

Adsorption configuration and dissociative reaction of NH₃ on anatase (101) surface with and without hydroxyl groups

Supporting information

Verification

Verifications of the accuracy of the model adopted herein are carried out by computing the bulk properties and then adsorption reactions for the TiO₂ anatase (101) surface. The model is shown in Fig. 1 with a size of 24[TiO₂] units for the anatase bulk, with the Monkhorst-Pack k-point set at 6x4x3, and the E_{cut} set as 450 eV. The lattice constants obtained for the anatase crystal are $a = 3.822$ Å, and $c = 9.653$ Å, which correspond well to the X-ray diffraction results of $a = 3.782$ Å and $c = 9.502$ Å⁵³. The lattice constant obtained from the bulk calculation is applied to the surface models with a 12.63 Å vacuum space.

In calculating the adsorption on the surface, with the exception of the Monkhorst-Pack k-point sampling changed to 3x2x1, all the others parameters are as above. The adsorption energy of H₂O on TiO₂(101) is predicted by the present DFT simulation to be 20.4 kcal/mol, which is close to the experimental range of 11.5 ~ 16.1 kcal/mol⁵⁴ and is in good agreement with the other simulation values from other literature of 16.6⁵⁵, 17.3⁵⁶ and 19.2 kcal/mol⁴¹. The calculation of the energetic of dissociated state of H₂O on the surface forming the H and OH—which adsorbed on 2c-O and 5c-Ti, respectively, i.e., H-O+HO-Ti—is 10.4 kcal/mol, which is close to the former literature (6.9⁵⁵ kcal/mol and 7.74⁴¹ kcal/mol), below the reference state of H₂O(g)+TiO₂. Other data in Table 1 for H₂O, OH co-adsorption with the hydroxyl group (H co-adsorbed on 2c-O) are denoted as H₂O-Ti^a and HO-Ti^a. The OH adsorbed on 2c-O on the clean surface, which is denoted as HO-Ti, is also listed. The adsorption energy of HO-Ti is also close to the values found in former literature⁴¹. Comparing HO-Ti^a and HO-Ti in Table S1, it is clear the OH adsorption is enhanced by the presence of the hydroxyl group. Finally, recall that to obtain the energetic of H-O+HO-Ti, we use

the total energy of a TiO₂ surface with the H and OH adsorbed on O and Ti, respectively, and subtract the total energy of a TiO₂ plus a isolated H₂O molecule. Alternatively, this energetic also can be obtained by the summation of the basic reactions with the dissociation energy of H₂O into H and OH (-124.8 kcal/mol), together with H-O (55.5 kcal/mol) and HO-Ti^a (79.6 kcal/mol), in which all the values in the parenthesis are calculated by VASP. The dissociation energy of H₂O into H and O in the first parenthesis calculated also agrees an experiment value of 117.8 kcal/mol reported in the reference⁵⁷. This verification also shows the hydroxyl group effect must be considered in order to obtain the correct energetic as well as reaction pathway.

A DFT simulation was also conducted to verify the geometries of NH₃(g), NH₂(g) and NH(g). Here we put the gas molecules into a (10 Å×10 Å×10 Å) cubic cell to isolate the mutual interaction across the cell boundary. These geometries were then compared to those found in the literature, as shown in the parentheses in Table S2. The geometries of NH₃, NH₂ and NH are in agreement with previous results^{58,59}. The dissociation energies are later used to calculate the reaction energetics.

Table S1. Adsorption configurations and adsorption energies of H₂O and its fragments on anatase (101) surface

Anatase	Ti-O (Å)	O-H1(Å)	O-H2(Å)	H-O(Å)	O _{2c} -Ti _{6c} (Å)	E _{ads} (kcal/mol)	other
H ₂ O-Ti	2.244	0.985	0.981			20.4	11.5~16.1 ⁵⁴
H ₂ O-Ti ^a	2.270	0.982	0.977	1.978	2.148	17.2	18.6 ⁴¹
HO-Ti	1.849	0.979				25.1	
HO-Ti ^a	1.862	0.977		2.292	2.108	79.6	75.0 ⁴¹

$$^a E_{\text{ads}} = E_{\text{mole}} + E_{\text{surface/H}} - E_{\text{mole/surface/H}}$$

