

REACTION DYNAMICS OF THE FIRST PROTON COUPLED ELECTRON TRANSFER FOR PHOTOTHERMAL CATALYTIC AMMONIA DECOMPOSITION REACTION ON TiO_2

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Abstract

Solar-driven photothermal catalysis presents a green and sustainable solution to the challenge of ammonia decomposition reaction (ADR) under mild conditions. However, the synergistic cooperation between photoelectric and photothermal effects in solar-driven ADR on TiO_2 has yet to be elucidated. Here, we performed density functional theory (DFT) calculations to investigate ADR on the anatase $\text{TiO}_2(101)$ slab surface model. Our results show that the rate-limiting step in the ADR on $\text{TiO}_2(101)$ surfaces is the removal of the first hydrogen, as it generally requires a high overpotential. The dynamics analysis of proton coupled electron transfer (PCET) indicates that electron transfer occurs only after proton transfer, and proton transfer is completed via thermal driving. The introduction of oxygen vacancies on the surface model (TiO_{2-x}) lowers the activation barrier for thermal proton transfer, bypassing the high photopotential for the first dehydrogenation, while slightly raising the electron-transfer barrier. The free energy surfaces calculations further confirm that thermally driven proton transfer can occur on TiO_{2-x} surfaces under mild conditions, facilitating subsequent electron transfer. Our research provides insights into the mechanism of photothermal synergistic catalytic ammonia decomposition under mild temperature conditions.

1 Introduction

The growing depletion of fossil fuels, coupled with the global shift towards a low-carbon green economy, has positioned solar energy as a key renewable resource for powering chemical transformations in the context of sustainable development. In particular, ammonia stands out as a highly promising hydrogen carrier, benefiting from its high hydrogen content (17.6 wt%), favourable liquefaction and transport properties, and mature industrial infrastructure for production and logistics. Hydrogen production through ammonia decomposition has become a key bridge between hydrogen storage and hydrogen utilization. [1-4] However, conventional thermocatalytic ammonia decomposition typically requires high temperatures above 400 °C to achieve practical hydrogen yields, which limits its viability for on-site hydrogen production applications. On the other hand, photocatalysis is driven predominantly by photogenerated charge carriers. Yet, the rupture of N–H bonds in ammonia demands a significant activation energy, which photons alone are unable to furnish. Consequently, solar-driven photothermal catalysis presents an elegant solution to the challenge by simultaneously harnessing the photoelectric and photothermal effects, achieving synergistic catalysis under mild conditions.

Considerable efforts have focused on lowering the reaction temperature of thermocatalytic ammonia decomposition by metal loading, yet temperatures of 400–500 °C remain required.[5, 6] Meanwhile, surface plasmon resonance (SPR)

in metal nanostructures can generate high-energy hot carriers under visible light, enabling bond cleavage and thus low-temperature decomposition.[7-9] Photo-generated charges in semiconductors under solar irradiation also play an important role in ammonia decomposition.[10-12] Despite these advances, existing research has largely focused on characterizing macroscopic reaction activity. A fundamental understanding of the synergistic interplay between photochemical and thermal contributions at the atomic scale remains elusive, owing to experimental characterization challenges and difficulties in selecting appropriate computational simulation methods and models.

Despite experimental challenges in probing the atomic-scale photothermal synergy, computational simulations provide a viable path forward. Density functional theory (DFT) with implicit solvation models enables static free energy calculations of elementary steps, as exemplified by Li et al., who systematically investigated the photocatalytic oxygen evolution reaction on anatase TiO_2 surfaces using an implicit solvent model and confirmed that the initial proton removal step suffers higher free energy changes (0.61–0.69 eV).[13] More accurate descriptions of interfacial interactions can be achieved with explicit solvation models in both static and thermodynamic frameworks. For instance, Chen et al. employed first-principles calculations with explicit water molecules to reveal that the first proton coupled electron transfer (PCET) during water oxidation follows a stepwise mechanism: proton transfer (PT) precedes electron transfer (ET), exhibiting an activation barrier of 0.2–0.5 eV, while the

