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Supplementary material

Insight into both Coverage and Surface Structure Dependent CO Adsorption and Activation on Different Ni Surfaces From DFT and Atomistic Thermodynamics

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Part 1. Thermodynamic Correction

For the stepwise CO adsorption at different coverage, the stepwise CO adsorption free energy correction ΔE_{ads}(correction) is defined by the following equation:

$$\Delta E_{ads}(correction) = (E_{ZPE} + U^{\theta} - TS^{\theta})_{CO\ n+1/slab} - \left[(E_{ZPE} + U^{\theta} - TS^{\theta})_{CO\ n/slab} + (E_{ZPE} + H^{\theta} - TS^{\theta})_{CO}\right]$$

On the other hand, for the stepwise CO dissociation process, the dissociation free energy barrier correction ΔE_a(correction) is defined by the following equation:

$$\Delta E_a(correction) = (E_{ZPE} + U^{\theta} - TS^{\theta})_{TS} - (E_{ZPE} + U^{\theta} - TS^{\theta})_{IS}$$

The dissociation reaction free energy correction ΔE_{dis}(correction) is defined by the following equation:

$$\Delta E_{dis}(correction) = (E_{ZPE} + U^{\theta} - TS^{\theta})_{FS} - (E_{ZPE} + U^{\theta} - TS^{\theta})_{IS}$$

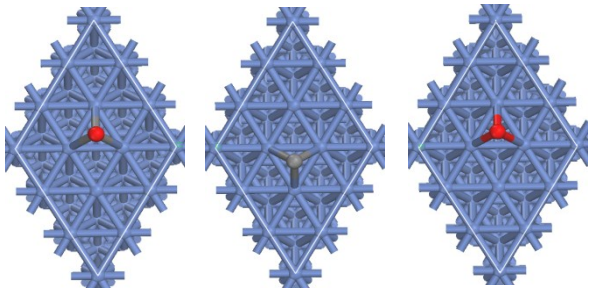
Table S1 The stepwise CO adsorption energies (eV) for the most stable adsorption configurations of CO on Ni surfaces at different coverage with and without the dispersion correction. Zero-point energy corrections, thermal energy corrections and entropies are not included.

Method	Surface	nCO								
		1	2	3	4	5	6	7	8	9
DFT	Ni(111)	-1.93	-1.92	-1.87	-1.47	-1.12	-0.86	-0.16	-0.04	4.68
DFT-D		-1.93	-1.92	-1.87	-1.47	-1.12	-0.86	-0.16	-0.04	4.68
DFT	Ni(100)	-2.01	-1.98	-1.91	-1.88	-1.68	-1.54	-1.46	-1.63	-0.51
DFT-D		-2.01	-1.97	-1.92	-1.88	-1.68	-1.54	-1.46	-1.64	-0.51
DFT	Ni(110)	-1.83	-1.82	-1.76	-1.83	-1.72	-1.76	-1.50	-1.33	-1.42
DFT-D		-1.83	-1.82	-1.76	-1.83	-1.72	-1.76	-1.51	-1.33	-1.42

Table S2 The test results about the effect of vacuum thickness, supercell size and slab layers on the energy of the single CO molecule on different Ni(111), (100) and (110) surface models. Zero-point energy corrections, thermal energy corrections and entropies are not included.

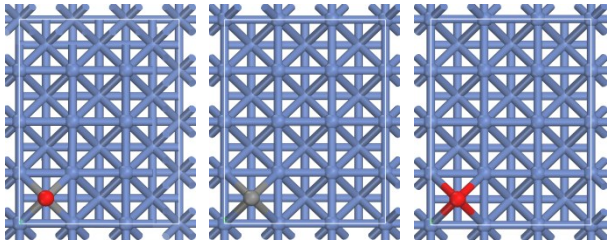
	Ni(111) surface models		E_{ads}/eV
Vacuum thickness	**10 Å**	4 layers-*p*(3×3)	-1.93
	12 Å		-1.93
	15 Å		-1.92
Slab thickness	3 layers	*p*(3×3)-10 Å	-1.82
	4 layers		-1.93
	5 layers		-1.96
Supercell size	***p*(3×3)**	4 layers-10 Å	-1.93
	p(3×4)		-1.95
	p(4×4)		-1.96
	Ni(100) surface models		E_{ads}/eV
Vacuum thickness	**10 Å**	4 layers-*p*(3×3)	-1.96
	12 Å		-1.96
	15 Å		-1.96
Supercell size	3 layers	*p*(3×3)-10 Å	-2.00
	4 layers		-2.01
	5 layers		-1.98
Slab thickness	*p*(3×3)	4 layers-10 Å	-1.96
	***p*(3×4)**		-2.01
	p(4×4)		-2.03
	Ni(110) surface models		E_{ads}/eV
Vacuum thickness	**10 Å**	4 layers-*p*(3×3)	-1.95
	12 Å		-1.95
	15 Å		-1.98
Supercell size	***p*(3×3)**	4 layers-10 Å	-1.95
	p(3×4)		-1.98
	p(4×4)		-2.00
Slab thickness	4 layers	*p*(3×3)-10 Å	-1.95
	5 layers		-1.83
	6 layers		-1.87

Figure S1 The most stable adsorption configurations of CO, C and O atoms on Ni(111), (100) and (110) surfaces. The Ni, C and O atoms are shown in the blue, grey and red balls, respectively. Zero-point energy corrections, thermal energy corrections and entropies are not included.



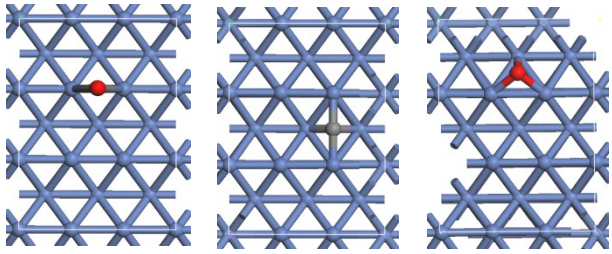
CO (-1.93 eV) **C (-6.87 eV)** **O (-5.80 eV)**

(a) Ni(111)



CO (-2.01 eV) **C (-8.38 eV)** **O (-6.08 eV)**

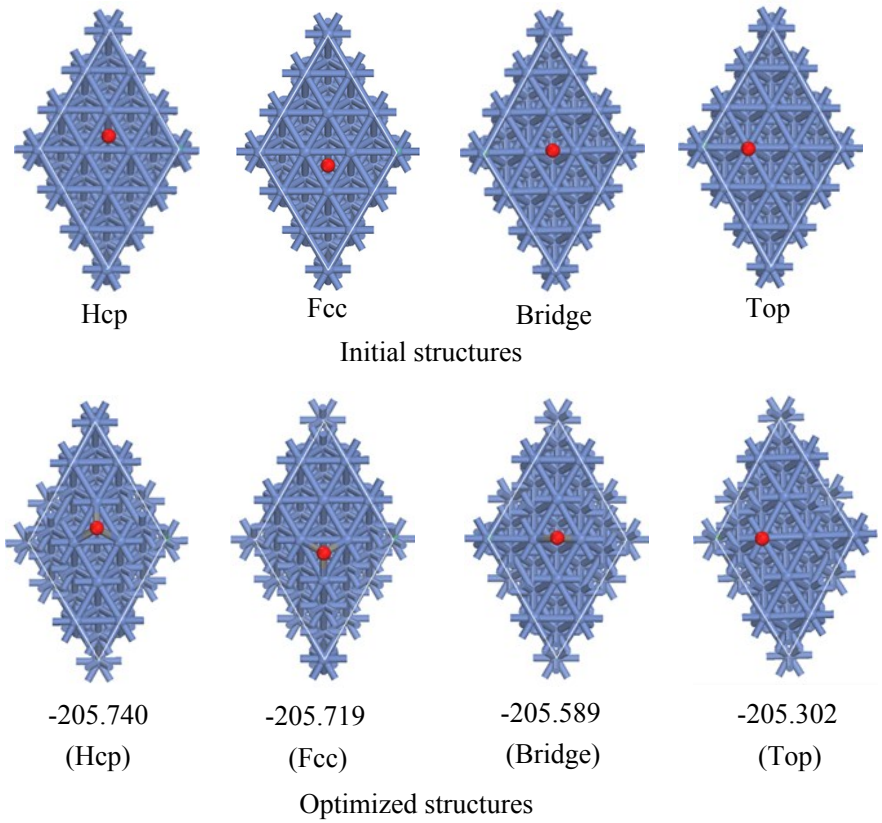
(b) Ni(100)



CO (-1.83 eV) **C (-7.48 eV)** **O (-5.99 eV)**

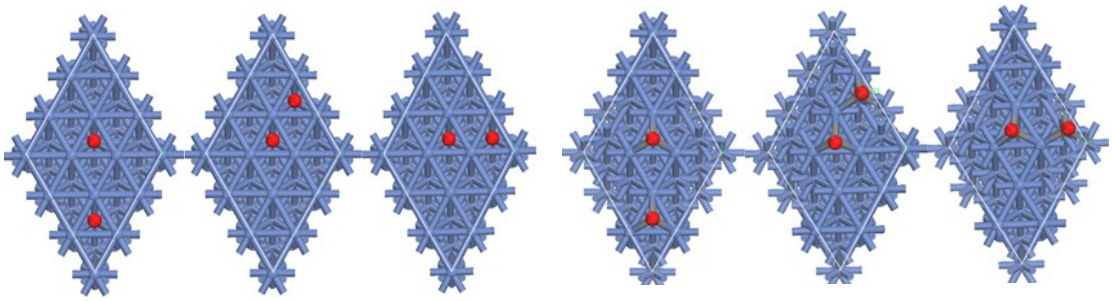
(c) Ni(110)

Figure S2 The initial and optimized structures, as well as the total energy (eV) with adsorbed CO molecules on Ni(111) surface at different coverage. The blue, grey and red balls stand for Ni, C and O atoms, respectively. Zero-point energy corrections, thermal energy corrections and entropies are not included.



