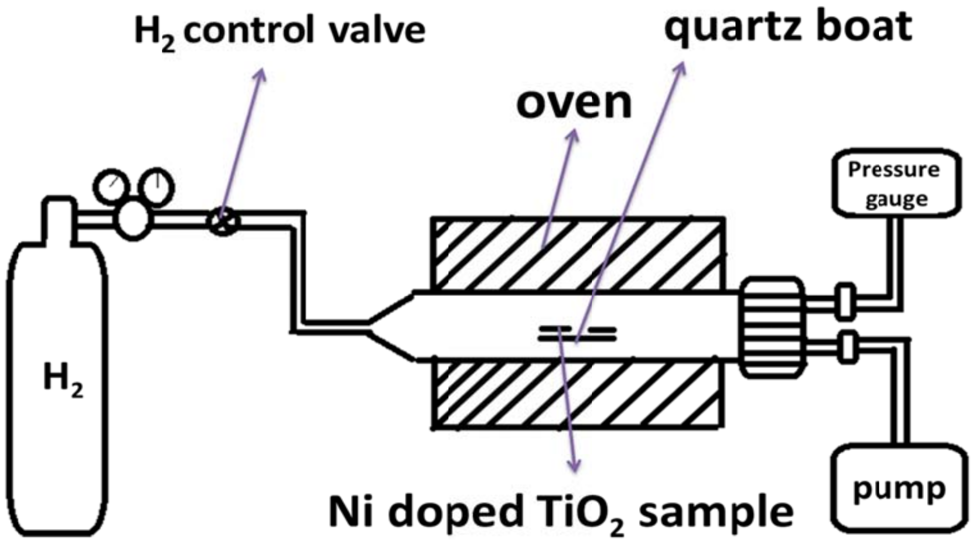
Supporting Information

We conducted the hydrogenation of Ni-doped TiO_2 samples using the homemade low-pressure hydrogenation system as shown in the Figure below.



In the hydrogenation reaction, Ni doped TiO_2 samples were placed in a quartz boat. After evacuation, the system was purged with low-pressure H_2 for about five minutes; the H_2 pressure was then slowly increased to 800 Torr. The temperature of the oven was maintained at 300 ^{O}C for 3 hrs.

Table S1: Hydrogen production rates (mmol/g-Hr) of Ni-doped TiO_2 and hydrogenated Ni-doped TiO_2 with 0.5% and 5% Ni-doping NPs under 1-hr illumination using 10% ethanol as sacrificial agent and 2 W Xe-lamp output.

Sample	**0.5% Ni Doped TiO_2**	**5% Ni Doped TiO_2**	**H-0.5% Ni Doped TiO_2**	**H-5% Ni Doped TiO_2**
H_2 Production (mmol/g-Hr)	0.17	0.40	0.25	1.64

Table S2: Comparison of predicted energies for the dissociative adsorption of H_2 and migration of H on 1- and 2-Ni doped TiO_2 and on undoped TiO_2 surfaces at the DFT+U level of theory.

System	**(1-2) Ni-TiO_2**	**Undoped TiO_2**[9]
H_2(g)+1Ni-TiO_2	**0.0**	
H_2…1Ni-TiO_2 (a)	0.9	
TS1	12.1	
H-O_{3C}, H-Ni-1Ni-TiO_2 (a)	-16.6	
TS2	-13.2	
H-O_{3C},H-O_{2C}-1Ni-TiO_2 (a)	-94.9	
H_2(g)+1Ni-TiO_2	**0.0**	**0.0**
H_2…O_{2C}-1Ni-TiO_2(a)	1.21	-0.3
TS3	6.1	47.8
2H-O_{2C}-1Ni-TiO_2 (a)	-98.2	-18.3
H_2(g)+2Ni-TiO_2	**0.0**	
H_2…2Ni-TiO_2 (a)	0.8	
TS4	17.4	
H-O_{3C}, H-Ni-2Ni-TiO_2 (a)	-15.6	
TS5	-14.6	
H-O_{3C}, H-O_{2C}-2Ni-TiO_2 (a)	-92.5	
H_2(g)+2Ni-TiO_2	**0.0**	**0.0**
H_2…O_{2C}-2Ni-TiO_2 (a)	0.2	-0.3
TS6	12.4	47.8
2H-O_{2C}-2Ni (a)	-94.8	-18.3
TS6a	-72.6	2.5

$H-O_{3C}$,$H-O_{2c}$-2Ni (a)	-79.7	-8.7
TS6b	-64.8	9.9
$H-O_{sub2}$,$H-O_{2c}$-2Ni (a)	-81.0	-9.5
2H-O_{sub2}-2Ni (b)	-76.3	7.3
TS6c	-50.7	29.3
H_2O-2Ni(b)	-68.7	19.0

Table S3: Comparison of predicted energies for H-atom adsorption and migration on 1- and 2-Ni doped TiO_2 and those on the un-doped TiO_2 surface as well as those for 2H atoms on O_{2c} sites and migration into the bulk at the DFT+U level of theory

System	**1Ni-TiO_2**	**Undoped TiO_2[9]**			
$H-O_{2C}$-1Ni-TiO_2 (a)	**0**	**0**			
TS7	23.5	27.8			
$H-O_{3C}$-1Ni-TiO_2 (a)	18	17.6			
TS8	32.9	35.6			
H_{BD1}-1Ni-TiO_2 (a)	14.3	13.7			
TS9	30.3				
H_{BD2}-1Ni-TiO_2 (a)	21				
System	**2Ni-TiO_2**	**Undoped TiO_2[9]**	**System**	**2Ni-TiO_2**	**Undoped TiO_2[9]**
$H-O_{2C}$-2Ni-TiO_2(a)	**0.0**	**0.0**	**2H-O_{2c}-2Ni(a)**	**0.0**	**0.0**
TS10	22.7	27.8	TS6a	22.2	20.8
$H-O_{3C}$-2Ni-TiO_2 (a)	18.2	17.6	$H-O_{3c}$,$H-O_{2c}$-2Ni(a)	15.1	9.6
TS11	33	35.6	TS6b	30.0	28.2
H_{BD1}-2Ni-TiO_2 (a)	15	14.33	$H-O_{BD1}$,$H-O_{2c}$-2Ni(a)	13.8	14.2
TS12	29.6		TS6b1	16.4	20.0
H_{BD2}-2Ni-TiO_2 (a)	19.9		$H-O_{sub2}$,$H-O_{2c}$-2Ni(a)	4.8	8.8
			2H-O_{sub2}-2Ni(b)	18.5	25.6
			TS6c	44.1	47.6

			H_2O-2Ni(b)	26.1	37.3

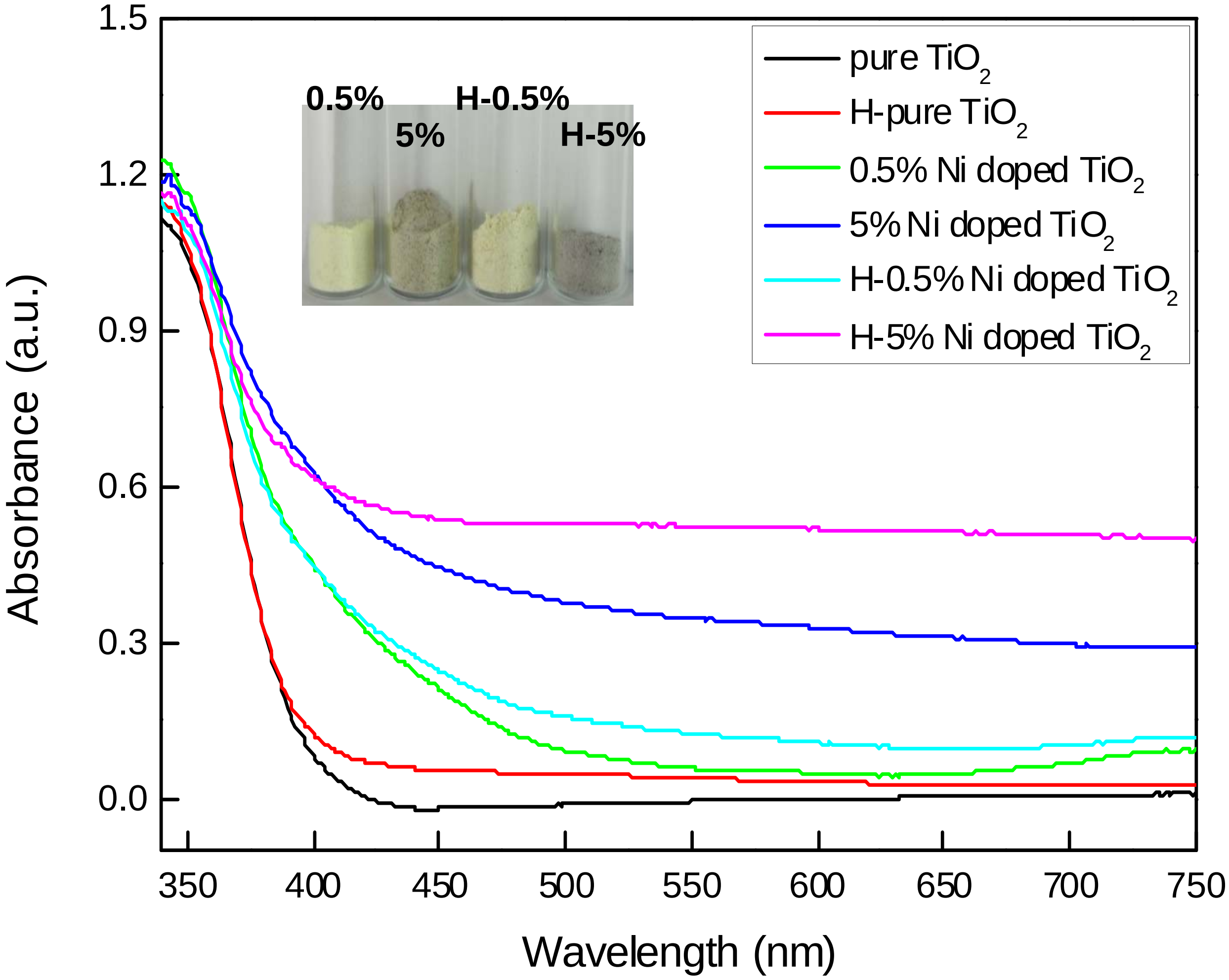
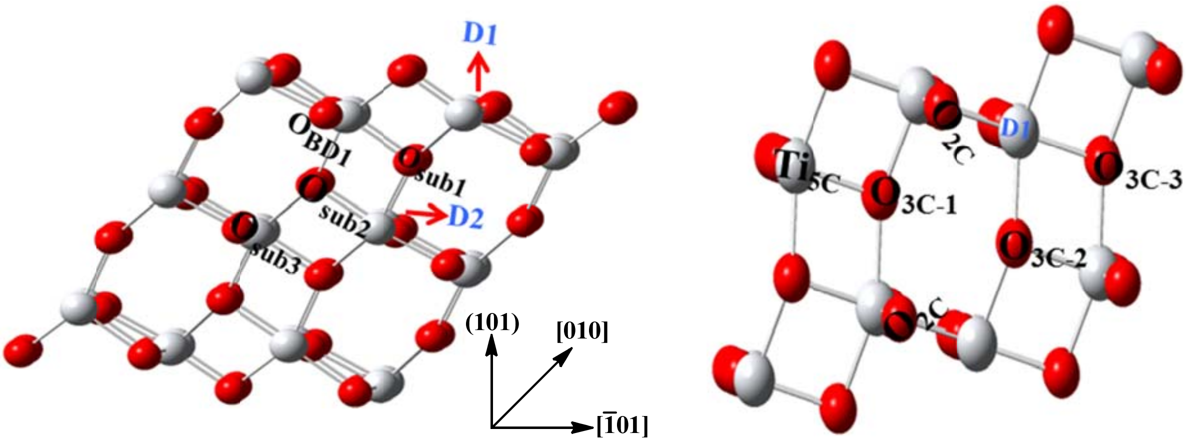