subsequent electron transfer is barrierless.[14] Beyond static descriptions, molecular dynamics (MD) simulations with explicit solvent models capture dynamic proton transfer processes. However, initio molecular dynamics simulations (AIMD) are limited to small system sizes and short time scales (typically tens of picoseconds). To overcome this, deep neural network potential models have been developed to extend simulations to larger systems and longer time scales while retaining near-DFT accuracy. Such an approach demonstrated that molecular and dissociated water coexist at the water/TiO₂ interface with a free energy difference of ~ 0.08 eV and a dissociation barrier of ~ 0.33 eV; this indicates that the aqueous environment can provide hydroxyl groups to capture photogenerated holes.[15] Nevertheless, it remains unclear whether the PCET mechanism established for water splitting can be generalized to photocatalytic ammonia decomposition, as the latter involves N–H bond cleavage and distinct intermediates. Furthermore, oxygen vacancies on TiO₂ surfaces are frequently considered as active sites in catalytic reactions, and they are readily formed under photothermal conditions. However, a microscopic understanding of their specific role in photothermal synergistic catalysis is still lacking.

Herein, we perform a systematic computational investigation of photocatalytic ammonia decomposition on TiO₂ surfaces. Using a vacuum slab model, we first identify the rate-limiting step under a given overpotential, thereby establishing the kinetic bottleneck for the reaction. We then analyze the PCET dynamics during the dehydrogenation step, with a particular focus on the sequential roles of proton and hole transfer. This allows us to clarify how photogenerated holes and thermally driven proton transfer jointly enable the cleavage of the N–H bond under mild conditions. Given that surface oxygen vacancies (O_v) are commonly present on TiO₂ under photothermal conditions and are known to influence charge transfer and adsorption energy, we further examined their effects on both proton and electron transfer. Our results reveal how defect engineering modulates the free energy surface and, consequently, the overall catalytic activity.

2 Methodology

All DFT calculations were performed using the CP2K/QUICKSTEP software package, which implements a hybrid Gaussian and plane wave (GPW) approach in combination with GTH pseudopotentials to describe the core–valence interaction.[16] The Gibbs free energies of elementary steps along the reaction pathways were calculated using the hybrid PBE0 exchange–correlation functional augmented with Grimme dispersion corrections to account for London dispersion interactions. Static geometry optimization and AIMD were performed using a DZVP basis set, and the TZV2PX basis set was used to calculate vibrational frequencies for Gibbs free energy corrections. Static geometry optimization employed the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method until the maximum force acting on each relaxed atom fell below 0.00045 Ry/bohr. The AIMD simulations performed under the generalized gradient approximation (GGA) using the PBE

functional, the 3d electron self-interactions of Ti were realized by the DFT+U method with a U value of 5.4 eV, and hydrogen was replaced by deuterium. The time step for the MD run is 1.0 fs, and a canonical ensemble (NVT) condition was imposed by a Nosé–Hoover chain method thermostat with a target temperature of 330 K. In calculations using the hybrid PBE0, the real-space grid cutoff was set to 400 Ry for the vacuum slab model, 280 Ry for the explicit solvent model. We used the exchange correlation functional of hybrid PBE0 for static geometry calculations, and an auxiliary density matrix method was used to speed up. Due to the large size of this cell, k-sampling was restricted to the Γ point. To accelerate MD simulations and extend both the time and length scales accessible to AIMD sampling, we employed a deep neural network (DNN) to represent the potential energy surface. The DNN potential was trained using the Deepmd-kit package with initial interatomic forces and energies derived from AIMD simulations. [17, 18] We sampled PT transition states by applying a harmonic restraint to an initial DNN potential, recalculated the sampled configurations with DFT, and iteratively added them to the training set for potential refinement.

The anatase TiO₂(101) surface periodically slab model of three TiO₂ layers, and rectangular unit cells are utilized for the surface slabs of 10.210×11.328 Å², corresponding to 36 TiO₂ formula units. The vacuum slab model was used in the static calculation of the reaction pathway, with ammonia molecules adsorbed onto the exposed surfaces on both sides of the model to saturate the uncoordinated Ti atom sites. In the aqueous explicit solvent NH₃/TiO₂ model, 36 NH₃ molecules were used as the solvent.

