

Supporting Information

for

The Photo-catalytic Activity and Hole Scavenging Behaviors on Rutile TiO₂(100) Surfaces: a Theoretical Study

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1, pDOS of amines on rutile $\text{TiO}_2(100)$ surface

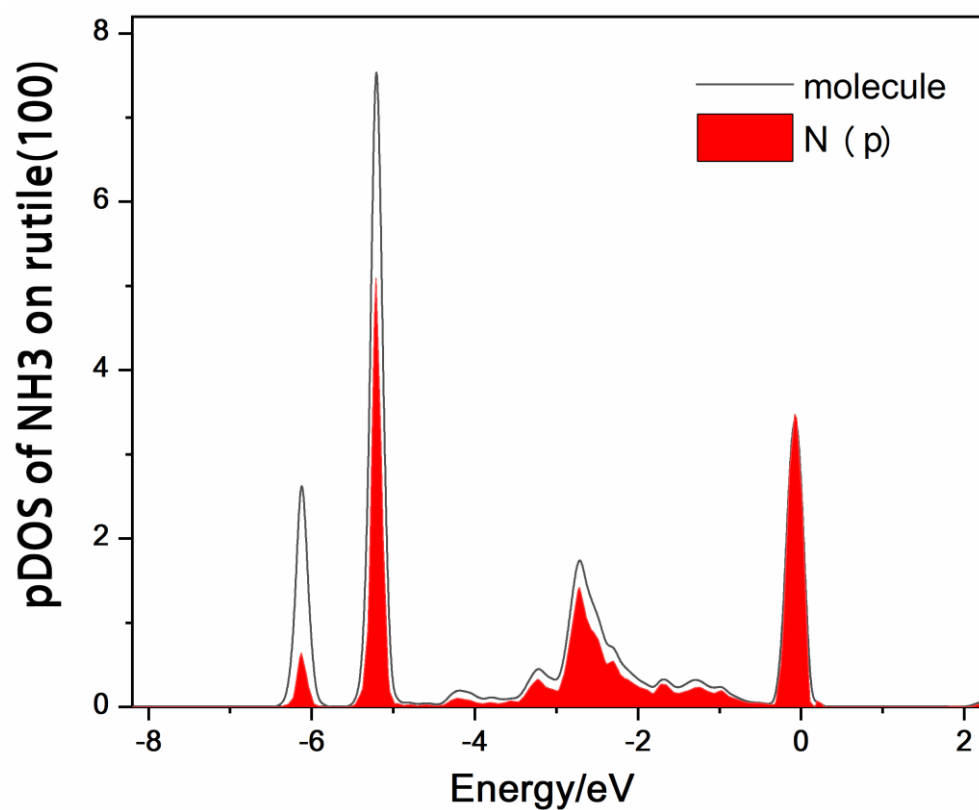


Figure S1. Partial density of states calculated of the dissociated NH_3 absorbing on rutile $\text{TiO}_2(100)$ surface, including the DOS of the whole NH_3 (black,molecule) and of the N_{2p} orbitals in NH_3 (red).

