Supporting information

Mechanistic insights into effect of sulfur on the selectivity of cobalt catalyzed Fischer-Tropsch Synthesis: A DFT study

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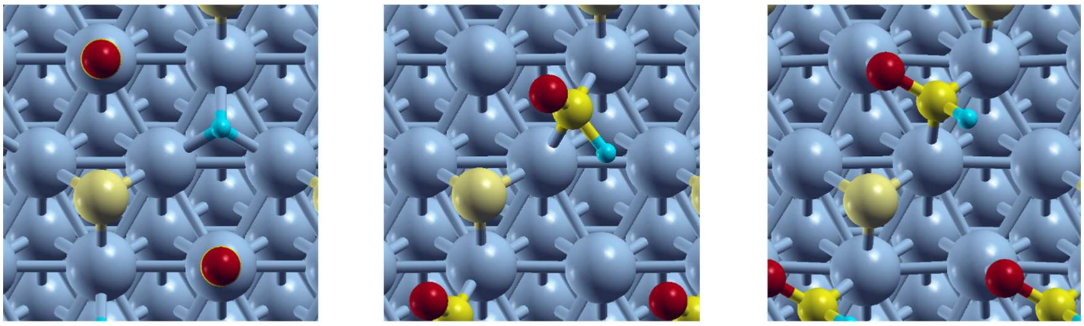
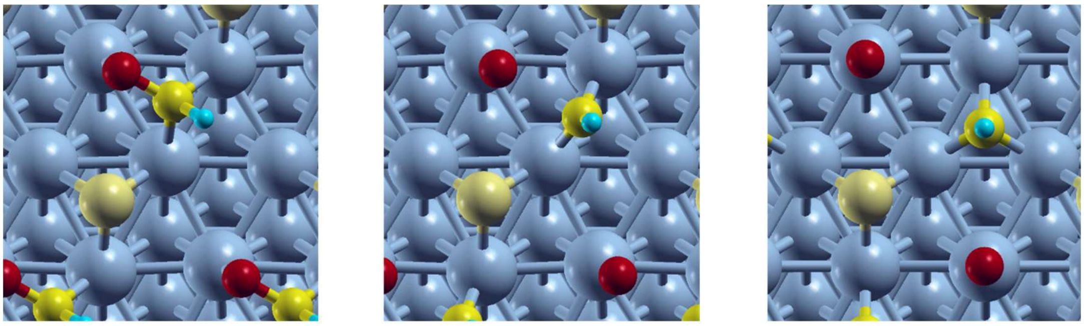
1. Top views for the initial states, transition states and final states of the investigated elementary reactions on S-Co(111) for 0.25 ML sulfur coverage



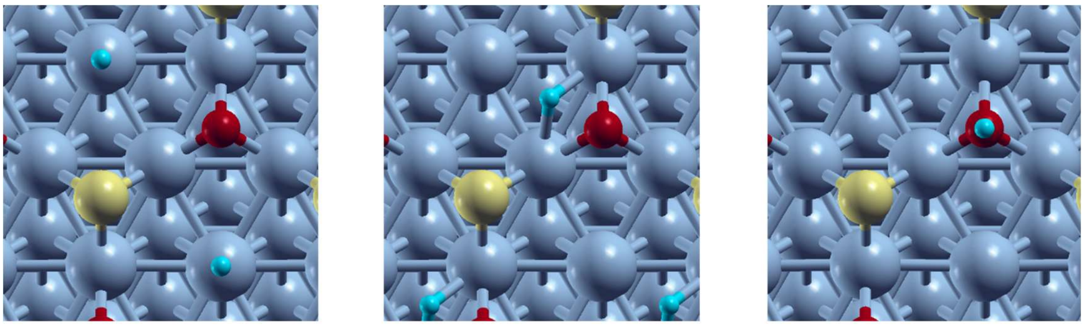
IS **TS** **FS**

Figure S1. Initial state (IS), transition state (TS) and final state (FS) for HCO formation (H+CO→HCO) on S-Co(111) (Color coding: Sulfur: Pale yellow, C: Bright yellow, O: Red, H: Blue, Co: Grey).