3 Results

3.1 Pathways of photocatalytic ADR

To investigate the rate-limiting step in photocatalytic ammonia decomposition under a given photopotential, we first calculated the Gibbs free energy profiles of the elementary steps using a vacuum slab model. The theoretical ideal electrode potential for the electrocatalytic OER is 1.23 V, and the 0.70 V (i.e., $U = 1.93$ V vs SHE) overpotential is theoretically the low limit for OER to occur on TiO₂ surfaces at room temperature.[13] Further, isotope tracing of room-temperature photocatalytic ammonia decomposition in aqueous solutions confirms that hydrogen originates mainly from ammonia, not water, indicating that proton removal from ammonia is more favorable than water oxidation.[19] Therefore, the theoretical thermodynamic water-splitting electrode potential on TiO₂ surfaces at room temperature, i.e., the photopotential $U = 1.93$ V, was adopted as a meaningful benchmark in our study.

We assume that photogenerated holes at the valence band edge of anatase TiO₂(101) drive photocatalytic ADR via one-electron transfer steps. We examined three distinct decomposition pathways on the TiO₂ surface (labeled P1, P2, P3), as well as one pathway on an oxygen-vacancy surface (TiO_{2-x}, labeled P4). The Gibbs free energy profiles and intermediate conformations are shown in Fig. 1a–c, and the

corresponding reaction energy and Gibbs free energy changes are listed in Table 1. The three reaction pathways differ in the coupling steps after the initial dehydrogenation on the TiO_2 surface: P1 involves N–O bond formation with a surface bridge oxygen (O_{br}), P2 proceeds via an N_2H_4 intermediate formed by the coupling of NH_2 with a free NH_3 , and P3 involves coupling between two adjacent NH_2 species. Despite these differences, across all three pathways on the TiO_2 surface, the first dehydrogenation step is the rate-determining step. Removing the first hydrogen from NH_3 ($1 \rightarrow 2$) requires overcoming an energy of 0.805 eV even at an overpotential of 0.70 V (Table 1), leading to substantial energy losses. As shown in Fig. 1d, the Ti atom bonded to NH_2 is slightly pulled up from the surface, and the adsorbed NH_2 exists in a spin-unpolarized state rather than as a free radical.

Furthermore, we calculated the ADR pathway on the TiO_{2-x} surface, referred to as P4, as shown in Fig. 1a and 1b. In contrast to the perfect TiO_2 surface, the Gibbs free energy decreases significantly on the TiO_{2-x} surface after the first hydrogen atom is removed ($16 \rightarrow 17$). The subsequent steps follow a sequence similar to pathway P1, except that the resulting N_2 molecule is strongly adsorbed at the O_v and requires a desorption energy of 0.701 eV to be released. Spin charge density analysis (state 17, Fig. 1d) shows that the adsorbed NH_2 radical readily captures holes at the O_v site, lowering the system energy.