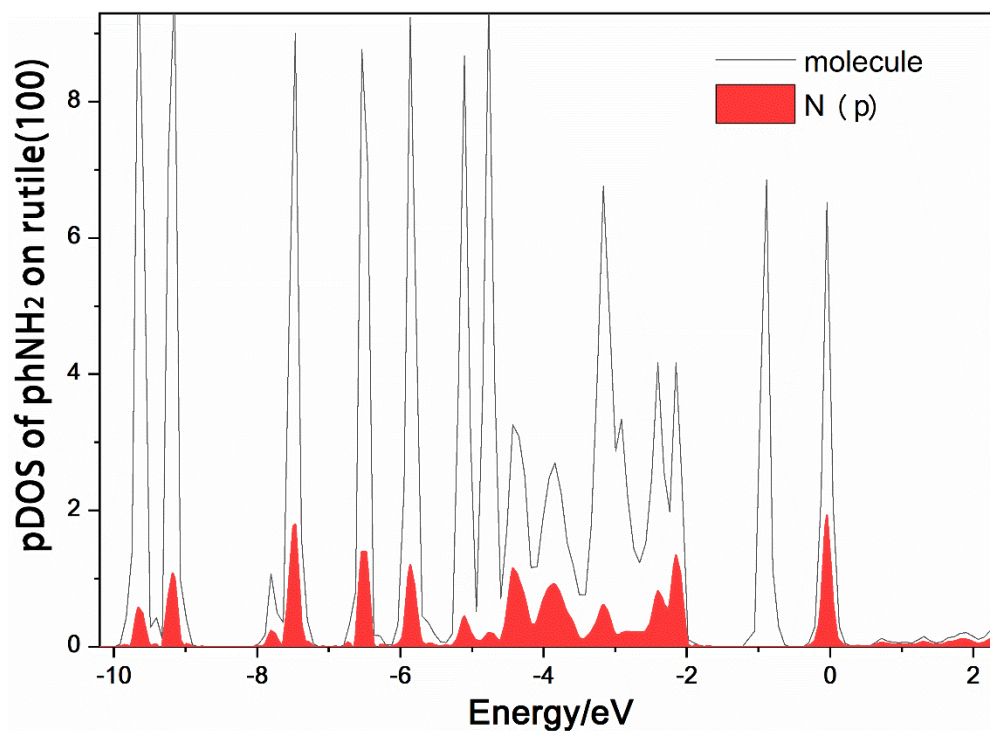


Figure S2. Partial density of states calculated of the dissociated phNH_2 absorbing on rutile $\text{TiO}_2(100)$ surface, including the DOS of the whole phNH_2 (black,molecule) and of the N_{2p} orbitals in phNH_2 (red).

2, DFT+U results of water and methanol on rutile TiO₂(110)

We have simulated the surface hole on rutile TiO₂(110) with DFT+U($U_d=4.2\text{eV}$ and $U_p=6.0\text{eV}$) methods according to previous studies^{1,2}, and the results are shown in FigureS3 and Table S1 below.

In the (110) case, we can see that the discrepancy in adsorption energy for IS0 from IS1, which comes from the influence of hydrogen bond.

In addition, we analyzed the hole-mediated kinetics with the methanol photo-dissociation on rutile TiO₂(110) surface as model system. With the state energy in Table S1, the initial state is IS2' while the final state is FS1'. As we have explained in manuscript, the hole trapping with positive charge would destroy the hydrogen bond. Then, it is reasonable that the initial hole-trapping Ob in our work is not the same one that the dissociative H bond to(Ob2).

The kinetic results are shown in Figure S4. The site-projected magnetic moment and spin-density image of TS' shows that the hole remains on the initial hole-trapping Ob site in transition state, which means that the hole in the system has no direct dynamic effect in the dissociation. However, the dissociation reaction becomes thermodynamically easier when hole exists since the dissociative state can be stabilized with hole trapped on methoxyl. Besides, The DFT+U results show that the hole location has no change when the H atom dissociative H already moves half way, which means that H atom moves solely without electron coupled. Thus, actually, electrons in the system redistribute when the dissociative H atom already bonded to Ob2 and then the hole-trapping site changes.

Besides, the hole trapped on neighbor site can represent general remote-hole cases with similar adsorption energy, thus we can imply that the electron redistribution happens no matter where the initial hole-trapping site is.

In addition, the kinetic results would not be influenced by the hole with similar energy barriers.