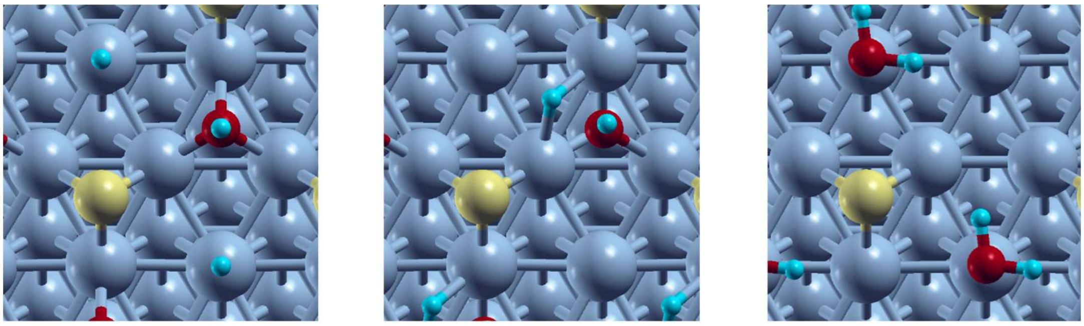
IS **TS** **FS**

Figure S2. Initial state (IS), transition state (TS) and final state (FS) for HCO dissociation (HCO→HC+O) on S-Co(111).



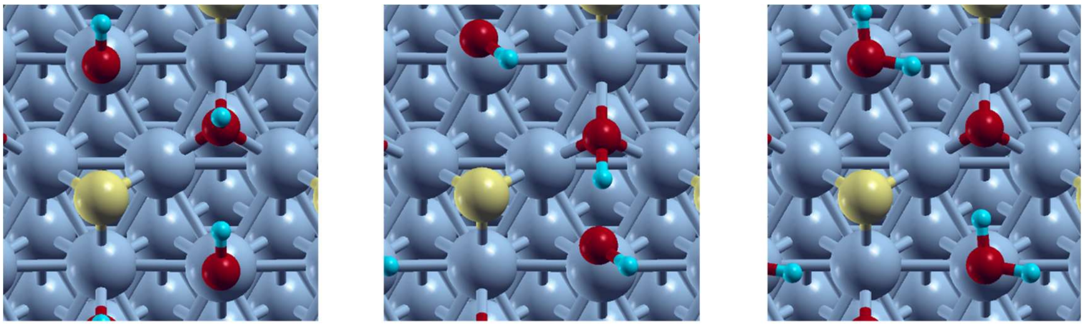
IS **TS** **FS**

Figure S3. Initial state (IS), transition state (TS) and final state (FS) for OH formation (O+H→OH+*) on S-Co(111).



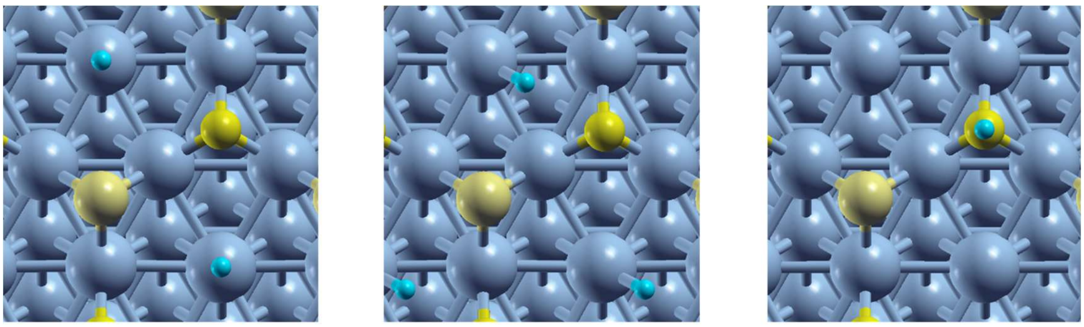
IS TS FS

Figure S4. Initial state (IS), transition state (TS) and final state (FS) for OH hydrogenation ($OH+H \rightarrow H_2O+*$) on S-Co(111).



IS TS FS

Figure S5. Initial state (IS), transition state (TS) and final state (FS) for OH coupling ($OH+OH \rightarrow H_2O+O$) on S-Co(111).



IS TS FS

Figure S6. Initial state (IS), transition state (TS) and final state (FS) for CH formation ($C+H \rightarrow CH+*$) on S-Co(111).