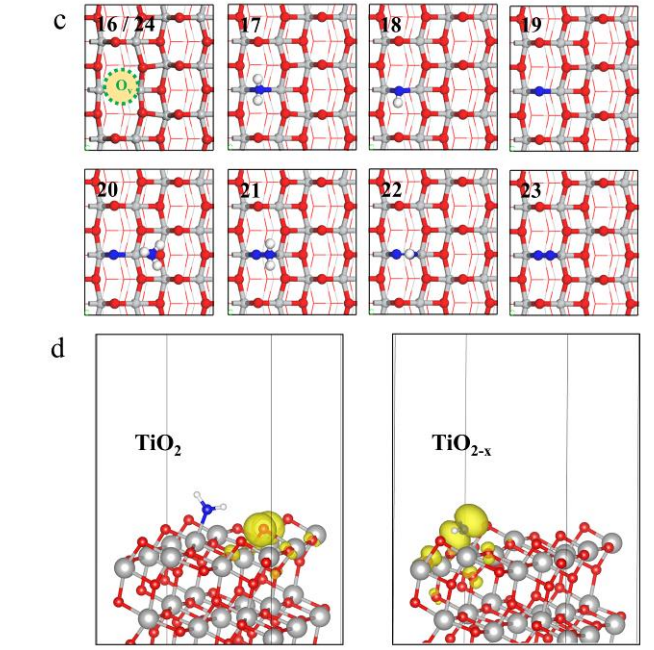
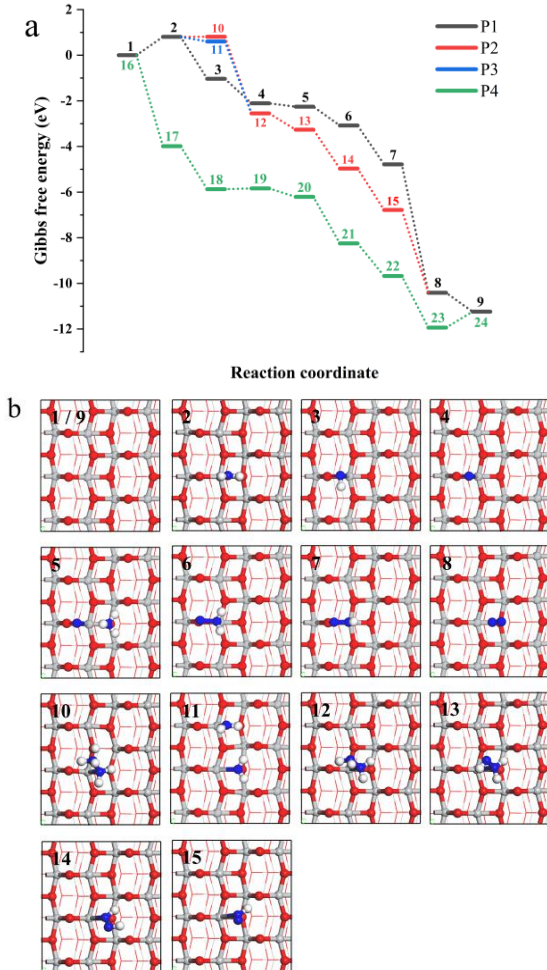


Fig. 1 Gibbs free energy profiles (a) and intermediate structures (b, c) for ADR on the TiO_2 and TiO_{2-x} surfaces, along with spin charge density of the adsorbed NH_2 (d, isosurface = 0.01 a.u.). Color code: Ti, gray; O, red; N, blue; H, white.

Table 1: Reaction energy and Gibbs free energy for the elementary steps in ADR.

elementary step	ΔE (eV)	ΔG (eV)
$1 + \text{NH}_3 + \text{h}^+ \rightarrow 2 + \text{H}^+$	2.590	0.805
$2 + \text{h}^+ \rightarrow 3 + \text{H}^+$	0.361	-1.838
$3 + \text{h}^+ \rightarrow 4 + \text{H}^+$	1.205	-1.076
$4 + \text{NH}_3 \rightarrow 5$	-0.709	-0.149
$5 + \text{h}^+ \rightarrow 6 + \text{H}^+$	1.438	-0.822
$6 + \text{h}^+ \rightarrow 7 + \text{H}^+$	0.532	-1.706
$7 + \text{h}^+ \rightarrow 8 + \text{H}^+$	-3.233	-5.628
$8 \rightarrow 9 + \text{N}_2$	0.317	-0.825
$2 + \text{NH}_3 \rightarrow 10$	-0.638	0.002
$10 + \text{h}^+ \rightarrow 12 + \text{H}^+$	-1.110	-3.359
$12 + \text{h}^+ \rightarrow 13 + \text{H}^+$	1.664	-0.714
$13 + \text{h}^+ \rightarrow 14 + \text{H}^+$	0.514	-1.704
$14 + \text{h}^+ \rightarrow 15 + \text{H}^+$	0.568	-1.812
$15 + \text{h}^+ \rightarrow 8 + \text{H}^+$	-1.404	-3.632
$2 + \text{h}^+ \rightarrow 11 + \text{H}^+$	0.972	-0.204
$11 + \text{NH}_3 \rightarrow 12$	-2.720	-3.153
$16 + \text{h}^+ \rightarrow 17 + \text{H}^+$	-2.250	-3.988
$17 + \text{h}^+ \rightarrow 18 + \text{H}^+$	0.419	-1.884
$18 + \text{h}^+ \rightarrow 19 + \text{H}^+$	2.267	0.035
$19 + \text{NH}_3 \rightarrow 20$	-0.877	-0.371
$20 + \text{h}^+ \rightarrow 21 + \text{H}^+$	0.131	-2.039
$21 + \text{h}^+ \rightarrow 22 + \text{H}^+$	0.901	-1.432
$22 + \text{h}^+ \rightarrow 23 + \text{H}^+$	-0.022	-2.261
$23 \rightarrow 24 + \text{N}_2$	1.932	0.701

