

Role of Hydroxyl Groups in the NH_x ($x = 1-3$) Adsorption on the TiO_2 Anatase (101) Surface Determined by a First-Principles Study

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A spin-polarized density functional theory calculation was carried out to study the adsorption of NH_x species ($x = 1-3$) on a TiO_2 anatase (101) surface with and without hydroxyl groups by using first-principles calculations. It was found that the present hydroxyl group has the effect of significantly enhancing the adsorption of monodentate adsorbates $\text{H}_2\text{N}-\text{Ti}(\text{a})$ compared to that on a bare surface. The nature of the interaction between the adsorbate (NH_x) and the hydroxylated or bare surface was analyzed by the Mulliken charge and density of states (DOS) calculations. This facilitation of NH_2 is caused by the donation of coadsorbed H filling the nonbonding orbital of NH_2 , resulting in an electron gain in NH_2 from the bonding. In addition, the upper valence band, which originally consisted of the mixing of O 2p and Ti 3d orbitals, has been broadened by the two adjacent H 1s and NH_2 σ_y^p orbitals joined to the bottom of the original TiO_2 valence band. The results are important to understand the OH effect in heterogeneous catalysis.

1. Introduction

To achieve better device functionality of dye-sensitizer solar cells,¹⁻³ different kinds of gas-phase molecules have been reacted with the TiO_2 surface at the Ti cation site (or O anion site) to form specific adsorbates that functionalize the TiO_2 surface. The adsorbates may then act as precursors⁴⁻¹² that allow gas molecules to subsequently react, anchoring groups¹³⁻²⁰ that provide

better electron transfer or doping molecules²¹⁻²⁶ that narrow the band gap or band shift^{27,28} to increase the photovoltaic efficiency. Thus, understanding the reactivity of gas molecules and the reaction mechanism is not only of fundamental scientific interest but also of use in anticipating the success of an engineering process.

Moisture (water) certainly exists in catalytic systems. It is widely accepted that H_2O can readily dissociate on the O vacancy of the TiO_2 surface to form two hydroxyl groups.^{29,30} The free-energy barrier related to forming these hydroxyl groups is only 0.11 eV.^{29,30} Thus, the natural formation of hydroxyl groups on the surface occurs as a result of the surface defects as well as the presence of moisture itself. Tilocca et al.³¹ studied the adsorption and reactivity of O_2 on a hydroxylated TiO_2 surface in the presence of two OH groups, and Liu et al.³² studied the O_2 adsorption on one OH group existing on the surface. Both of them pointed out that surface properties might be significantly modified by the hydroxyl groups; even only one OH can facilitate O_2 adsorption on the TiO_2 rutile surface. This phenomenon also has been confirmed by other recent publications that examine the hydroxyl's effect on reaction pathways on the anatase surface such that the hydroxyl group's presence on the surface might influence the adsorption of other molecules, such as CH_3OH ,³³ $\text{B}(\text{OH})_3$,¹¹ HN_3 ,⁴ NH_3 ,³⁴ H_2S ,³⁵ and HNO_3 .³⁶

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on the TiO₂ anatase surface. In addition, Zapol and co-worker³⁷ also reported that the morphology of TiO₂ nanocrystals is affected by the presence of water and the consideration of hydrated nanocrystal surfaces is necessary to accurately predict the correct size dependence of the anatase-to-rutile phase transition. Prezhdo et al.³⁸ studied the electron transfer (ET) dynamics of wet electrons on the partially hydroxylated TiO₂ surface with one monolayer of water coverage and found that ET is fast because of the strong coupling between TiO₂ and water. However, the reason for the effect of the hydroxyl groups on the reactivity of the gas molecule has not been explained in detail.

The TiO₂ nanoparticle film is a polycrystalline material with different phases. The rutile (110) and anatase (101) surfaces, which have the lowest surface energies with similar characteristics, may coexist in a nanoparticle film.³⁹ Theoretically, the (101) surface is the most stable surface in anatase as reported by Labat et al.⁴⁰ Therefore, the objective of this article is to study the adsorption of NH_x ($x = 1-3$) only on the TiO₂ anatase (101) surface in the presence of hydroxyl groups. NH_x is selected because it is usually used as the precursor of N-doped TiO₂. In addition, it is also important to remove ammonia from air or water for environmental preservation. Selective catalytic oxidation of NH₃ to N₂ and H₂O has attracted interest with respect to the reduction of NH₃ pollution in waste streams.⁴¹ Although two OH groups are always produced in a vacancy, in this study only one OH group existed on the TiO₂ surface. In this article, we present the molecular structures, bonding energies, and detailed bonding interactions between NH_x and the surface by density functional theory (DFT) calculations. The interactions of NH_x on the hydroxylated surface have been analyzed by the Mulliken charge and density of states (DOS) calculations.

2. Computational Model and Method

All geometrical structures are optimized using the DMol3⁴²⁻⁴⁴ package in Material Studio (version 4.3) and are calculated on the basis of DFT. The physical plane wave functions are expanded in terms of a double-numeric-quality basic set with polarization functions (DNP).^{45,46} The core electrons are treated with DFT semicore pseudopotentials (DSPPs).⁴⁷ The generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE)⁴⁸ formulation is used for all calculations and has been shown to work well for the bonding energy.⁴⁸ The spin-polarization effects are also included in the calculations for the open-shell systems. The Brillouin zone is sampled with the chosen Monkhorst-Pack⁴⁹ k points, which ensures the convergence of the whole system. The convergence criteria for the self-consistent field (SCF) energy and displacement are set to 1×10^{-6} Ha and 5×10^{-3} Å, respectively. The slab model with 24 TiO₂ units used in this study is shown in Figure 1. The dimensions of this supercell are 11.08 Å × 7.65 Å × 22.47 Å. There are four adsorption

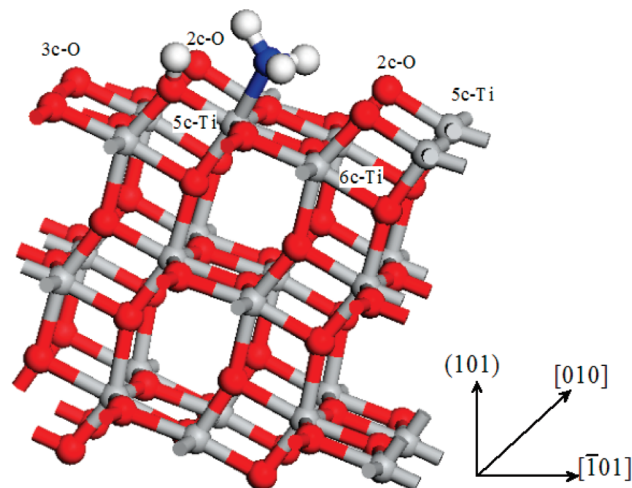


Figure 1. Schematic diagram of the TiO₂ (101) surface with the NH₃ adsorbate and one hydroxyl group, where red atoms are O, dark-gray atoms are Ti, blue atoms are N, and white atoms are H.

sites: 2-fold-coordinate O, 3-fold-coordinate O, 5-fold-coordinate Ti, and 6-fold-coordinate Ti atoms, as indicated by 2c-O, 3c-O, 5c-Ti, and 6c-Ti, respectively, which have been labeled on the TiO₂ surface (Figure 1.). Usually, the 2c-O and 5c-Ti atoms are more reactive than the 3c-O and 6c-Ti atoms because of their unsaturated coordination. All slabs are separated by a vacuum space of greater than 13 Å, which guarantees no interaction between the slabs.