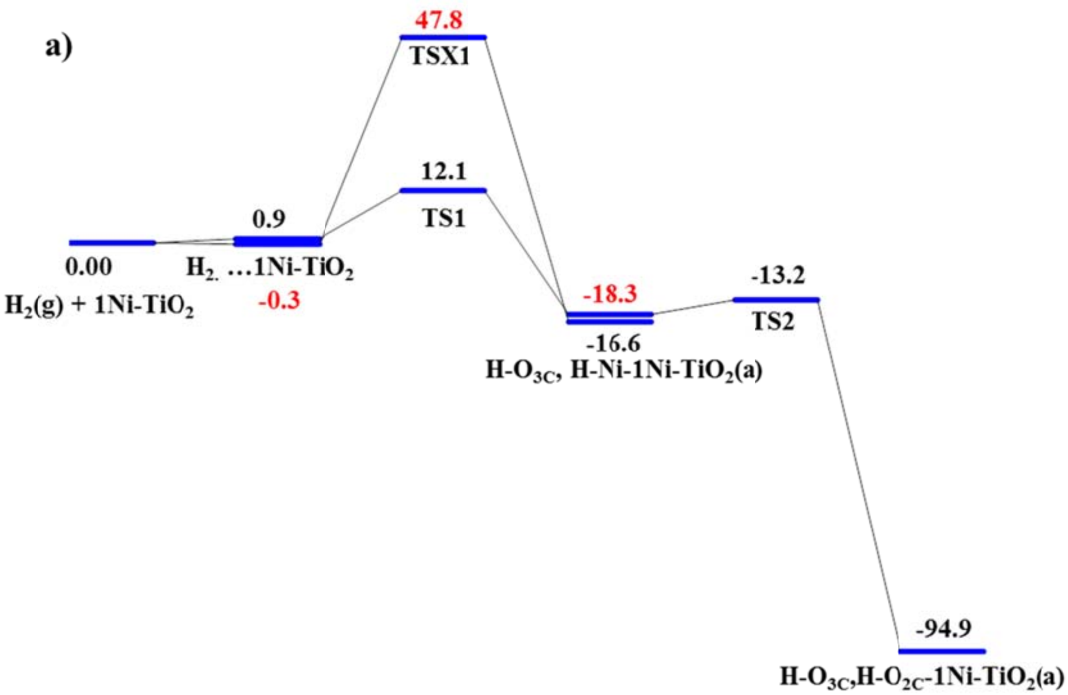
Figure S1. The picture of Ni doped TiO_2 powders and the UV-Vis absorption spectra of the powders.

