Water adsorption on rutile titanium dioxide (110): Theoretical study of the effect of surface oxygen vacancies and water flux in the steady state case

F. Bouzidi[a,d,*], M. Tadjine[a], A. Berbri[a] and A. Bouhekka[b,c]
[a]*Department of Physics, Faculty of Exact Sciences and Informatics, Hassiba Benbouali University of Chlef,*
P. B. 78 C, National Road N° *19, Ouled Fares 02180, Chlef, Algeria.*
[b]*Department of Materials Sciences, Faculty of Sciences and Technology,*
Tissemsilt University, Algeria.
[c]*Thin-Film Physics Laboratory and Materials for Electronics, Oran 1 Ahmed Ben Bella University,*
P.B. 1524, El M'naouar 31000, Oran, Algeria.
[d]*Laboratory of Mechanics and Energy, Hassiba Benbouali University of Chlef,*
Hay Salem, National Road N° *19, 02000, Chlef, Algeria.*
[*]*e-mail: bouzidifatima94@gmail.com*

Received 16 May 2022; accepted 4 November 2022

The aim purpose of the present work is highlighting the impact of surface oxygen vacancies and H_2O flux on the behavior of water adsorption at the rutile titanium dioxide (110). Therefore, a theoretical model, based on molecular and dissociation mechanisms at different surface atomic sites, was formulated in a system of partial differential coupled equations. The proposed model used to study, in an atomic scale, this complex phenomenon of adsorption governed by several factors including surface vacancies defects and water flux. The findings of the solution of the system of equations in the steady state case, presented in this paper, strongly indicated that the rate coverage of surface oxygen vacancies has an important role in the dissociation of H_2O as well as the flux which is a key factor in the behavior of water adsorption on the rutile TiO_2 (110) and the rate coverage of OH groups.

Keywords: Water adsorption; rutile titanium dioxide (110); oxygen vacancies; hydroxyls groups; H_2O flux; steady state.

DOI: https://doi.org/10.31349/RevMexFis.69.031004

1. Introduction

Among a lot of important materials, titanium dioxide (TiO_2) takes a particular attention in the recent years in several industrial applications especially in the elimination of organic contamination, sensor, splitting of water, self-cleaning and photocatalytic [1–5]. Furthermore, TiO_2 is abundance [3], inexpensive, nontoxic [4], inert and chemical stability [5, 6]. Rutile TiO_2 (110) surface is the lowest surface energy, thus is very important in studying, especially in catalysis [7]. Furthermore, TiO_2 has a high refractive indexranges between 2.4-2.6.Unfortunately, one of the drawbacks of TiO_2 is the wide band gap of 3-3.2 eV, reacts only in the (UV) light under (380 nm), that is available only around 5% in solar energy [8–11]. Many researchers treated this deficiency by generating electronic states inside the forbidden gap via inducing defects (oxygen vacancy, Ti interstitial, dislocation,...) and doping with impurities (metal transition, noble metal,..) in the structures of TiO_2. This leads to extend its response in the visible light and near infrared (NIR) region [12–17]. One of the most important applications of TiO_2 surface is water splitting. The H_2O can be adsorbed in two different mechanisms either molecular or dissociative onto rutile TiO_2 (110) surface [18, 19]. But this is an intriguing phenomenon, because the adsorption process is affected by many factors (phase components, temperature, vacancies, water coverage...) [20]. Several theoretical methods (Langmuir, Freundlich, Langmuir-Hinshelwood...) are widely used to study the kinetics of adsorptions [21–25]. These phenomena have been studied by using various ab inition quantum mechanical approximations highlighting on the important factors that affect on the adsorption and the dissociation of H_2O such as (DFT and DFT-PW and HF...) calculations and molecular dynamics([21] and references therein) which have provide numerous groundbreaking insight into the water -TiO_2 interface. However, it is not possible to get adsorption information taking in consideration all the surface sites at the same time. Experimentally, the infrared spectroscopy, especially in Situ ATR-FTIR, is one of the most important and powerful technique used to investigate the water molecules adsorption at solid surfaces [26]. But in experimental, it is not clear and easy to get details at the atomic scale level of adsorption therefore; the theory becomes a useful tool. In light of the above information, we are interested in this context, to study the effect of oxygen vacancies concentration at rutile TiO_2 (110) surface and water flux on the behavior of H_2O molecules adsorption using a system of nonlinear differential equations, carried out taking into account the different cases of adsorption and all surface available sites. This indicates a better understanding of structural and dynamical properties changes of the behavior of H_2O on rutile TiO_2 (110) surface. Thereby, these factors greatly enhancing chemical/catalytic reactivity (among other properties) as well as the splitting of water and self-cleaning. At the end, a summary will be given together with

