Electronic Supplementary Information

Mechanistic Studies on Millerite Chlorination with Ammonium Chloride

Xiaolu Xiong [a], Guangshi Li[a], Xionggang Lu[a,b,*], Hongwei Cheng[a], Qian Xu[a], Shenggang Li[b,c,*]

[a.] *State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advances Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, 99 Shangda Road, Shanghai 200444, P. R. China*

[b.] *School of Physical Science and Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210, China.*

[c.] *CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institue, Chinese Academy of Sciences, 100 Haike Road, Shanghai 201210, China.*

* Corresponding authors: luxg@shu.edu.cn (X. Lu); lisg@sari.ac.cn (S. Li)

List of Supplementary Figures and Tables

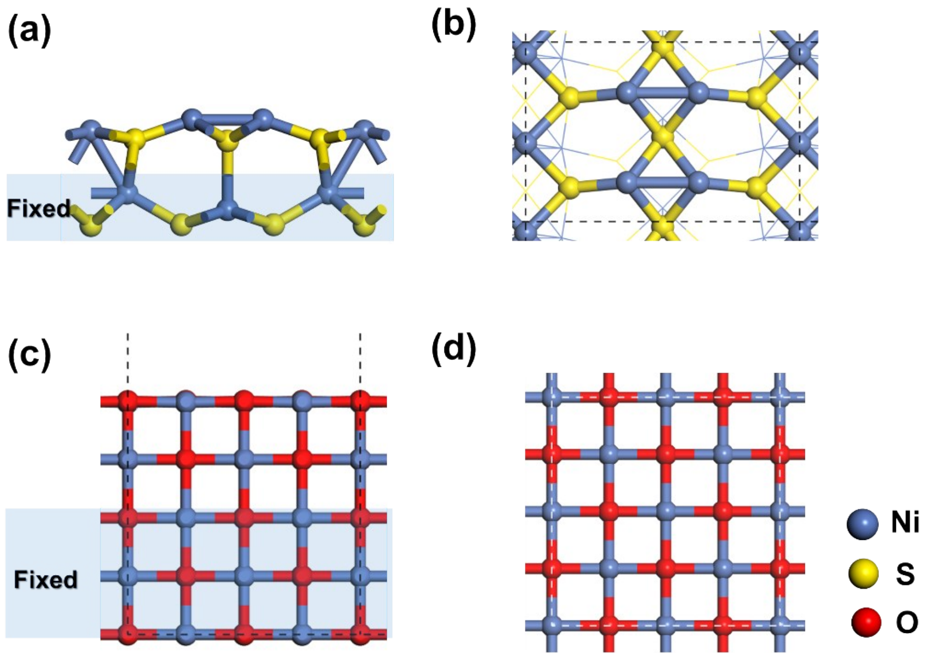

Figure S1. (a) Side view and (b) top view of the NiS(100) surface; (c) Side view and (d) top view of the NiO(100) surface.

