} = 2.18/2.14$
$d_{Mo-C} = 2.15$ $d_{Co-C} = 2.25$

$d_{Mo-H1} = 1.79$ $d_{Mo-C} = 2.22$
$d_{Co-H1} = 1.77$ $d_{S-C} = 1.77$

$d_{C-H1} = 1.59$ $d_{S-C} = 1.78$

$d_{S-C} = 1.84$

$d_{S-H1} = 1.36$

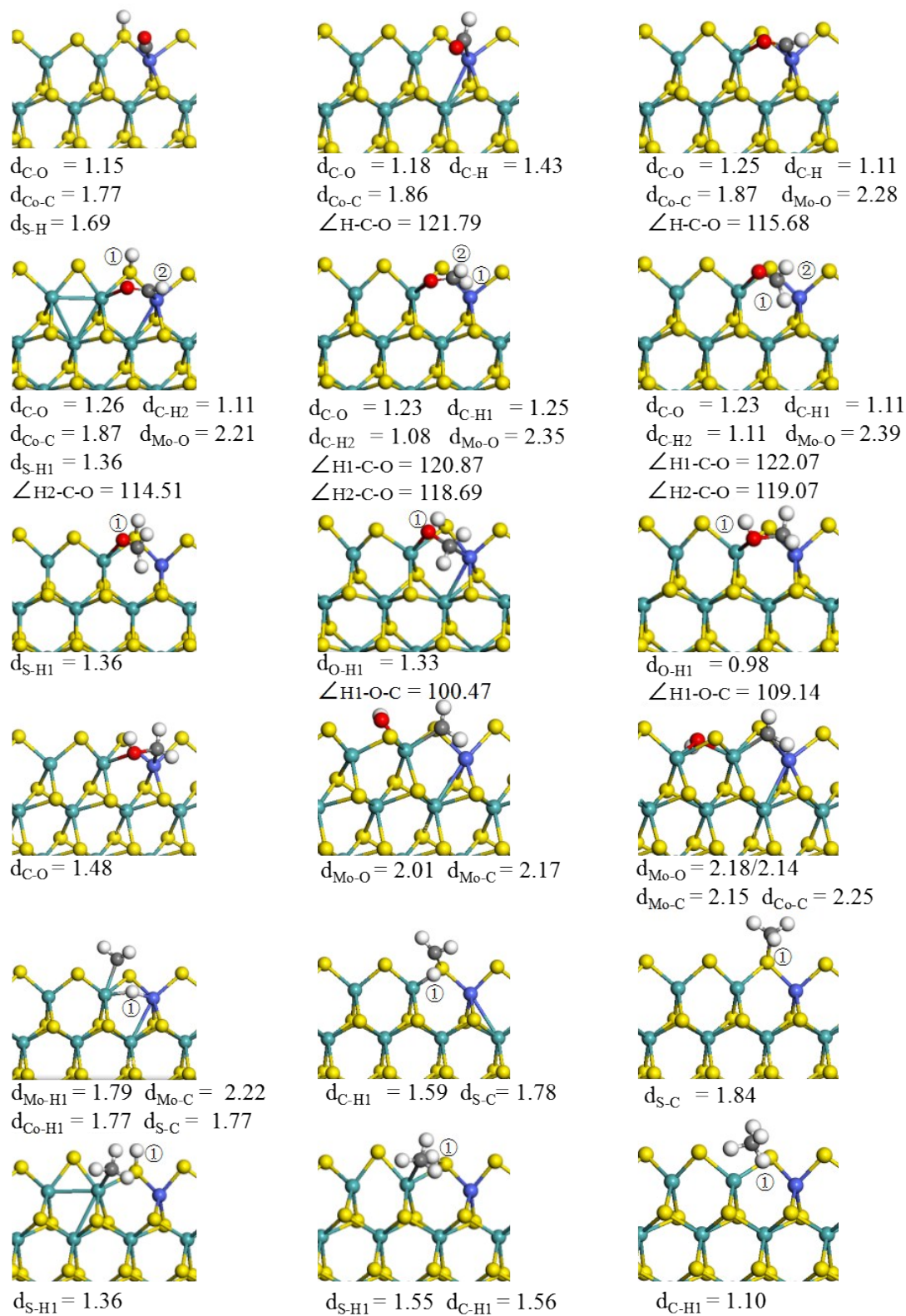$d_{S-H1} = 1.55$ $d_{C-H1} = 1.56$

$d_{C-H1} = 1.10$