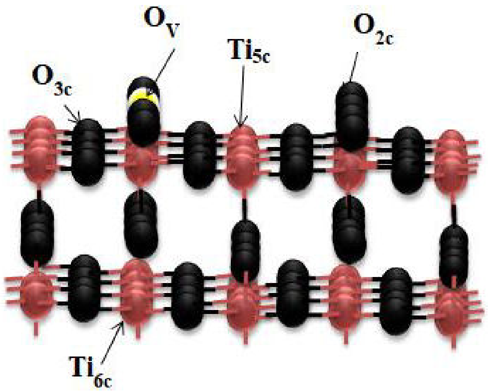

FIGURE 1. Structure of rutile TiO_2 (110) surface in the z-direction, black balls represent O atoms of the bridge-bonded O species (O_{2c}) and three coordinated (O_{3c}), red balls are fivefold coordinated surface Ti (Ti_{5c}) and six fold coordinated Ti atoms (Ti_{6c}), white ball is single oxygen vacancies (O_V).

a brief outlook towards challenges and prospects for future theoretical studies [27, 28].

2. The surface structure of rutile TiO_2 (110)

Naturally, TiO_2 exists in three different crystallography forms rutile, anatase and brookite. The structure of each form is described as a chain of octahedron (one atom of Ti surrounded by six oxygen atoms) as shown in Fig. 1. Among the three structures anatase (101) and rutile (110) are the most stable faces and more reactive especially in photocatalytic applications [7].

The different surface sites illustrated in this figure play a crucial role in the adsorption and the behavior of water molecules. It is still not clear to distinguish which kind of site is primordial in controlling the adsorption phenomenon. In the following part, we give the possible mechanisms of adsorption used to formulate the proposed theoretical model.

3. Kinetics model description of H_2O - rutile TiO_2 (110) surface interactions

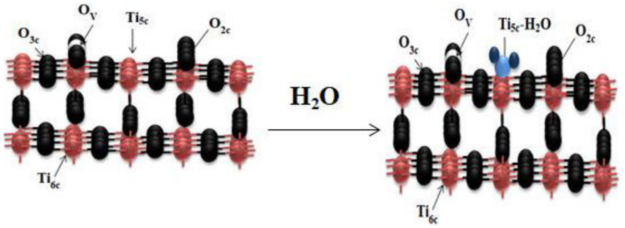

FIGURE 2. The adsorption of molecular water on free defect surface, dark (light) blue balls hydrogen (oxygen of water) atoms, K_1, K_2 are the rates constants of adsorption and desorption respectively.

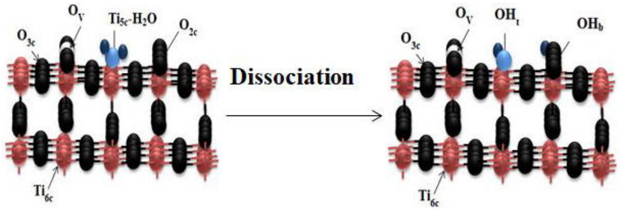

FIGURE 3. The dissociative adsorption of water on Ti_{5c} sites, where K_3 and K_4 are the rates constants of dissociation and recombination reaction, respectively.