The adsorption energy is calculated for all possible adsorbates, NH_x, on the clean surface (without the presence of hydroxyl group) as follows

$$E_{\text{ads}} = E_{\text{mole}} + E_{\text{surface}} - E_{\text{mole/surface}} \quad (1)$$

where E_{mole} is the energy of an isolated molecule that represents NH_x, E_{surface} is the energy of a clean TiO₂ anatase (101) surface, and $E_{\text{mole/surface}}$ is the total energy of the same molecule adsorbed on the TiO₂ anatase (101) surface. Note that a positive value for E_{ads} suggests stable adsorption.

In the presence of the hydroxyl group's coadsorption on the surface, where the H atom is adsorbed on the 2c-O, the adsorption energy is calculated according to the equation

$$E_{\text{ads}} = E_{\text{mole}} + E_{\text{surface/H}} - E_{\text{mole/surface/H}} \quad (2)$$

The term $E_{\text{surface/H}}$ represents the energy of the surface including the hydroxyl group. $E_{\text{mole/surface/H}}$ is the total energy of the surface including the hydroxyl group and NH_x coadsorbed elsewhere on the surface. It should be mentioned that we also perform calculations for NH₃ adsorption on two OH groups' surfaces corresponding to a coverage of $1/2$ ML using the most stable configurations. It is shown that the OH group coverage effect becomes less important because of the almost unchanged adsorption energy and structural parameters of the adsorbed NH₃ (Table 3). Liu et al.³² also showed that only one OH group existed on the TiO₂ surface, which has a significant effect on adsorption. Therefore, in the present study we use only one OH adsorbed on the surface corresponding to a coverage of $1/4$ ML as the hydroxylated surface model.

3. Results and Discussion

3.1. Verification. The lattice constant of TiO₂ is first obtained by using the same calculation conditions as above, adding 4 TiO₂ units and with $7 \times 3 \times 3$ k points. The optimized parameters of bulk TiO₂ are $a = 3.823$ Å, $c = 9.672$ Å, $2\theta = 155.328^\circ$, $d_{\text{eq}} = 1.957$, and $d_{\text{ap}} = 2.000$, where d_{eq} is the equatorial Ti–O bond

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Table 1. Comparison of the Calculated Structure Parameters and Band Gap of TiO₂ Anatase with Previous Studies

Structural Parameters					
	this work	ref 50	ref 51	ref 25	exp ⁵³
<i>a</i> (Å)	3.823	3.692	3.763	3.785	3.782
<i>c</i> (Å)	9.672	9.471	9.851	9.715	9.502
<i>d</i> _{eq} (Å)	1.957	1.893	1.939		1.932
<i>d</i> _{ap} (Å)	2.000	1.948	1.995		1.979
<i>c/a</i>	2.530	2.566	2.618		2.512
<i>u</i> (= <i>d</i> _{ap} / <i>c</i>)	0.207	0.206	0.202	0.206	0.208
2θ (deg)	155.328	154.4	152.1		156.3
Band Gap					
	this work	ref 26	refs 25 and 28	ref 52	exp ^{54,55}
<i>E</i> _g (eV)	2.163	2.39	2.14	2.0	3.2

length, *d*_{ap} is the apical Ti–O bond length, and *θ* is half of the angle spanned by two *d*_{eq} lengths. Our calculated results are consistent with the previous theoretical^{25,26,28,50–52} and experimental^{53–55} results listed in Table 1.

The band structure and density of states (DOS) of the TiO₂ anatase (101) surface is also calculated. The direct band gap is found a Γ point of 2.163 eV, consistent with the previously calculated values in the literature^{25,26,28,52} but still far smaller than the experimental values,^{54,55} as seen in Table 1. The DOS of the TiO₂ surface is shown in Figure 2. The underestimation characteristic of the band gap is due to the failure of well-known shortcoming in the DFT calculations,^{56–58} which use the local exchange-correlation functional. It can be corrected by introducing an empirical scissors correction that is effectively a rigid shift of the conduction band with respect to the valence band when there is experimental information about the electronic structure. However, to deal with the band gap problem, a new exchange-correlation functional such as a nonlocal exchange-correlation functional should be developed. As seen in Figure 2, the valence band consists of a peak and a band, both below the Fermi level. The first peak present at the lowest energy (approximately at –17.5 eV) is mainly the O 2s orbital. The bonding of Ti and O primarily involves the mixing of O 2p and Ti 3d orbitals and is located in the upper part of the valence band just below the Fermi level. The upper valence bandwidth of approximately 5.0 eV is also consistent with values in the literature—5.05 eV⁵⁰ and 5.0 eV.^{25,28} The conduction band above the Fermi level primarily consists of the Ti 3d orbital.

As summarized in Table 2, the calculated geometric parameters of gas-phase NH_x in a 15 Å³ cubic box are consistent with the literature.^{59,60} In addition, the adsorption energy of H₂O adsorbed

on the TiO₂ anatase surface is 19.8 kcal/mol, which is close to the experimental result⁶¹ and is in good agreement with the other simulation values from the literatures of 16.6,⁶² 17.3,⁶³ and 19.2¹¹ kcal/mol. The energy, which uses H₂O plus TiO₂ as the energy reference of H–O(a) + HO–Ti(a), is obtained as 12.7 kcal/mol, which is close to 10.2,⁶² 11.7,²⁰ and 19.3⁶⁴ kcal/mol found in the literature. This also indicates that molecular water adsorption is more favorable than dissociative adsorption on a perfect TiO₂ surface. The other verifications of the adsorption energies of H–O(a) + H₂O–Ti(a), H–O(a), and HO–Ti(a) are compared in Table 2. All show agreement with the literature.¹¹

3.2. NH_x Adsorption with and without a Hydroxyl Group. The adsorption energy and configuration of most stable NH_x with and without a hydroxyl group are listed in Table 3 and Figure 2. Other possible structures are display in Figure S1 (Supporting Information). For the hydroxylated surface, H is adsorbed on 2c–O (i.e., H–O(a)). The adsorption energy is 58.0 kcal/mol, and the H–O_{2c} bond length is 0.977 Å. The bonding between H and 2c–O involves the mixing of the H 1s orbital and O 2s and 2p orbitals. The H atom plays the role of an electron donor because of the high electronegativities of 2c–O. In the present work, we discuss only the interaction between the most stable NH_x adsorption and surface (bare or hydroxylated surface).