Table S2 Optimized bond lengths, bond angle

	r(N-H)	∠HNH
NH ₃ (g)	1.022(1.012) ⁵⁸	107.7°(106.7°) ⁵⁸
NH ₂ (g)	1.037(1.024) ⁵⁸	103.0°(103.4°) ⁵⁸
NH(g)	1.053(1.036) ⁵⁹	

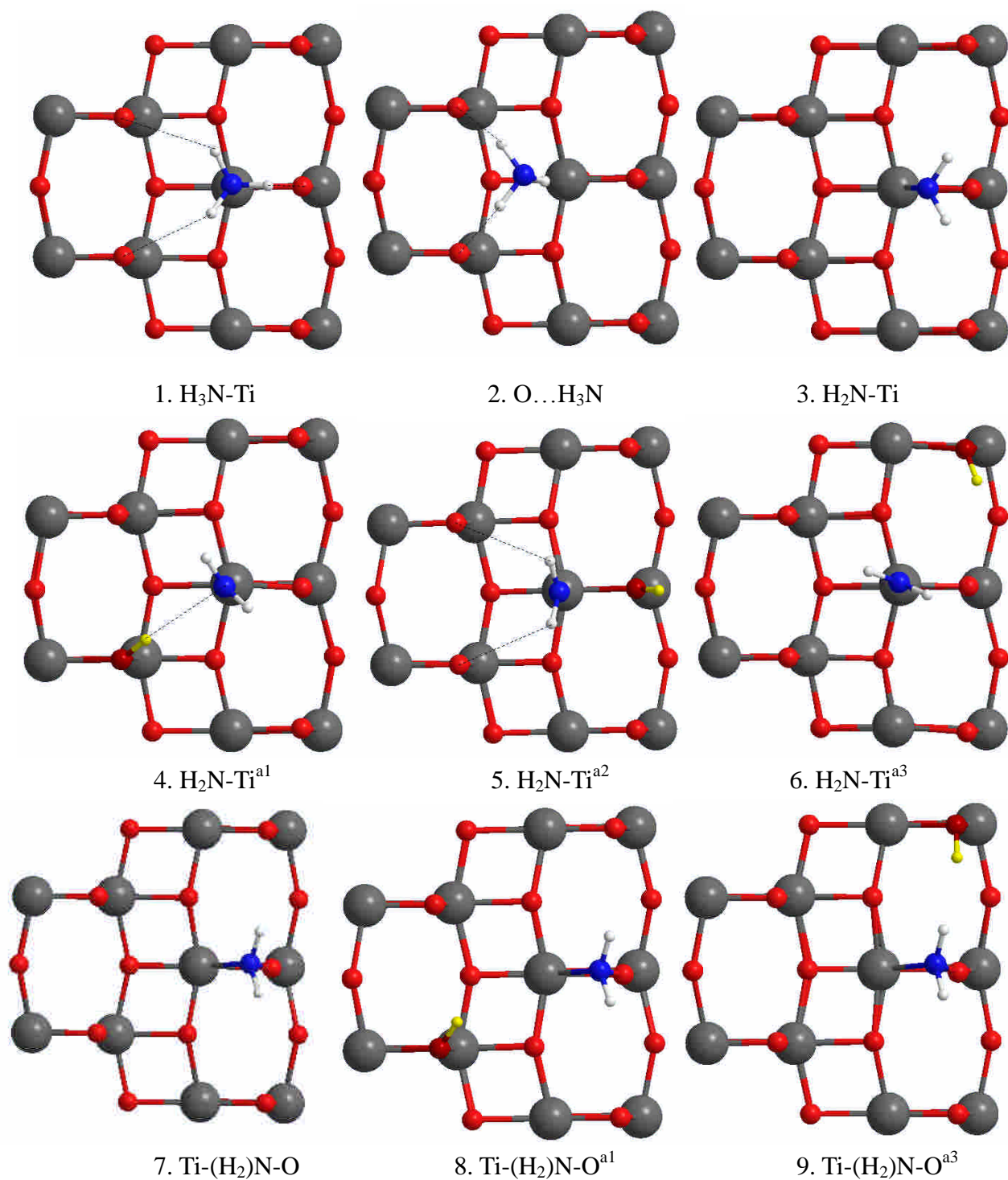


Figure S1 Top views of configurations in Fig. 2. Note that the atoms at the lower right of each are repeated from upper right.