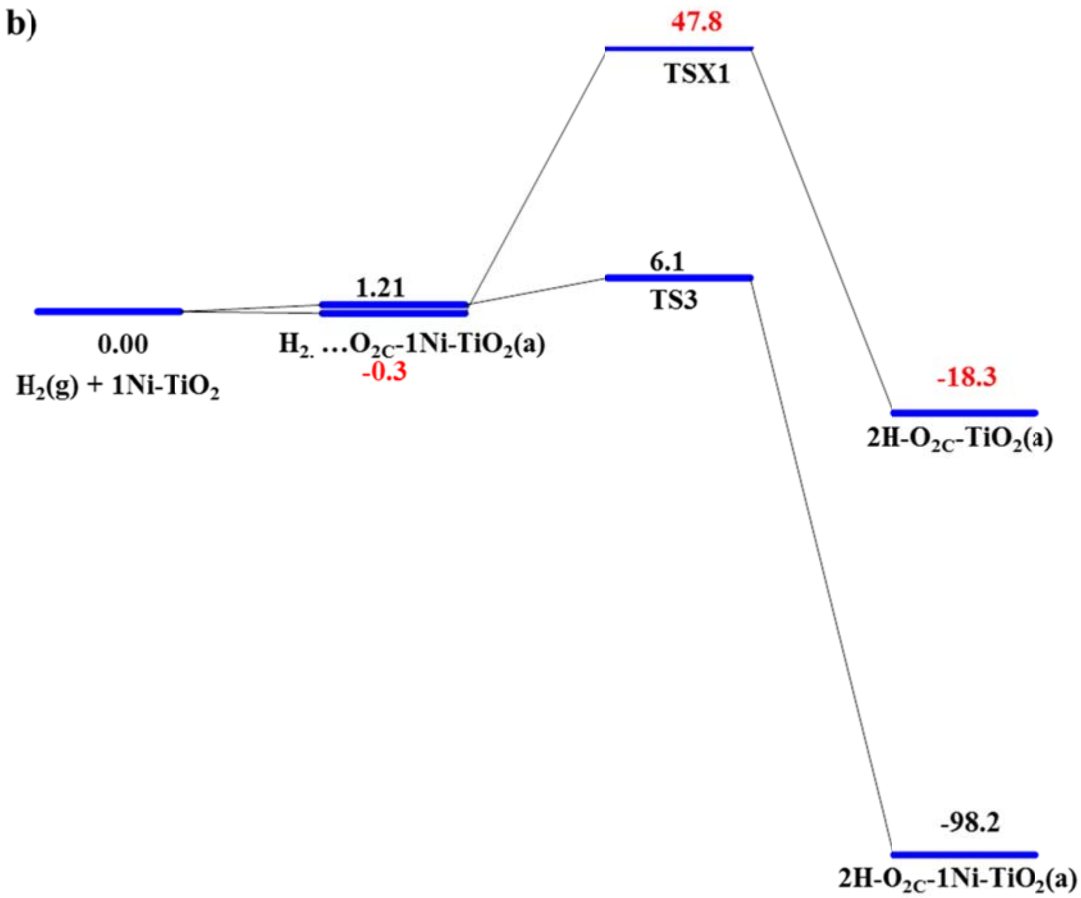


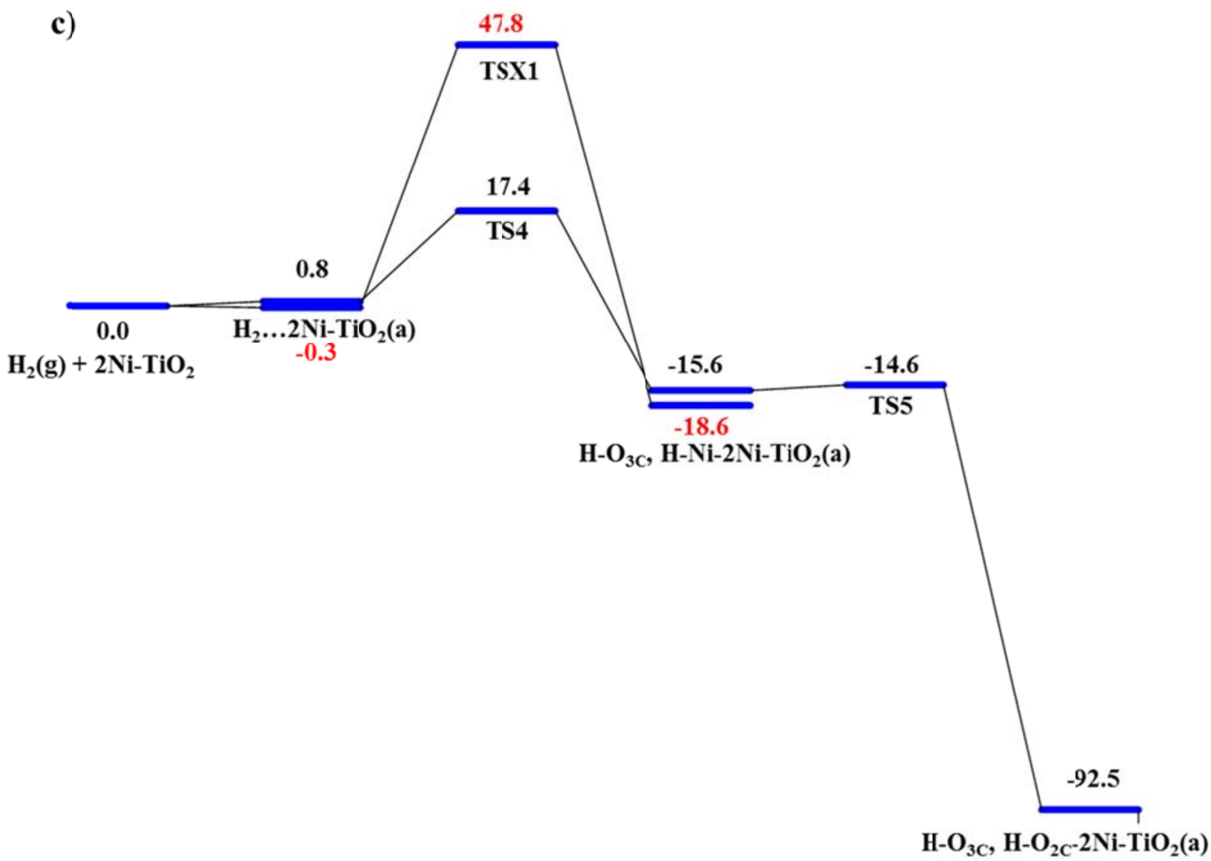
TiO_2 side view

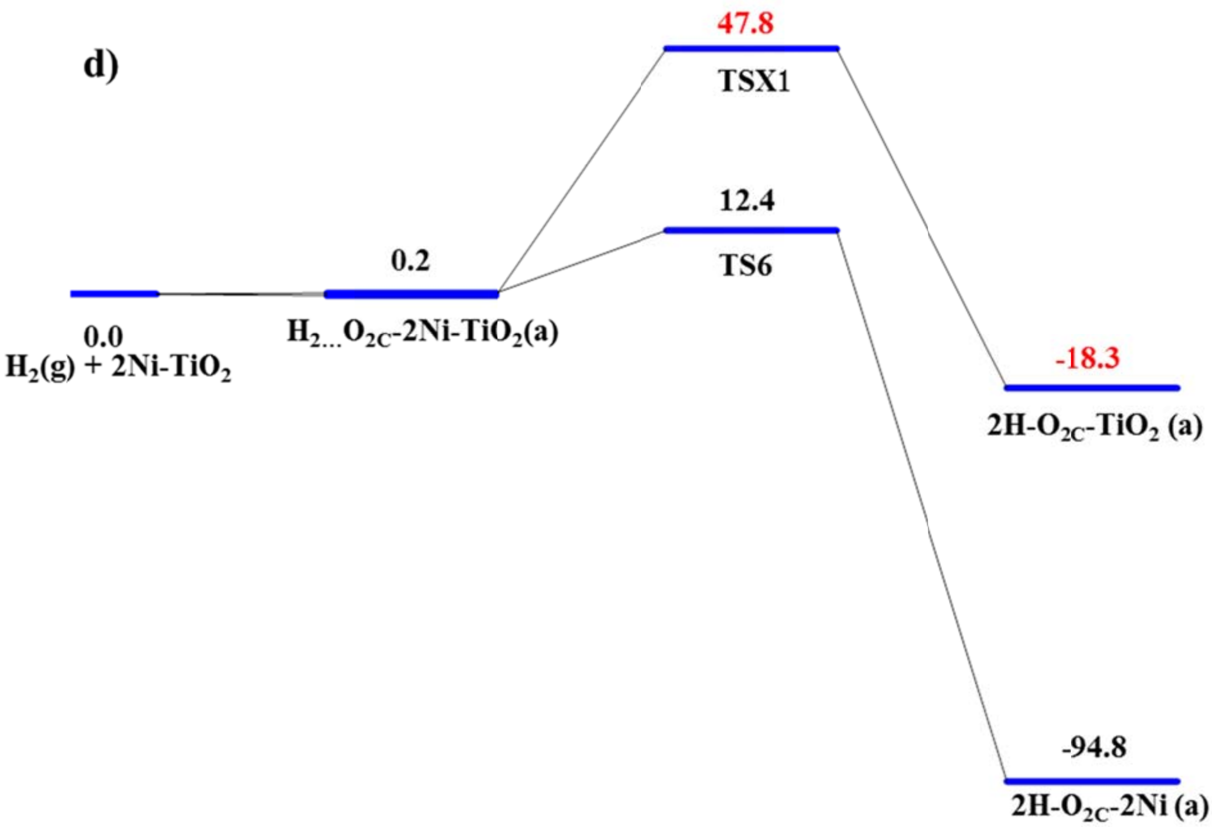
TiO_2 top view

Figure S2. Perspective view of the TiO_2(101) surface slab model usedin the present study.


a)
47.8
TSX1
12.1
TS1
0.9
0.00
H2. …1Ni-TiO2
-0.3
H2(g) + 1Ni-TiO2
-18.3
-13.2
TS2
-16.6
H-O3C, H-Ni-1Ni-TiO2(a)
-94.9
H-O3C,H-O2C-1Ni-TiO2(a)


b)
47.8
TSX1
6.1
TS3
1.21
0.00
H2. …O2C-1Ni-TiO2(a)
-0.3
H2(g) + 1Ni-TiO2
-18.3
2H-O2C-TiO2(a)
-98.2
2H-O2C-1Ni-TiO2(a)


c)
47.8
TSX1
17.4
TS4
0.8
0.0
H2…2Ni-TiO2(a)
-0.3
H2(g) + 2Ni-TiO2
-15.6
-14.6
TS5
-18.6
H-O3C, H-Ni-2Ni-TiO2(a)
-92.5
H-O3C, H-O2C-2Ni-TiO2(a)


d)
47.8
TSX1
12.4
TS6
0.2
0.0
H2(g) + 2Ni-TiO2
H2…O2C-2Ni-TiO2(a)
-18.3
2H-O2C-TiO2 (a)
-94.8
2H-O2C-2Ni (a)

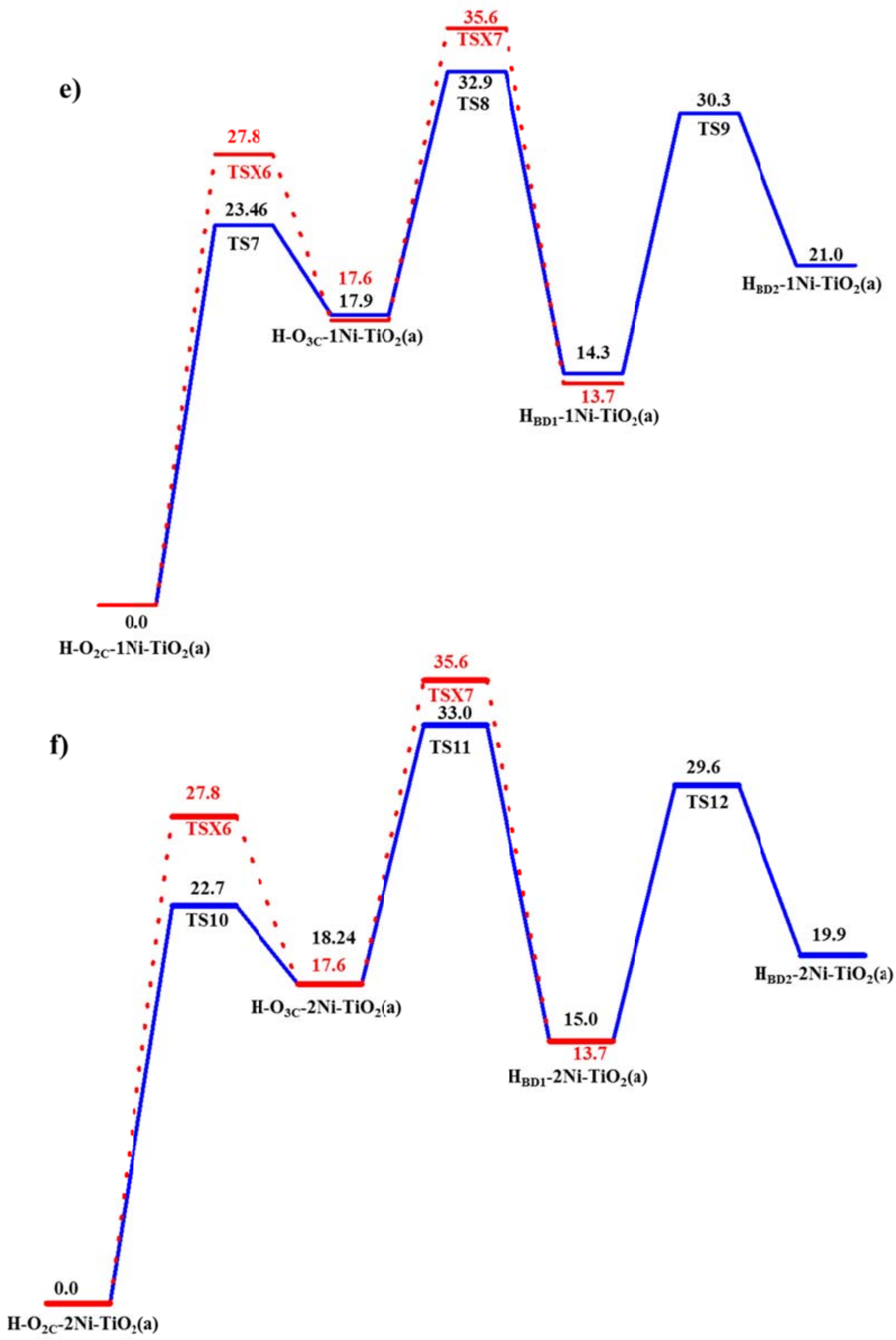


Figure S3. Calculated potential energy diagrams for (a) H_2 dissociation on 1Ni doped TiO_2 surface (on Ni site), (b) H_2 dissociation on the Ni-doped TiO_2 surface (at O_{2C} site), (c) H_2 dissociation on the 2Ni-doped TiO_2 surface (at Ni site) (d) H_2 dissociation on the 2Ni-doped TiO_2 surface (at O_{2C} site), (e) H migration on the 1Ni- doped TiO_2 from the O_{2C} site to bulk, (f) H migration on the 2Ni-doped TiO_2 from the O_{2C} site to bulk. The results of H_2 dissociation and migration on undoped TiO_2(101) shown in red color are taken from Raghunath et al.[9]