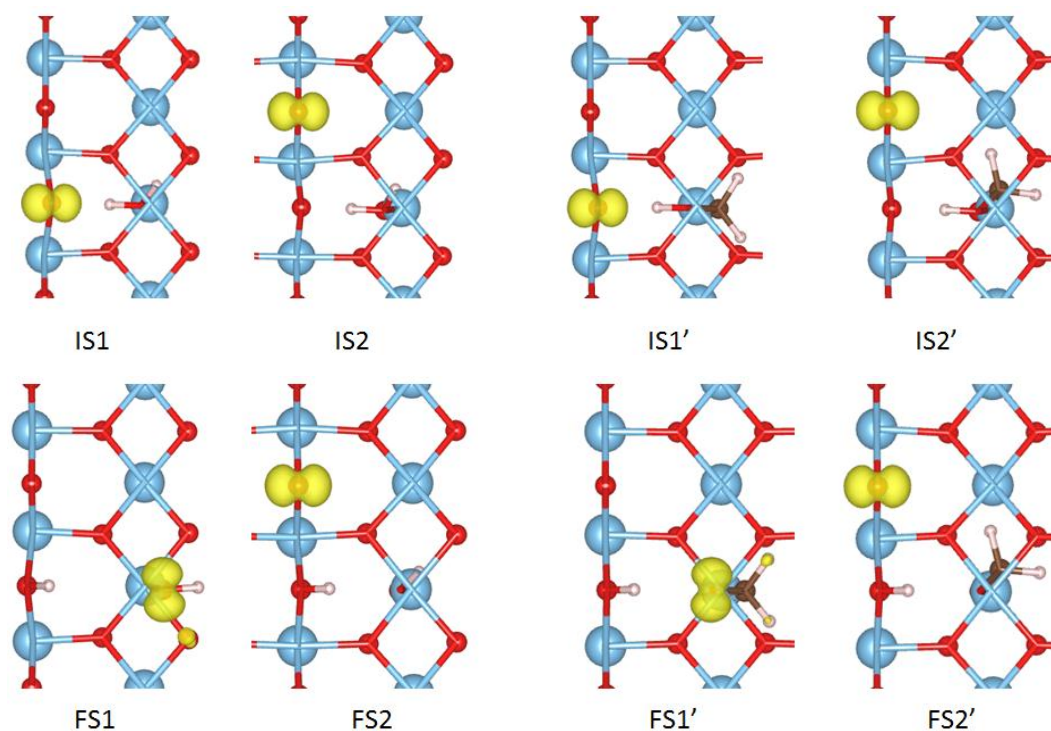


Figure S3. Top-view structure with spin density (iso-value=0.02) of optimized possible associative and dissociative states of water and methanol absorbed on rutile $\text{TiO}_2(110)-(1 \times 1)$ surface. (a) Water molecule with hole trapped on nearest Ob1 site and second-nearest Ob2 site are shown as IS1 and IS2, methanol molecule with hole trapped on Ob1 and Ob2 site are shown as IS1' and IS2'. (b) Dissociative water molecule with hole trapped on hydroxyl and initial Ob2 site are shown as FS1 and FS2, Dissociative methanol molecule with hole trapped on methoxyl and initial Ob2 site are shown as FS1' and FS2'.

Table S1. Calculated results of optimized possible associative and dissociative states of water and methanol on rutile $\text{TiO}_2(110)-(1 \times 1)$ surface. Optimization is achieved with DFT+U method and hybrid functional(HSE06) is used for validation. IS0 (IS0') and FS0 (FS0') refer to associative and dissociative states of water (methanol) on $\text{TiO}_2(110)-(1 \times 1)$ surface without hole existence (No F atom injected in the system). Ow and Om refers to the Oatom in absorbed water and methanol.

| Water absorbed on rutile $\text{TiO}_2(110)-(1 \times 1)$ | | | | | | |
|--|------|-----------------|-------|-------|---------|--------|
| | | Bond distance/Å | | | Eads/eV | |
| | | Ow-Ti | Ow-H | Ob1-H | DFT+U | HSE06 |
| Associative States | IS0 | 2.196 | 0.998 | 1.768 | -1.093 | -0.754 |
| | IS1 | 2.264 | 0.977 | 2.081 | -0.754 | -0.709 |
| | IS2 | 2.199 | 1.001 | 1.736 | -1.087 | -0.806 |
| Dissociative States | FS0 | 1.897 | 1.932 | 0.985 | -1.145 | -0.726 |
| | FS1 | 2.191 | 3.298 | 0.969 | -0.812 | -0.734 |
| | FS2 | 1.893 | 1.989 | 0.983 | -1.133 | -0.832 |
| Methanol absorbed on rutile $\text{TiO}_2(110)-(1 \times 1)$ | | | | | | |
| | | Bond distance/Å | | | Eads/eV | |
| | | Om-Ti | Om-H | Ob1-H | DFT+U | HSE06 |
| Associative States | IS0' | 2.166 | 0.995 | 1.799 | -1.163 | -0.826 |
| | IS1' | 2.223 | 0.972 | 2.137 | -0.956 | -0.693 |
| | IS2' | 2.171 | 0.994 | 1.800 | -1.191 | -0.913 |
| Dissociative States | FS0' | 1.889 | 1.948 | 0.984 | -1.254 | -0.837 |
| | FS1' | 2.298 | 2.273 | 0.971 | -1.362 | -1.237 |
| | FS2' | 1.870 | 1.994 | 0.982 | -1.256 | -0.998 |