NH₃ can form a monodentate adsorbate on 5c–Ti (i.e., H₃N–Ti(a)), where the N–Ti bond length is 2.285 Å and the adsorption energy is 28.4 kcal/mol. Comparing the N–H bond lengths of the adsorbate to those of NH₃(g), they are nearly unchanged. This is because the bonding between NH₃ and 5c–Ti involves mainly the nonbonding (lone pair) electron in the *P_z* (π_z^{nb}) orbital, which is perpendicular to the bonding plane of N and H atoms. Although the H atom is present in the coadsorption configuration, where the bond length between H and 2c–O is 0.978 Å, the N–Ti bond length becomes longer (2.306 Å) and the adsorption energy consequently becomes slightly smaller (26.9 kcal/mol). In addition, similar to the previous case, the N–H bond lengths are almost as the same as those of NH₃(g). The closeness in adsorption energy of these two adsorbates, H₃N–Ti(a) and H₃N–Ti, H–O_{2c}(a), indicates that there is no influence to facilitate or diminish the adsorption of NH₃ on 5c–Ti(a). The reason for the longer N–Ti bond length is that H-electron donation alleviates the donation of NH₃ (which will be discussed in detail in the next section), which is why the adsorption energy of H₃N–Ti(a)^a is smaller than that of H₃N–Ti(a).

As presented in Figure 2, NH₂ is favorably adsorbed on 5c–Ti, forming the monodentate adsorbate of H₂N–Ti(a). The less stable bidentate configuration is displayed in Figure S1. The N–Ti bond length of monodentate H₂N–Ti(a) is 2.224 Å, and the adsorption energy is 24.5 kcal/mol. In addition, the N–H bond lengths become slightly shorter compared to those of H₃N–Ti(a) because the bonding between NH₂ and 5c–Ti involves the σ bond of NH₂. Although H is present in the coadsorption configuration, the adsorption energy increases to 55.7 kcal/mol. The larger adsorption energy is due to the stronger bonding between NH₂ and the surface and the formation of a hydrogen bond. (The N–Ti bond length and hydrogen bond of H₂N–Ti, H–O_{2c}(a) are 1.839 and 2.487 Å, respectively.) The adsorption energy increases by 31.2 kcal/mol in the presence of H as compared to that of NH₂(a), a significant increase in the adsorption

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Table 2. Optimized Geometric Parameters of $\text{NH}_x(\text{g})$, Adsorption Energy of Adsorbates H_2O , HO , and H , and Energy of $\text{H}_2\text{O}-\text{Ti}(\text{a}) \rightarrow \text{H}-\text{O}(\text{a}) + \text{HO}-\text{Ti}(\text{a})$

species	this work				other work
	$r(\text{N}-\text{H}1)$	$r(\text{N}-\text{H}2)$	$r(\text{N}-\text{H}3)$	$\angle \text{H-N-H}$	$\angle \text{H-N-H}, r(\text{N}-\text{H})$
$\text{NH}_3(\text{g})$	1.023	1.023	1.023	105.3°	106.7°, 1.012 ⁵⁹
$\text{NH}_2(\text{g})$	1.038	1.038		101.7°	103.4°, 1.024 ⁵⁹
$\text{NH}(\text{g})$	1.052				1.036 ⁶⁰
adsorbates	$r(\text{O}-\text{Ti})$	$r(\text{O}-\text{H}1)$	$r(\text{O}-\text{H}2)$	E_{ads}	E_{ads}
$\text{H}_2\text{O}-\text{Ti}(\text{a})$	2.293	0.978	0.974	19.8	11.5–16.1, ⁶¹ 16.6, ⁶² 17.3, ⁶³ 19.2 ¹¹
$\text{HO}-\text{Ti}(\text{a})$	1.822	0.970		25.1 ^b	1.851, ¹¹ 24.9 ¹¹
$\text{H}-\text{O}(\text{a})$	0.977 ^a			58.0	0.970, ¹¹ 56.2 ¹¹
	$r(\text{O}-\text{Ti})$	$r(\text{O}-\text{H})$		E_{ads}	E_{ads}
$\text{H}-\text{O}(\text{a}) + \text{HO}-\text{Ti}(\text{a})$	1.826	0.970		12.7 ^c	10.2, ⁶² 11.7, ²⁰ 19.3 ⁶⁴

^a The value is the bond length of $\text{H}-\text{O}_{2\text{c}}$. ^b $E_{\text{ads}} = E(\text{TiO}_2 \text{ surface}) + E(\text{HO}) - E(\text{HO}-\text{Ti}(\text{a}))$ ^c $E_{\text{ads}} = E(\text{TiO}_2 \text{ surface}) + E(\text{H}_2\text{O}) - E(\text{H}-\text{O}(\text{a}) + \text{HO}-\text{Ti}(\text{a}))$

Table 3. Adsorption Energy (kcal/mol) and Adsorption Structure of NH_x with and without a Hydroxyl Group

adsorbate	$r(\text{N}-\text{Ti})$	$r(\text{N}-\text{O})$	$r(\text{N}-\text{H}1)$	$r(\text{N}-\text{H}2)$	$r(\text{N}-\text{H}3)$	$\text{H}-\text{O}_{2\text{c}}$	E_{ads}
Hydroxyl Group							
$\text{H}-\text{O}(\text{a})$						0.977	58.0
			NH_3				
$\text{H}_3\text{N}-\text{Ti}(\text{a})$	2.285		1.023	1.023	1.026		28.4
$\text{H}_3\text{N}-\text{Ti}, \text{H}-\text{O}(\text{a})$	2.306		1.023	1.023	1.027	0.978	26.9
$\text{H}_3\text{N}-\text{Ti}, 2\text{H}-\text{O}(\text{a})^a$	2.298		1.023	1.023	1.026	0.978	27.4
			NH_2				
$\text{H}_2\text{N}-\text{Ti}(\text{a})$	2.224		1.029	1.032			24.5
$\text{H}_2\text{N}-\text{Ti}, \text{H}-\text{O}(\text{a})$	1.839		1.023	1.021		0.978	55.7
			NH				
$\text{Ti}-(\text{H})\text{N}-\text{O}(\text{a})$	1.991	1.402	1.034				41.7
$\text{Ti}-(\text{H})\text{N}-\text{O}, \text{H}-\text{O}(\text{a})$	1.954	1.439	1.035			0.984	43.7

^a $\text{H}_3\text{N}-\text{Ti}, 2\text{H}-\text{O}(\text{a})$ represents NH_3 adsorbed on a hydroxylated TiO_2 surface in the presence of two OH groups.

energy of $\text{H}_2\text{N}-\text{Ti}, \text{H}-\text{O}_{2\text{c}}(\text{a})$ that indicates that the hydroxyl group is present to facilitate NH_2 adsorption on 5c-Ti. Actually, the adsorption of NH_2 , which is similar to the adsorption of NH_3 , involves the donation of excess electrons and mixing with the 3d orbital of the 5c-Ti surface atom. However, the H atom plays a similar role because of the relatively large electronegativities of $2\text{c}-\text{O}$ that attract its electron. In fact, the delocalized electron over 5c-Ti will diminish the adsorption of NH_2 , an explanation that seems valid for $\text{H}_3\text{N}-\text{Ti}(\text{a})$ but not for $\text{H}_2\text{N}-\text{Ti}(\text{a})$. The enhancement of the adsorption of NH_2 by the hydroxyl group cannot be simply explained by this but instead is a result of the bonding characteristics, as explained in the following section.