(a) CO Adsorption at different sites at the coverage of 1/9 ML

(1) The corresponding structures at the Hcp site

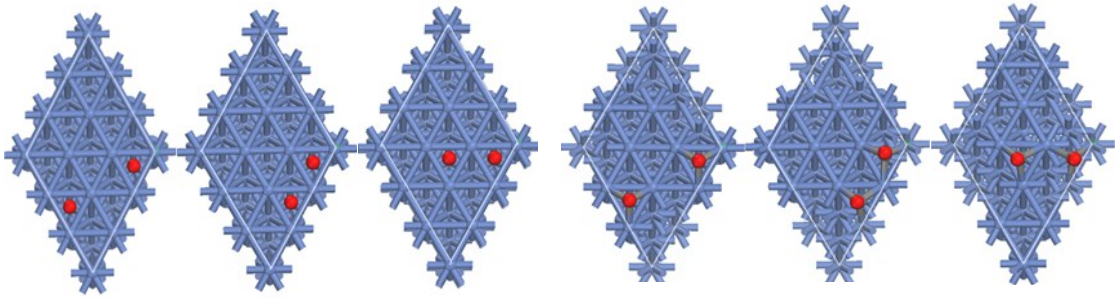


-222.447 -222.276 -222.276

Initial structures

Optimized structures

(2) The corresponding structures at the Fcc site

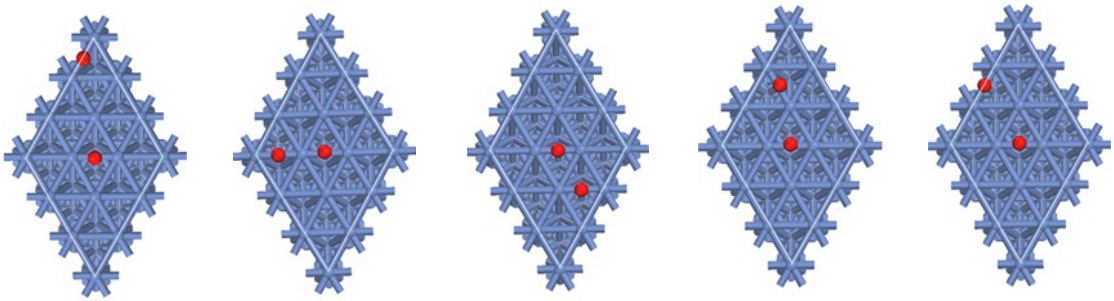


-222.400 -222.253 -222.252

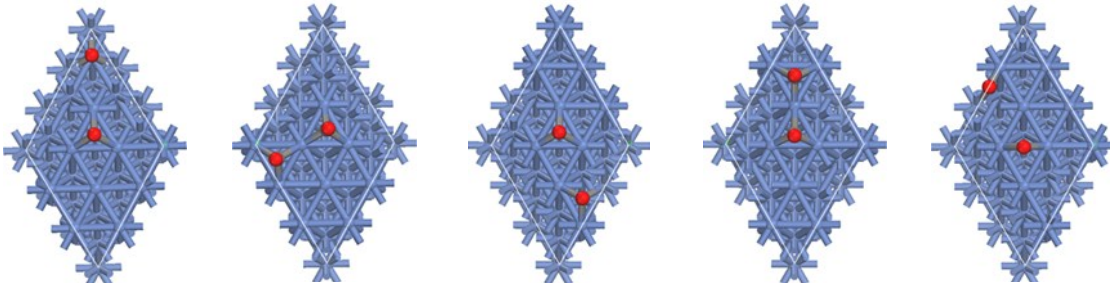
Initial structures

Optimized structures

(3) The corresponding structures at the Bridge site



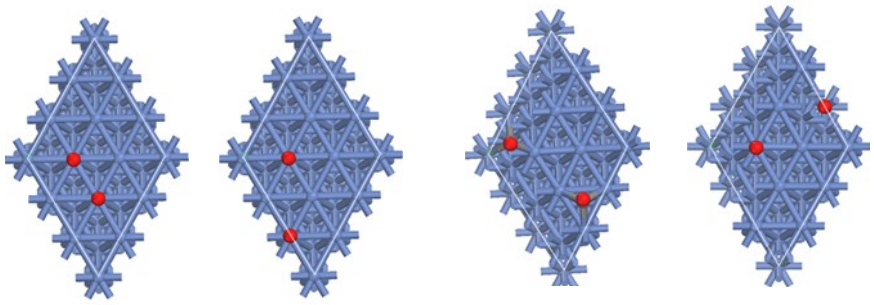
Initial structures



-222.446 -222.399 -222.389 -222.399 -222.147

Optimized structures

(4) The corresponding structures at the Top site

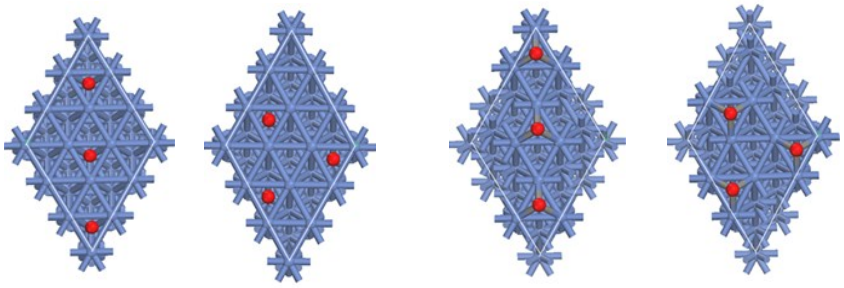


Initial structures

Optimized structures

(**b**) CO Adsorption at different sites at the coverage of 2/9 ML

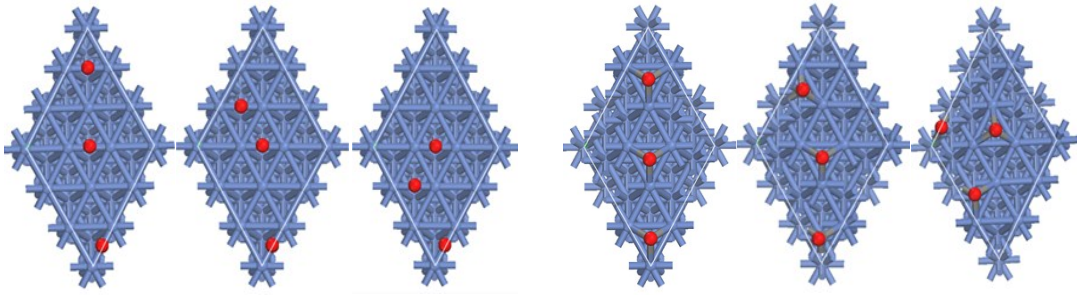
(1) The corresponding structures at the Hcp and Fcc site respectively



Initial structures

Optimized structures

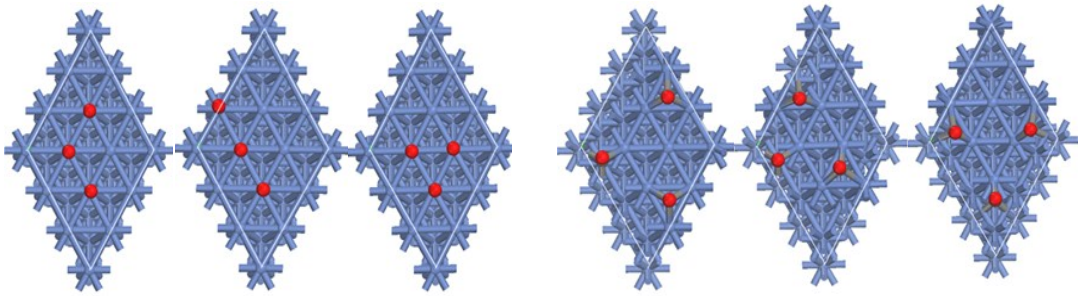
(2) The corresponding structures at the Bridge site



Initial structures

Optimized structures

(3) The corresponding structures at the Top site

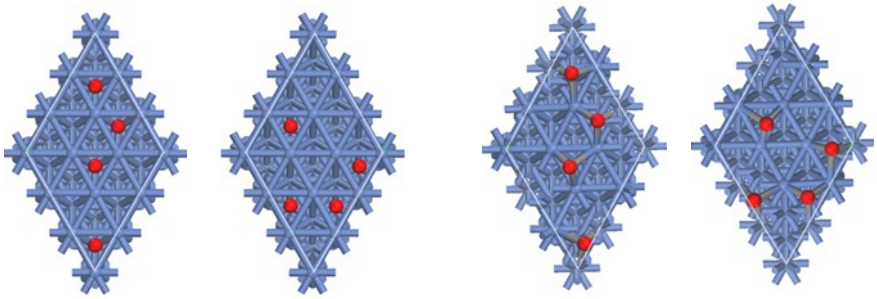


Initial structures

Optimized structures

(**c**) CO Adsorption at different sites at the coverage of 3/9 ML

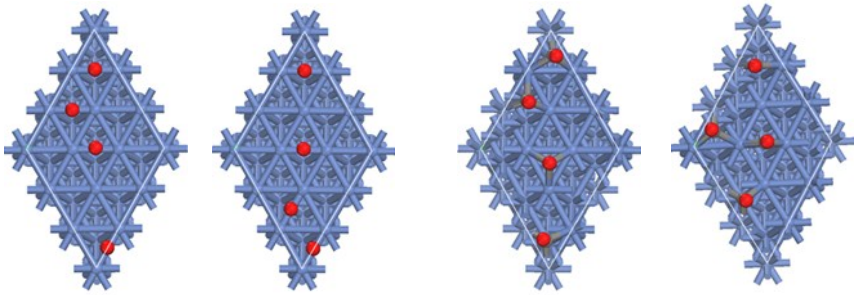
(1) The corresponding structures at the Hcp and Fcc site respectively



Hcp Fcc -255.132 (Hcp) -255.093 (Fcc)

Initial structures Optimized structures

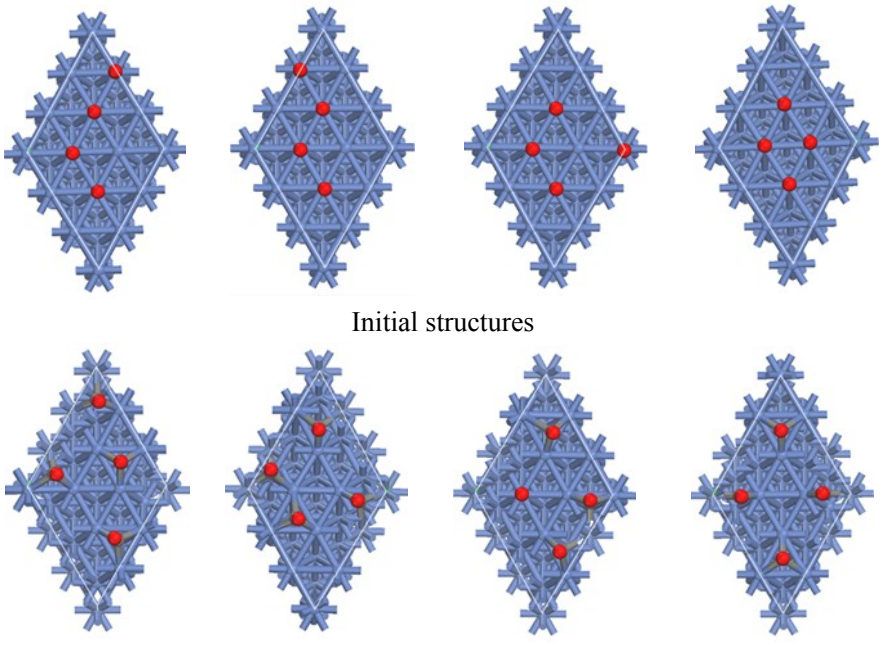
(2) The corresponding structures at the Bridge site



