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PHYSICAL CHEMISTRY 2014

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NEAR-SURFACE HYDROGEN DYNAMICS IN TITANIA

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ABSTRACT

The hydrogen interaction with the TiO₂ (110) surface has been investigated using pseudopotential and PAW methods with addition of U Hubbard term. The hydrogen diffusion behavior and thermodynamic properties were calculated by means of full relaxation of structure in every step of bulk diffusion. The results show the existence of potential barriers close to every atomic layer, the trends of barriers and overall system energy lowering away from surface and the occurrence of preferential H sites within each interlayer basin. These findings go in favor of previously experimental findings of TiO₂ low surface H coverage and observed easy diffusion of hydrogen from reduced surface into the TiO₂ bulk or at least in near surface region.

INTRODUCTION

Titania (rutile-structure TiO₂) attracts a lot of interest because of its many achieved and possible future applications, non-toxicity and safe usage. This material is used as a white pigment and for optical coating [1], as a photocatalyst for air and water purification and as a self-cleaning surface [2] and for hydrogen production using photochemical splitting of water [3]. Modified TiO₂ films could be promising alternative for spin-based electronic devices [4]. TiO₂ is also known as a good catalyst [5,6].

Another possible application of TiO₂ is in improvement of (de)sorption properties of hydrides. A large number of experimental studies confirm that the addition of metal oxides, such as TiO₂, has beneficial effect on destabilization of MgH₂ matrix and can cause improvement of this material's kinetic properties [6-10]. Further, several numerical studies on hydrogen motion through oxide surface has been done to understand the mechanism of the reaction [11,12].

Yin *et al.* [13] have investigated hydrogen coverage on TiO₂ (110) surface under different experimental conditions of exposure to atomic hydrogen. They obtained that maximum H monolayer coverage on TiO₂ (110) surface is only 70% at room temperature, regardless of applied partial pressure of

hydrogen. This result was confirmed using scanning tunneling microscopy and high-resolution electron energy loss spectroscopy. The same authors confirmed that during the heating of the hydrogenated sample, H atoms have migrated *into* the TiO₂ bulk. This is unusual since desorption of H₂ (or H₂O) molecules into the gas phase is common behavior of reduced oxides surface. Filippone *et al.* carried out research which showed that hydrogen behaves as a deep donor in rutile phase and forms an OH⁺ complex, where H forms bond with a prevailing ionic character [15]. With addition of Hubbard term U, they showed that electronic localization effects have major influence on nature of bonding and charge distribution as a consequence of hydrogen interstitial. Also, Ti⁺³ species are formed as a result of localization of H and OH⁺ electronic levels on some Ti neighbors [15]. The reduction of Ti⁺⁴ atoms to Ti⁺³ raises the possibility that all hydrogen atoms are adsorbed as protons onto outer oxygen atoms [11].

In this paper we have investigated the interaction of H atom with TiO₂ (110) surface and its behavior in the near-surface region of rutile TiO₂.

DETAILS OF CALCULATIONS

Investigation of atomic hydrogen behavior on rutile TiO₂ (110) surface and in the near-surface region were done using two methods available in Abinit code [16-18]. Plane waves based calculations with Troullier - Martins norm-conserving pseudopotentials (PP) and projected augmented waves (PAW with GGA+U) methods were used. The value of U_{eff} was 2.0 eV. The energy cut-off of the plane wave basis set was 816 eV.

In case of PP calculations (1x1)(110) supercell with 12 atomic layers and 25 atoms was constructed. Slab supercell (2x1)(110) with 21 atomic layers and 85 atoms was constructed in the case of PAW calculation. The surface of the supercells was

separated from its periodic image by 15 Å of vacuum. Three bottom layers were fixed to simulate the bulk. The rest of supercell atoms were subject to

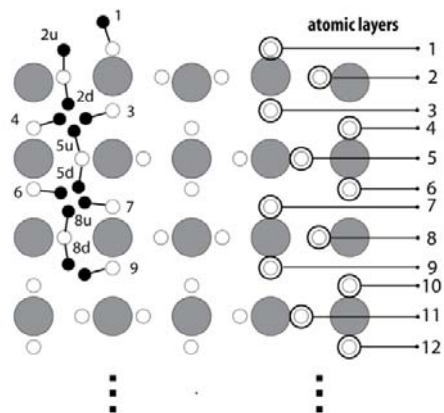


Figure 1. Side view of slab supercell - atomic layers and initial positions of H atoms.

the relaxation of atomic positions. It is assumed that hydrogen atom forms short OH bonds and that diffusion consists of “jumps” between neighboring O sites. Further, calculations were performed to obtain relaxed structures with different arrangements, where H atom was bounded to O atoms in different atomic layers.

RESULTS AND DISCUSSION

In Fig. 2, the energy differences as function of H distance from surface are given for both PP and PAW (GGA+U) calculations. Energy differences were shown on x axis, with energy of configuration **1** used as reference, marked with horizontal line. As distance reference from surface, z-coordinate of O_{2s} atom in slab supercell without H was used, marked as vertical short-dashed line. The characteristic “periodic” dependence of energy on hydrogen position depth is visible. In case of PP calculations “degeneration” of opposite configurations (i.e. 2d and 5u, 3 and 4) was not observed. According to [13,15] the barriers for jump from one oxygen atom to another range from 0.5 to 1.1 eV, depending on the position of bonding oxygen atoms and distance from surface. These barriers could be overcome at modest temperatures (in accordance with [13]). The details of energy profile, like barriers, are not visible in approach presented here. However, initial and final states, corresponding to jump from one O atom to the next can provide details and possible pathways of hydrogen drift from and to the surface.

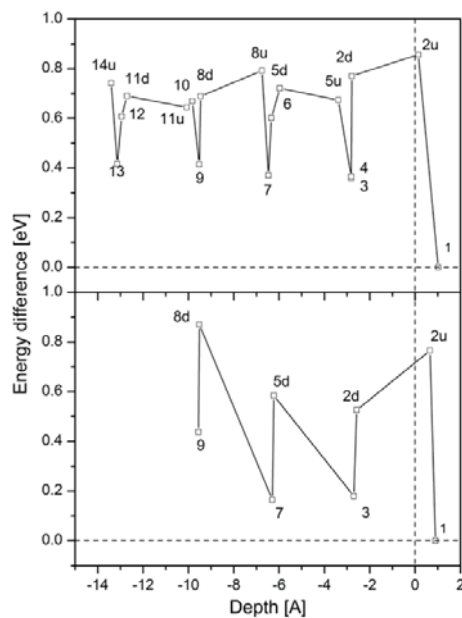


Figure 2. Slab system energy change as a function of hydrogen atom distance from the surface. Top) PAW, bottom) PP.

CONCLUSION

In this paper we have presented the results of electronic structure calculations of (1x1) and (2x1) (110) slabs of TiO₂ – H system. The degree

of H influence on host lattice clearly depends on H concentration and charge redistribution mechanism (GGA or GGA+U). In case of PP calculations, there is a preferred direction perpendicular to surface in a sense of preference of closer-to-surface configurations, at least in the few atomic layers close to the surface. This preference was not observed in PAW calculations. The characteristic energy profile of close-to surface area show that atomic layers parallel to surface act like barriers for hydrogen drift into the bulk. At the same time, hydrogen should “jump” within the same interlayer basin fairly easy. The rise of energy of configurations close to bottom surface of slab supercell can be attributed to non relaxed and stressed structure due to fixed positions of the lowest atomic layers. From the same reason it is hard to estimate how deep influence of surface goes. Larger supercell calculations showed that the influence of surface is constrained to only few atomic layers closest to vacuum.

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