3.2 Dynamics of the First Proton Coupled Electron Transfer

Our Gibbs free energy calculations with a vacuum slab model confirm that the first dehydrogenation of adsorbed ammonia is the rate-limiting step for photocatalytic ADR on the TiO_2

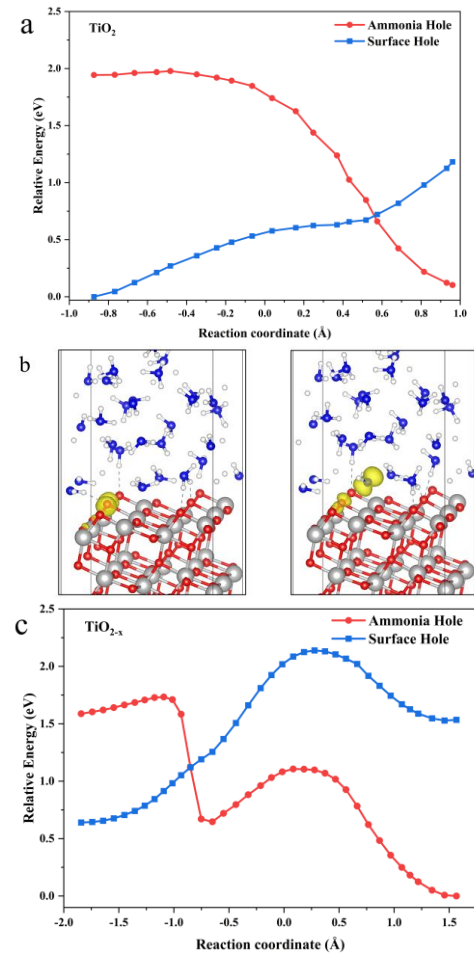
surface due to a high overpotential, yet this model overlooks the proton-accepting role of solvent molecules and their interfacial influence, which hinders kinetic studies in solvated environments. To address this, we employ an explicit solvent model to explore the PCET of the first dehydrogenation.

To generate well-equilibrated configurations of the interface, we carried out AIMD simulations of 12 ps duration and 2 ps equilibration relaxation before the production trajectories to eliminate initial modeling effects. Subsequently, we selected three well-separated configurations from the AIMD trajectory, removed one electron (i.e., created a hole) from each, and performed geometry optimization with the hybrid PBE0 functional. Specifically, for each configuration studied, we calculated the PT energy profiles in the two electronic states associated with ET, the state with the hole localized on the nitrogen (N_d) of an adsorbed ammonia molecule (denoted ammonia hole state), and that with the hole localized on an O_{br} close to N_d (denoted surface hole state). We defined the distance difference between N_d-H and N_a-H bonds, $\Delta d_{NHN} = d(N_d-H) - d(N_a-H)$, as the reaction coordinate of PT, where H is the transferred proton, N_d and N_a are proton donors and acceptors, respectively.