Initial structures -255.366 -255.170

Optimized structures

(3) The corresponding structures at the Top site



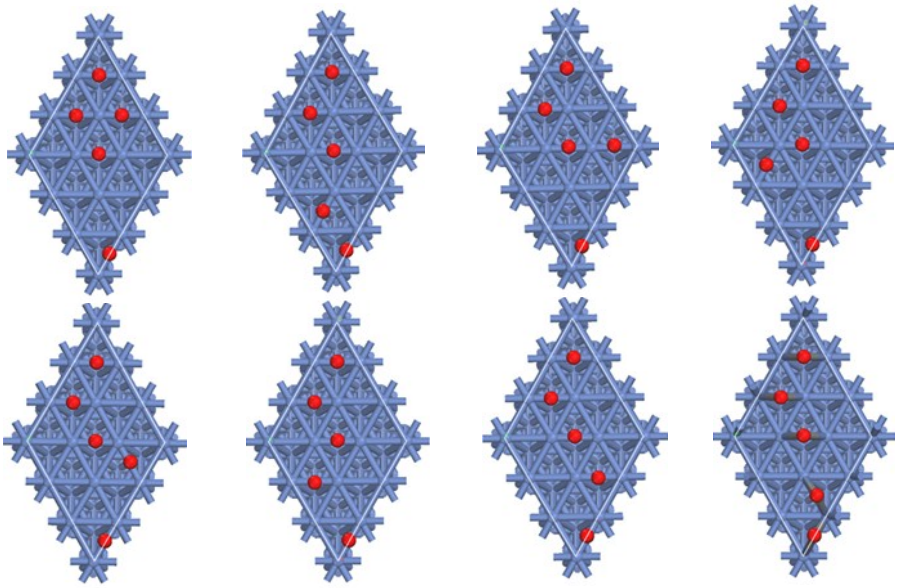
Initial structures

-255.365 -255.285 -255.088 -255.189

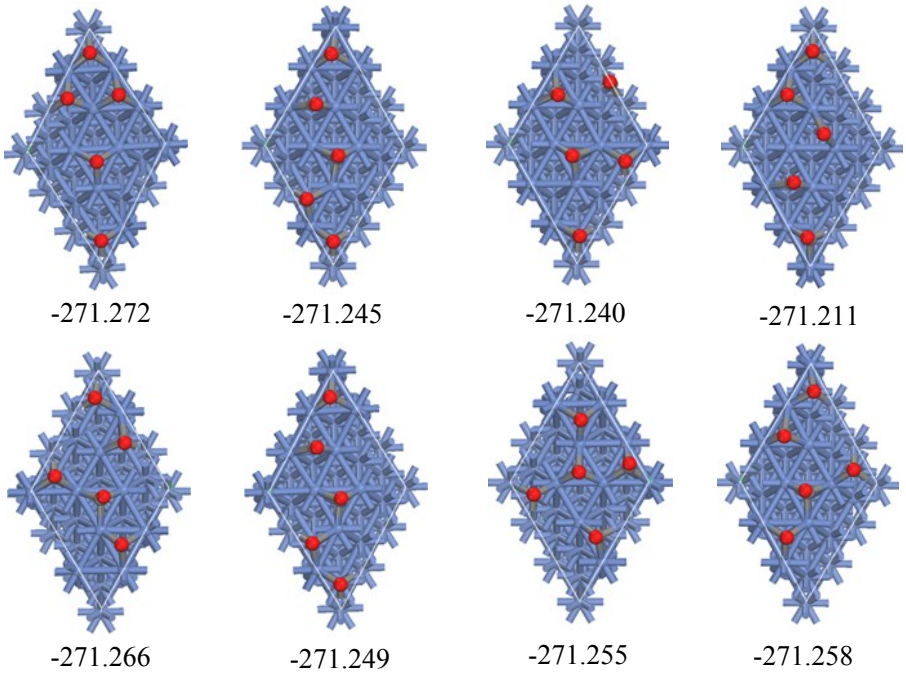
Optimized structures

(**d**) CO Adsorption at different sites at the coverage of 4/9 ML

(1) The corresponding structures at the Bridge site

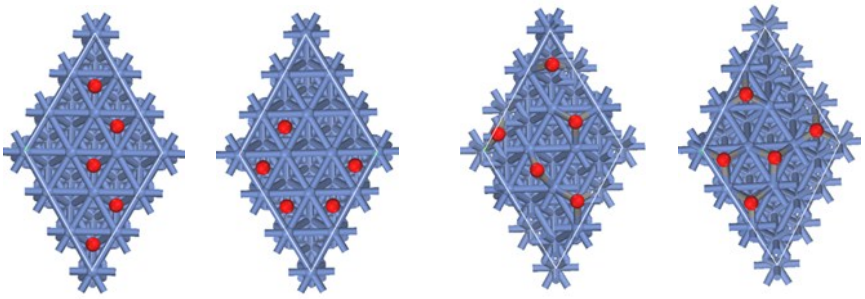


Initial structures

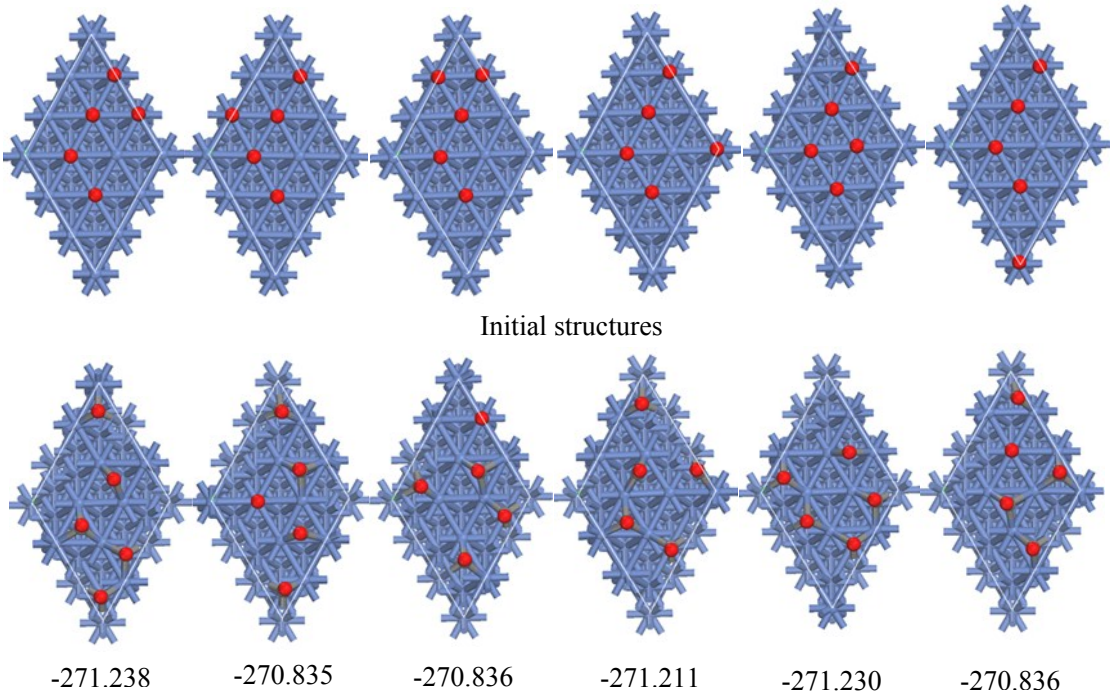


Optimized structures

(2) The corresponding structures at the Hcp and Fcc site respectively

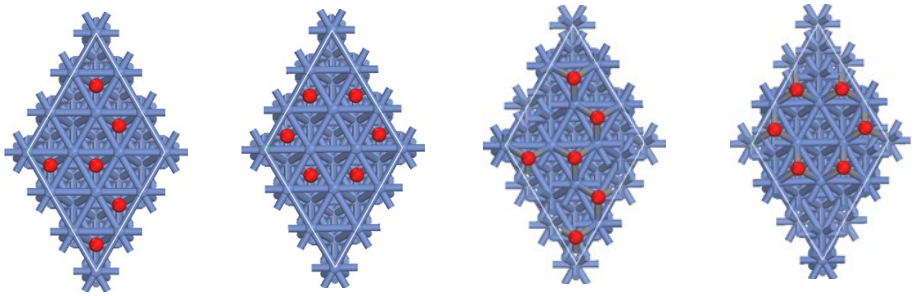


(3) The corresponding structures at the Top site

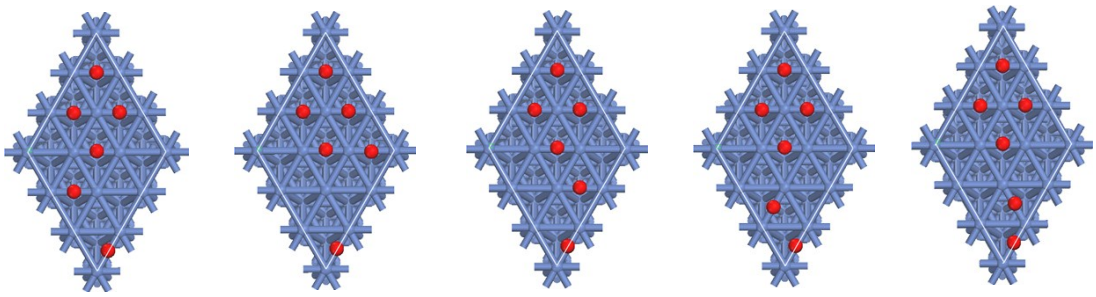


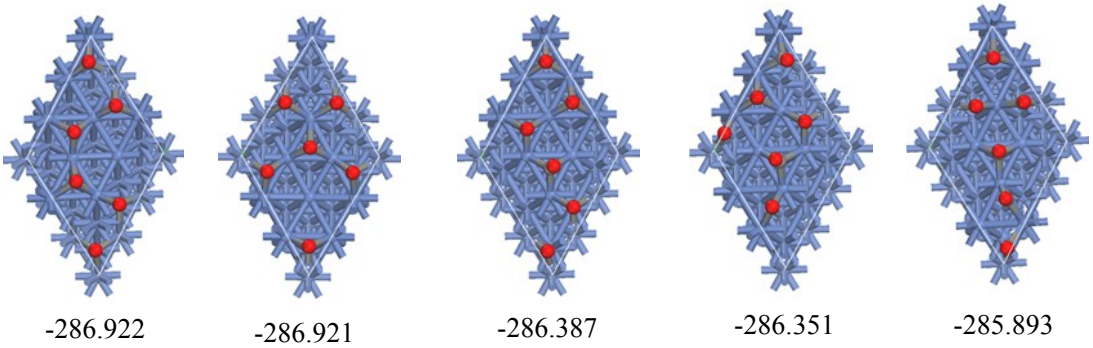
(**e**) CO Adsorption at different sites at the coverage of 5/9 ML