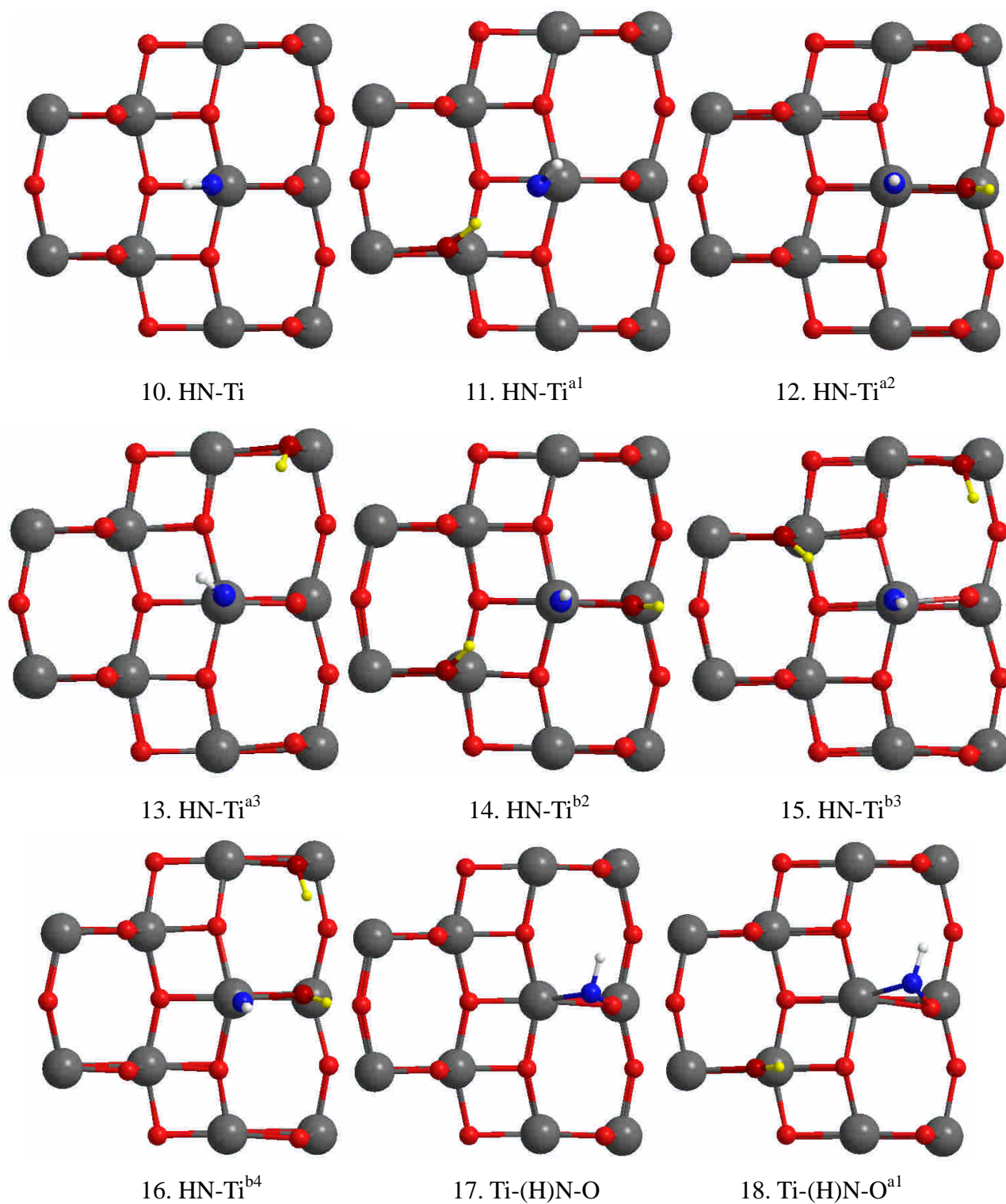


Figure S1 (continued) Top views of configurations in Fig. 2. Note that the atoms at the lower right of each are repeated from upper right.