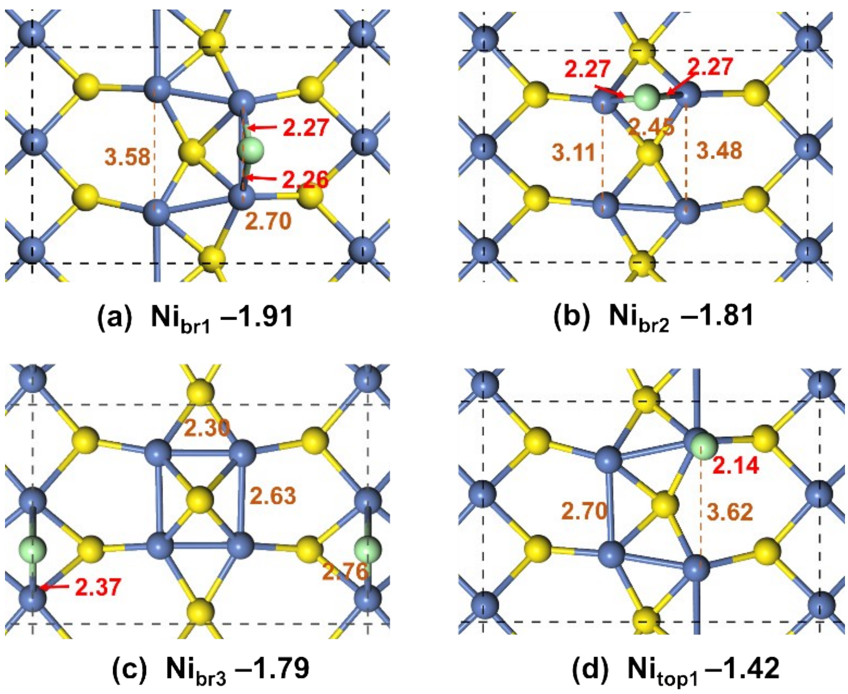

Figure S2. Adsorption configurations of a single Cl atom on the NiS(100) surface.

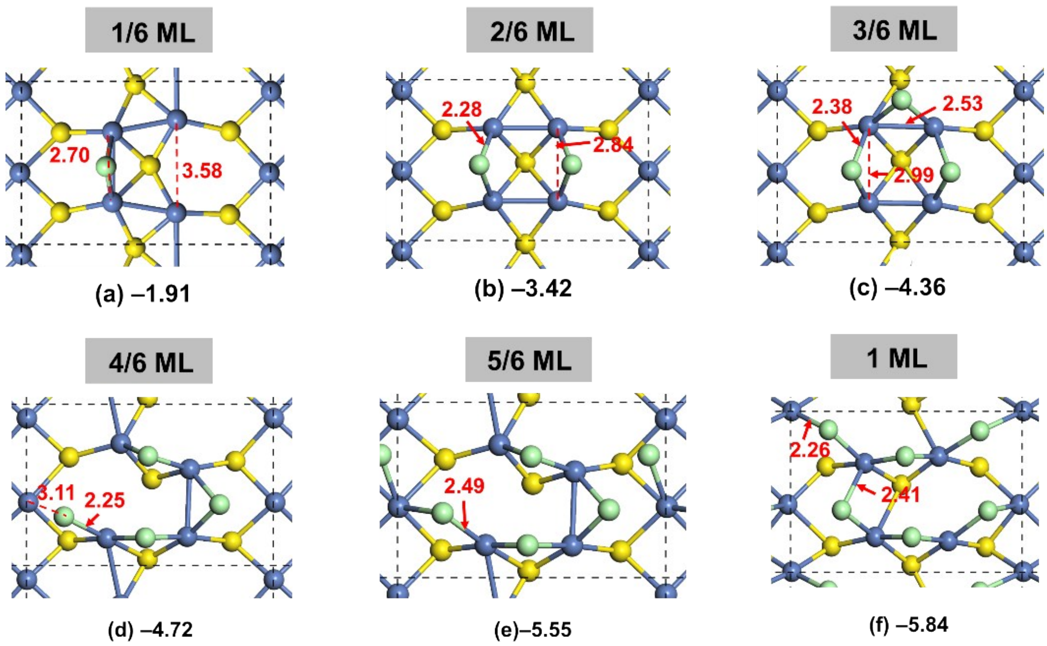

Figure S3. Adsorption configurations for multiple Cl atoms on the NiS(100) surfaces at different surface coverages.