(1) The corresponding structures at the Hcp and Fcc site respectively

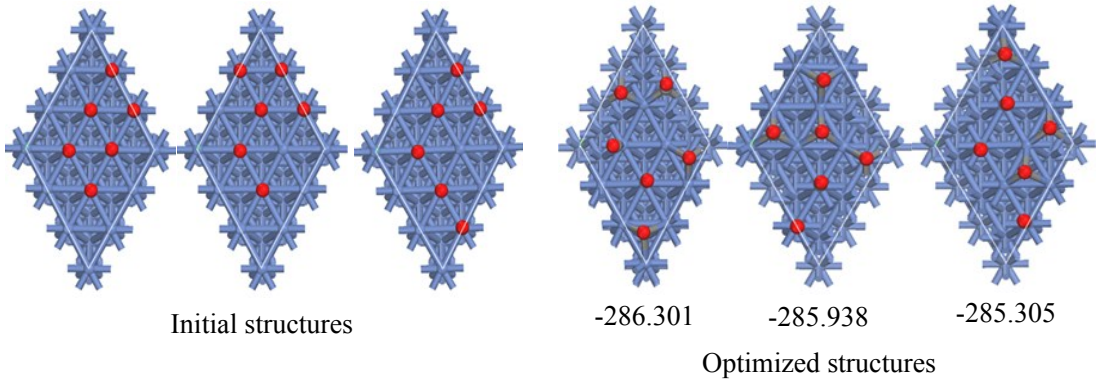


(2) The corresponding structures at the Bridge site



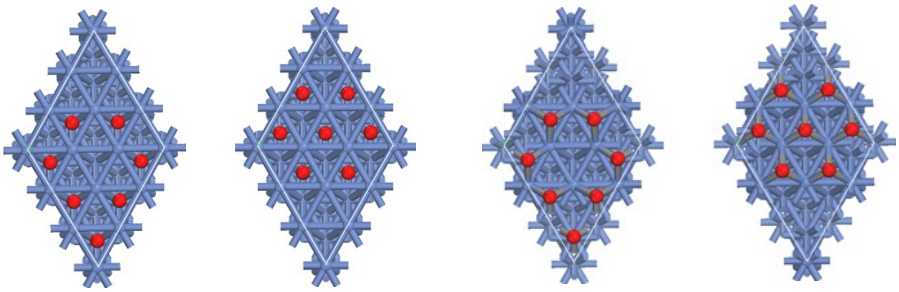


(3) The corresponding structures at the Top site



(**f**) CO Adsorption at different sites at the coverage of 6/9 ML

(1) The corresponding structures at the Hcp and Fcc site respectively

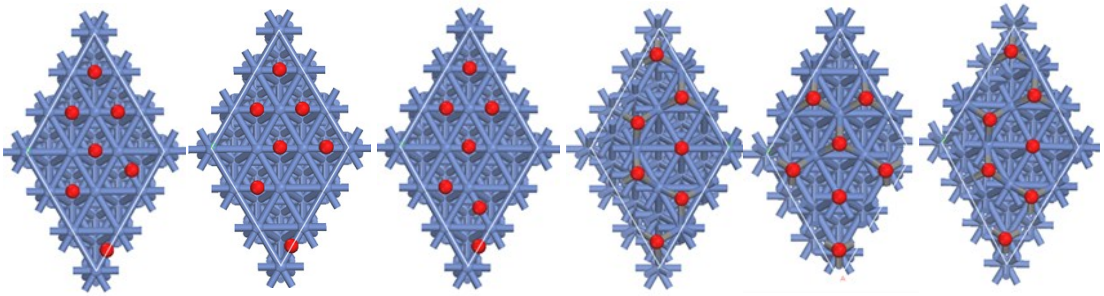


Hcp Fcc -299.303 -299.373

Initial structures (Hcp) (Fcc)

Optimized structures

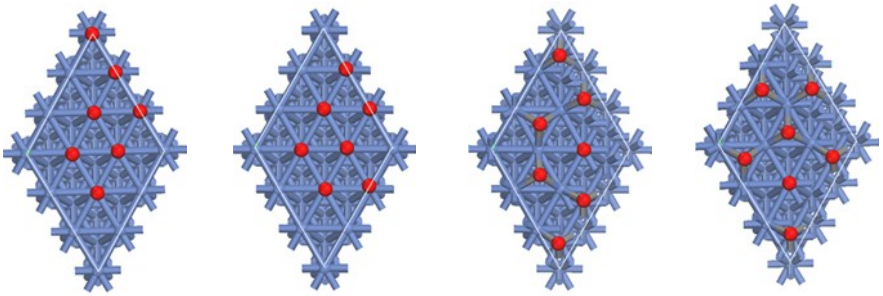
(2) The corresponding structures at the Bridge site



Initial structures -301.870 -301.865 -301.868

Optimized structures

(3) The corresponding structures at the Top site

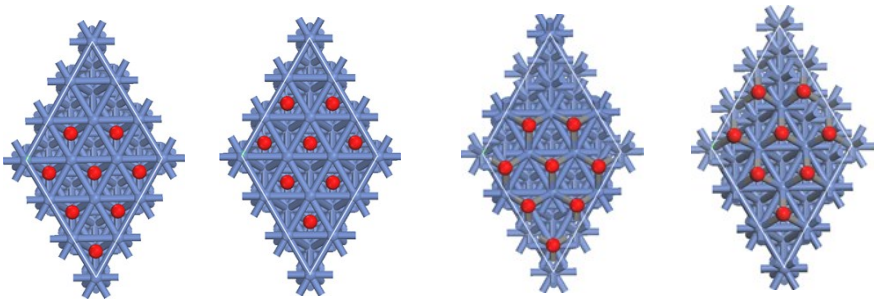


Initial structures -301.869 -301.866

Optimized structures

(**g**) CO Adsorption at different sites at the coverage of 7/9 ML

(1) The corresponding structures at the Hcp and Fcc site respectively

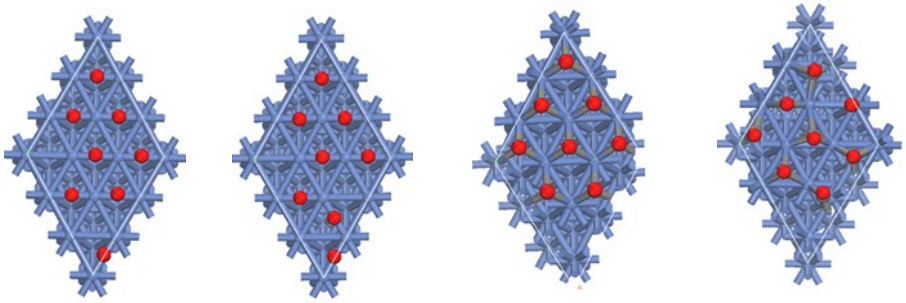


Hcp Fcc -313.357 -313.455

Initial structures (Hcp) (Fcc)

Optimized structures

(2) The corresponding structures at the Bridge site

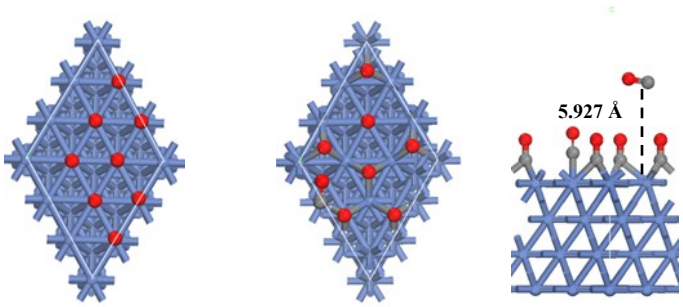


-313.450 -313.010

Initial structures

Optimized structures

(3) The corresponding structures at the Top site



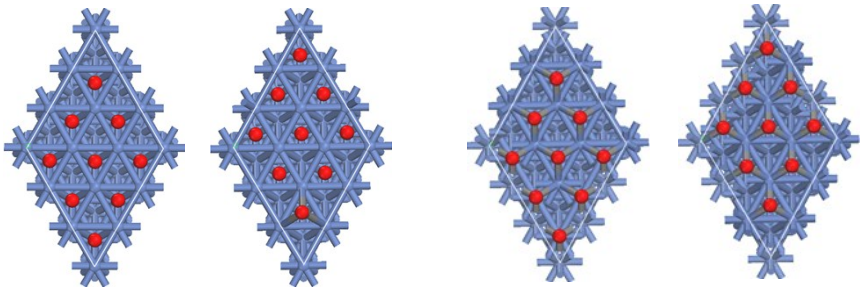
Top view Side view

Initial structure

Optimized structure -316.697

(**h**) CO Adsorption at different sites at the coverage of 8/9 ML

(1) The corresponding structures at the Hcp and Fcc site respectively

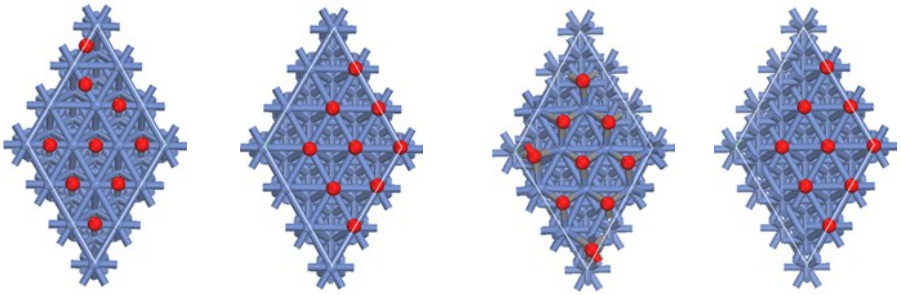


Hcp Fcc -326.703 -326.805

Initial structures (Hcp) (Fcc)

Optimized structures

(2) The corresponding structures at the Bridge and Top site respectively



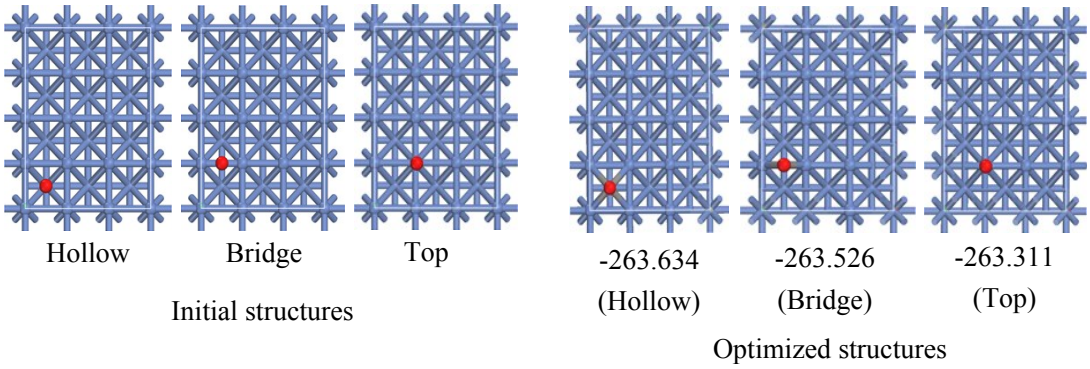
Bridge Top -322.243 -322.486

Initial structures (Bridge) (Top)

Optimized structures

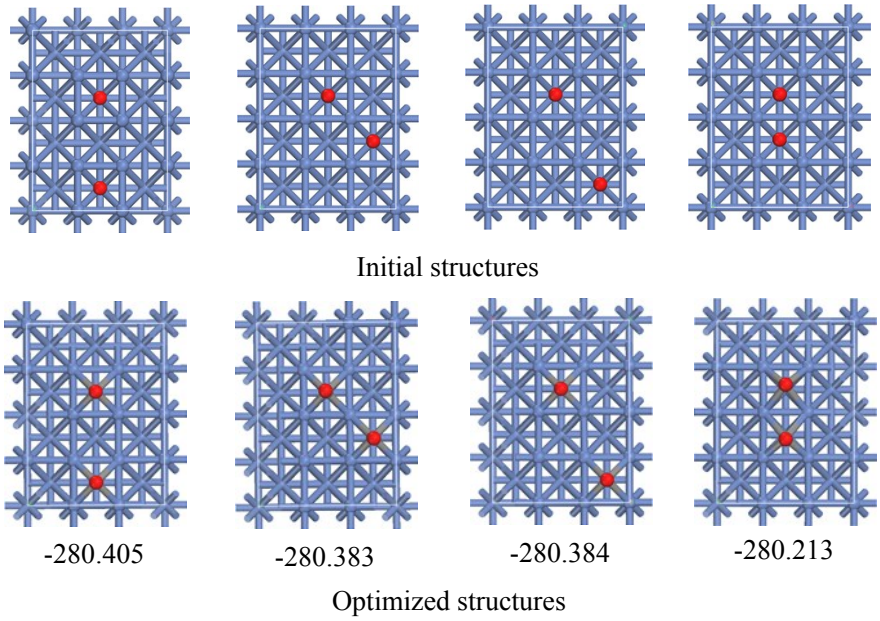
(i) CO Adsorption at different sites at the coverage of 9/9 ML

Figure S3 The computed structures and total energy (eV) with adsorbed CO molecules on Ni(100) surface at different coverage. The blue, grey and red balls stand for Ni, C and O atoms, respectively. Zero-point energy corrections, thermal energy corrections and entropies are not included.

