



Facet-Dependent Hydrogenation of the Anatase TiO₂

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Abstract. TiO₂, known for its low cost and natural abundance, is a prominent semiconductor utilized in photocatalysis and solar energy storage applications. However, the substantial energy gap of 3.2 eV restricts its capacity to absorb sunlight. Hydrogenation, by introducing an amorphous layer, enhances the capture of light in the visible spectrum. The understanding of the hydrogenation mechanism is crucial for the development of black TiO₂ and its applications, especially the relationship between the hydrogenation process and the surface configuration. This review will present a comprehensive overview of the pertinent research findings within this domain.

Keywords: hydrogenation mechanism; TiO₂; surface structure.

1 Introduction

Titanium dioxide (TiO₂) finds extensive use in photocatalysis, wastewater treatment, reduction of carbon dioxide, catalytic H₂ production, and solar energy storage, owing to its superior optoelectronic properties¹⁻⁴. However, wide bandgap limits its absorption of sunlight to the ultraviolet region. Black TiO₂ significantly expanded the absorption spectrum, due to the introduction of the defect states through hydrogenation⁵. Hydrogenation is closely related to the surface structure of TiO₂. Therefore, understanding the intricate relationship between surface structure and the hydrogenation mechanism is essential for the study of black TiO₂. In this paper, we strive to construct a detailed and comprehensive description of how surface structure impacts the hydrogenation process.

2 Facet-Dependent Hydrogenation

The surface exposed structure of anatase TiO₂ is characterized by variations in the number of unsaturated coordinated oxygen (O) and titanium (Ti) atoms, which endow it with distinct properties. Previous studies have shown that different exposed surfaces of anatase TiO₂ possess distinct surface energies, which influence their reactivity⁶. These energy differences are thought to modulate the surfaces' interactions with reactants, thus impacting reaction kinetics. The (001) surface's high reactivity towards water dissociation is attributed to the lower coordination of O atoms on this surface⁷. In

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contrast, the (101) facet demonstrates superior photocatalytic activity for CO₂ reduction compared to the (001) facet⁸. The hydrogenation reaction of TiO₂ is closely associated with its surface structure, leading to two predominant theories explaining the mechanisms on differently exposed surfaces. The first theory proposes that the adsorption and diffusion energy barriers for hydrogen (H) within the TiO₂ lattice are major determinants of the reaction rate. In contrast, the second theory links hydrogenation kinetics to the formation energy and diffusion energy barriers of oxygen vacancies (V_O). Following sections will provide a detailed analysis of each theory.

2.1 Anisotropic Diffusion of H

The H₂ transfer process is intricately linked to the surface structure of the TiO₂^{9, 10}. The energy barriers for H transfer are influenced by the specific sites on the TiO₂ surface where the O atoms reside. For instance, O atoms with lower coordination numbers, such as those at the O_{2c} position, may present different adsorption energies compared to those in more coordinated environments, like the O_{3c} position^{11, 12}. The formation of V_Os during the hydrogenation process, a phenomenon observed in various studies, can also affect the diffusion pathways and energy barriers for H¹³. These vacancies can facilitate the movement of H species across the surface, potentially lowering the activation energy for certain steps in the hydrogenation process^{14, 15}.

Sun et al. have demonstrated that hydrogen incorporation varies between the (101) and (001) facets of TiO₂ nanocrystals through experimental observations and density functional theory (DFT) calculations¹⁶. Hydrogen adsorption and desorption measurements suggest that the (101) surface promotes hydrogen incorporation more effectively than the (001) surface, due to its higher hydrogen retention capacity at 1.4% (Fig.1). DFT calculations indicate a reduced energy threshold for hydrogen uptake on the (101) surface, which is contrary to the calculations results of Wei's group¹⁵. They calculated that the (001) surface had the lowest activation and diffusion barrier, which was inconsistent with Sun's experimental results.

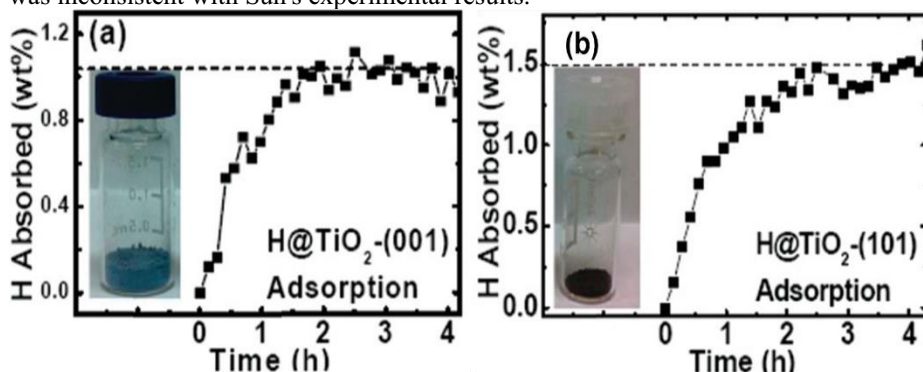


Fig. 1. Profiles of hydrogen adsorption on (a) (001) and (b) (101) surface. Reproduced with permission from Ref. 16. Copyright 2011, American Chemical Society.