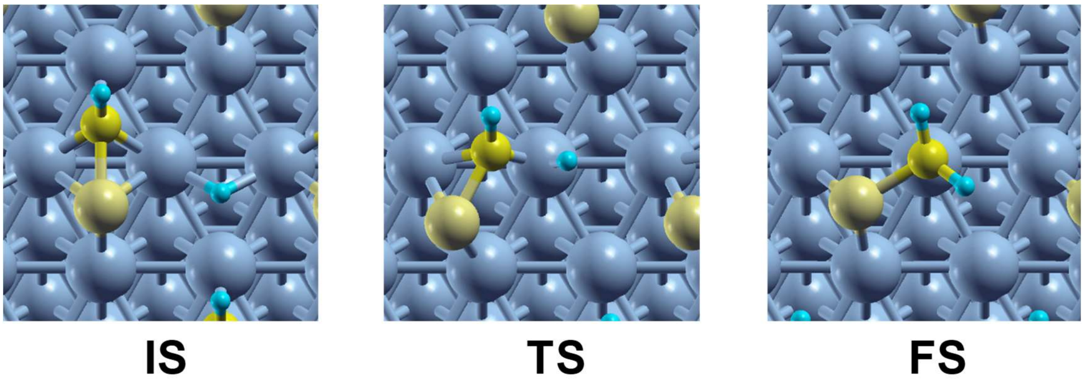


Figure S7. Initial state (IS), transition state (TS) and final state (FS) for CH_2 formation ($CH+H \rightarrow CH_2+*$) on S-Co(111).

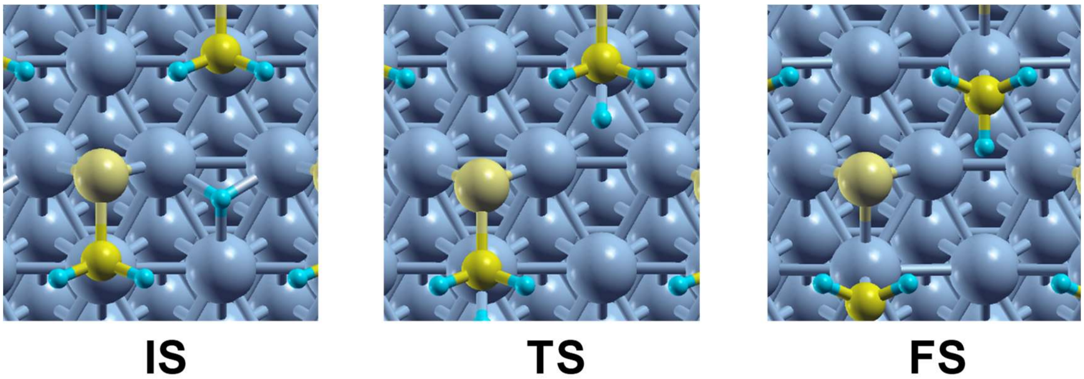


Figure S8. Initial state (IS), transition state (TS) and final state (FS) for CH_3 formation ($CH_2+H \rightarrow CH_3+*$) on S-Co(111).

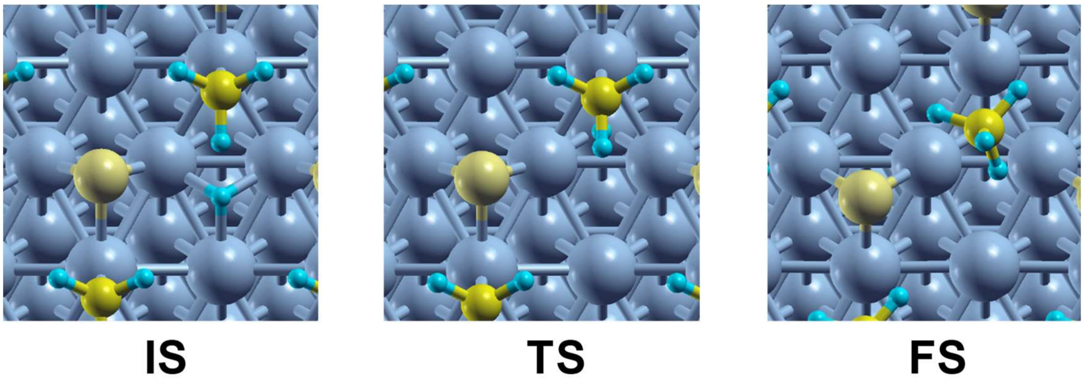


Figure S9. Initial state (IS), transition state (TS) and final state (FS) for CH_4 formation ($CH_3+H \rightarrow CH_4+*$) on S-Co(111).