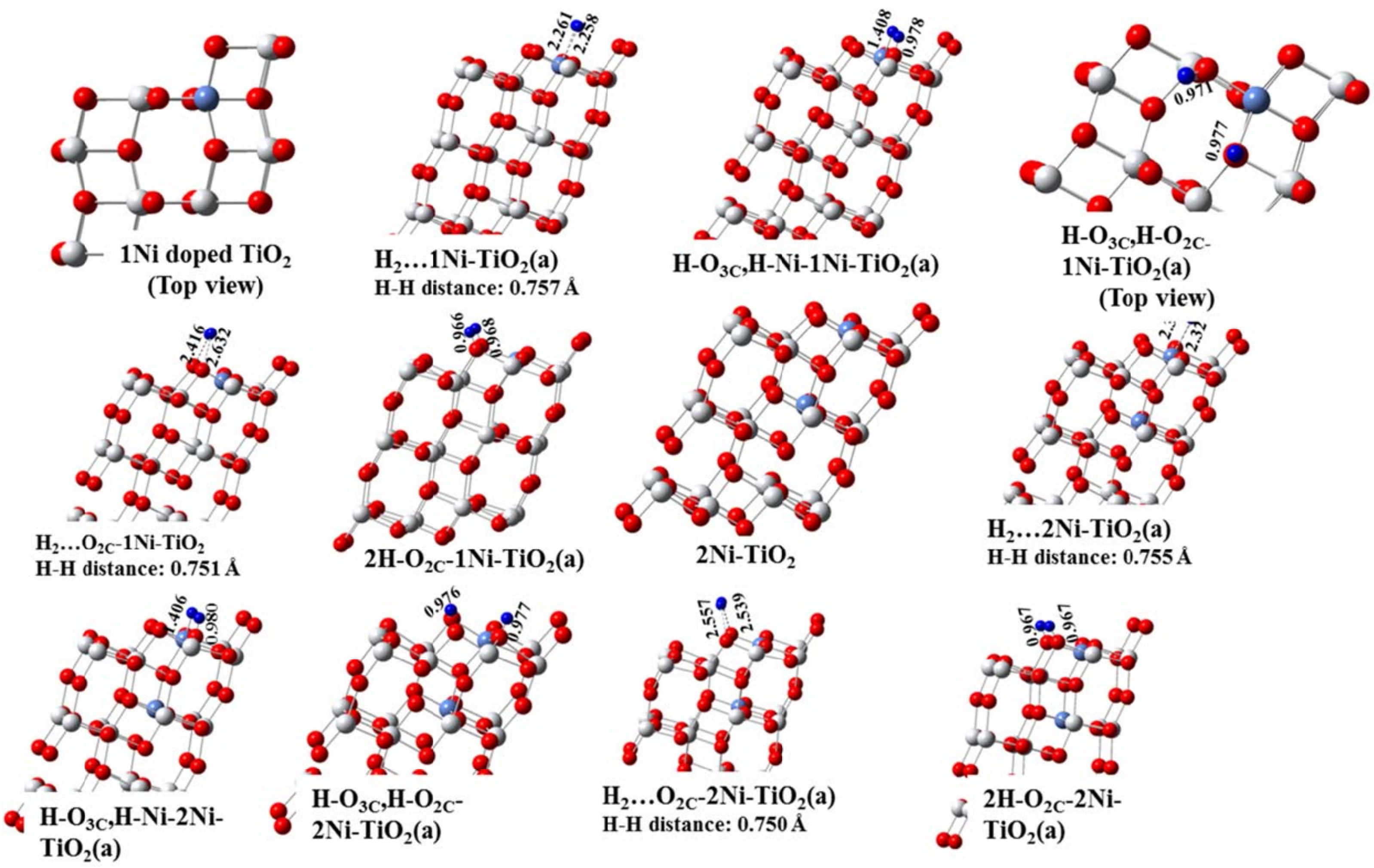
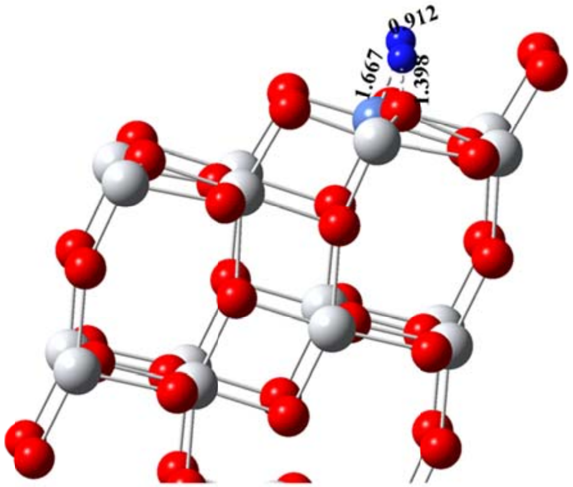
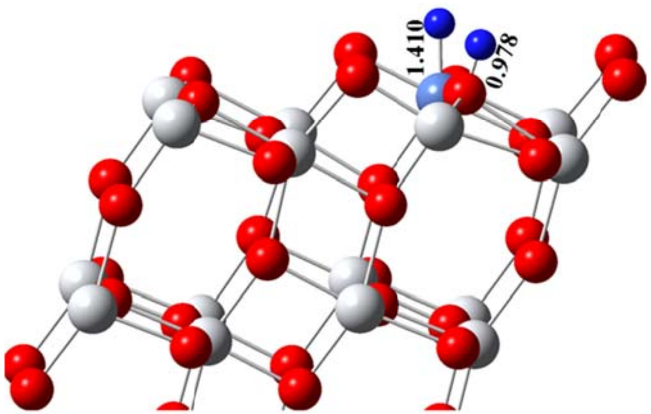


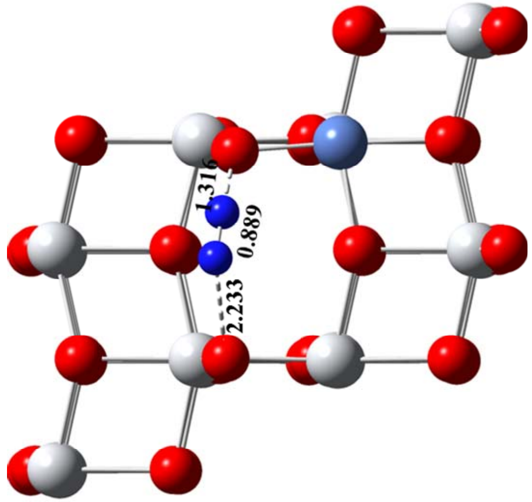
Figure S4. Optimized configurations of TiO_2, H and H_2 on (1 to 2) Ni-TiO_2 (101). (Grey: Titanium; Red: Oxygen; Royal Blue: Nickel; Blue: Hydrogen). The distance (Å) between the surface and H are shown in the optimized structure.



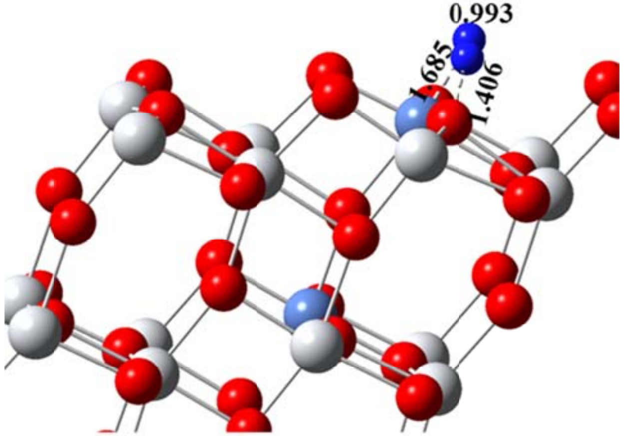
TS1



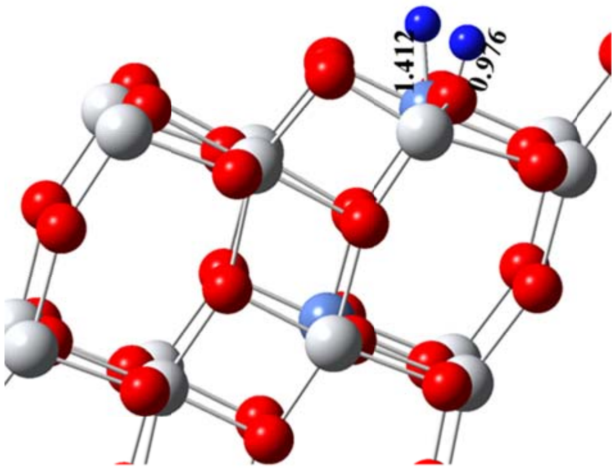
TS2



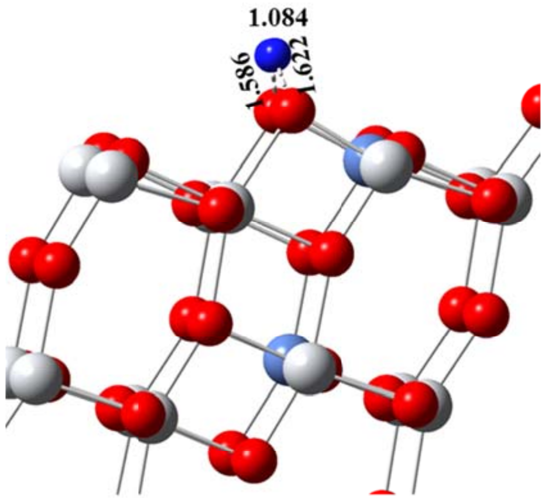
TS3



TS4



TS5



TS6

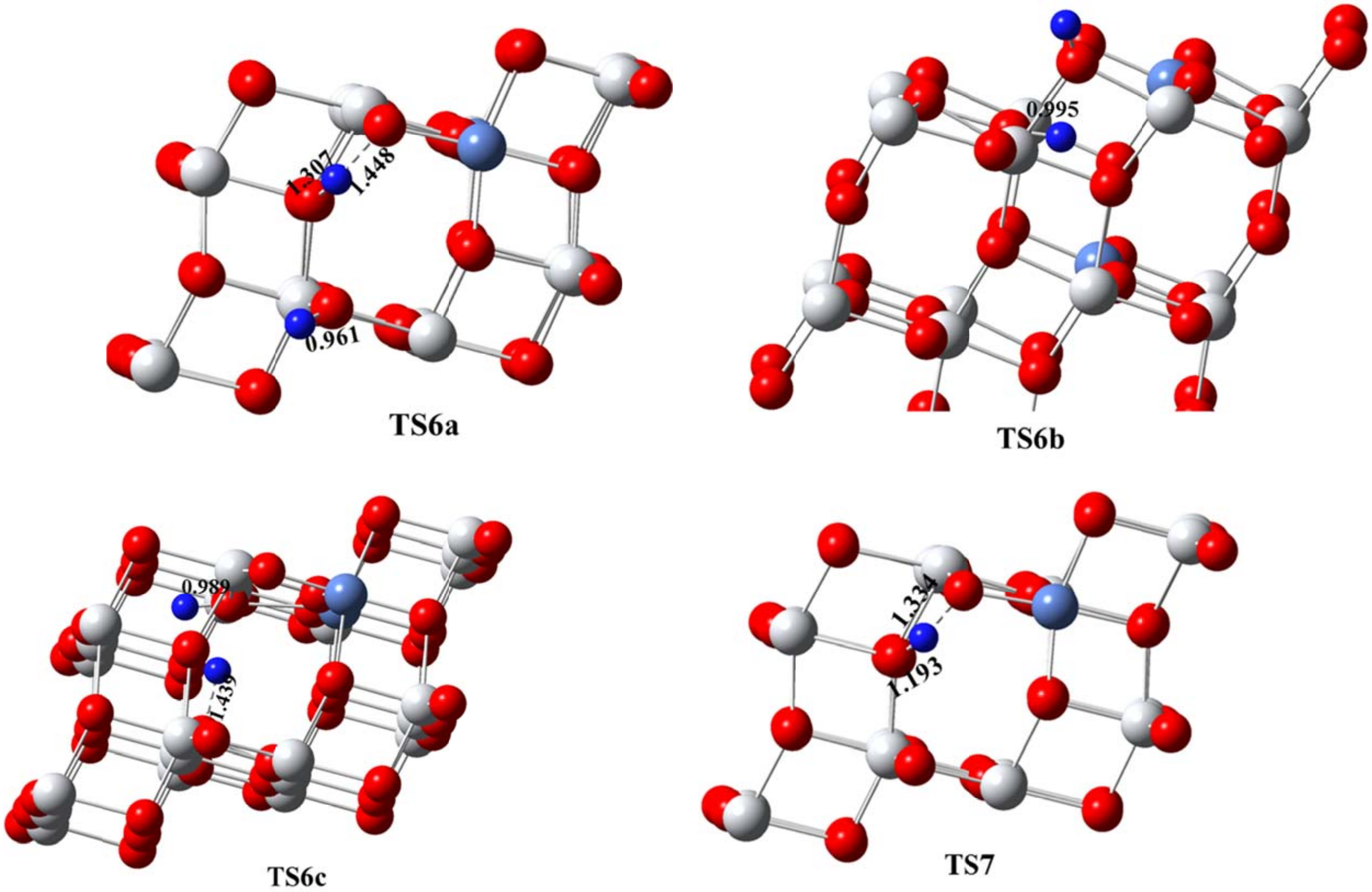


Figure S5. Optimized transition state configurations for H_2 dissociation and migration on (1 - 2) Ni-TiO_2. (Grey: Titanium; Red: Oxygen; Royal Blue: Nickel; Blue: Hydrogen). The distance (Å) between the surface and H are shown in the optimized structure.