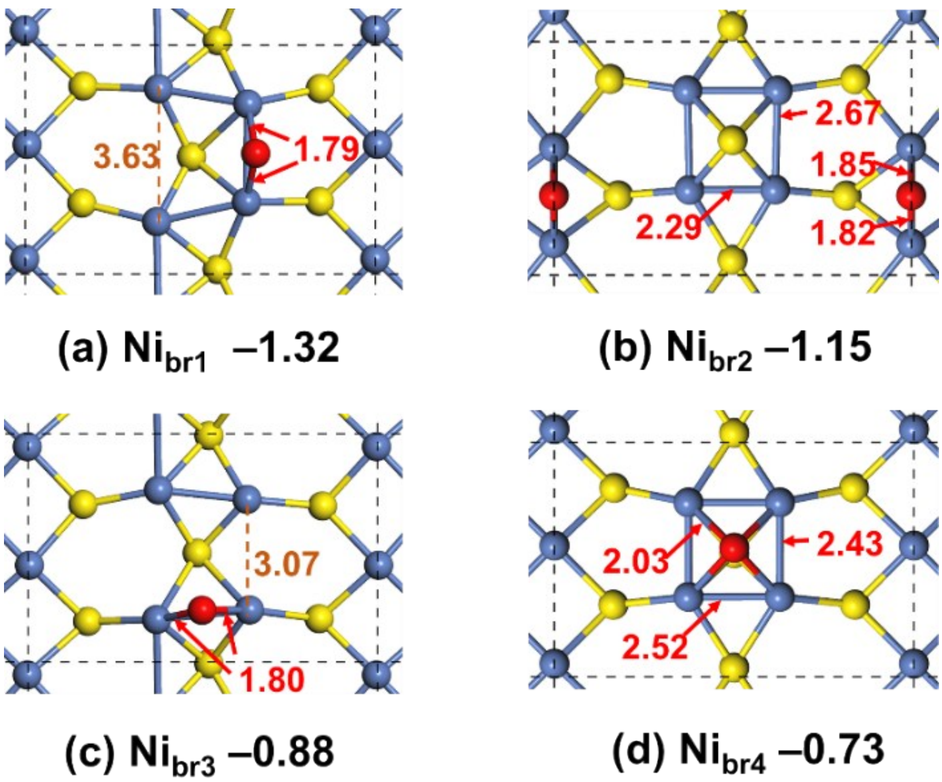

Figure S4. Adsorption configurations of a single O atom on the NiS(100) surface.

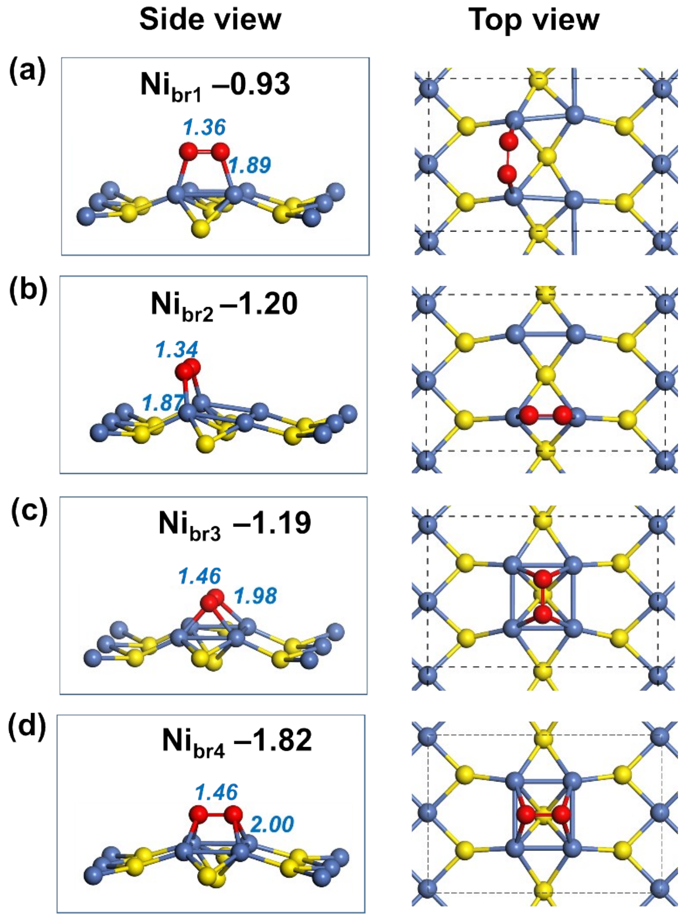

Figure S5. Adsorption configurations of a single O_2 oxygen on the NiS(100) surface.