Fig. 2a and 2c show the two electronic states' energy profile of selected snapshots in PCET. Only one of the selected configurations is presented for convenience because the other two exhibit similar trends in electronic state energy. The minimum energy path of the PT is first determined using the Nudged Elastic Band (NEB) method, and then additional points are interpolated along the PT path, the electronic wavefunction of the points were optimized using constrained DFT (CDFT) minimization, with the wavefunction from the previous point employed as the initial guess to make the energy profile as close as possible to the adiabatic potential energy surface. The sequence of proton and electron transfer in PCET can be inferred from the intersection of the two potential energy surfaces. If the intersection occurs near the PT transition state, e.g., at $\Delta d_{NHN} \sim 0$ Å, the PCET proceeds via a concerted mechanism; if it occurs near the PT initial or final state, the PCET follows a sequential mechanism. As shown in Fig. 2a, the energy profile of the surface hole and ammonia hole becomes intersecting around the final state of PT, suggesting that the first PCET of the ADR on TiO_2 is sequential, with ET typically following PT. In contrast to the vacuum slab model, in the presence of an explicit solvent environment, as shown in Fig. 2b, the hole localized at the O_{br} site readily transfers to the NH_2 after a proton is released from the NH_3 . The reason for this difference is that, in a solvent environment, the plane defined by the three atoms of NH_2 forms a low forward tilt angle ($\sim 30^\circ$) with respect to the TiO_2 surface, which configuration is favorable for the hole localization on NH_2 . We calculated that the ET energy barrier is 0.20 eV, which is much smaller than the PT activation energy barrier of 0.62 eV, suggesting that ET can occur at room temperature, but it is limited by PT due to its sequential mechanism.

When the NH_3 dissociates at the O_v site, the formed NH_2 group adopts a tilt angle of 60° relative to the TiO_2 surface and binds to two Ti atoms, a configuration that stabilizes the

hole specifically on the surface three coordinate oxygen (O_{3c}) atom (Fig. 2d). By contrast, in the vacuum slab model, the N-H bond of NH_2 points towards an O_{br} atom, which instead favours hole localization at that site. We further used CDFT to calculate the energy profile curves of the ammonia hole and surface hole along the reaction coordinate for the second dehydrogenation reaction of the NH_3 molecule at the O_v site, and found that the second dehydrogenation follows a sequential mechanism of PCET, with ET occurring before PT. This implies that during the slight movement of the NH_2^- along the hydrogen-bonding pathway in the process of releasing the second proton at the oxygen vacancy site, the NH_2^- species captures a hole to form an NH_2 radical, where NH_2^- no longer acts as a hydrogen-bond acceptor but rather as a hydrogen-bond donor, thereby establishing a configuration favourable for hole localization. We calculated the activation energy barrier for the first dehydrogenation to be 0.45 eV, and for the second proton dissociation process, the activation energy barrier that must be overcome for ET upon a slight displacement of NH_2 is 0.46 eV, the complete dissociation of the second proton requires 0.44 eV, comparable to the preceding ET step. Equivalent to the first PCET of the NH_3 molecule at the O_v site, ET occurs after PT. In summary, the first PCET in ammonia decomposition is primarily limited by the difficulty of PT, whereas introducing an O_v on the TiO_2 surface allows PT and ET to proceed sequentially, thereby alleviating the high energy barrier of the PT process, although simultaneously increasing the energy consumption for ET.



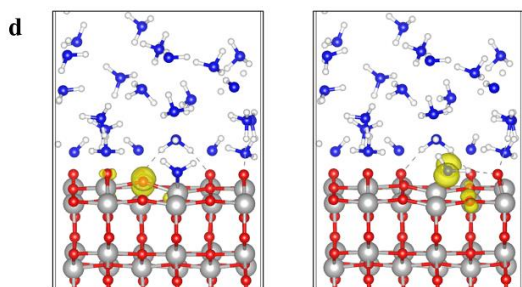


Fig. 2 PT energy profiles (a, c) for ammonia hole and surface hole states on the TiO_2 and TiO_{2-x} surfaces; (b, d) corresponding spin charge density before and after ET.