Different from H_2N , the NH fragment is likely to form bidentate adsorbate $\text{Ti}-(\text{H})\text{N}-\text{O}(\text{a})$. The less stable monodentate configuration is displayed in Figure S1. The adsorption energy of bidentate adsorbate $\text{Ti}-(\text{H})\text{N}-\text{O}(\text{a})$ is 41.7 kcal/mol, the N–Ti bond length is 1.991 Å, and the N–O bond length is 1.402 Å. As compared to the bond length of N–H of the NH fragment, the N–H bond length (1.034 Å) becomes shorter than in its gas phase (1.052 Å). This reveals that the bonding of NH adsorbed on both $2\text{c}-\text{O}$ and 5c-Ti involves the σ orbital of NH. Although the hydroxyl group is present, the adsorption energy changes only slightly to 43.7 kcal/mol, only a 2.0 kcal/mol increase as compared to that of $\text{Ti}-(\text{H})\text{N}-\text{O}(\text{a})$. In addition, the N–Ti bond length is slightly decreased (1.954 Å) and the N–O bond length is slightly increased (1.439 Å) as compared to

those of $\text{Ti}-(\text{H})\text{N}-\text{O}(\text{a})$. The $\text{H}-\text{O}_{2\text{c}}$ bond length increases (0.984 Å), showing that the adsorption of NH on the surface also influences the adsorption of H on $2\text{c}-\text{O}$. One should note that the present hydroxyl group has a significant effect on the adsorption of monodentate $\text{HN}-\text{Ti}(\text{a})$ compared to that of bidentate $\text{Ti}-(\text{H})\text{N}-\text{O}(\text{a})$ (Figure S1). Similar to monodentate $\text{H}_2\text{N}-\text{Ti}(\text{a})$, the adsorption energy increases from 13.3 to 40.0 kcal/mol because of the stronger bonding between NH and the surface and the formation of a hydrogen bond. (The N–Ti bond length and hydrogen bond length of $\text{HN}-\text{Ti}, \text{H}-\text{O}_{2\text{c}}(\text{a})$ are 1.866 and 1.891 Å, respectively.) One should expect that monodentate $\text{HN}-\text{Ti}(\text{a})$ has a similar effect to monodentate $\text{H}_2\text{N}-\text{Ti}(\text{a})$.

In addition, to characterize the key reaction pathways of the NH_3 adsorption/dissociation processes on the TiO_2 anatase (101) surface, we employ the energetically most stable configurations obtained from the NH_x adsorption to map out the potential energy surface (PES) using the NEB method⁶⁵ by connecting the local minima. As shown in Figure 3, NH_3 first adsorbs on the surface without an intrinsic transition state, producing $\text{NH}_3-\text{Ti}(\text{a})$ with an exothermicity of 28.4 kcal/mol, followed by the dissociation process ($\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$) to form $\text{H}_2\text{N}-\text{Ti}(\text{a}), \text{H}-\text{O}(\text{a})$. The dissociating H atom primarily attaches to an adjacent bridging $\text{O}_{2\text{c}}$ anion, forming an O–H bond via TS1 with a

(65) Henkelman, G.; Uberuaga, B. P.; Jonsson, H. *J. Chem. Phys.* **2000**, *113*, 9901.

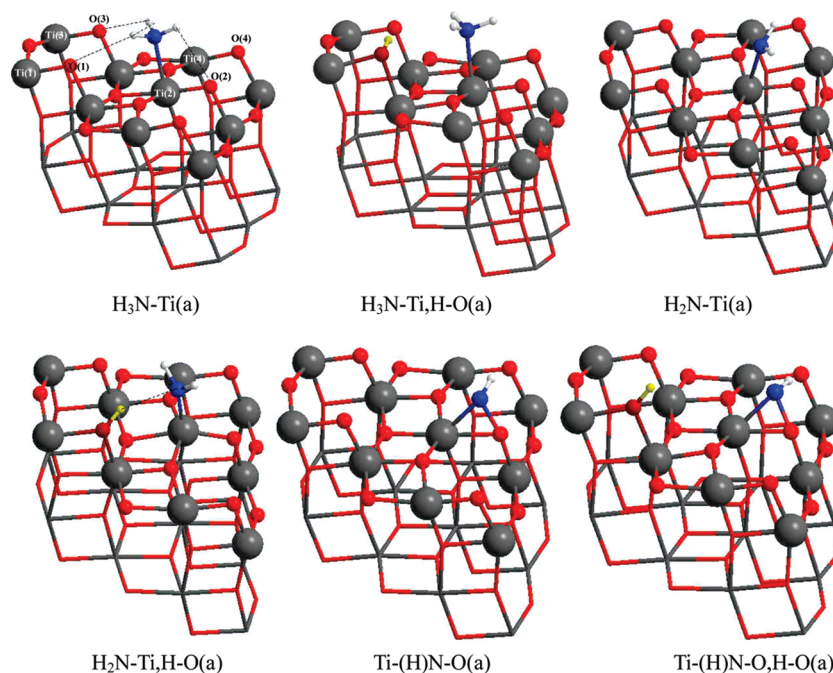


Figure 2. Adsorption configurations of NH_x ($x = 1-3$) on an anatase (101) surface with and without hydroxyl groups where red atoms are O, dark-gray atoms are Ti, blue atoms are N, and white and yellow atoms are H.