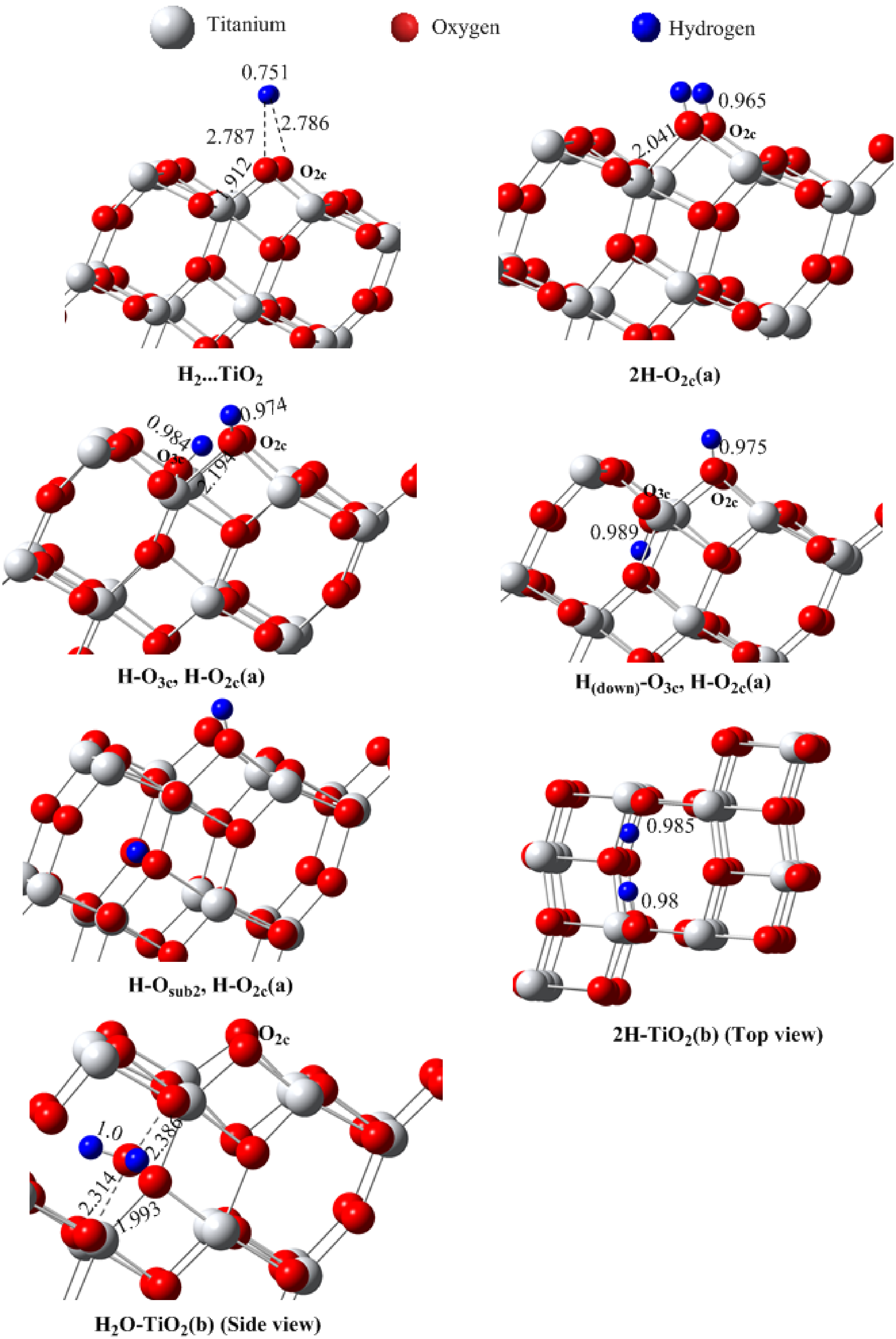
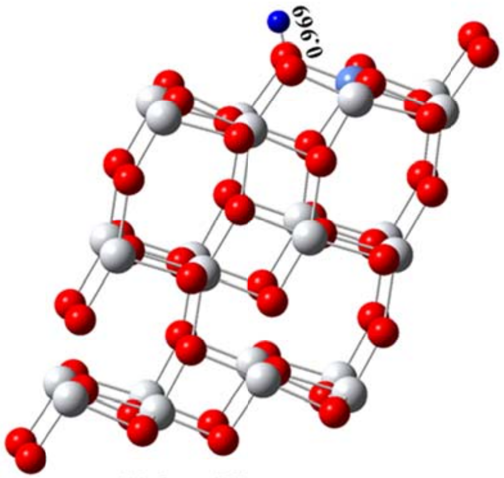
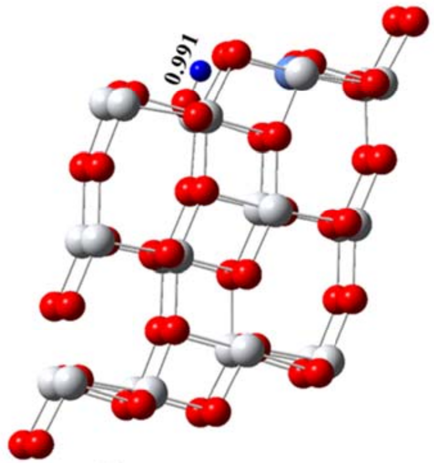


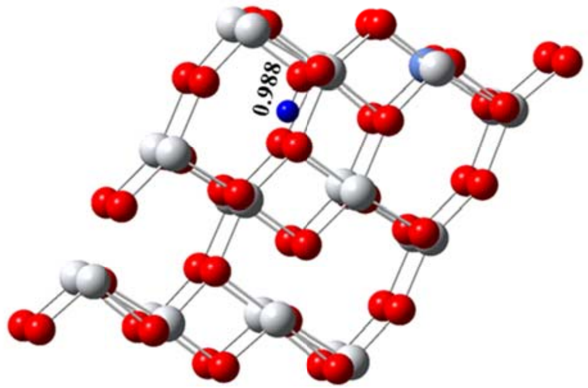
Figure S6. Optimized configurations of species from H_2 dissociation and migration from surface into to subsurface layers of the un-doped TiO_2 anatase presented in Figure 3a.



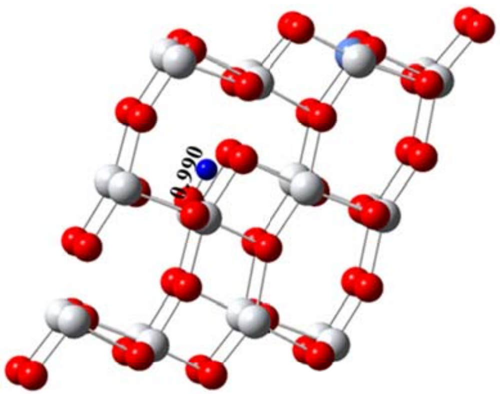
H-O_{2C}-1Ni-TiO_2(a)



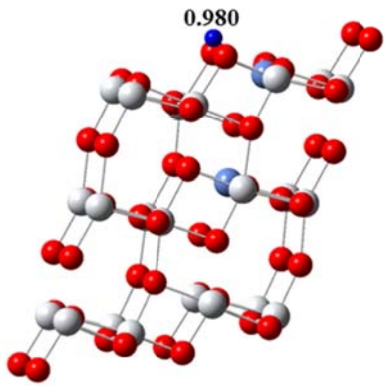
H-O_{3C}-1Ni-TiO_2(a)



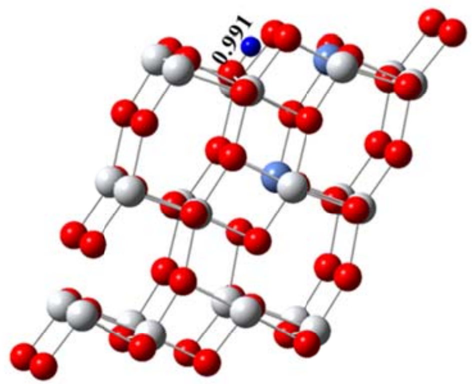
H_{BD1}-1Ni-TiO_2(a)



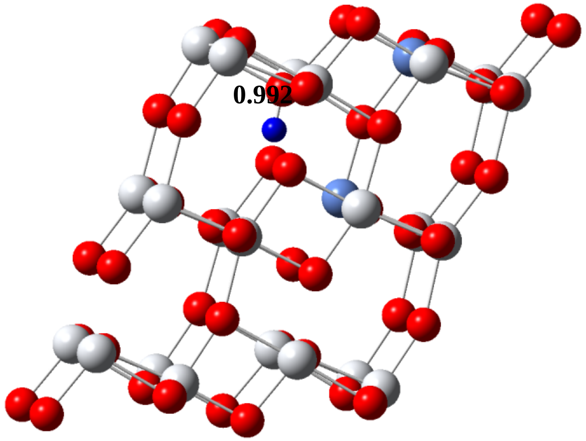
H_{BD2}-1Ni-TiO_2(a)



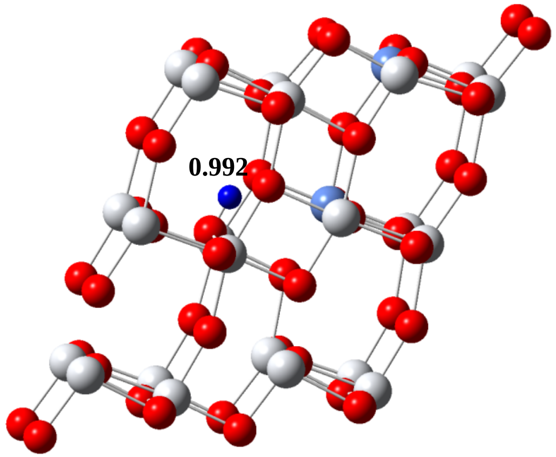
H-O_{2C}-2Ni-TiO_2(a)



H-O_{3C}-2Ni-TiO_2(a)



H_{BD1}-2Ni-TiO_2(a)



H_{BD2}-2Ni-TiO_2(a)

Figure S7. Optimized configurations of H-species on (1 - 2) Ni-TiO_2 surfaces and in their bulks (Grey: Titanium; Red: Oxygen; Royal Blue: Nickel; Blue: Hydrogen). The distance (Å) between the surface and H are shown in the Figure.