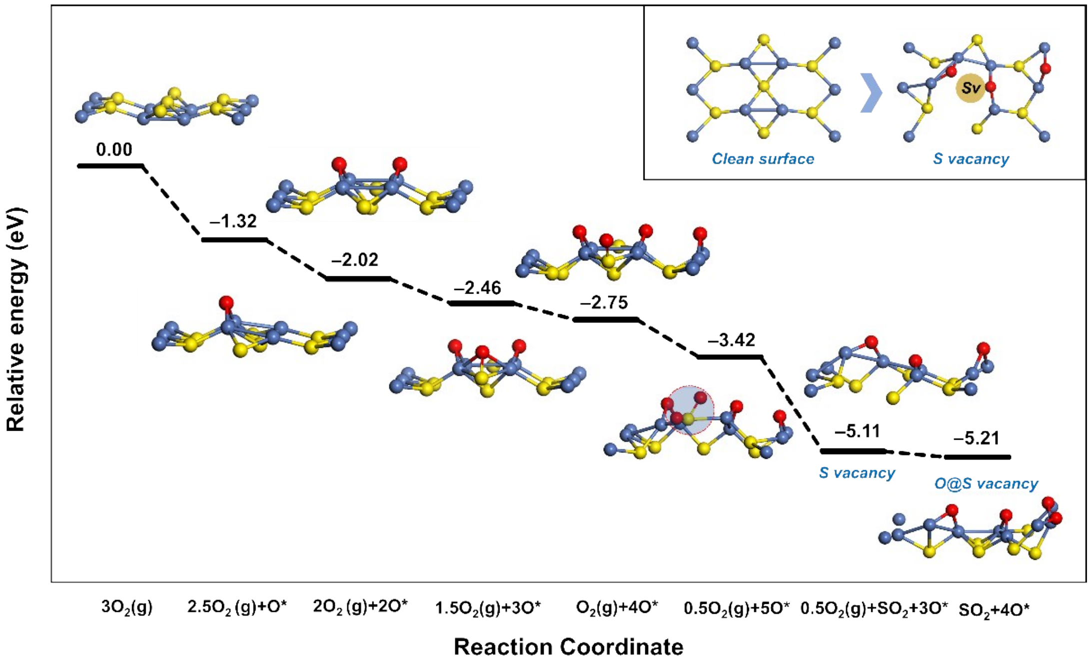

Figure S6. The formation of SO_2 on the NiS(100) surface.

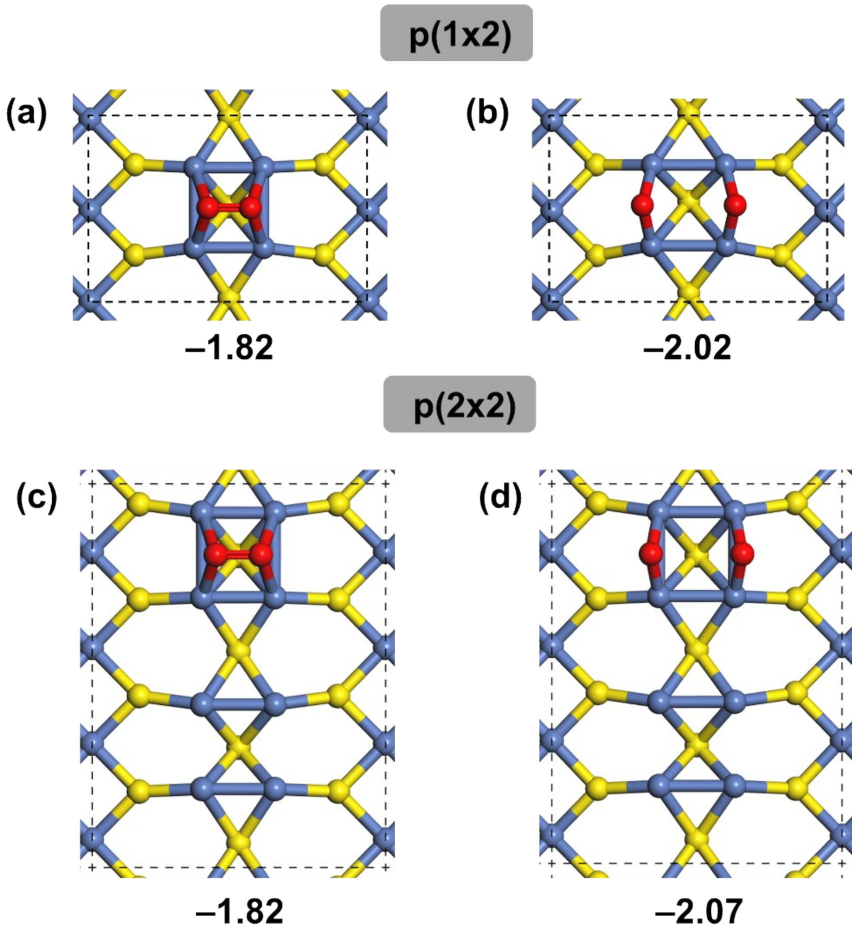

Figure S7. (a) Molecular O_2 chemisorption and (b) dissociative adsorption on the p(1 × 2) supercell of the NiS(100) surface; (c) Molecular O_2 chemisorption and (d) dissociative adsorption on the p(2 × 2) supercell of the NiS(100) surface.