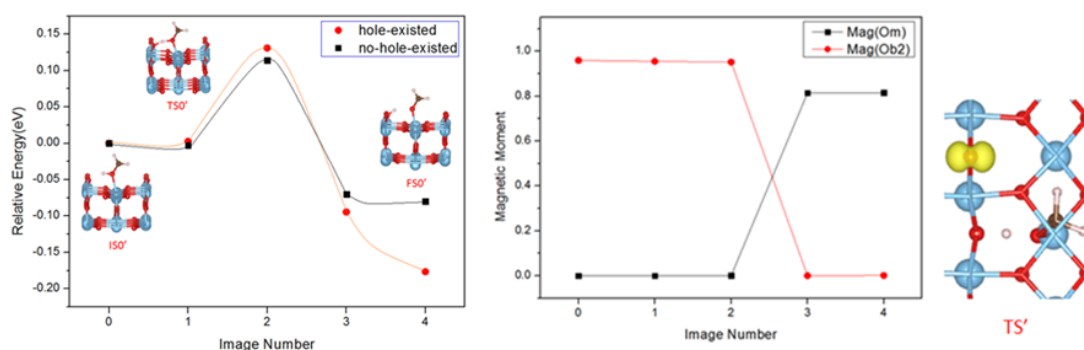


Figure S4. Results of methanol dissociation on $\text{TiO}_2(110)$ surface: (a) The potential energy surface with (red) and without (black) the existence of hole and structures in the no-hole system are shown; (b) Site-projected magnetic moment of the O atom on absorbed molecule site (black) and initial hole-trapping Ob2 site (red) during dissociation process with hole existence, and the spin-density image of transition state (TS') is also shown.

3 , DFT+U hole scavenging calculations for water and methanol on different surfaces

In the (110) case above, to analyze the hole scavenging behaviors, we calculate $E_{\text{hole}}(\text{R})$ as $E_{\text{hole}}(\text{R})=E_{\text{FS2}}-E_{\text{FS1}}$. Then, for DFT+U calculation on (110) surface, $E_{\text{hole}}(\text{OH})=-0.32\text{eV}$ while $E_{\text{hole}}(\text{OCH}_3)=0.11\text{eV}$.

With same strategy, we have calculated the hole scavenging energies for hydroxyl and methoxyl group on different surfaces with the above DFT+U methods($U_d=4.2\text{eV}$ for Ti and $U_p=6.0\text{eV}$ for O) as a reference and the results are shown in Table S2 below. We found the trend of hole scavenging energies is rutile (100)> anatase (101) > rutile (110), which is in accordance with the high photo-activity of rutile (100) surface observed experimentally and our $E_{\text{orb}}(\text{R})$ results.

Table S2. Calculated results of the hole scavenging energies for hydroxyl($E_{\text{hole}}(\text{OH})$) and methoxyl($E_{\text{hole}}(\text{OCH}_3)$) group on different surfaces. R(110), R(100) and A(101) represent rutile $\text{TiO}_2(110)$, rutile $\text{TiO}_2(100)$ and anatase.

| | R(110) | R(100) | A(101) |
|---------------------------------|--------|--------|--------|
| $E_{\text{hole}}(\text{OH})$ | -0.321 | 0.200 | 0.122 |
| $E_{\text{hole}}(\text{OCH}_3)$ | 0.106 | 0.589 | 0.587 |

4 , DFT+U hole scavenging calculations on rutile TiO₂(100) surface

The reliability of the DFT+U method in hole simulation was evaluated. The $E_{\text{hole}}(\text{R})$ of H₂O, CH₃OH, CH₃NH₂, (CH₃)₂NH and C₂H₆ were shown in Figure S5. According to introduction, the U_p correction would lead to unbiased results and it is a problem to choose appropriate U_p value for different elements. And we just set the same U_p value for both O and the element of the adsorbed atom as an example to show the sensitivity of U_p correction.

With U_d always set as 4.2eV for Ti, the results of $U_p=6.0$, 4.0 and 3.0 eV are shown. In fact, we have tried to set $U_p=0.0$ and 2.0 eV but failed to simulate the localized hole. Thus, when U_d is applied to Ti, U_p is necessary.

Actually, for alcohols and amines with O and N atom absorbing on the surface, the calculated hole scavenging ability is not sensitive to the U_p value. However, the U_p corrections to C atoms shall be used with caution, since its hole scavenging ability is strongly related with the U_p value used in the calculation. When we need to take extensive kinds of molecules(including alkane) into consideration, it would be a problem in choosing approximate U_p for different elements.