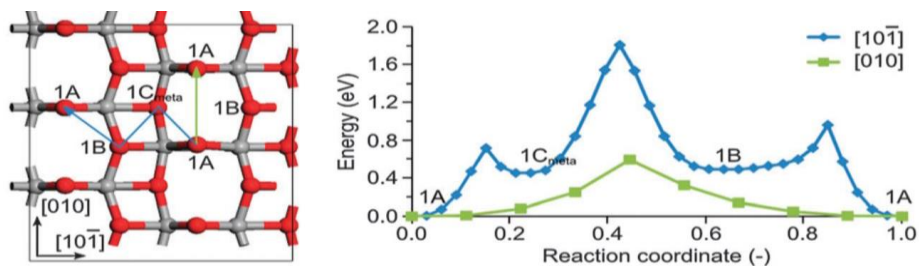


Fig. 2. Lowest energy trajectories for H diffusion on the anatase TiO₂ (101) surface, following the [010] direction (green) and the [101] direction (blue), at a coverage of 1/6 ML. Reprinted with permission from ref. 17. Copyright 2012, The Royal Society of Chemistry.

Aschauer et al. calculated the minimum diffusion energy barriers for hydrogen along the [100] and [101] directions, as shown in Fig. 2¹⁷. The results reveal a minimal hydrogen diffusion energy barrier in the [010] direction, indicating anisotropic diffusion within the TiO₂ crystal lattice. Liu et al. (2022) demonstrated that H atoms on the anatase TiO₂ (101) surface exhibit the lowest energy barrier for hopping between adjacent oxygen atoms¹⁸. The varying surface structures, with different compositions of oxygen atoms, lead to distinct adsorption energies⁹. The arrangement of oxygen atoms in different directions from the surface to the subsurface influence hydrogen diffusion, contributing to the anisotropy of the hydrogenation process.

2.2 Anisotropic Diffusion of V_O

During the hydrogenation process, a significant number of V_Os are generated, leading to an alternative hypothesis that posits the anisotropic diffusion of V_Os as the primary cause. Initially, V_Os are more prone to form at the O_{2c} sites, which have unsaturated coordination, as opposed to the O_{3c} atoms with saturated coordination¹⁹. The formation energy for these vacancies at the O_{2c} position is lower than that for the O_{3c} sites. Upon the formation of V_Os, they are observed to diffuse from the surface layer into the subsurface region^{20, 21}. Consequently, the energy barrier associated with the diffusion of V_Os is proposed to be the underlying reason for the varying rates of hydrogenation observed on different exposed surfaces of TiO₂²².

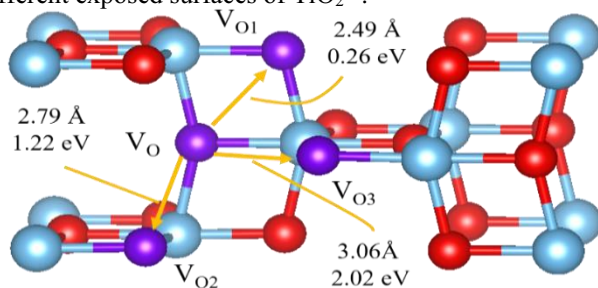


Fig. 3. Activation energies for the different diffusion pathways of the V_O²³. The purple ball represents the V_O position, and the orange arrow represents the direction of V_O diffusion.

Paris et al. conducted theoretical calculations on the diffusion energy of V_O along different directions²³. Fig. 3 shows that the diffusion barrier along the V_{O1} direction is the lowest at 0.26 eV, markedly lower than the 0.6 eV required for H diffusion. In 2018, the Selcuk group's kinetic calculations indicated that H movement in TiO_2 surface is isotropic, in contrast to the anisotropic diffusion of V_O ²⁴. Fig. 4 illustrates the diffusion direction of V_O on different exposed surfaces, aligning with others group's calculated results^{25, 26}. V_O are more likely to diffuse along the [010] direction, resulting in the V_O diffusion of (001) surface being parallel to the surface plane²⁶. The diffusion energy of V_O follows the order: (010) > (101) > (001). Their calculations suggest that the diffusion energy of H atoms is significantly higher than that of V_O , indicating that V_O primarily influences the kinetics of surface hydrogenation. Additionally, several research groups have theoretically determined that V_O s on the anatase TiO_2 surface are more prone to diffusing from the surface to the subsurface, thereby enhancing the hydrogenation reaction²⁷.

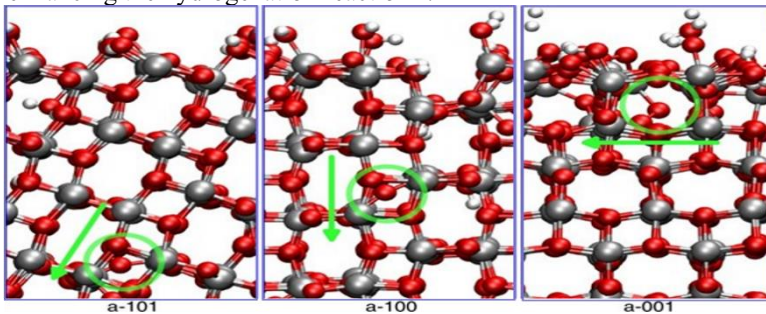


Fig. 4. Molecular-level specifics regarding the movement of V_O s across various surfaces. Reprinted with permission from Ref. 24. Copyright 2018, Springer Nature.

3 Conclusions

Currently, there are two predominant theories about the hydrogenation mechanism of TiO_2 with different exposed surfaces: hydrogen diffusion and oxygen vacancy diffusion. Theoretically, the (010) surface is predicted to have the highest hydrogenation reactivity, while the (001) surface is lowest. However, experimental support for these theories is scarce, highlighting the need for *in situ* experiments to confirm hydrogenation mechanisms. This kind of verification can deepen our comprehension of the formation process and aid in the advancement of material science based on black TiO_2 .

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