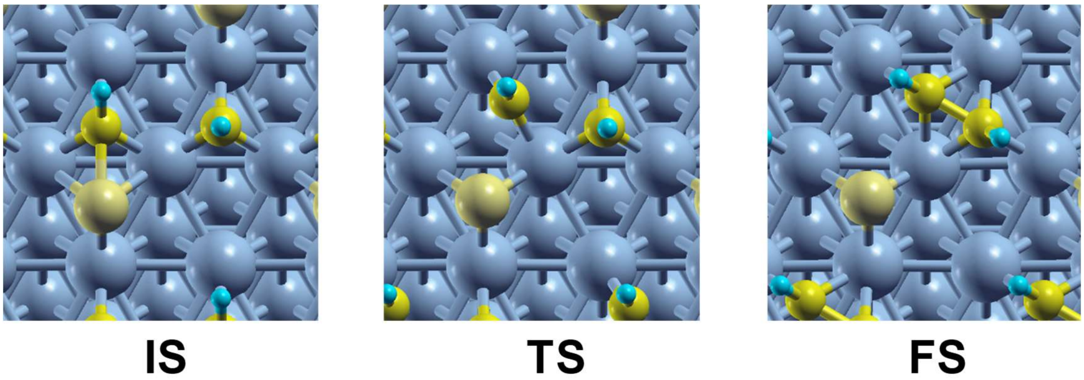


Figure S10. Initial state (IS), transition state (TS) and final state (FS) for C_2H_2 formation ($CH+CH \rightarrow C_2H_2+*$) on S-Co(111).

2. Top and side views of S-Co(111) for 0.25 ML sulfur coverage

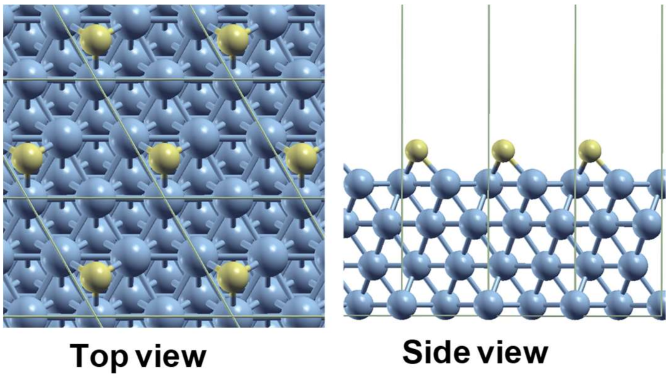


Figure S11. Top and side views of S-Co(111) for 0.25 ML sulfur coverage.

3. Comparison of the calculated adsorption energies (E_{ad}) and activation barriers (E_a) with literature

Table S1. Comparison of the calculated E_{ad} with literature

	Our study	Our study	Literature	Literature
Adsorbates	0.25 ML	0.06 ML	0.25 ML	0.04 ML
CO	-140	-134	-176[b]	-174[a]
H	-288	-283	-284[b]	-269[a]
C	-647	-640	-695[b]	-680[a]
CH	-635	-619	-642[b]	-624[a]
C_2H_2	-206	-209	NA	-257[a]
O	-545	-542	-542[c]	-586[a]
OH	-385	-397	-345[c]	-361[a]

a. PBE functional, Co(111)[25] , b. PBE functional, Co(111)[33] , c. PBE functional, Co(0001)[34] .

Table S2. Comparison of the calculated activation barriers (E_a) with literature

	Our study	Literature	Literature
	0.25 ML	0.04 ML	0.25 ML
H+CO→HCO	121	130[a]	146[b]
HCO→HC+O	74	63[a]	90[b]
C+H→CH	77	69[a]	77[c]
CH+H→CH_2	65	58[a]	66[c]
CH_2+H→CH_3	49	56[a]	47[c]
CH_3+H→CH_4	93	95[a]	82[c]
CH+CH→C_2H_2	67	62[a]	NA
O+H→OH	122	48[a]	116[d]
O+H→H_2O	142	151[a]	111[d]
OH+OH→H_2O+O	5	47[a]	5[d]

a. PBE functional, Co(111)[25] , b. PBE functional, Co(0001)[37], c. PBE functional, Co(111)[33] , d. rPBE functional, Co(111)[40] .

4. E_{ad} values for adsorbates for 0.25 ML, 0.11 ML and 0.06 ML adsorbate/sulfur coverages on Co(111)/S-Co(111)

Table S3. E_{ad} values for adsorbates for 0.25 ML, 0.11 ML and 0.06 ML adsorbate/sulfur coverages on Co(111)/S-Co(111)

	Co(111)	S-Co(111)	Co(111)	S-Co(111)		Co(111)	S-Co(111)	
Adsorbates	0.25ML	0.25ML	0.11 ML	0.11ML (Zone1)	0.11ML (Zone2)	0.06 ML	0.06ML (Zone1)	0.06ML (Zone2)
CO	-140	-70	-129	-117	-127	-134	-121	-132
H	-288	-262	-278	-266	-283	-283	-269	-283
C	-647	-562	-632	-597	-624	-640	-611	-637
CH	-635	-600	-615	-592	-615	-619	-592	-619
C_2H_2	-206	-6	-201	-163	-197	-209	-189	-207
O	-545	-451	-535	-494	-527	-542	-494	-536
OH	-385	-288	-391	-361	-390	-397	-363	-393
S	-491	NA	-481	NA	NA	-487	NA	NA