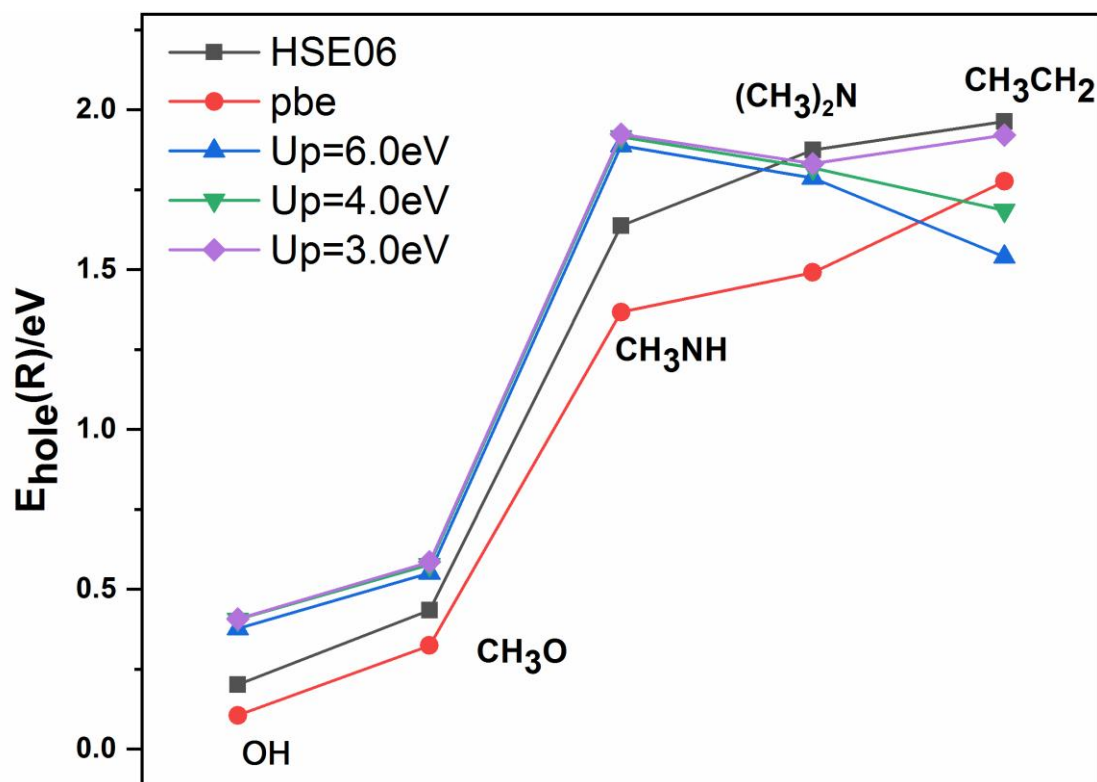


Figure S5. The $E_{\text{hole}}(\text{R})$ calculation results of different adsorbates on rutile TiO₂(100) surface with different computational methods, including static calculation with hybrid functional(HSE06) , DFT calculation(PBE), DFT+U calculation with $U_d=4.2\text{eV}$ to Ti atoms and different U_p ($U_p=6.0\text{eV}$, $U_p=4.0\text{eV}$ and $U_p=3.0\text{eV}$) to O and other absorbing atoms(O and N for CH₃NH₂ and CH₃NHCH₃ case, while O and C for CH₃CH₃ case).

5 , DFT+U hole scavenging calculations on anatase TiO₂(101) surface

The $E_{\text{hole}}(\text{R})$ of water, alcohols and amides on anatase (101) surface were calculated with DFT+U ($U_{\text{d}} = 4.2\text{eV}$ for Ti, $U_{\text{p}} = 6.0\text{eV}$ for O and N) methods. According to the discussions in the manuscript, such DFT+U results could only be used as a reference to show the trend.

In Figure S6 we have listed the correlation of $E_{\text{orb}}(\text{R})$ and $E_{\text{hole}}(\text{R})$ for studied groups on anatase (101). The correlation for homologues is still valid.