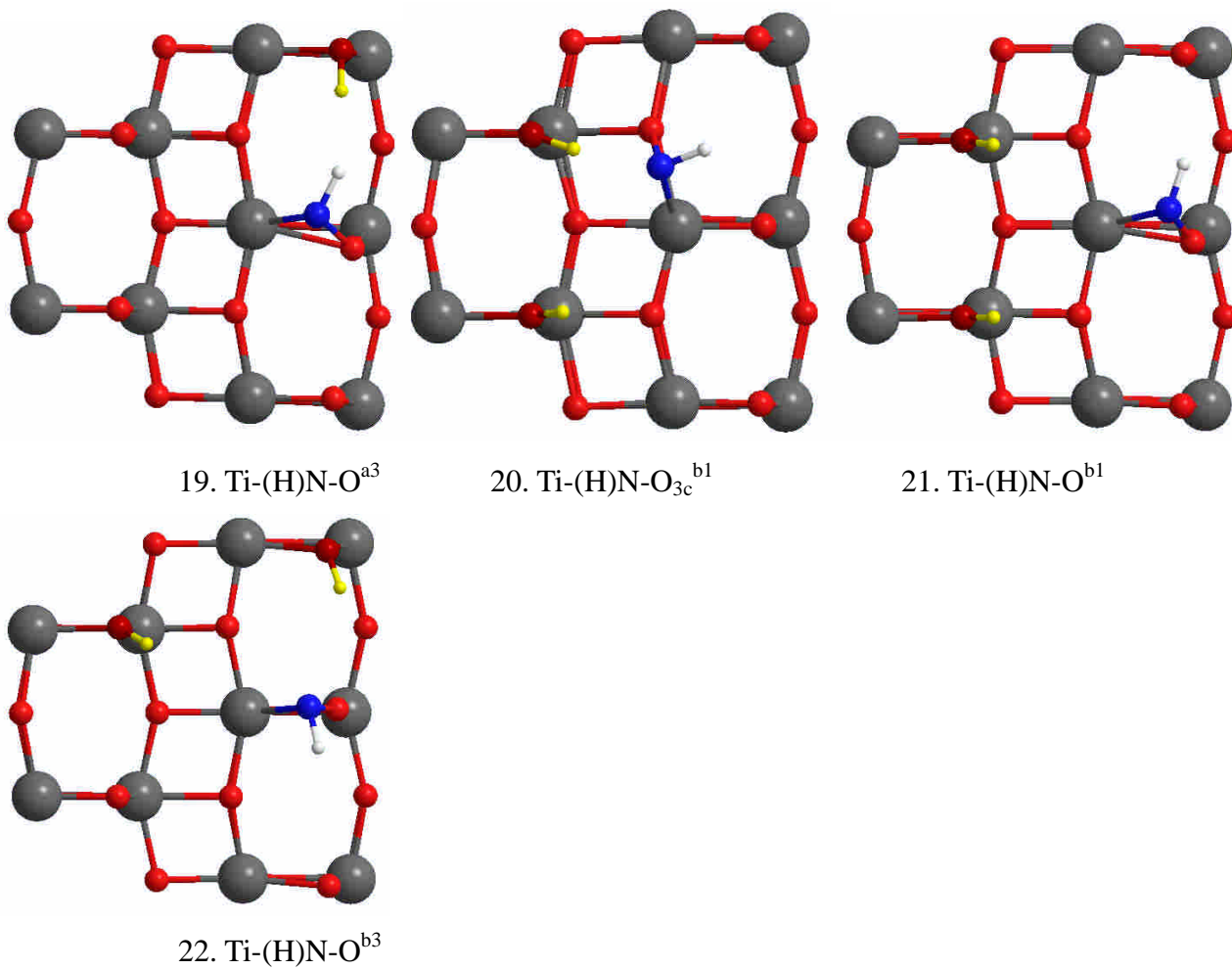


Figure S1 (continued) Top views of configurations in Fig. 2. Note that the atoms at the lower right of each are repeated from upper right.