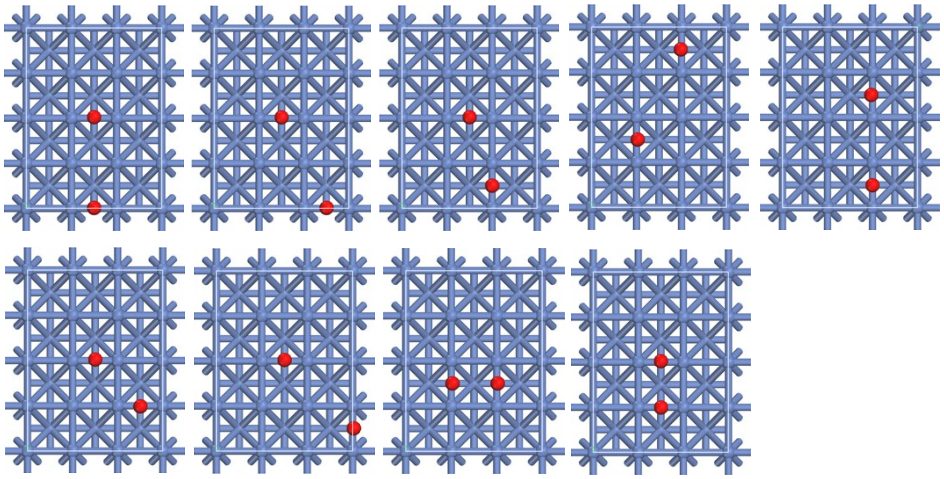


(a) CO Adsorption at different sites at the coverage of 1/12 ML

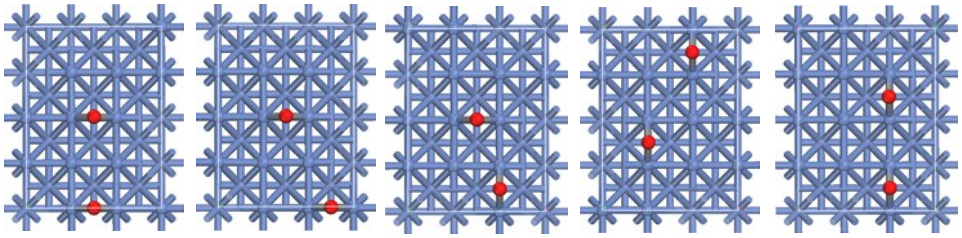
(1) The corresponding structures at the Hollow site



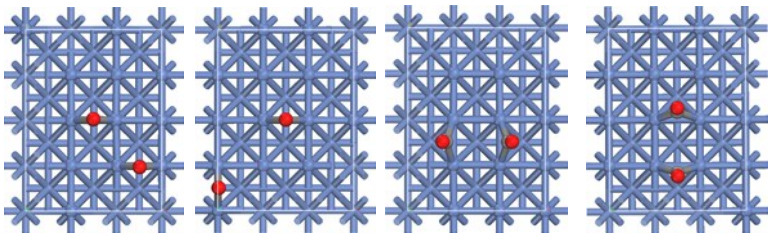
(2) The corresponding structures at the Bridge site



Initial structures



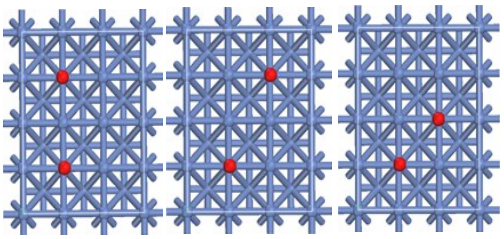
-280.210 -280.192 -280.192 -280.173 -280.164



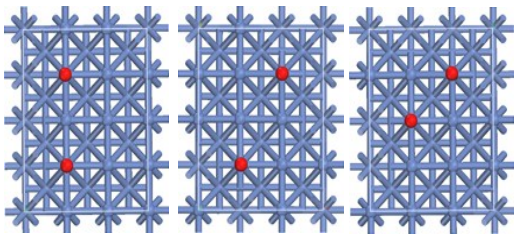
-280.161 -280.154 -280.151 -280.115

Optimized structures

(3) The corresponding structures at the Top site



Initial structures

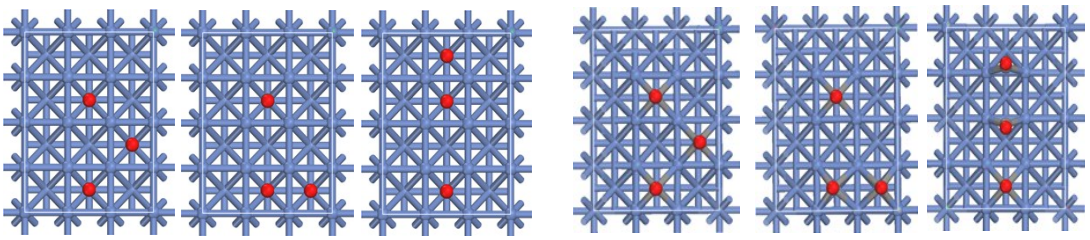


-279.795 -279.764 -279.742

Optimized structures

(**b**) CO Adsorption at different sites at the coverage of 2/12 ML

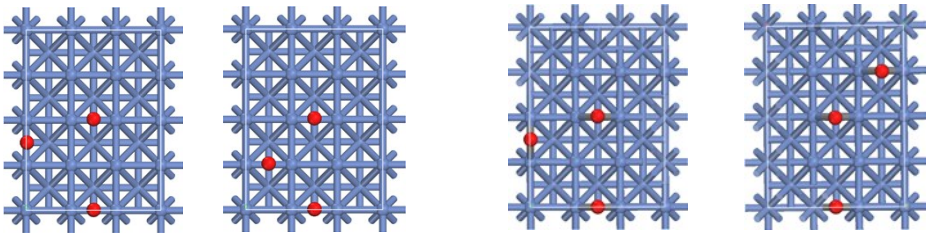
(1) The corresponding structures at the Hollow site



Initial structures

Optimized structures

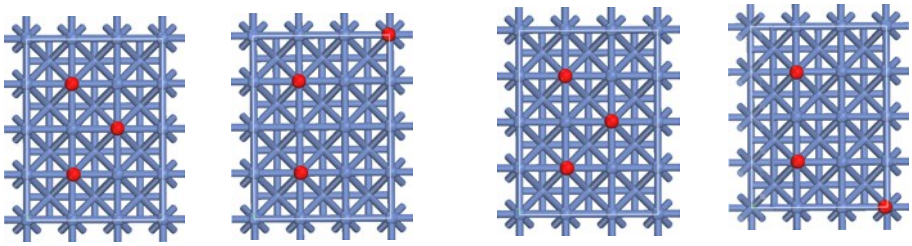
(2) The corresponding structures at the Bridge site



Initial structures

Optimized structures

(3) The corresponding structures at the Top site

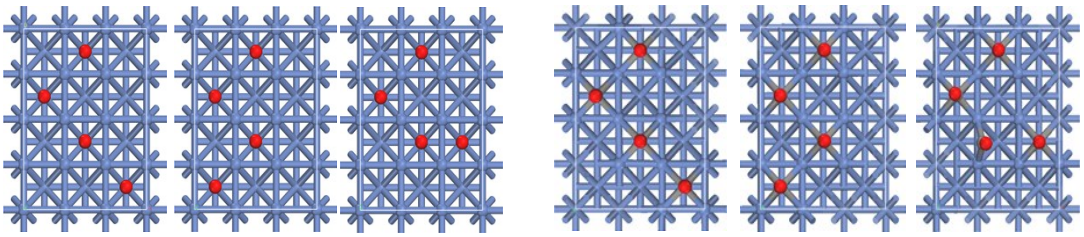


Initial structures

Optimized structures

(**c**) CO Adsorption at different sites at the coverage of 3/12 ML

(1) The corresponding structures at the Hollow site

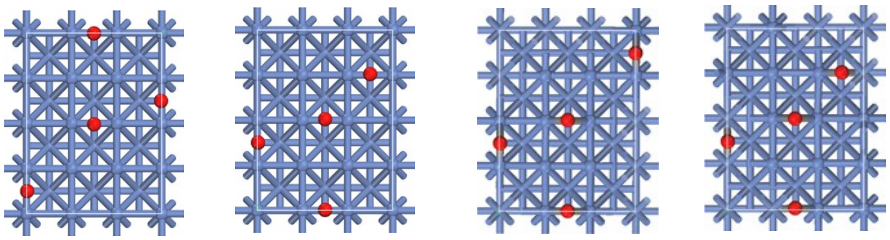


Initial structures

-313.779 -313.760 -313.668

Optimized structures

(2) The corresponding structures at the Bridge site

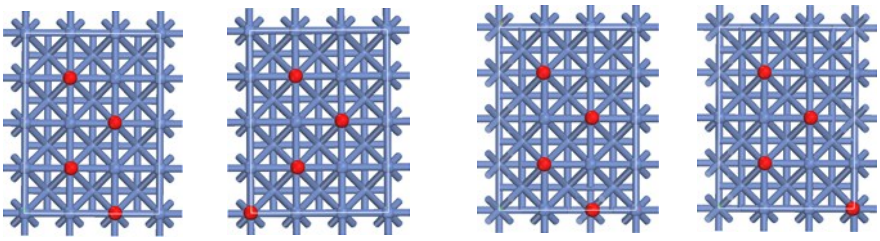


Initial structures

-313.438 -313.424

Optimized structures

(3) The corresponding structures at the Top site



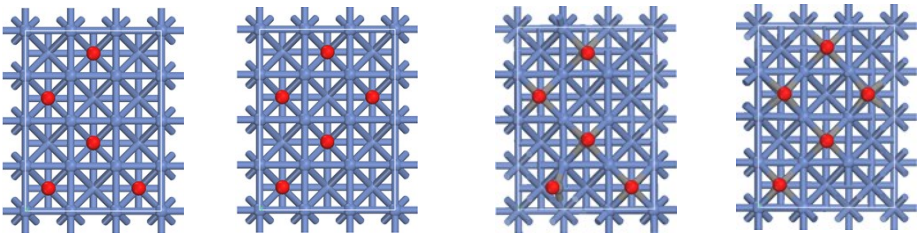
Initial structures

-312.666 -312.612

Optimized structures

(**d**) CO Adsorption at different sites at the coverage of 4/12 ML

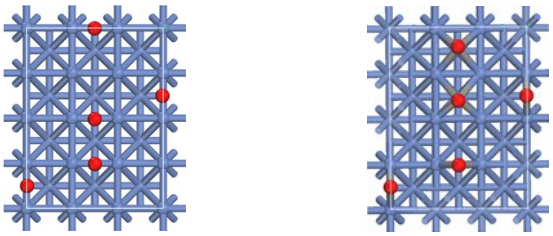
(1) The corresponding structures at the Hollow site