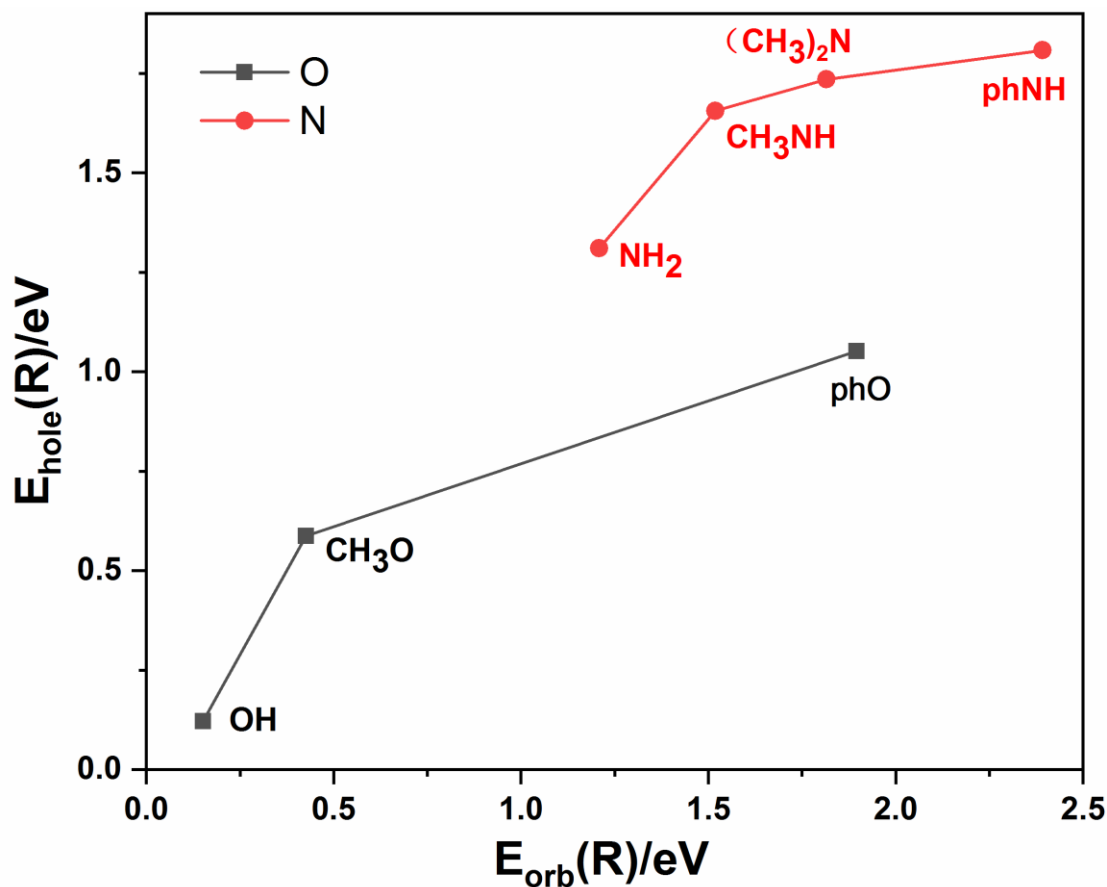


Figure S6. The correlation of $E_{\text{hole}}(\text{R})$ and $E_{\text{orb}}(\text{R})$ on anatase TiO₂(101) surface.

6 , Hole simulating on TiO₂(100) surface

As is shown in Figure S7, we have simulated the hole with hybrid functional(HSE06) as a reference and get similar unlocalized hole on TiO₂(100) surface. Thus, it is an inherent property for the TiO₂(100) surface.

The hole-containing O_b and the corresponding subsurface O_{3c} bond to the same two unsaturated Ti_{5c} atoms and form the O-Ti-O multi-center bonding. Actually, as is shown in the figure below, the HOMO orbital for O_b atoms are also shared with corresponding surface O_{3c} atoms. It suggests that the HOMO of the surface is a multi-center π bond composed of p orbital O_b and the corresponding O_{3c}, as well as one d orbital of the Ti_{5c}. Of them the contribution from Ti_{5c} is small, while the contributions from the two oxygen atoms are similar.

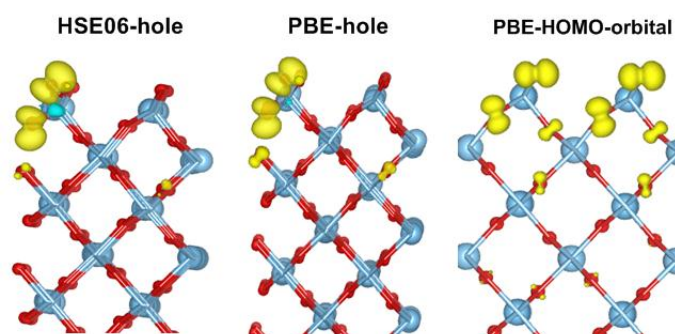


Figure S7. (a),(b) Structures with spin density(iso-value=0.02) of the hole containing TiO₂(100) surface by hybrid functional(HSE06, Figure S6a) and DFT(PBE, Figure S6b). (c)The HOMO orbital of the TiO₂(100) surface with DFT(PBE) calculation.