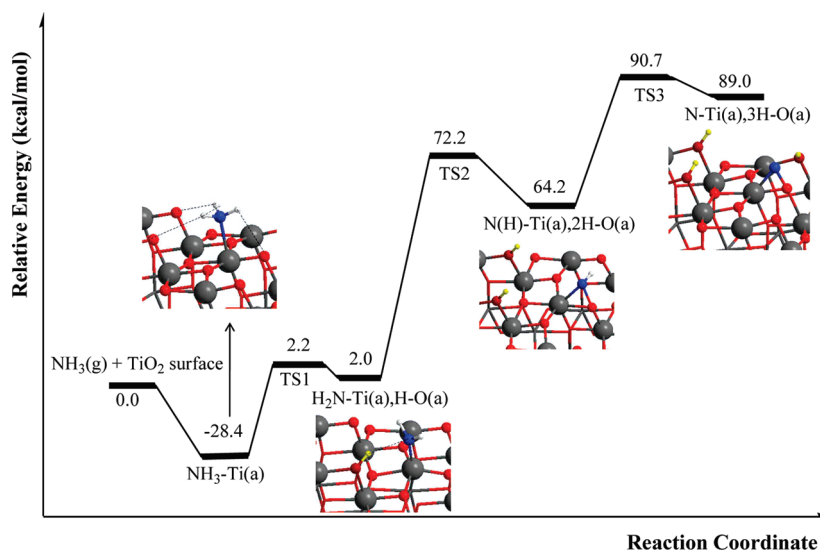


Figure 3. Potential energy profile of NH_3 dissociation on the anatase (101) surface.

reaction barrier of 30.6 kcal/mol. The second dissociation step ($\text{NH}_2 \rightarrow \text{NH} + \text{H}$) takes place by overcoming a very high reaction barrier of 70.0 kcal/mol at TS2, producing $\text{N(H)-Ti(a), 2H-O(a)}$ with an endothermicity of 62.0 kcal/mol. Finally, $\text{N(H)-Ti(a), 2H-O(a)}$ dissociates and produces N-Ti(a), 3H-O(a) via TS3 by passing an energy barrier of 26.5 kcal/mol. The overall reaction of $\text{NH}_3(\text{g}) \rightarrow \text{NH}_2 + \text{H} \rightarrow \text{NH} + 2\text{H} \rightarrow \text{N} + 3\text{H}$ on the TiO_2 anatase (101) surface is endothermic by 89.0 kcal/mol. According to the PES, $\text{NH}_3\text{-Ti(a)}$ is the most stable intermediate and may dissociate to $\text{NH}_2\text{-Ti(a)}$ whereas the dissociation of $\text{NH}_2\text{-Ti(a)}$ to HN-Ti(a), 2H-O(a) , and N-Ti(a), 3H-O(a) is unlikely because of the high barrier and endothermicity. However, under the experimental condition

(UV irradiation),⁶⁶ adsorbed NH_3 can generate NH_2 , which has a short lifetime and readily reacts with an oxygen anion radical species to result in the formation of NO. Then, NO can react with NH_2 to produce N_2 . Our PES calculation supported the experimental result that $\text{H}_2\text{N-Ti(a)}$ might be formed by passing only a barrier of 30.6 kcal/mol but easily reverses because of the very small reverse barrier of 0.2 kcal/mol (short lifetime).

3.3. Density of States. The discussion in the following section related to the density of states and the orbitals of the gas-phase molecules of NH_x ($x = 1-3$) can be referenced in the Supporting Information. Before starting our analysis, one should note that the DFT approach has some limitations in the description of electronic energy levels: (1) underestimating the band gap substantially and (2) delocalizing the Ti^{3+} electronic states. However, the charge transfer between the surface and adsorbate can be adequately described by the DFT calculations.³¹

(66) Yamazoe, S.; Okumura, T.; Hitomi, Y.; Shishido, T.; Tanaka, T. *J. Phys. Chem. C* **2007**, *111*, 11077.

3.3.1. H–O(a). Figure 4b shows the local density of states (LDOS) of H–O(a), where only four 2c-O and four 5c-Ti atoms on the anatase (101) surface are selected. The bonding of the H atom on 2c-O mainly arises from the mixing of the H 1s orbital with the O 2s orbital and also with the O 2p orbital, which are represented in the two smaller additional peaks, one to the left of the O 2s peak and the other just below the upper valence band, respectively, as shown in Figure 4b. This also can be seen in Table 4 for the Mulliken population analysis, where the electron of the O 2s orbital decreases to 1.792e (O(1) of H–O(a) in the Table) and the electron of the O 2p orbital increases to 4.815e, as compared to the data for the clean surface or its neighboring 2c-O atoms. This means that for the O surface atom there is electron loss for the O 2s orbital and electron gain for the O 2p orbital. In total, the net electron loss of the H atom (0.346e) is delocalized to enrich the electrons of the 5c-Ti atoms on the surface; then the net charges of Ti(2), Ti(3), and Ti(4) decrease when compared to those of the clean surface.

3.3.2. NH₃ Adsorption with and without Hydroxyl Groups. The LDOS of H₃N–Ti(a) is shown in Figure 5a. The bonding of

NH₃ on 5c-Ti arises mainly from the donation of the lone pair of electrons of NH₃, which occupy the π_z^{nb} orbital and mix with Ti 3d and Ti 4p orbitals. The other σ orbitals of NH₃ are present at the peak just below the upper valence band in Figure 5a with no mixing with the d-band structure of TiO₂ (one other σ orbital, the σ_s^b , consists of the N 2s orbital and the H 1s orbital). The other two orbitals, $\sigma_{x,y}^b$, consist of a H 1s orbital and an N 2p orbital, with the latter $\sigma_{x,y}^b$ orbitals occupying a higher energy level than σ_s^b , as can be referenced in Figure S2 in the Supporting Information. The energy range of the lower-energy σ_s^b orbital of NH₃ is within the O 2s energy range of TiO₂, thus enhancing the peak intensity of the leftmost peak without producing another peak. Table 5 for the Mulliken population analysis shows that NH₃ loses 0.281e and the Ti(2) atom (where NH₃ is adsorbed) gains the electron, with the net charge of Ti(2) decreasing to 1.356e. In addition, the net charge of the electron in the Ti 3d and 4p orbitals increases to 2.067e and 0.306e, as compared to that of neighboring Ti atoms.

Figure 5b displays the LDOS of the coadsorption configuration of H₃N–Ti, H–O_{2c}(a). As compared to Figure 5a, the

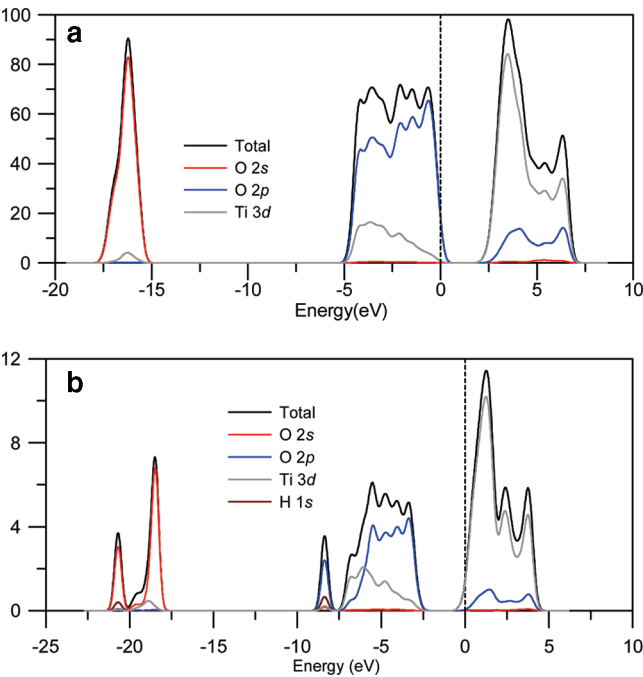


Figure 4. LDOS of surface atoms for (a) a clean surface and (b) H–O(a).