Initial structures -330.247 -330.177

Optimized structures

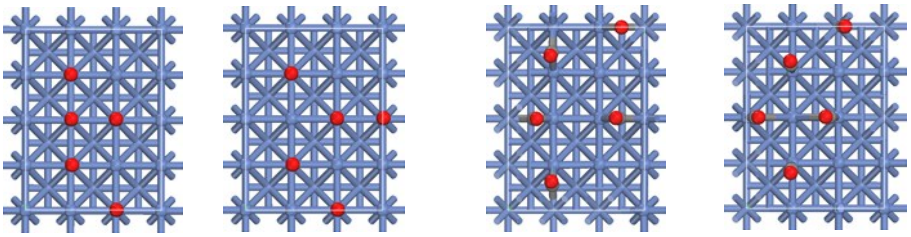
(2) The corresponding structures at the Bridge site



Initial structures -330.068

Optimized structures

(3) The corresponding structures at the Top site

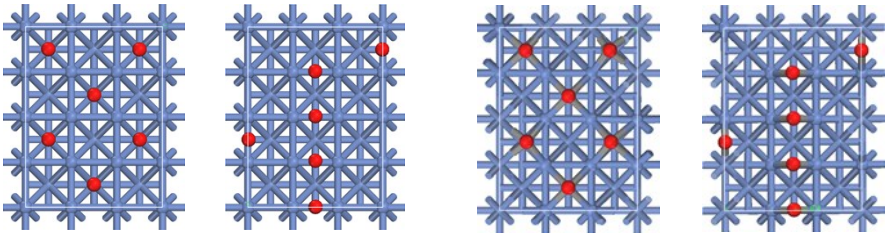


Initial structures -329.971 -329.026

Optimized structures

(**e**) CO Adsorption at different sites at the coverage of 5/12 ML

(1) The corresponding structures at the Hollow and Bridge site

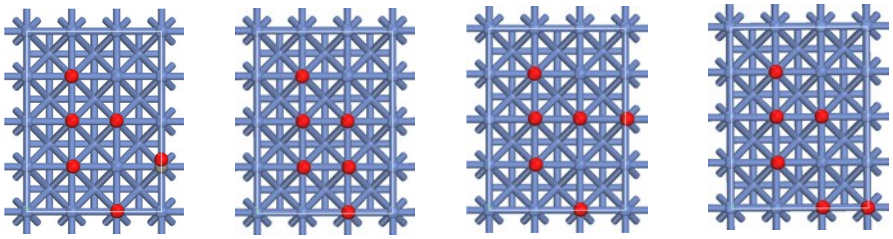


Hollow Bridge -346.531 -344.724

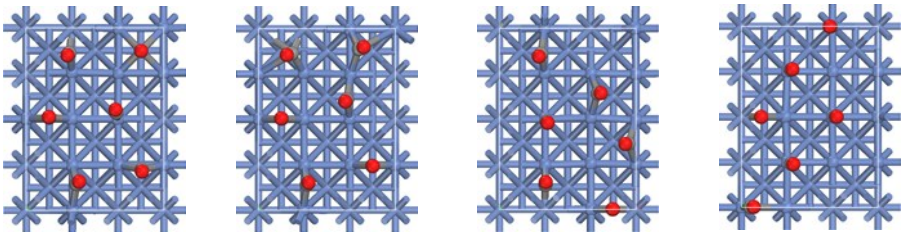
Initial structures (Hollow) (Bridge)

Optimized structures

(2) The corresponding structures at the Top site



Initial structures

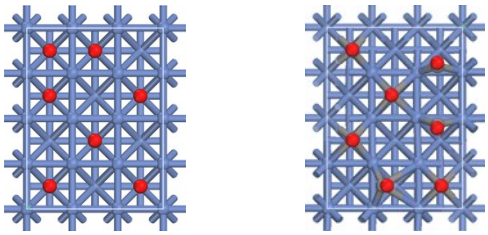


-346.575 -346.553 -346.265 -344.879

Optimized structures

(**f**) CO Adsorption at different sites at the coverage of 6/12 ML

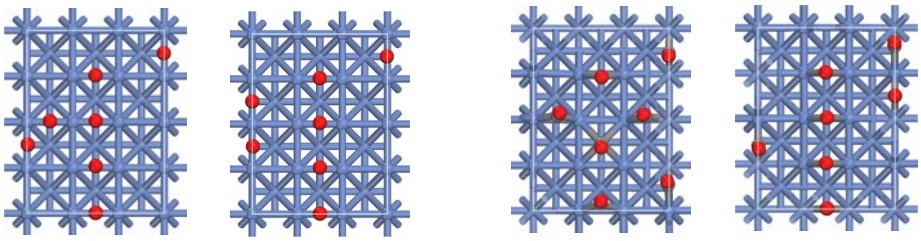
(1) The corresponding structures at the Hollow site



Initial structures -362.821

Optimized structures

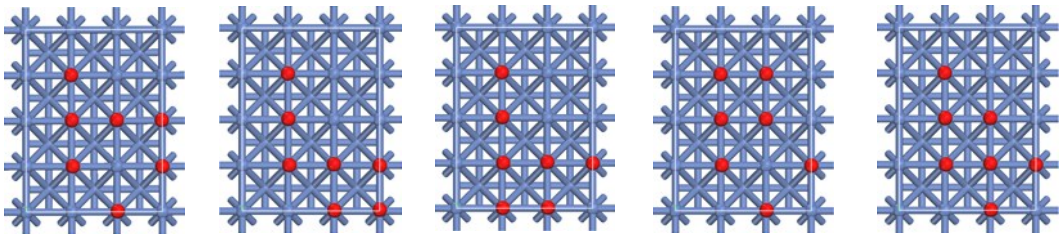
(2) The corresponding structures at the Bridge site



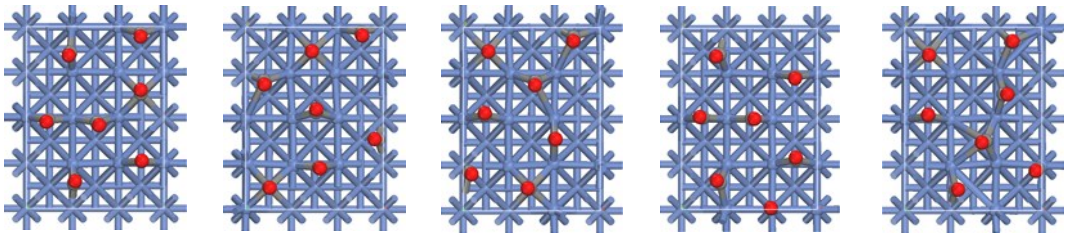
Initial structures -362.777 -361.104

Optimized structures

(3) The corresponding structures at the Top site



Initial structures

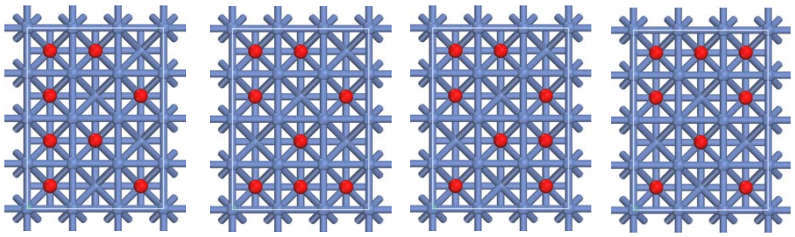


-362.779 -362.729 -362.651 -362.534 -362.501

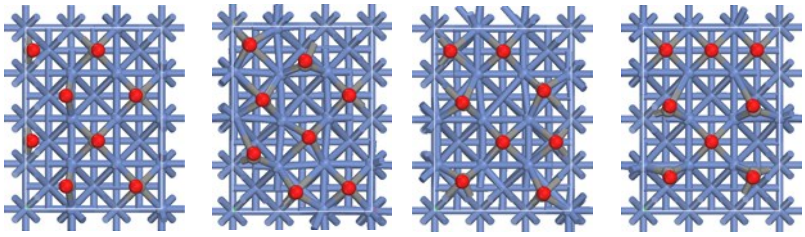
Optimized structures

(**g**) CO Adsorption at different sites at the coverage of 7/12 ML

(1) The corresponding structures at the Hollow site



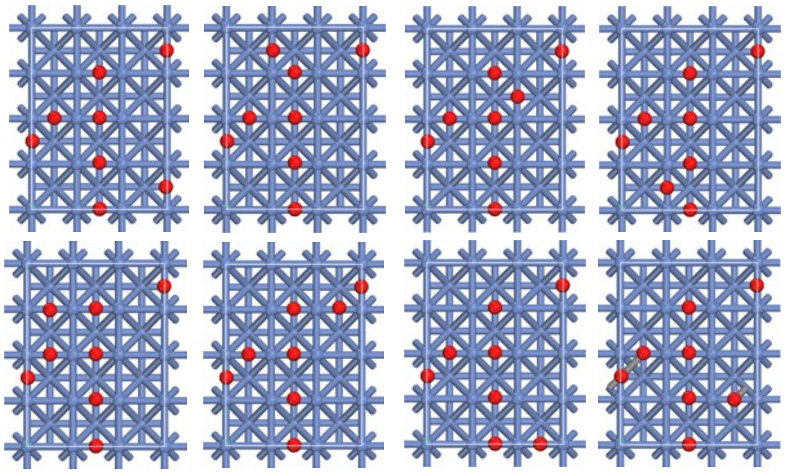
Initial structures



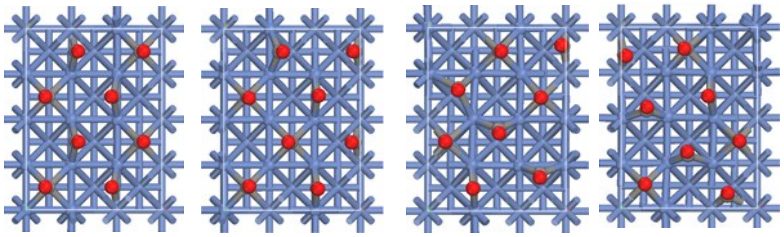
-379.241 -378.761 -378.710 -377.871

Optimized structures

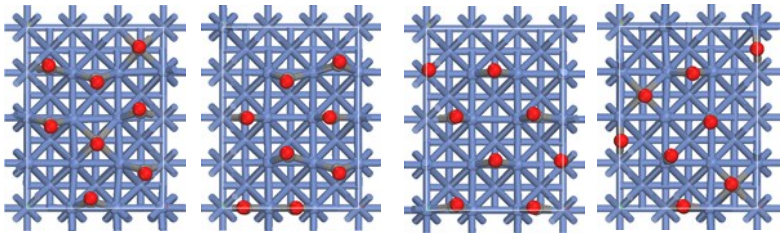
(2) The corresponding structures at the Bridge site