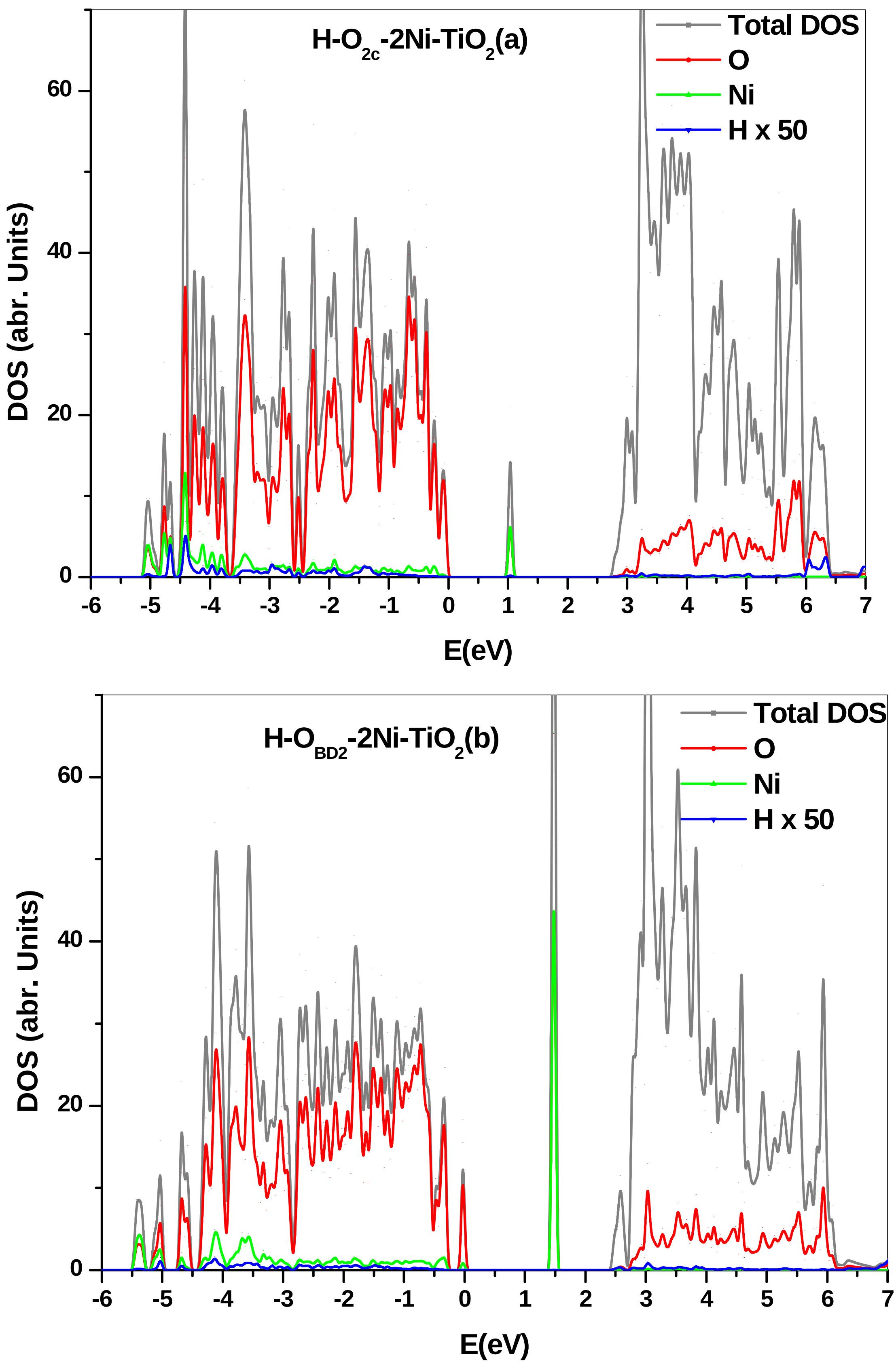
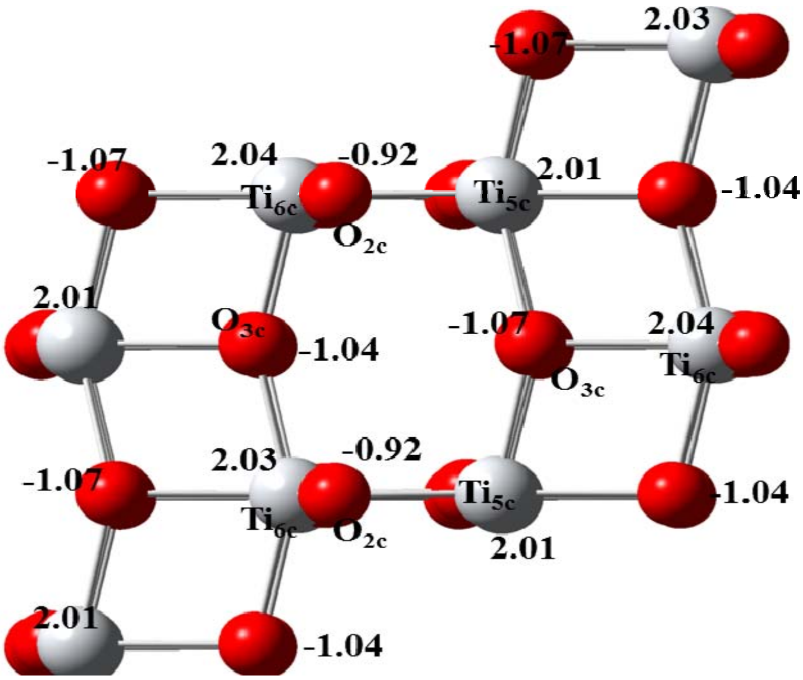
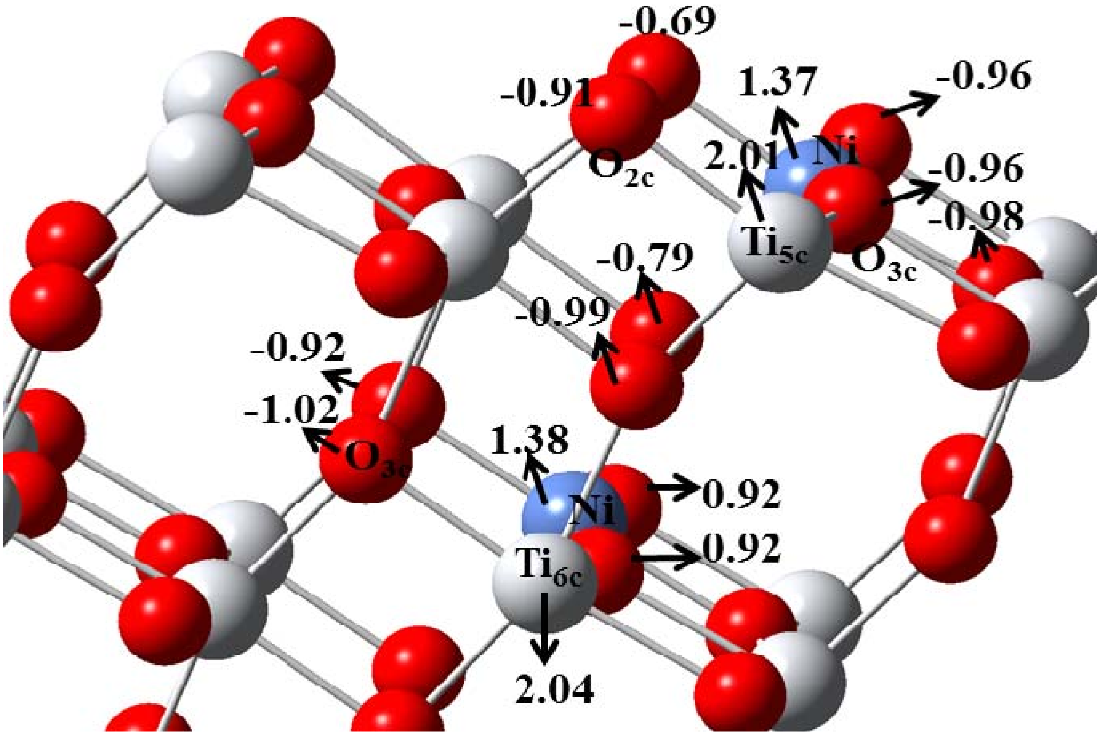


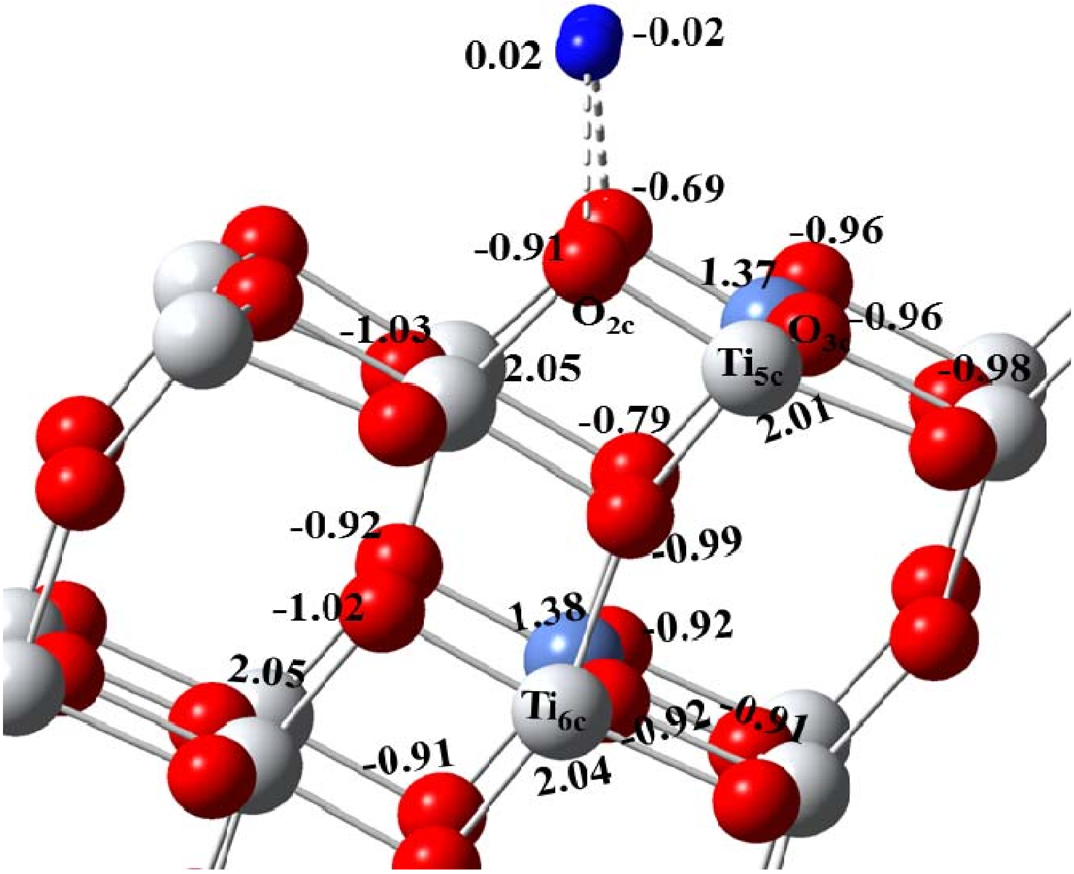
Figure S8. Densities of states (DOS) for the H atom bonding with O at the surface O_{2c} site of 2Ni-TiO_2 (H-O_{2c}-2Ni-TiO_2(a)) and the H atom bonding with O in the bulk O_{sub3} site of 2Ni-TiO_2 (H-O_{sub3}-2Ni-TiO_2(b)) calculated at the DFT + U level (U = 4.0 eV for Ni and Ti) (for clarity, H and Ni PDOS peaks are magnified). Their optimized geometries and Bader charges are shown in Fig S7 and S9, respectively.