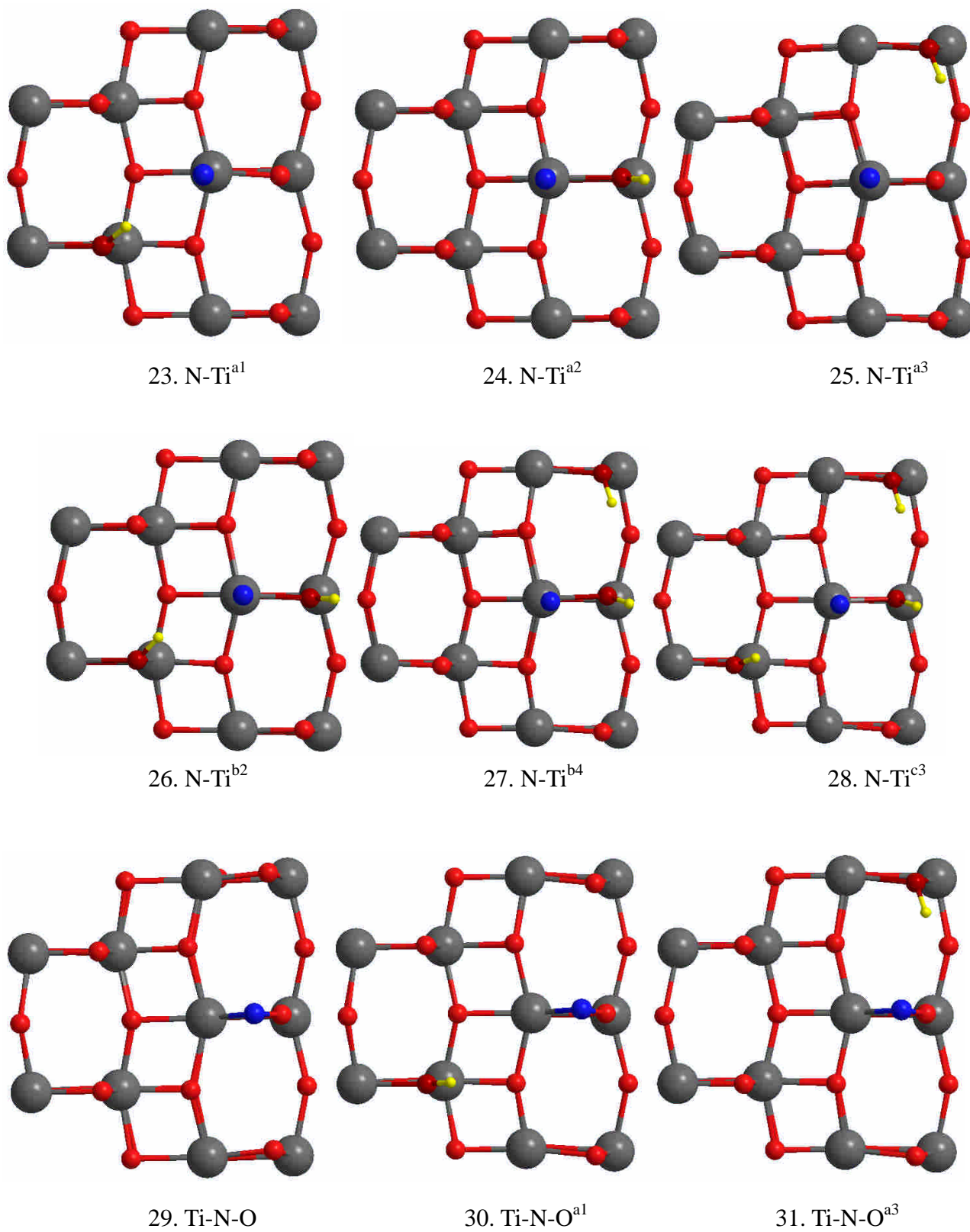


Figure S2 Top views of configurations in Fig. 3. Note that the atoms at the lower right of each are repeated from upper right.