Initial structures



-379.247 -379.156 -378.837 -378.826

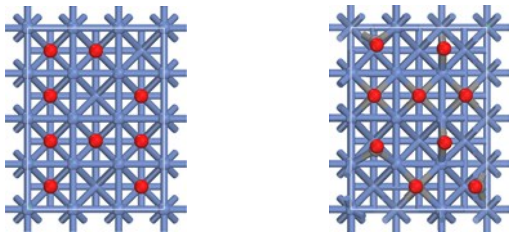


-378.533 -378.510 -378.231 -377.891

Optimized structures

(**h**) CO Adsorption at different sites at the coverage of 8/12 ML

(1) The corresponding structures at the Hollow site

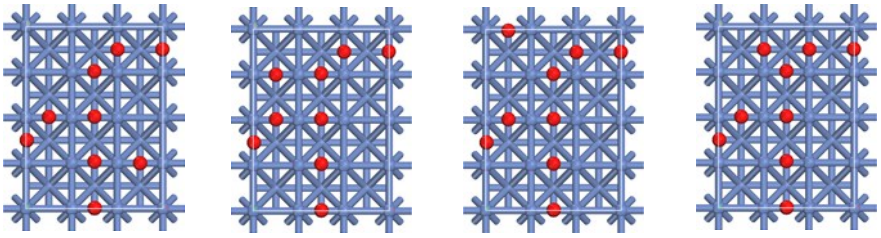


Initial structures

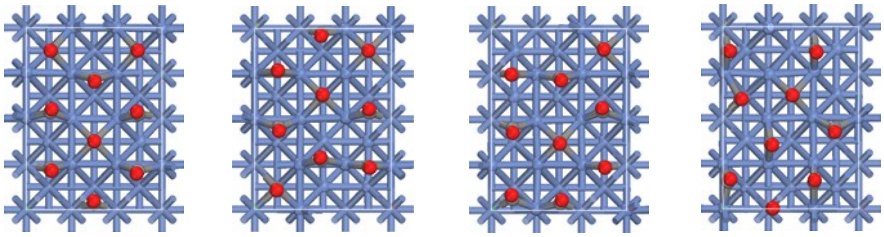
-393.547

Optimized structures

(2) The corresponding structures at the Bridge site



Initial structures

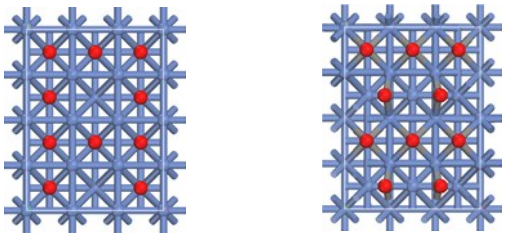


-394.545 -394.485 -394.412 -393.783

Optimized structures

(i) CO Adsorption at different sites at the coverage of 9/12 ML

(1) The corresponding structures at the Hollow site

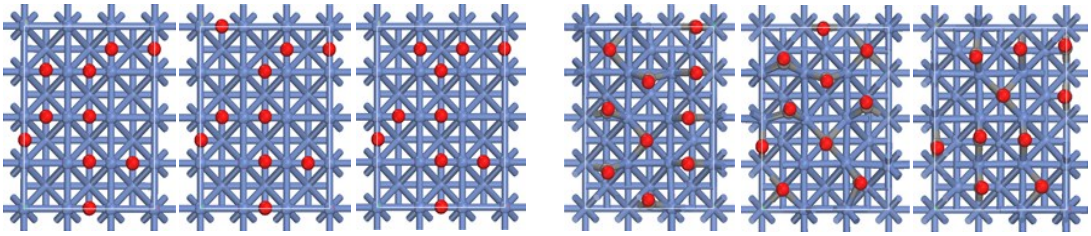


Initial structures

-407.470

Optimized structures

(2) The corresponding structures at the Bridge site



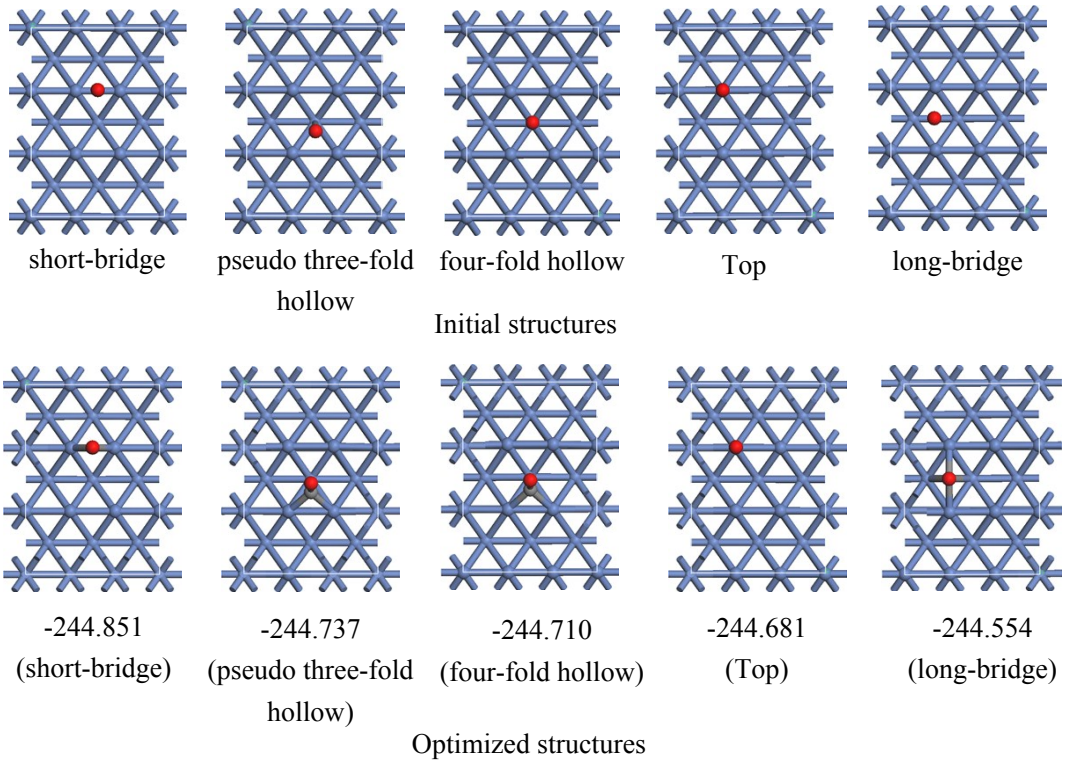
Initial structures

-408.988 -408.760 -408.083

Optimized structures

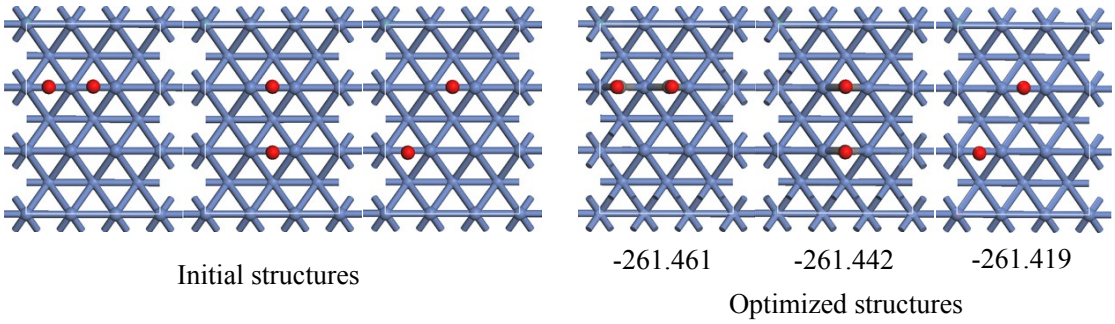
(**j**) CO Adsorption at different sites at the coverage of 10/12 ML

Figure S4 The computed structures and total energy (eV) with adsorbed CO molecules on Ni(110) surface at different coverage. The blue, grey and red balls stand for Ni, C and O atoms, respectively. Zero-point energy corrections, thermal energy corrections and entropies are not included.



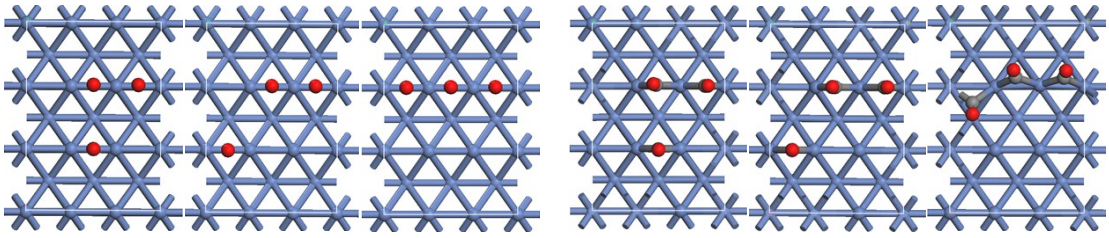
(**a**) CO Adsorption at different sites at the coverage of 1/9 ML