Fig. 7. Configuration of reactants, transition states, and products in the optimal pathways on S termination of Co-MoS$_2$ catalysts (bond distances in Å and angles in °)
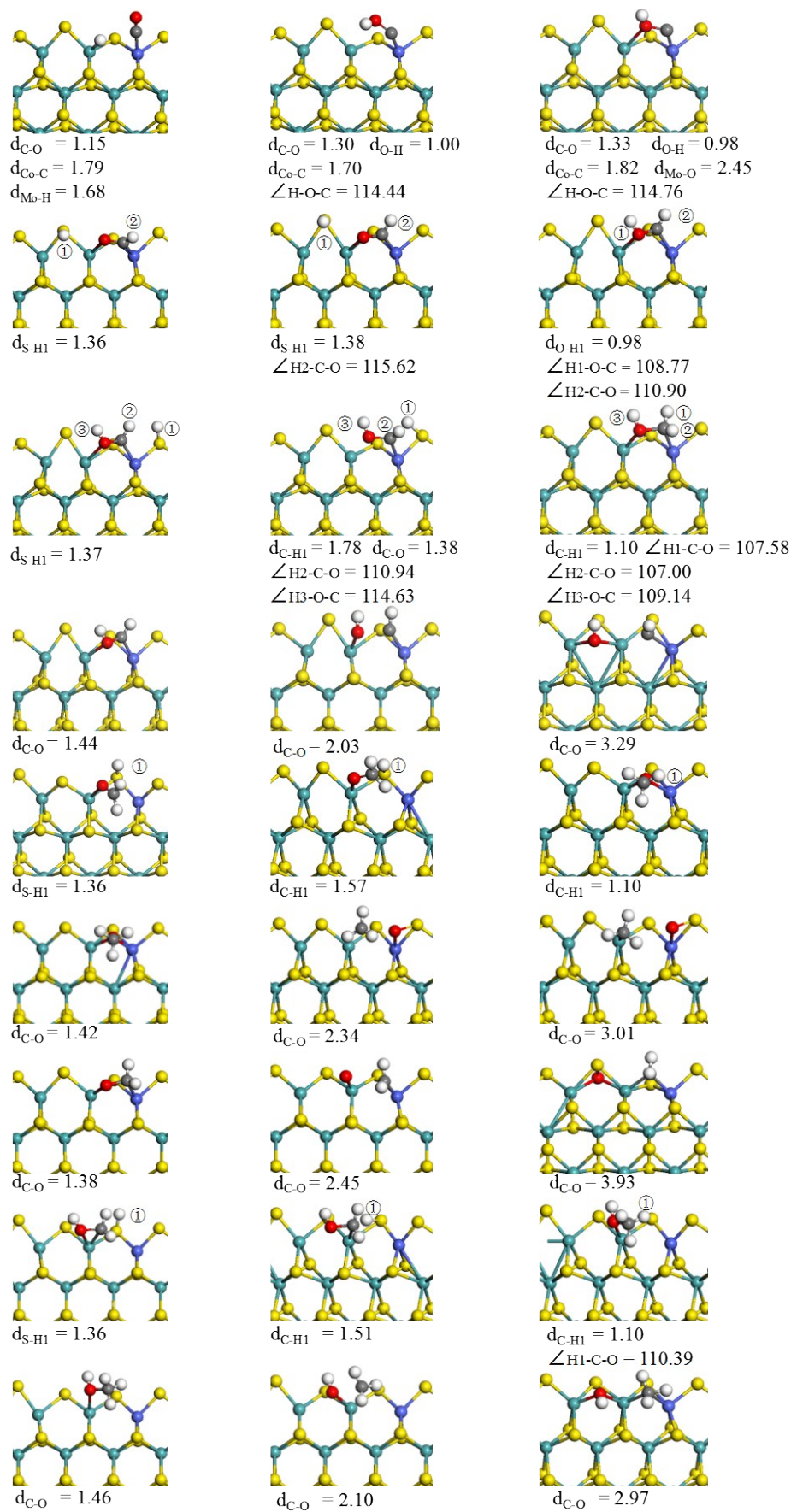
Fig. 8. Configuration in the other feasible pathways on S termination of Co-MoS$_2$ catalysts(bond distances in Å and angles in °)