7 , Geometric symmetry on rutile TiO₂(110) and (100) surface

We have shown the symmetry of the Ti center in bulk, rutile TiO₂(110) surface, and TiO₂(100) surface in Figure S8.

In the bulk structure of rutile TiO₂, each Ti⁴⁺ anion is coordinated with 6 O²⁻ anions, forming four shorter ($r_{\text{Ti-O1}}=1.95 \text{ \AA}$) and two longer ($r_{\text{Ti-O2}}=1.97 \text{ \AA}$) Ti-O bonds. The Ti center has a distorted octahedral structure with D_{4h} symmetry..

On rutile TiO₂(110) surface, the Ti_{5c} atom is coordinated with 4 surface O_{3c}(O1) atoms and one subsurface O_{3c}(O2) atom, forming the C_{4v} symmetry.

On rutile TiO₂(100) surface, the Ti_{5c} atom is coordinated with 2 bridge O_{2c}(O_b) atoms, 2 subsurface O_{3c}(O1) atoms and one 2nd layer O_{3c}(O2) atom, forming the C_{2v} symmetry.

The symmetry of the Ti center decreases in the order of bulk TiO₂, TiO₂ (110) surface and TiO₂ (100) surface.

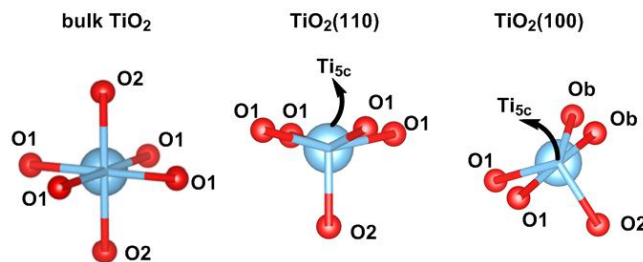
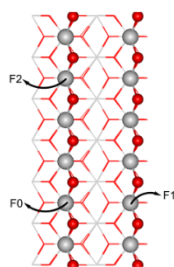


Figure S8. Geometric structures of Ti_{6c} in bulk rutile TiO_2 and Ti_{5c} on rutile $TiO_2(110)$ and (100) surface.

8 , Analysis of the introduction of bottom-absorbing F atom

We have calculated several states with F on two different sites other than the initial F0 in main text. The relative energy (ΔE) of the new slabs are shown below and we can see that the position has little influence to the situation. We think this is because the slab is thick enough to separate the adsorbates and F atom.

Table S3: The relative energies of the slabs with F on different sites. The positions for F adsorbing in F0, F1 and F2 are shown in the top-view figure below. For bare surface, CH_3OH -ads and CH_3NHCH_3 -ads the hole is located on Ob, while for CH_3OH -dis and CH_3NHCH_3 -dis the hole is located on the dissociative CH_3O and $(CH_3)_2N$ groups.



| ΔE (eV) | F0 | F1 | F2 |
|-------------------|-------|-------|--------|
| Bare surface | 0.000 | 0.039 | -0.007 |
| CH_3OH -ads | 0.000 | 0.073 | 0.015 |
| CH_3OH -dis | 0.000 | 0.043 | -0.001 |
| CH_3NHCH_3 -ads | 0.000 | 0.030 | -0.021 |
| CH_3NHCH_3 -dis | 0.000 | 0.071 | 0.018 |

9 , Analysis of the solvation effect

Vasp-sol was applied to analyze the solvation effect. We have calculated the $E_{hole}(R)$ in vacuum and in aqueous solution with the same method as that used in manuscript.

Although the adsorption with solvation effect is dramatically weaker than that in vacuum (e.g. $E_{ad}(CH_3OH)_{vac}=-1.075eV$, $E_{ad}(CH_3OH)_{sol}=-0.589eV$; $E_{ad}(CH_3NH_2)_{vac}=-1.228eV$, $E_{ad}(CH_3NH_2)_{sol}=-0.843eV$), the discrepancy in hole scavenging energy is acceptable. In fact, no matter the hole is trapping on the Ob or the adsorbates, there is always a positive charge on the surface and thus reasonable in showing similar polarity.