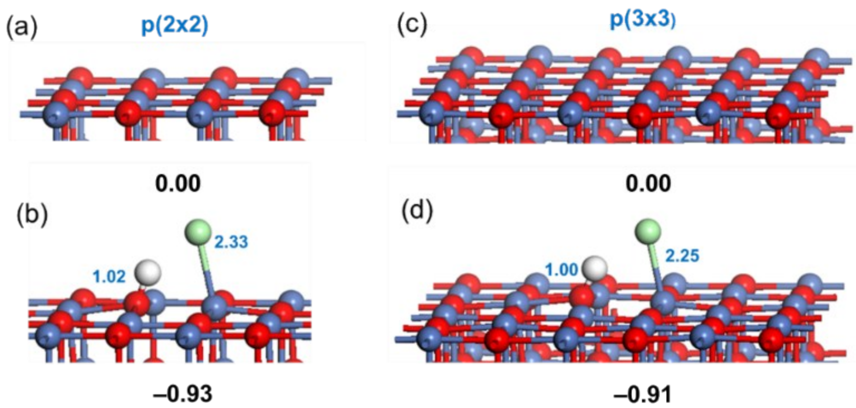

Figure S8. The (a) p(2 × 2) and (c) p(3 × 3) supercells of the NiO(100) surface; dissociative adsorption of molecular HCl on the (b) and (d) p(3 × 3) supercells of the NiO (100) surface.