A kinetics model of H_2O on rutile TiO_2 (110) surface, in bellow figures, was developed to describe the behavior of H_2O adsorption, assumed to adsorb in reversible states; different forms model, two types of features found on rutile TiO_2 (1x1) (110) surface as indicated in Fig. 2 and reaction (1). H_2O molecules adsorb in molecular form on defect-free sites (Ti_{5c}) at low temperature around 160 K [29] is due a Ti -H_2O bond length (2.16 - 2.29) Å [30], with adsorption energy around (0.5 - 0.7 eV) [1, 28, 33–35]. When annealing the surface below room temperature, only the H_2O molecules are desorbed from surface with energy ranges between 0.7 eV to 0.8 eV depending on the water rate coverage [36]. In the other hand, The H_2O has the possibility to dissociate on (Ti_{5c}) sites, however, the second proton H^+ transfer to the neighbouring bridging oxygen (O_{2c}) and forms two OH hydroxyl groups OH_t and OH_b respectively, which was discussed in details in Ref. [3] with dissociation energy toward 0.36 eV and 0.41 eV, when annealing the surface to room temperature under reaction (2) [31–33] as shown in Fig. 3. This competition between molecular and dissociated adsorption is mostly governed by the basic strength of the bridging O atom receiving the H.

$$\mathrm{Ti}_{5c} + \mathrm{H_2O} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \mathrm{Ti}_{5c} - (\mathrm{H_2O}). \tag{1}$$

A missing of an oxygen atom, by removing the oxygen bridging (O_{2c}) from the surface using electron bombardment or other methods, leads to the creation of a surface oxygen vacancy (O_V) (none thermally). This was discussed in more details in Ref. [2].

$$\mathrm{Ti}_{5c} - (\mathrm{H_2O}) + \mathrm{O}_b \underset{K_4}{\overset{K_3}{\rightleftarrows}} \mathrm{OH}_t + \mathrm{OH}_b. \tag{2}$$

With its concentration around 15% ML (Mono Layer) (1 ML is defined with respect to the coverage of Ti_{5c} sites of 5.2. 10^{14} cm^{-2}) from the surface of TiO_2 (110) [34, 35]. The water favoured dissociate in the oxygen defect at below temperature (130-200 K) and forms two OH hydroxyl groups in the O_V and the H^+ proton of water transfer nearby bridging oxygen and creates the other hydroxyl for every vacancy as given in Fig. 4 [36–39], the recombination of the two OH occurs at temperature above 490 K [3, 18]. This reaction can be written as Eq. (3) indicates.

$$\mathrm{H_2O} + \mathrm{O}_v + \mathrm{O}_b \underset{K_6}{\overset{K_5}{\rightleftarrows}} \mathrm{OH}_b + \mathrm{OH}_t. \tag{3}$$

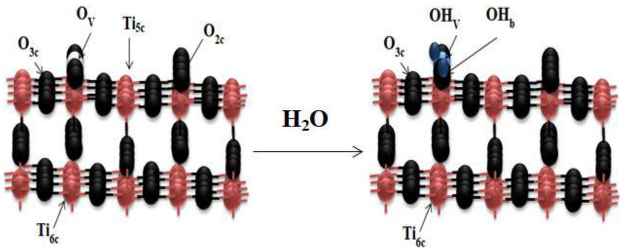

FIGURE 4. The dissociative adsorption of water on the surface oxygen vacancy, where the K_5 and K_6 are the dissociation and recombination rates constants, respectively

4. Model and method

A mathematical description of these equations (1)-(3) for the adsorption of water in different cases onto rutile TiO_2 (110) surface can be derived using an adaptation of the Langmuir adsorption model. This model is the most commonly applied of single component liquid-solid adsorption. Based on the kinetics principle, Langmuir isotherm model assuming that only monolayer adsorption exists; no impurities (CO_2, O_2...) are considered at the surface and to avoid interactions between water molecules the incident H_2O flux density can be supposed very weak and more addition the adsorbent surface is uniform with the same adsorption probability [22,24]. Therefore, the adsorption rate of each chemical reaction can be presented as following Eq. (4):

$$\frac{d\theta}{dt} = \Phi P_{\text{ads}} - K\theta, \tag{4}$$

where $\Phi, \theta, P_{\text{ads}}, K$ are the flux, the surface sites coverage, the probability of the molecule will find adsorption sites and the desorption rate constant, respectively. The probability of adsorption is given by the following Eq. (5).