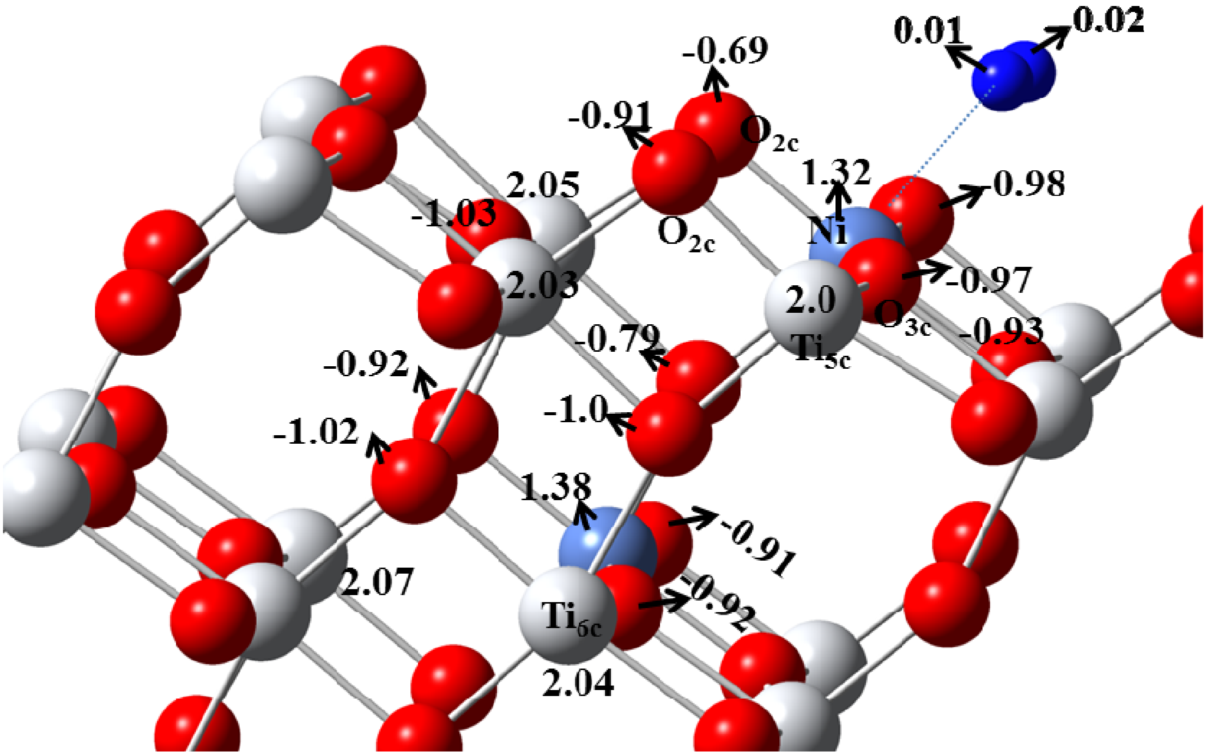
a) TiO_2 (Top View)