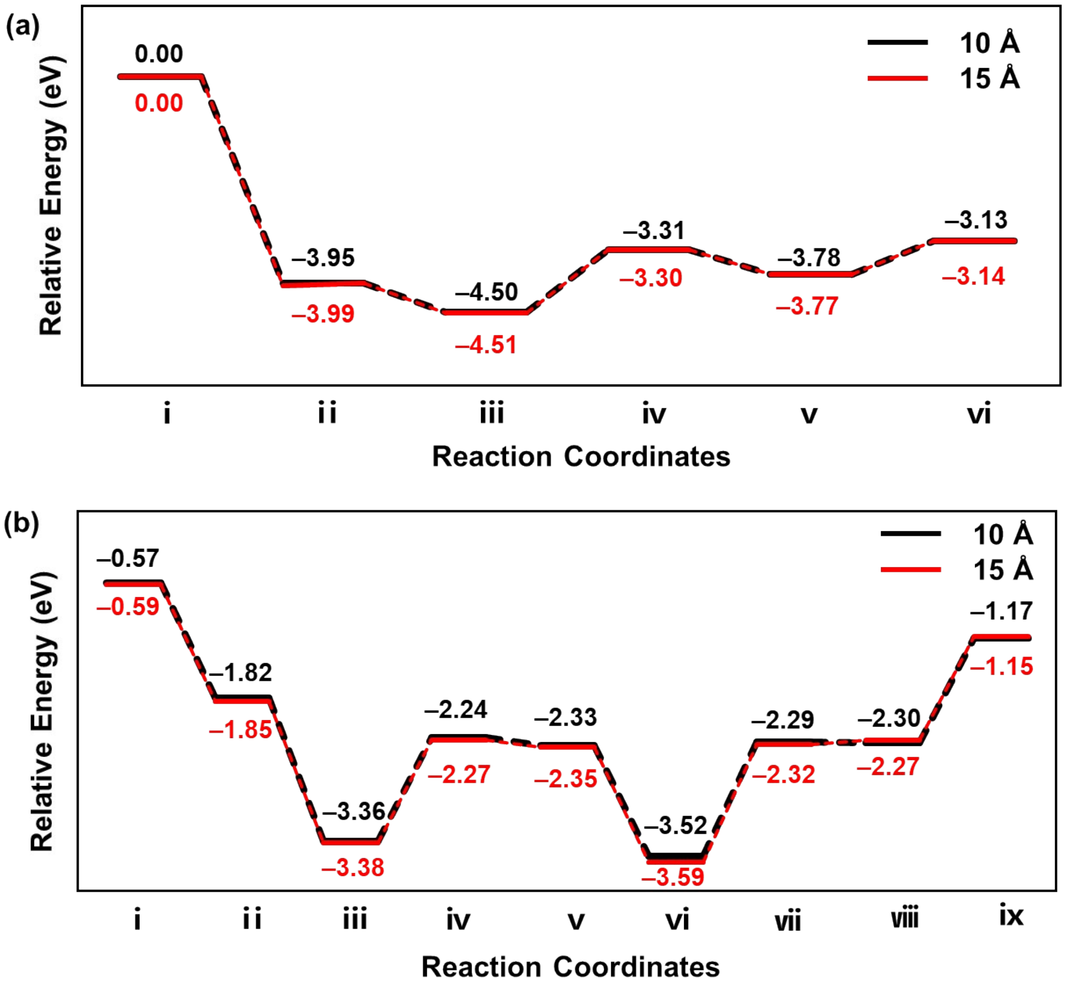

Figure S9. Potential energy surfaces for NH_4Cl adsorption on (a) the NiS(100) surface and (b) the NiO (100) surface with vacuum spacings of 10 Å (black) and 15 Å (red), respectively. These potential energy surfaces are presented in Figures 4(a) and 7(a), respectively, where a vacuum spacing of 10 Å is used.

Table S1. Entropy contributions ($-T*\Delta S$, eV) to the adsorption and dissociation energies of O_2 and Cl_2 on the NiS(100) surface at 600 K. Experimental entropies of molecular O_2 and Cl_2 (226.451 J K^{-1} mol^{-1} and 247.849 J K^{-1} mol^{-1}) from the NIST Chemistry WebBook (https://webbook.nist.gov/chemistry/) were used. Entropic corrections lead to less negative or more positive adsorption and dissociation energies, thus destabilize the surface species, although their effect on the relative energies between the adsorption, transition, and dissociation structures are rather small at <01 eV.

Species	**NiS(100)**
O_2*	
adsorption	+0.73
transition state	+0.81
dissociation	+0.72
Cl_2*	
adsorption	+0.82
transition state	+0.92
dissociation	+0.81

Table S2. Adsorption energies (eV) on the NiS(100) and NiO(100) surfaces in Figure 4 and Figure 7 at the PBE level without (PBE) and with the D2 empirical dispersion correction (PBE-D2). Although inclusion of the dispersion correction leads to significantly more negative adsorption energies, its effect on the energy barrier is negligible.

Surfaces	**Species**	**Adsorption energy (eV)**	
		PBE	**PBE-D2**
NiS(100)	Figure 4		
	i	0.00	0.00
	ii	–3.95	–4.79
	iii	–4.50	–5.31
	iv	–3.40	–3.96
	TS	–3.27	–3.80
	v	–3.78	–4.33
	vi	–3.13	–3.35
NiO(100)	Figure 7		
	i	–0.57	–1.07
	ii	–1.82	–2.42
	iii	–3.36	–4.58
	iv	–2.24	–3.33
	v	–2.33	–3.16
	vi	–3.52	–4.63
	vii	–2.29	–2.98
	viii	–2.30	–3.35
	ix	–1.17	–1.67

Table S3. Fractional coordinates of the relaxed NiS(100) surface.