(1) The corresponding structures at the short-bridge site



(**b**) CO Adsorption at the coverage of 2/9 ML

(1) The corresponding structures at the short-bridge site



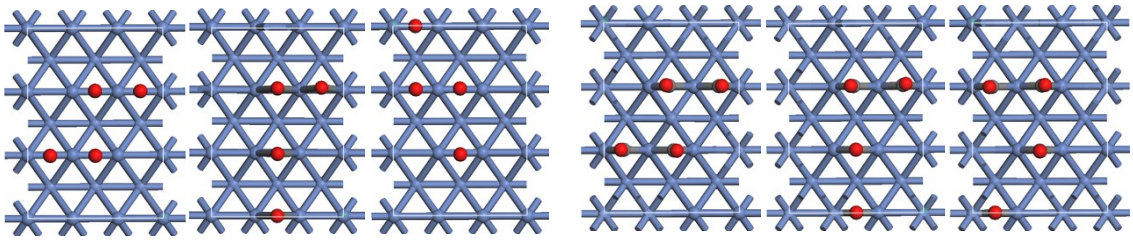
Initial structures

-278.015 -278.014 -277.875

Optimized structures

(**c**) CO Adsorption at the coverage of 3/9 ML

(1) The corresponding structures at the short-bridge site



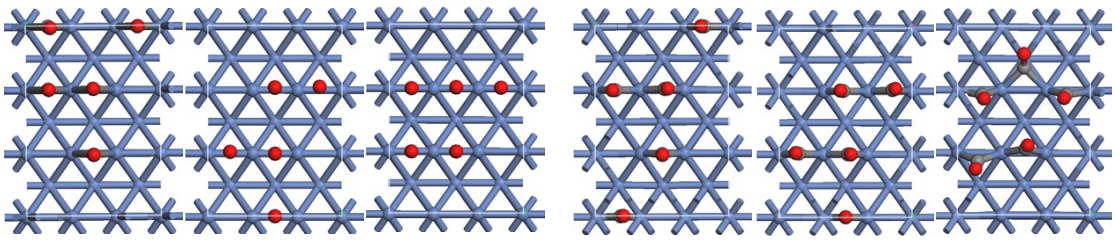
Initial structures

-294.633 -294.579 -294.574

Optimized structures

(**d**) CO Adsorption at the coverage of 4/9 ML

(1) The corresponding structures at the short-bridge site



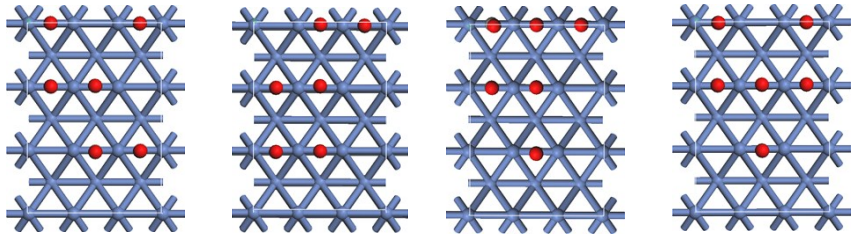
Initial structures

-311.141 -311.137 -311.006

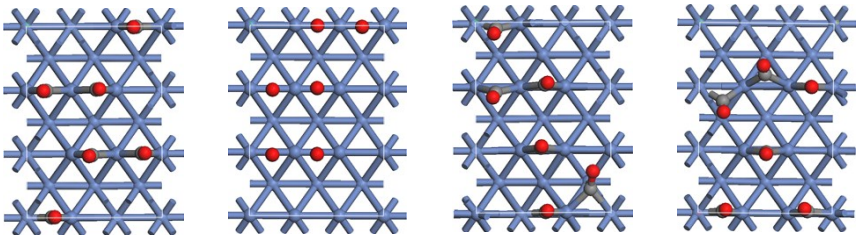
Optimized structures

(**e**) CO Adsorption at the coverage of 5/9 ML

(1) The corresponding structures at the short-bridge site



Initial structures

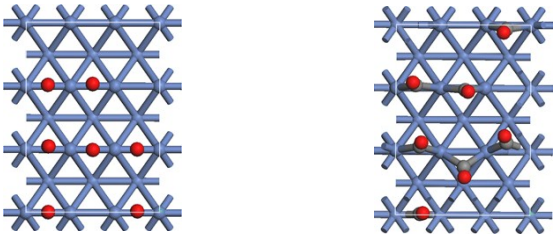


-327.690 -327.682 -327.533 -327.486

Optimized structures

(**f**) CO Adsorption at the coverage of 6/9 ML

(1) The corresponding structures at the short-bridge site



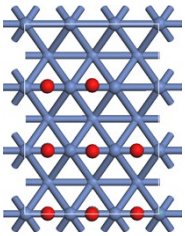
Initial structures

-343.985

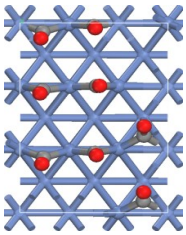
Optimized structures

(**g**) CO Adsorption at the coverage of 7/9 ML

(1) The corresponding structures at the short-bridge site



Initial structures

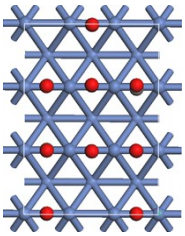


-360.102

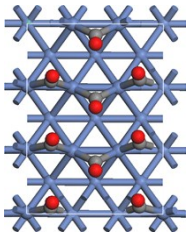
Optimized structures

(**h**) CO Adsorption at the coverage of 8/9 ML

(1) The corresponding structures at the short-bridge site



Initial structures



-376.309

Optimized structures

(**i**) CO Adsorption at the coverage of 9/9 ML

Figure S5 The computed structures of initial states (ISs), transition states (TSs) and final states (FSs) involved in the dissociations of CO molecules on Ni(111) surface at different coverage.

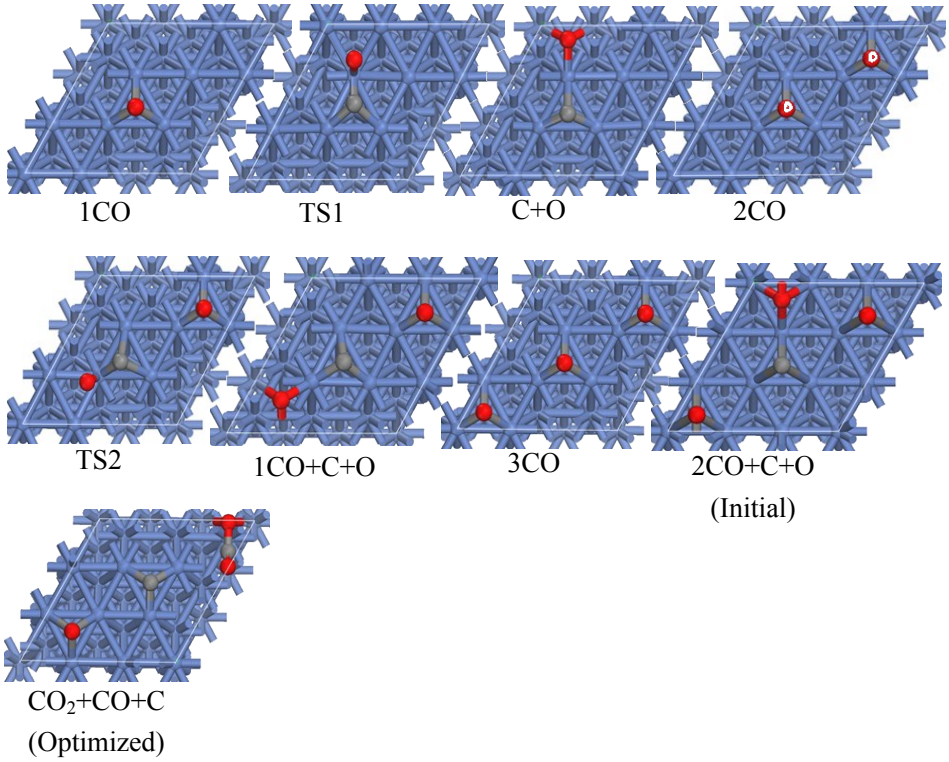


Figure S6 The computed structures of initial states (ISs), transition states (TSs) and final states (FSs) involved in the dissociations of CO molecules on Ni(100) surface at different coverage.

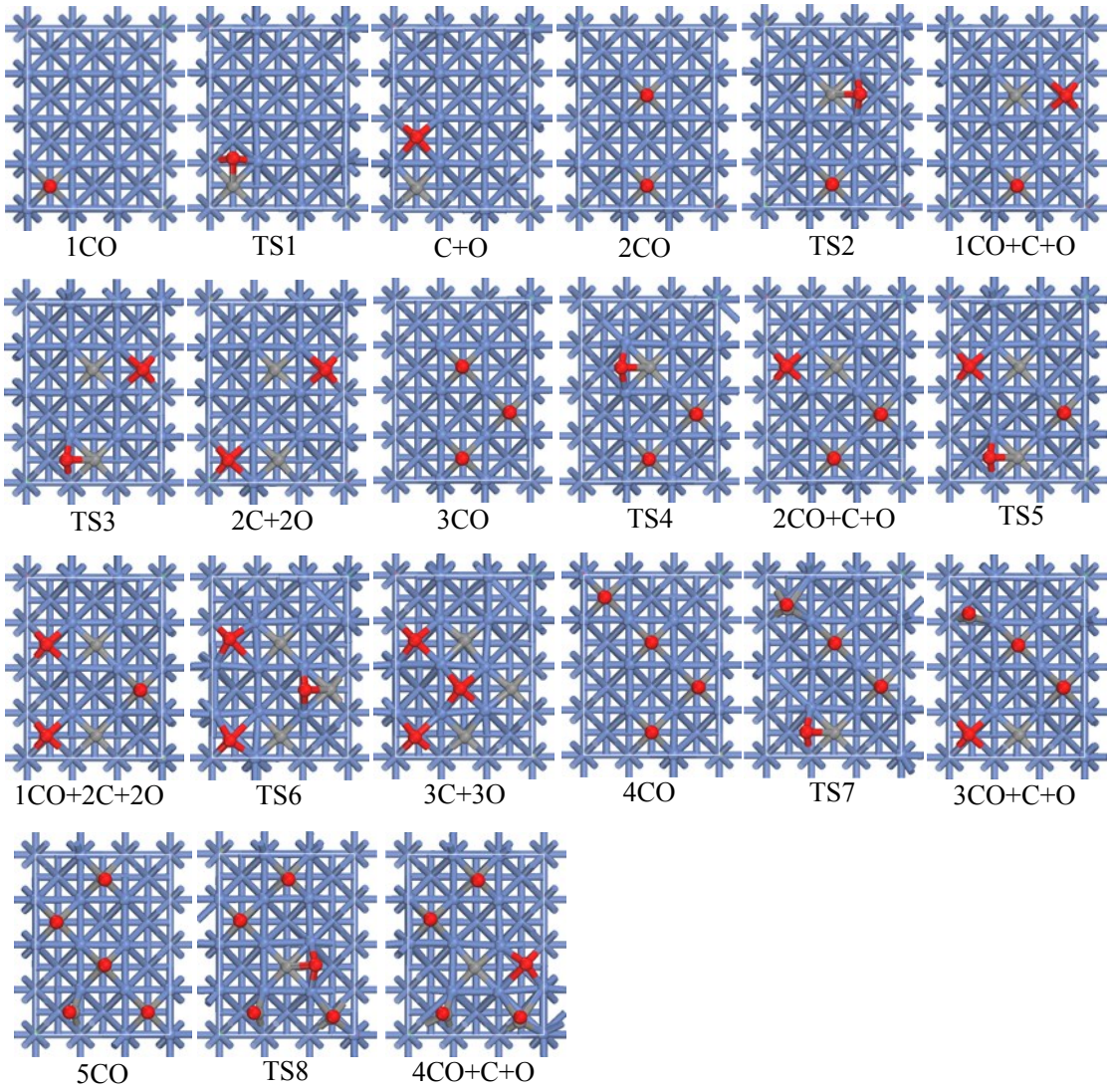
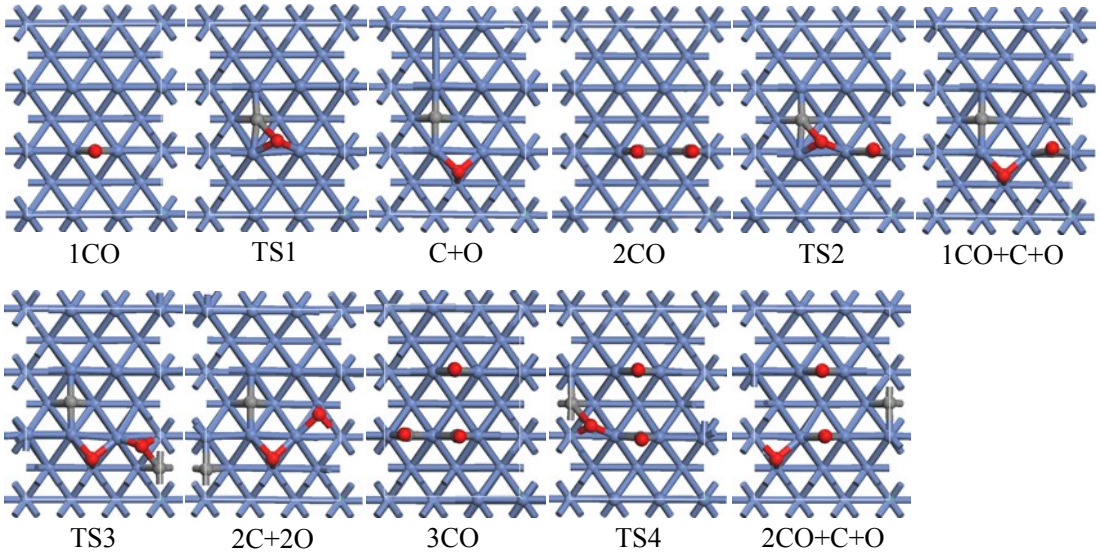



Figure S7 The computed structures of initial states (ISs), transition states (TSs) and final states (FSs) involved in the dissociations of CO molecules on Ni(110) surface at different coverage.