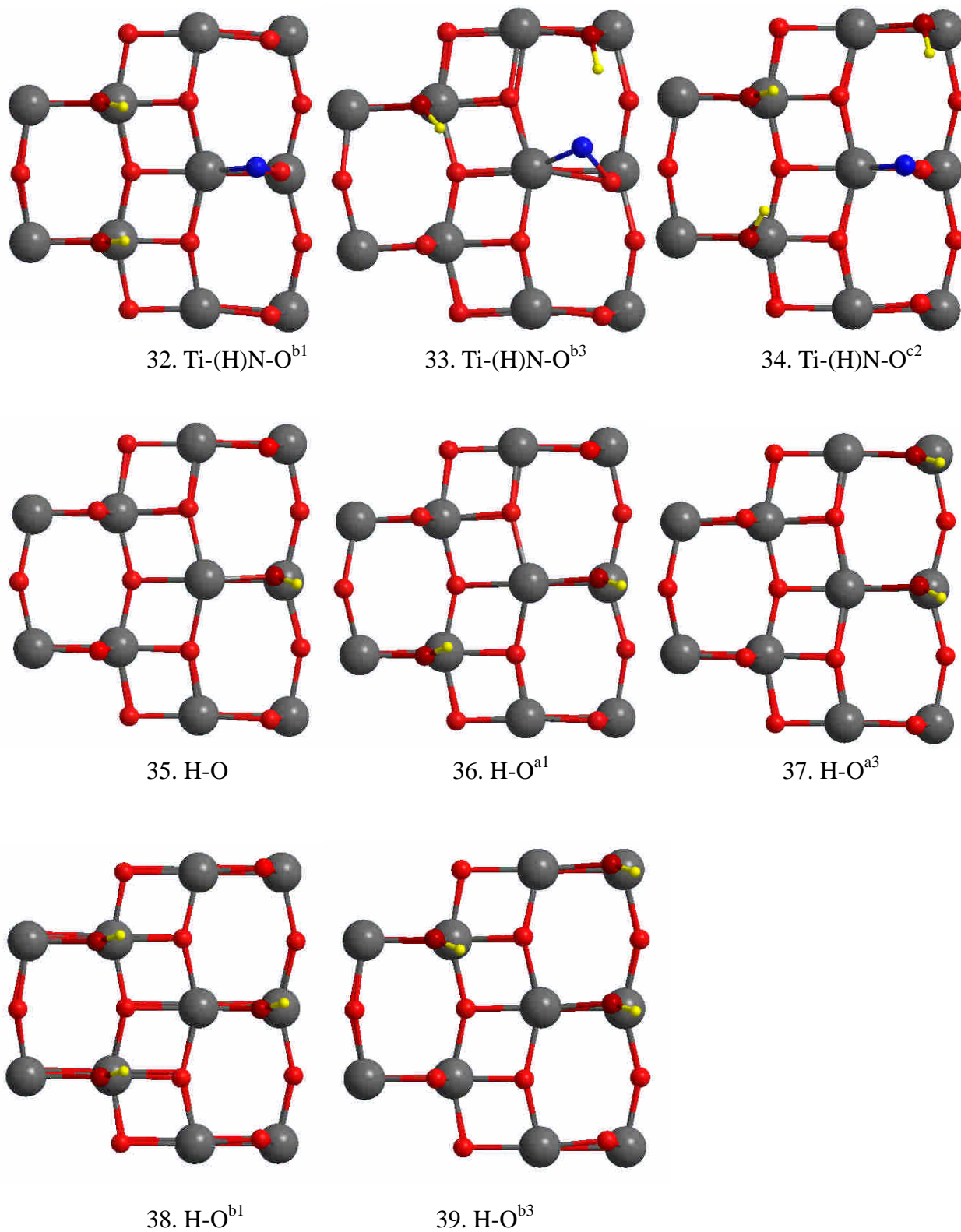


Figure S2 (continued) Top views of configurations in Fig. 3. Note that the atoms at the lower right of each are repeated from upper right.