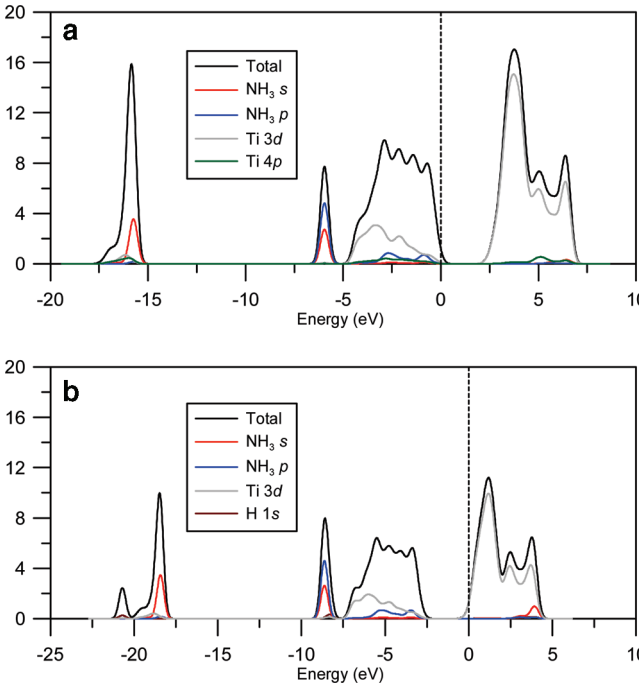


Figure 5. LDOS of surface atoms for (a) H₃N–Ti(a) and (b) H₃N–Ti, H–O(a).

Table 4. Mulliken Population^a of Surface Atoms for a Clean (101) Surface and H–O(a)

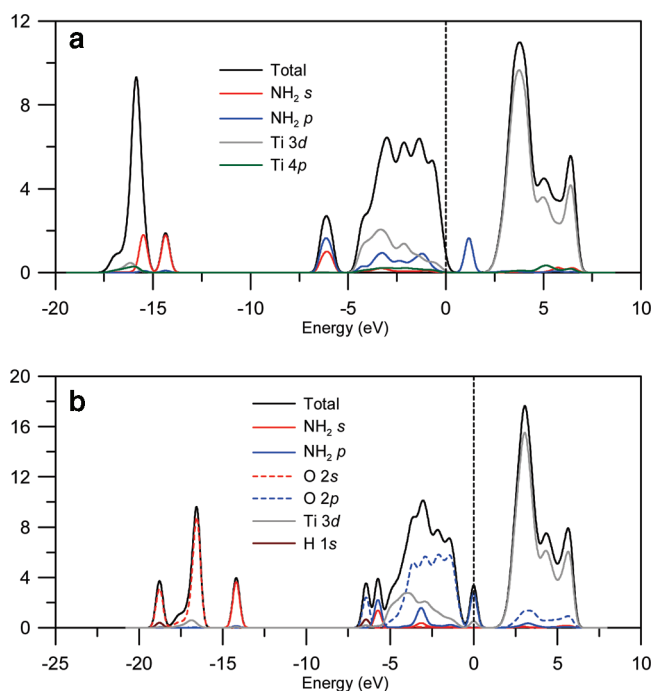
adsorbate/orbital		surface atoms							
clean surface		O(1)	O(2)	O(3)	O(4)	Ti(1)	Ti(2)	Ti(3)	Ti(4)
s		–0.589 ^b	–0.589	–0.592	–0.592	1.442 ^b	1.442	1.441	1.441
		1.919 ^b	1.919	1.919	1.919	0.266	0.266	0.267	0.267
	p	4.651	4.651	4.654	4.654	0.249	0.249	0.251	0.251
	d	0.019	0.019	0.019	0.019	2.043	2.043	2.042	2.042
H–O(a)		O(1) ^{*d}	O(2)	O(3)	O(4)	Ti(1)	Ti(2)	Ti(3)	Ti(4)
0.346 ^c		–0.624	–0.619	–0.598	–0.594	1.448	1.418	1.419	1.419
s		1.792	1.916	1.918	1.918	0.270	0.270	0.269	0.269
		4.815	4.685	4.661	4.657	0.255	0.253	0.252	0.249
	p	4.815	4.685	4.661	4.657	0.255	0.253	0.252	0.249
	d	0.016	0.018	0.020	0.020	2.029	2.059	2.059	2.062

^a Indicates net charge transfer, with negative (positive) denoting charge gain (loss). ^b The relationship for O(1) is –0.589 = (6.000 – 1.919 – 4.651 – 0.019); Ti(1) is 1.442 = (4.000 – 0.266 – 0.249 – 2.043). ^c The net charge transfer of H adsorbate. ^d O(1)* indicates the site where the H is adsorbed on.

Table 5. Mulliken Population of the Surface Atoms for H₃N–Ti(a) and H₃N–Ti, H–O(a)

adsorbate/orbital		surface atoms							
H ₃ N–Ti(a)		O(1)	O(2)	O(3)	O(4)	Ti(1)	Ti(2)* ^c	Ti(3)	Ti(4)
s p d	0.28 ^a	−0.609	−0.605	−0.631	−0.626	1.421	1.356	1.435	1.434
		1.917	1.915	1.916	1.916	0.271	0.272	0.271	0.271
		4.674	4.671	4.697	4.692	0.252	0.306	0.254	0.253
		0.018	0.018	0.018	0.018	2.055	2.067	2.041	2.041
H ₃ N–Ti, H–O(a)		O(1)* ^c	O(2)	O(3)	O(4)	Ti(1)	Ti(2)*	Ti(3)	Ti(4)
s p d	0.268 ^a , 0.349 ^b	−0.636	−0.634	−0.642	−0.632	1.425	1.322	1.414	1.414
		1.798	1.912	1.916	1.915	0.274	0.278	0.273	0.272
		4.820	4.705	4.710	4.699	0.258	0.304	0.255	0.253
		0.015	0.017	0.018	0.018	2.042	2.086	2.060	2.061

^a The net charge transfer of H₃N adsorbate. ^b The net charge transfer of H adsorbate. ^c O(1)* and Ti(2)* indicate the sites where the H and H₃N are adsorbed on, respectively.