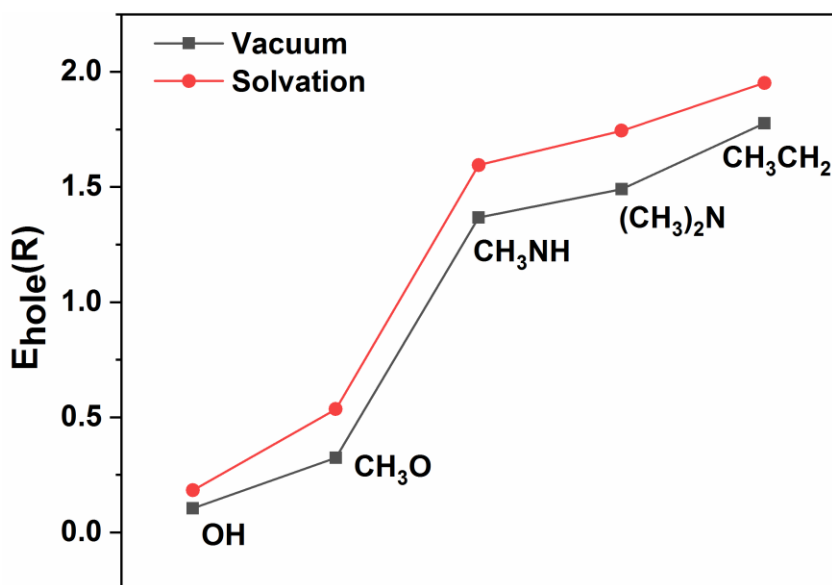


Figure S9: $E_{\text{hole}}(R)$ for OH, CH₃O, CH₃NH, ((CH₃)₂)N and CH₃CH₂ in vacuum(black) and in aqueous solution (red).

10 , Analysis of the hole concentration effect

We have analyzed the influence of hole concentration by introduce one and two holes in our simulation, and the results are shown in Table S4. The one-hole slab model is the same one used in the manuscript. While with the two-hole slab, the concentration of hole is doubled. We calculated the hole scavenging energy when one hole is scavenged by adsorbate, while another one is remaining on surface O_b. Generally, our calculation shows that the influence of the hole concentration to the hole scavenging energy is small.

We have analyzed the structures before and after the hole scavenging. Because of the repulsive force between positive charges, the two holes are not likely to be very close. After hole scavenging, the adsorbates are still binds to the surface strongly, and the distances between the two holes actually do not change obviously. We think this is the major reason for the weak influence of the hole concentration. In our calculation, the $E_{\text{hole}}(\text{CH}_3\text{NH})$ for two-hole slap is even slightly smaller than that for one-hole slab, in line with the reduced distance between the two holes in the hole scavenging (7.91 Å after the hole scavenging and 8.88 Å before), induced by the hydrogen bond between NH and O_b. However, this is strongly structural dependent, and there could also be other structures with different hydrogen bond pattern.

The concentration of the hole in our two-hole slab is already pretty large (1/6ML), therefore we do not expect a strong influence of the hole concentration in practical experimental conditions.

Table S4: $E_{\text{hole}}(R)$ for CH₃O, CH₃NH, and (CH₃)₂N in 6×2 slab model containing one hole and two holes (only one is scavenged by adsorbates).

| | 1 hole | 2 holes |
|--|--------|---------|
| $E_{\text{hole}}(\text{CH}_3\text{O})$ | 0.324 | 0.415 |
| $E_{\text{hole}}(\text{CH}_3\text{NH})$ | 1.368 | 1.266 |
| $E_{\text{hole}}((\text{CH}_3)_2\text{N})$ | 1.491 | 1.491 |

Reference:

- (1) Wang, D.; Wang, H.; Hu, P. Identifying the distinct features of geometric structures for hole trapping to generate radicals on rutile TiO₂(110) in photooxidation using density functional theory calculations with hybrid functional. *Phys. Chem. Chem. Phys.* **2015**, *17*, 1549-1555.
- (2) Zhang, J.; Peng, C.; Wang, H.; Hu, P. Identifying the Role of Photogenerated Holes in Photocatalytic Methanol Dissociation on Rutile TiO₂(110). *ACS Catal.* **2017**, *7*, 2374-2380.