3.3 Free energy surface of proton transfer

The PCET analysis above established that the first proton transfer step in ammonia dehydrogenation sets the stage for the subsequent hole transfer. However, the activation barriers derived from static calculations on selected configurations in the preceding section cannot adequately capture the temperature dependence of the PT kinetics over TiO_2 and TiO_{2-x} surfaces. To address this limitation, we performed MD simulations combined with umbrella sampling to quantify the free energy surfaces for thermally driven PT in a solvated environment. Two collective variables (CVs) based on interatomic distances were defined to describe the PT process. The first CV, denoted as d_{NO} , is the distance between the N atom of the adsorbed ammonia and the adjacent O_{br} atom, representing the separation between the proton donor and acceptor. The second CV is defined as the distance difference between $\text{N}_{\text{d}}\text{-H}$ bond and $\text{O}_{\text{br}}\text{-H}$ bond, $\Delta d_{\text{NHO}} = d(\text{N}_{\text{d}}\text{-H}) - d(\text{O}_{\text{br}}\text{-H})$, describes the progress of the proton transfer, and the positive and negative values correspond to dissociated and molecular state of the adsorbed ammonia molecule, respectively.

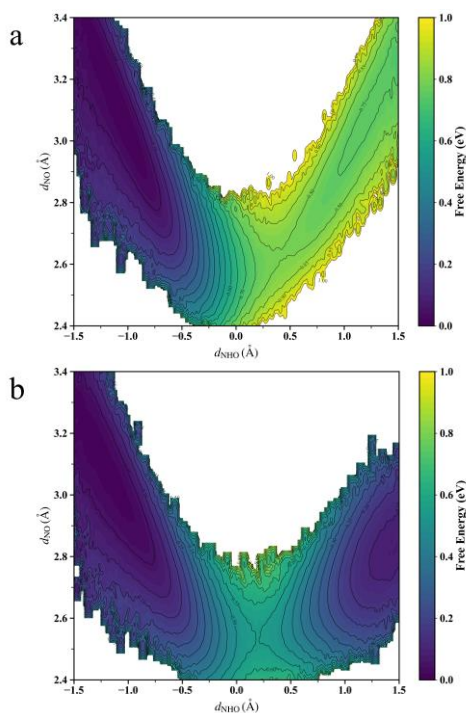


Fig. 3 Free energy surface of ammonia dissociation on the (a) TiO_2 and (b) TiO_{2-x} surfaces.

The resulting free energy surface (Fig. 3a and 3b) reveals two key features. First, on the stoichiometric TiO_2 surface, the molecular state of NH_3 is thermodynamically more stable than the dissociated state by 0.75 eV, indicating a strong preference for the intact adsorption configuration. Second, the free energy barrier for NH_3 dissociation on TiO_2 is 0.80 eV, which renders the ADR kinetically inaccessible at room temperature under pure solvated conditions. In striking contrast, when an O_v is introduced, the barrier for the first dehydrogenation step is substantially reduced to 0.55 eV, corresponding to a characteristic activation temperature of approximately 360 K, which can be readily achieved under solar (concentrated) photothermal catalysis conditions, above which the ADR becomes thermally feasible. Moreover, the resulting NH_2^- occupies a shallow free energy minimum on the reduced surface, indicating that the dissociated species can persist stably and thus serve as a favourable precursor for the subsequent ET step.

4 Conclusion

In summary, we identify the removal of the first hydrogen from adsorbed NH_3 as the rate-limiting step, which requires a substantial overpotential. Mechanistically, electron transfer occurs strictly after proton transfer, and proton transfer is thermally activated. The introduction of bridging oxygen vacancies on the TiO_2 surface lowers the activation barrier for proton transfer, enabling this step under mild conditions, while the barrier for electron transfer is slightly raised. Free energy surface calculations further confirm that thermally driven proton transfer on the TiO_{2-x} surface is kinetically feasible under mild conditions, thereby promoting the subsequent electron transfer. For the rational design of synergistic photothermal catalysts, active sites should lower the proton transfer barrier without excessively raising the electron transfer barrier, and the solvation environment must be sufficiently stabilizing for hole-trapping intermediates.

5 Acknowledgements

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