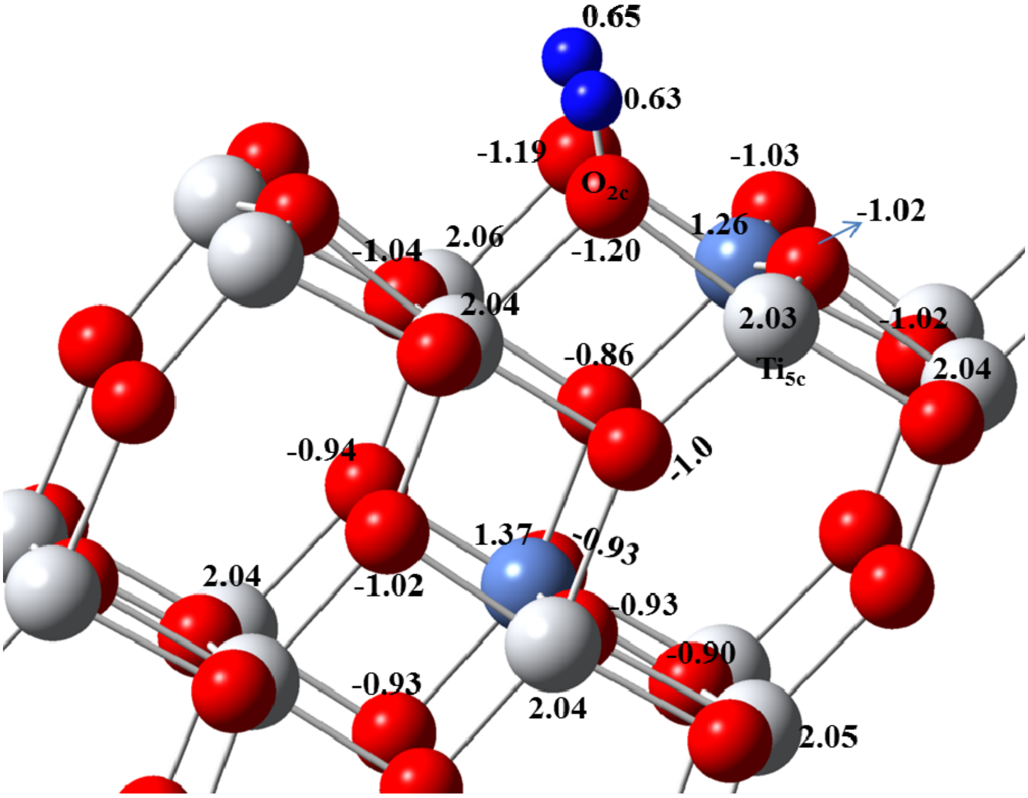
b) 2Ni-TiO_2



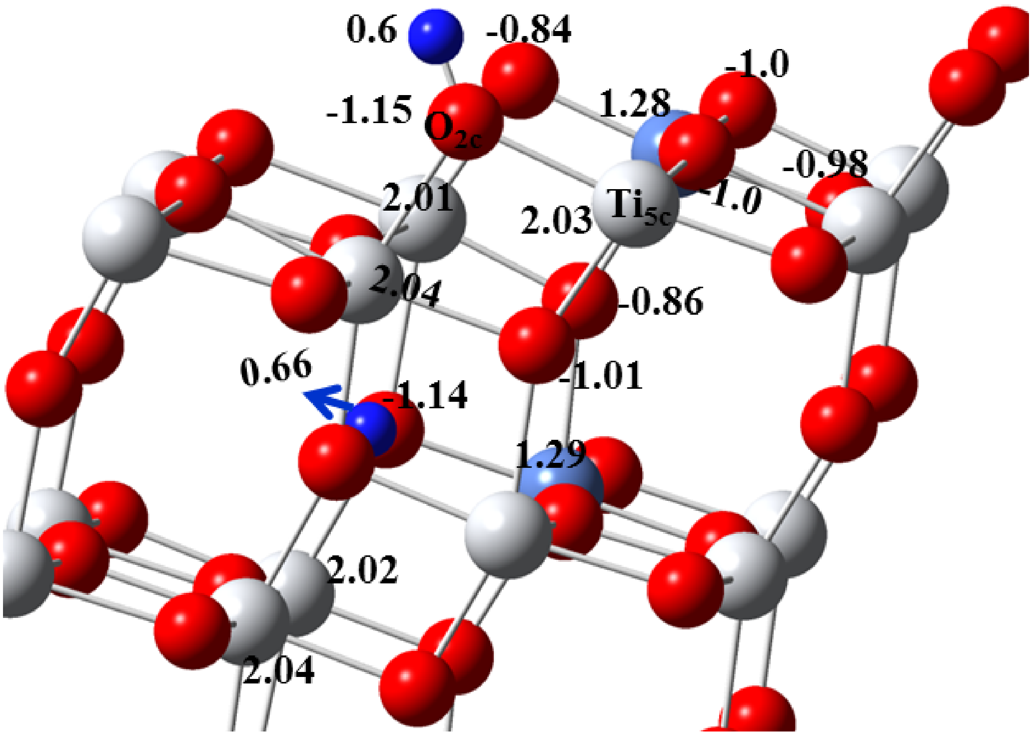
c) $H_2 \ldots O_{2c}$-2Ni



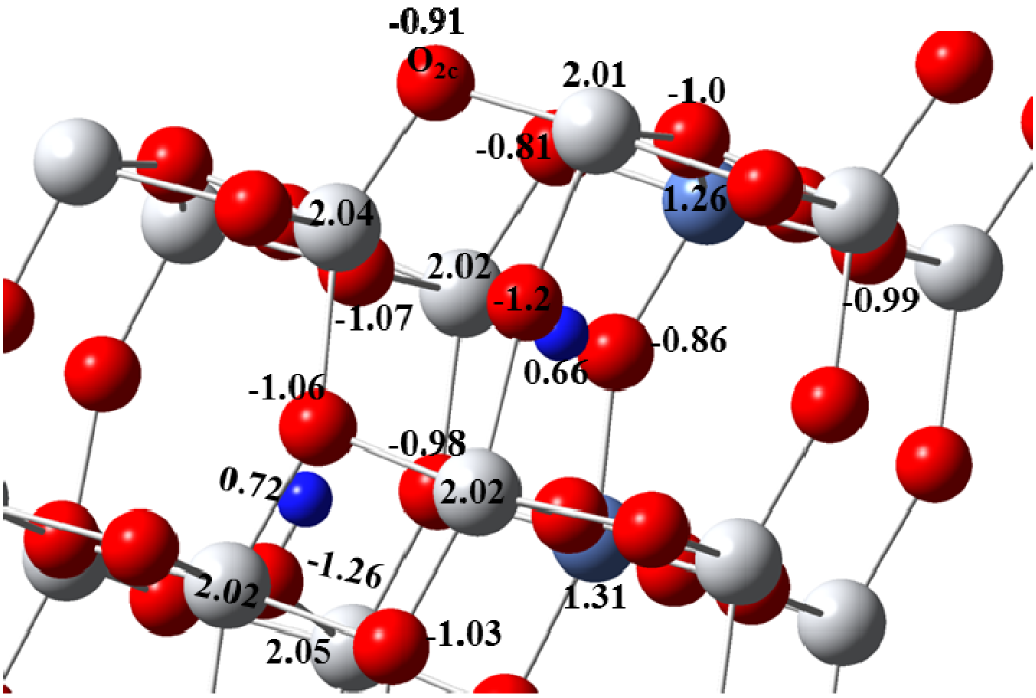
d) $H_2 \ldots 2Ni\text{-}TiO_2$



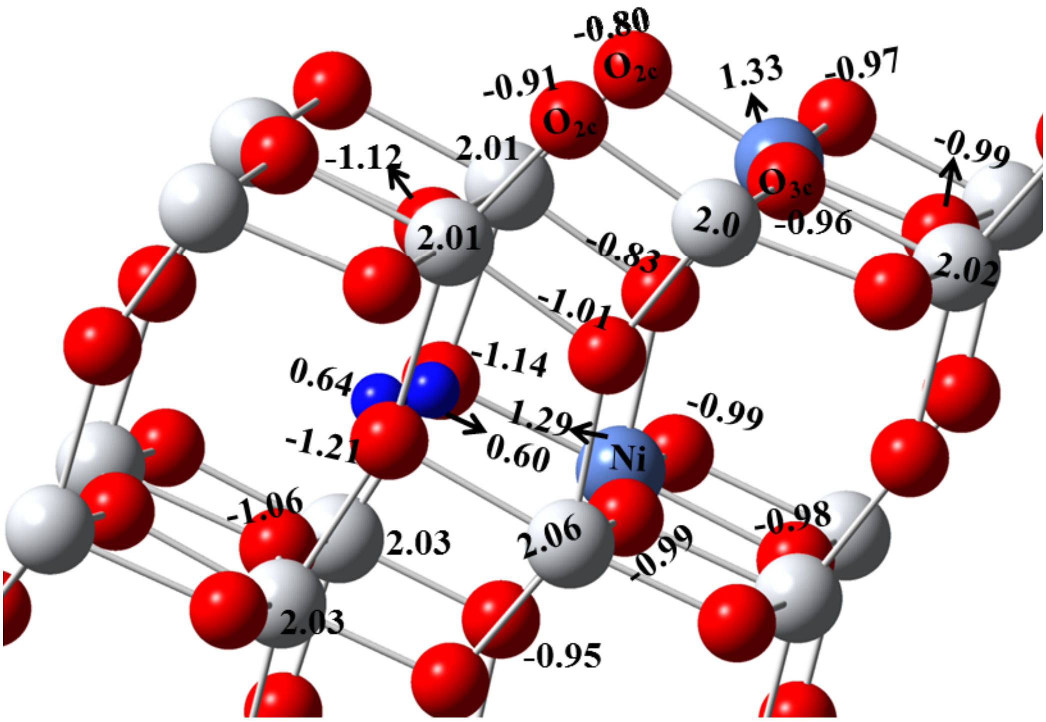
e) 2H-O_{2c}-2Ni(a)



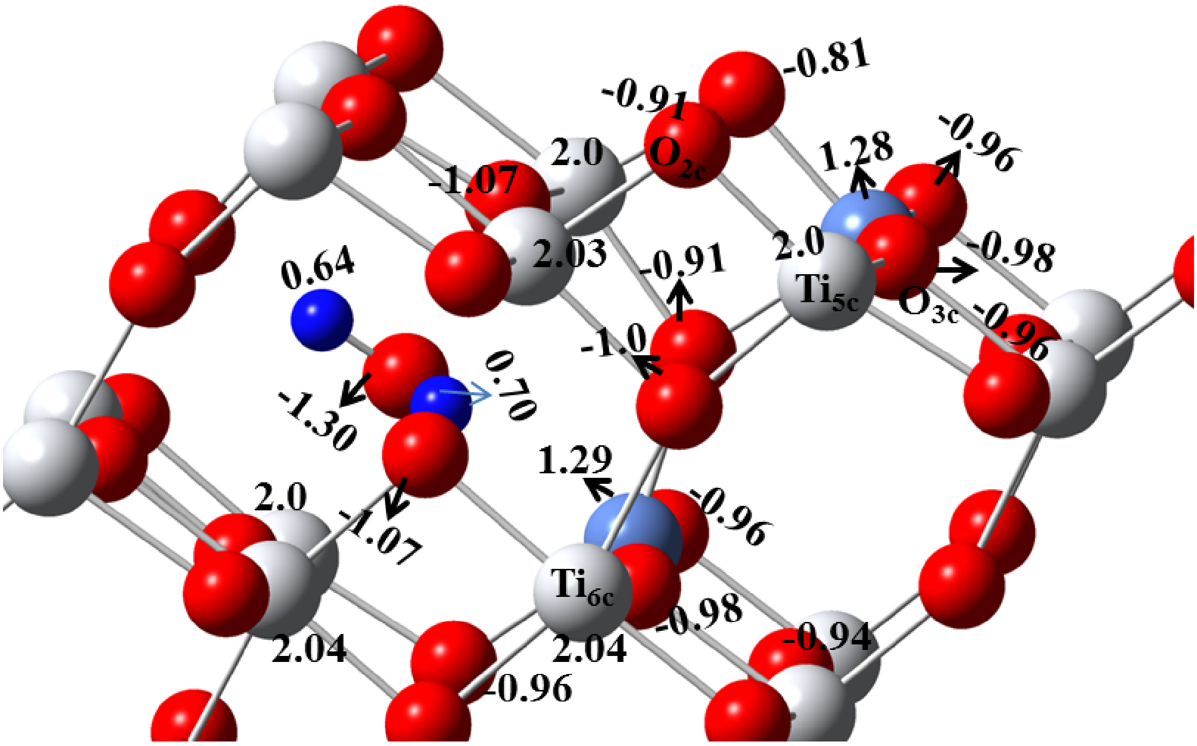
f) H-O_{sub2}, H-O_{2C}-2Ni(a)



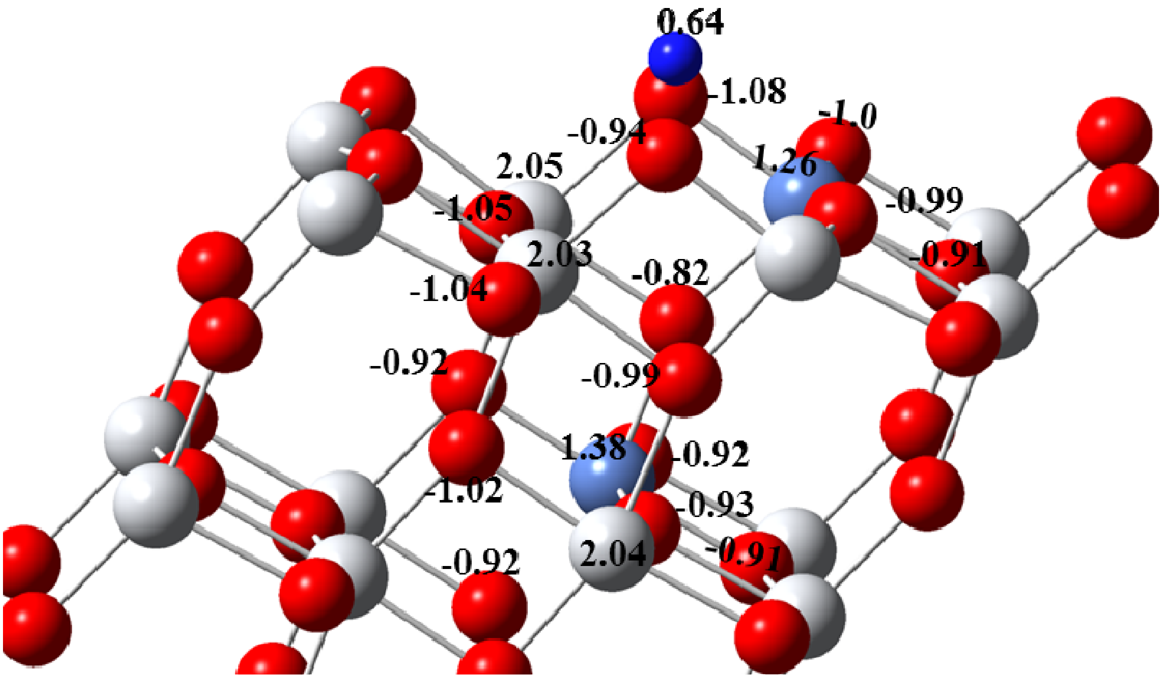
g) 2HO-2Ni(b)



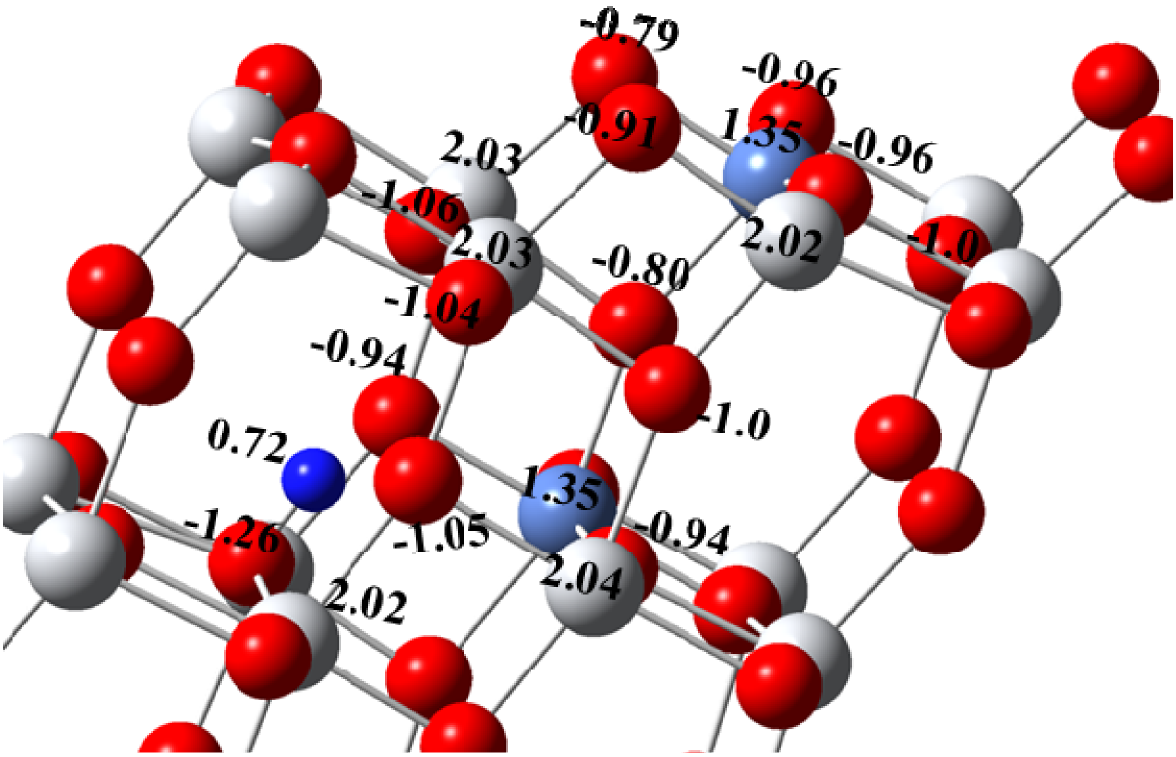
h) 2H-O_{sub2}-2Ni(b)



i) H_2O-2Ni(b)



j) H-O_{2C}-2Ni(a)



k) H-O_{sub3}-2Ni(b)

Figure S9. Bader atomic charges (*e*) for H, H_2, and H_2O adsorbed on the surface and/or subsurface layers of 2Ni-doped TiO_2 along with those of the clean TiO_2.