**Figure 6.** LDOS of surface atoms for (a) H₂N–Ti(a) and (b) H₂N–Ti, H–O(a).

leftmost peak, which designates the sum of O 2s and NH₃ s orbitals, is split into two peaks. Among the two split peaks, the smaller, leftmost one represents the mixing of the H 1s orbital with the O 2s orbital, thus the intensity of the O 2s peak decreases. Because both NH₃ and H play the same role of electron donor, the presence of H will alleviate the donor effect of NH₃. As shown in Table 5, the net charge on NH₃ decreases to 0.268*e* as compared to the previous case of 0.281*e* without the presence of H. In addition, the populations of the p and d orbitals for Ti(2) of H₃N–Ti(a), H–O_{2c}(a) do not significantly change as compared to those of H₃N–Ti(a). This is also true for the populations of s, p, and d orbitals for O(1) as compared to those of H–O(a) for O(1). This implies that the coadsorption of H does not significantly influence the adsorption of NH₃ on 5c-Ti.

3.3.3. NH₂ Adsorption with and without Hydroxyl Groups. The LDOS of H₂N–Ti(a) is shown in Figure 6a. There are three electrons of the gas-phase NH₂ involving the mixing of the d-band structure of TiO₂, which occupy the spin-up σ_x^b orbital, spin-down σ_x^b orbital, and spin-up π_z^{nb} orbital (Figure S3). The peak to the right of the O 2s peak is the σ_s^b spin-down orbital of NH₂.

The other σ_s^b spin-up orbital of NH₂ is within the O 2s peak, to the left of the σ_s^b spin-down orbital. The peak that lies below the upper valence band of TiO₂ is the σ_y^b orbital of NH₂, which is the sum of spin-up and spin-down σ_y^b orbitals. Special attention should be paid to the peak present within the band gap of TiO₂. This peak was originally the LUMO (lowest unoccupied molecular orbital) of NH₂ and occupies the spin-down π_z^{nb} orbital. In the related population analysis in Table 6, the net charge on NH₂ is 0.224*e*, indicating electron loss to form the bonding between N and 5c-Ti. In addition, the electron also increases for the 3d and 4p orbitals of Ti(2) as compared to those of Ti(2) of the clean TiO₂ surface in Table 4, finally leading to a smaller positive net charge of Ti(2) as compared to Ti surface neighboring atoms.

The LDOS of the coadsorption configuration of H₂N–Ti, H–O_{2c}(a) is depicted in Figure 6b. As compared to Figure 6a, one H peak is to the left of the O 2s peak and the second H peak is the leftmost peak below the TiO₂ upper valence band. In the former, H 1s orbital is mixing with O 2s orbital, and in the latter the H 1s orbital is mixing with O 2p orbital, similar to that of H–O(a) in Figure 4. The peak located to the right of the latter H peak, and just below the upper valence band is the σ_y^b orbital of NH₂, similar to that clearly shown in Figure 6a. In Figure 6b, the nonbonding orbital of NH₂ is partially filled and the Fermi level has shifted to the right. Furthermore, the upper valence band of TiO₂ has become broader because the H 1s orbital and the σ_y^b orbital of NH₂ are adjacent to the original upper valence band. In the related population analysis in Table 6, for O(1), there is electron loss for the O 2s orbital and electron gain for the O 2p orbital, similar to that of the H–O(a) case. However, for the Ti(2), there is a significant increase in the population of 3d orbital (2.138 *e*) as well as 4p orbital (0.324 *e*), when compared to H₂N–Ti(a). This leads to the smaller net charge of (1.229 *e*), indicating Ti(2) gains electron. Another obvious change is also found for the H₂N molecule, where the net charge becoming a negative value of –0.016 *e* implies the NH₂ LUMO is filled by the electron donated by the H atom. Note that the electron population in the 2p orbital of the N atom of NH₂ is 3.966 *e* for H₂N–Ti, H–O(a), which is 0.292 *e* higher than that of H₂N–Ti(a) (these two numbers are not shown in the table), indicating that the NH₂ gains electrons in the 2p orbital, also the nonbonding orbital of NH₂.

3.3.4. NH Adsorption with and without Hydroxyl Group. Figure 7a shows the LDOS of bidentate adsorbate of Ti–(H)N–O(a). In the Figure, the second peak from the left is the sum of spin-up and spin-down σ_s^b orbitals of NH, which mainly consist of H 1s and N 2s orbitals. The peak just below the upper valence band is attributed to the σ_x^b bond of NH, which consists of the mixing of the H 1s orbital and the N p_x orbital, where *x* is

Table 6. Mulliken Population of the Surface Atoms for H₂N–Ti(a) and H₂N–Ti, H–O(a)

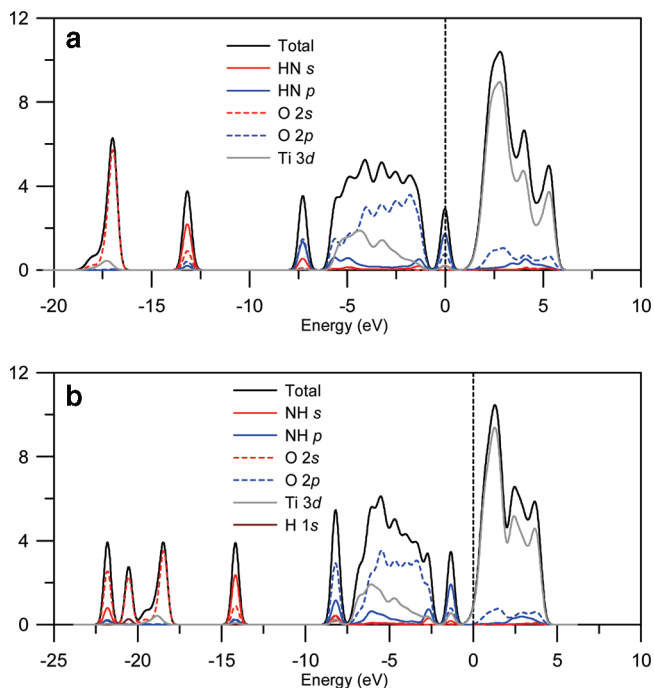
adsorbate/orbital		surface atoms							
H ₂ N–Ti(a)		O(1)	O(2)	O(3)	O(4)	Ti(1)	Ti(2)* ^c	Ti(3)	Ti(4)
s p d	0.224 ^a	−0.603	−0.601	−0.626	−0.625	1.428	1.337	1.469	1.435
		1.918	1.916	1.916	1.916	0.270	0.285	0.270	0.270
		4.667	4.666	4.693	4.691	0.250	0.305	0.254	0.254
		0.020	0.020	0.018	0.018	2.050	2.073	2.040	2.042
H ₂ N–Ti, H–O(a)		O(1)* ^c	O(2)	O(3)	O(4)	Ti(1)	Ti(2)* ^c	Ti(3)	Ti(4)
s p d	−0.016, ^a 0.351 ^b	−0.630	−0.644	−0.609	−0.606	1.457	1.229	1.424	1.426
		1.795	1.913	1.918	1.918	0.270	0.309	0.272	0.271
		4.818	4.713	4.672	4.670	0.245	0.324	0.257	0.254
		0.017	0.018	0.018	0.018	2.027	2.138	2.047	2.048

^a The net charge transfer of H₂N adsorbate. ^b The net charge transfer of H adsorbate. ^c O(1)* and Ti(2)* indicate the sites where the H and H₂N are adsorbed on, respectively.