NiS(100)

```
Ni S
   1.00000000000000
     9.5643530000000005    0.0000000000000000    0.0000000000000000
     0.0000000000000000    6.2519070000000001    0.0000000000000000
     0.0000000000000000    0.0000000000000000   13.8934940000000005
   Ni    S
    12    12
Selective dynamics
Direct
  0.0000061983025632  0.4360840146005185  0.2381628242159650   T   T   T
  0.3704632550808588  0.2177446922791972  0.2662000159987666   T   T   T
  0.6296006264012748  0.2176665529776214  0.2661980331247990   T   T   T
  0.4999815460596224  0.0754969643662307  0.0400907072043921   F   F   F
  0.8681193594590226  0.4088352561866344  0.0814769848390924   F   F   F
  0.1319482875632048  0.4088352561866344  0.0814769848390924   F   F   F
  0.0000101918916870  0.9360333673729939  0.2381562498928324   T   T   T
  0.3705242163936472  0.7174438172826776  0.2661815634364656   T   T   T
  0.6295659340229087  0.7175275334616079  0.2661953563769158   T   T   T
  0.4999815460596224  0.5755044020968327  0.0400907072043921   F   F   F
  0.8681193594590226  0.9088426939172294  0.0814769848390924   F   F   F
  0.1319482875632048  0.9088426939172294  0.0814769848390924   F   F   F
  0.1603191024318429  0.1874721251675117  0.2162931483313669   T   T   T
  0.8397383791101901  0.1874521062390378  0.2162722744927117   T   T   T
  0.4999706640654463 -0.0290906607995470  0.2132975341076685   T   T   T
  0.6685240496665088  0.3370171693212995  0.0021592840505065   F   F   F
  0.3315435973557257  0.3370171693212995  0.0021592840505065   F   F   F
  0.0000000000000000  0.1703480234110941  0.0000000000000000   F   F   F
  0.1603145291470820  0.6873680231228867  0.2162590026144629   T   T   T
  0.8397447608947789  0.6873774730890921  0.2162436537530862   T   T   T
  0.5000476812996296  0.4712371797452497  0.2131041278605445   T   T   T
  0.6685240496665088  0.8370246070518945  0.0021592840505065   F   F   F
  0.3315435973557257  0.8370246070518945  0.0021592840505065   F   F   F
  0.0000000000000000  0.6703554611416962  0.0000000000000000   F   F   F
```

Table S4. Fractional coordinates of the relaxed NiO(100) surface.

NiO(100)

Ni O

1.00000000000000

8.4085180000000008	0.0000000000000000	0.0000000000000000
0.0000000000000000	8.4085180000000008	0.0000000000000000
0.0000000000000000	0.0000000000000000	18.4085180000000008

Ni O

40 40

Selective dynamics

Direct

0.0000000000000000	0.2499845989507321	0.1141862696388714	F	F	F
-0.0000201649363186	0.2499832361798171	0.3432862574328524	T	T	T
0.2499845989507321	0.0000000000000000	0.1141862696388714	F	F	F
0.2499832361798171	-0.0000201649363186	0.3432862574328524	T	T	T
0.0000000000000000	0.0000000000000000	0.0000000000000000	F	F	F
0.0000000000000000	0.0000000000000000	0.2283725392777427	F	F	F
-0.0000167036537275	-0.0000167036537275	0.4551377383629027	T	T	T
0.2499845989507321	0.2499845989507321	0.0000000000000000	F	F	F
0.2499845989507321	0.2499845989507321	0.2283725392777427	F	F	F
0.2499828568825077	0.2499828568825077	0.4551416083386449	T	T	T
0.4999691979014642	0.2499845989507321	0.1141862696388714	F	F	F
0.4999704910036319	0.2499833058485644	0.3432862032726331	T	T	T
0.7499537968521892	0.0000000000000000	0.1141862696388714	F	F	F
0.7499740222929026	-0.0000202254407133	0.3432863836766034	T	T	T
0.4999691979014642	0.0000000000000000	0.0000000000000000	F	F	F
0.4999691979014642	0.0000000000000000	0.2283725392777427	F	F	F
0.4999708583296126	-0.0000168006339128	0.4551396267970097	T	T	T
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0.7499705974861021	0.2499829385225838	0.4551396267970097	T	T	T
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0.0000000000000000	0.4999691979014642	0.2283725392777427	F	F	F
-0.0000168006339128	0.4999708583296126	0.4551396267970097	T	T	T
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0.2499829385225838	0.7499705974861021	0.4551396267970097	T	T	T
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0.4999691979014642	0.4999691979014642	0.2283725392777427	F	F	F
0.4999709399696886	0.4999709399696886	0.4551416083386449	T	T	T
0.7499537968521892	0.7499537968521892	0.0000000000000000	F	F	F
0.7499537968521892	0.7499537968521892	0.2283725392777427	F	F	F
0.7499705005059167	0.7499705005059167	0.4551377383629027	T	T	T
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0.2499844546055862	0.2499844546055862	0.3431082589031133	T	T	T
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