Table 7. Mulliken Population of the Surface Atoms for Ti–(H)N–O(a) and Ti–(H)N–O, H–O(a)

adsorbate/orbital		surface atoms							
Ti–HN–O(a)		O(1)	O(2)* ^c	O(3)	O(4)	Ti(1)	Ti(2)* ^c	Ti(3)	Ti(4)
s p d	0.053 ^a	−0.607	−0.424	−0.590	−0.591	1.437	1.339	1.435	1.438
		1.918	1.854	1.918	1.918	0.266	0.238	0.272	0.272
		4.670	4.526	4.652	4.654	0.246	0.310	0.250	0.250
		0.020	0.046	0.020	0.020	2.050	2.116	2.042	2.038
Ti–(H)N–O, H–O(a)		O(1)* ^c	O(2)* ^c	O(3)	O(4)	Ti(1)	Ti(2)* ^c	Ti(3)	Ti(4)
s p d	0.048, ^a 0.371 ^b	−0.653	−0.501	−0.595	−0.592	1.452	1.289	1.400	1.419
		1.798	1.890	1.920	1.918	0.270	0.252	0.275	0.271
		4.838	4.568	4.658	4.655	0.250	0.314	0.258	0.249
		0.019	0.042	0.020	0.019	2.029	2.142	2.069	2.062

^a The net charge transfer of HN adsorbate. ^b The net charge transfer of H adsorbate. ^c O(1)* indicates the site where the H is adsorbed on; O(2)* and Ti(2)* are the sites where the NH are adsorbed on.

**Figure 7. LDOS of surface atoms for (a) Ti–(H)N–O(a) and (b) Ti–(H)N–O, H–O(a).**

defined as the bonding direction between N and H atoms. The peak close to the Fermi level is the lone pair electron of NH, which occupies the $\pi_{y,z}^{nb}$ orbitals. The bonding of NH on both 5c-Ti and

2c-O involves the donation of the lone pair electron of NH and its mixing with the d orbital of Ti, the electron in the σ_x^b orbital of NH mixing with the O 2p orbital, and the σ_s^b orbital of NH mixing with the O 2s orbital. In the related population analysis in Table 7, the net charge on Ti(2) decreases to 1.339e (implying an electron acceptor), the net charge on the electron in the d orbital increases to 2.116e, and the net charge on the electron in the 4p orbital increases to 0.310e. In addition, the net charge on O(2) increases to –0.424e (implying an electron donor). Furthermore, the net charges on the electrons of the 2s and 2p orbitals decrease to 1.854e and 4.526 e, respectively.

The LDOS of the coadsorption configuration of Ti–(H)N–O, H–O_{2c}(a) is illustrated in Figure 7b. The first H peak is located in the middle position of the three peaks on the left, and the second H peak is located just below the upper valence band. The former and the latter peaks represent H 1s orbital mixing with O 2s and O 2p orbitals, respectively. The mixing of the H 1s orbital with the O 2s orbital as well as the spin-up σ_s^b orbital of NH mixing with the O 2s orbital (the second and first peaks from the leftmost, respectively) leads to a significant decrease in the O 2s peak of TiO₂. The peak to the right of the O 2s peak is the spin-down σ_s^b orbital of NH. Note that the energy level for the σ_s^b orbital is split into two levels in this case, whereas in the previous case it is combined into one energy level. Similar to Figure 6a, the σ_x^b peak is located just below the upper valence band; however, the peak is intensified by the H 1s orbital, which possesses the same energy level as that of σ_x^b . The related population analysis in Table 7 shows that all of the surface atoms gain the electron donated by the H atom, thus most of the net charge of the surface atoms (O(1)–O(4) and Ti(2)–Ti(4)) decrease when compared to those

of Ti–(H)N–O(a). The changes for the bonding sites of O(2) and Ti(2) are not as significant as compared to those of Ti(2) for H₂N–Ti, H–O(a) in Table 6. Finally, the donation of NH also decreases in the presence of the H atom, with NH becoming 0.048e and showing no electron gain from bonding as did NH₂ in the previous case of H₂N–Ti, H–O(a).

4. Conclusions

This article investigates the adsorption of NH_x on the TiO₂ anatase (101) surface with respect to the role of hydroxyl groups by first-principles calculations. The results show that bidentate adsorbate Ti–(H)N–O(a) has the highest adsorption energy of 41.7 kcal/mol, whereas monodentate adsorbate H₂N–Ti(a) has the lowest adsorption energy of 24.5 kcal/mol on a clean surface. Nevertheless, H₂N–Ti(a) becomes the most stable with an adsorption energy of 55.7 kcal/mol on the hydroxylated surface. We find that the hydroxyl group plays a significant role in the adsorption energy of NH₂ but not in that of NH₃ and NH. The adsorption energy increases by 31.2 kcal/mol for H₂N–Ti, H–O(a) as compared to that for H₂N–Ti(a). On the basis of the Mulliken charge and density of states (DOS) analyses, this enhancement for NH₂ arises from the donation of coadsorbed H filling the nonbonding orbital of NH₂, resulting in the electron gain of NH₂ from the bonding. In addition, the upper valence band consisting of the mixing of the adsorption energy of the O 2p and Ti 3d orbitals has been broadened by the two adjacent H 1s and NH₂ σ_y^b orbitals joined to the bottom of the original upper valence band. Our observations show that the hydroxyl functional group plays a significant role in the adsorbed molecule and

its reactivity. In addition, we also study the reaction pathways of the NH₃ adsorption/dissociation processes on the TiO₂ anatase (101) surface. According to the PES, the NH₃–Ti(a) is the most stable intermediate and may dissociate to NH₂–Ti(a) whereas the dissociation of NH₂–Ti(a) to HN–Ti(a), 2H–O(a) and N–Ti(a), 3H–O(a) is unlikely to occur due to the high barrier and endothermicity. Further computational efforts aimed at unraveling coadsorbed OH group effects will improve our knowledge with respect to the molecular control of adsorption reactions on other metal oxide surfaces.

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Supporting Information Available: Other possible optimized geometries for NH₂ and NH adsorption on bare or hydroxylated anatase surfaces. The density state of the gas-phase molecules of NH_x ($x = 1-3$) and the orbitals. This material is available free of charge via the Internet at <http://pubs.acs.org>.