$$P_{\text{ads}} = K\left(\frac{n_a(1-\theta_a)}{n_s}\right), \tag{5}$$

where K, n_a, n_s, θ_a the adsorption rate constant (s^{-1}), the concentration of adsorption sites, the concentration of all atoms in the surface and the coverage of the adsorption sites respectively. The rate constant K_i can be expressed with an Arrhenius Eq. (6),

$$K_i = K_0 \exp\left(\frac{-E_a}{RT}\right), \tag{6}$$

where K_0, E_a, R and T are the attempt frequency (s^{-1}), the activation energy (Kj/mole, 1eV = 96.482 Kj), universal gas constant (8.314 J/mole.K) and the temperature K.

The different reactions (1) to (3) using Eq. (4) are organized below,

$$\mathrm{Ti}_{5c} + \mathrm{H_2O} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \mathrm{Ti}_{5c} - (\mathrm{H_2O})$$

$$r_1 : \Phi K_1\theta_{\text{Ti}} - K_2\theta_{\mathrm{H_2O}}, \tag{7}$$

$$\mathrm{O}_b + \mathrm{Ti}_{5c} - (\mathrm{H_2O}) \underset{K_4}{\overset{K_3}{\rightleftarrows}} 2\mathrm{OH}$$

$$r_2 : K_3\theta_{\mathrm{H_2O}}\theta_b - K_4\theta^2_{\text{OH}}, \tag{8}$$

$$\mathrm{O}_v + \mathrm{O}_b + (\mathrm{H_2O}) \underset{K_6}{\overset{K_5}{\rightleftarrows}} 2\mathrm{OH}$$

$$r_3 : \Phi K_5\theta_v\theta_b - K_6\theta^2_{\text{OH}}, \tag{9}$$

where θ_{Ti}, θ_{OH}, $\theta_{\mathrm{H_2O}}$, θ_b and θ_v are the coverage of titanium, hydroxyl groups, water, bridging oxygen and oxygen vacancies on the surface respectively. The adsorption rate is proportional to the H_2O flux arrived on surface and the coverage of active sites (Ti_{5c}, O_V and O_{2c}), desorption rate is proportional to the number of association and desorption adsorbed molecules, under such assumptions; in the adsorption process we have [39].

$$\begin{aligned}
\frac{d\theta_v}{dt} &= -r_3 = -\Phi K_5\theta_v\theta_b + K_6\theta^2_{\text{OH}},\\
\frac{d\theta_b}{dt} &= -r_3 - r_2 = -\Phi K_5\theta_v\theta_b + K_4\theta^2_{\text{OH}}\\
&\quad - K_3\theta_{\mathrm{H_2O}}\theta_b + K_6\theta^2_{\text{OH}},\\
\frac{d\theta_{\text{OH}}}{dt} &= +r_3 + r_2 = \Phi K_5\theta_v\theta_b - K_4\theta^2_{\text{OH}}\\
&\quad + K_3\theta_{\mathrm{H_2O}}\theta_b - K_6\theta^2_{\text{OH}},
\end{aligned}$$

TABLE I. Kinetic parameters used in the mathematical models of H_2O reactions on rutile TiO_2 (110), the rate constant (K_i) extracted from the Arrhenius Eq. (6).

Step,(i)	$K_0[s^{-1}]$	E_a [eV]	$T[K]$	K_0 [s^{-1}]	Reference
1.H_2O adsorption	10^{13}	$0.5 - 0.7$	$150 - 160$	0.0018	[1,3]
2.H_2O desorption	10^{12}	$0.73 - 0.8$	$200 - 275$	4.10^{-7}	
3.H_2O dissociation on free defect	10^{12}	$0.36, 0.44, 0.97$	$80 - 140$	0.0015	[29,30]
4.OH Association	10^{12}	0.355	$110 - 130$	$5.43.10^{-5}$	
5.H_2O dissociation on O_V	10^{13}	$0.93 - 1.5$	300, 187	0.0024	[41–47], [51,54]
6.OH recombination	10^{8}	$0.12 - 0.18$	$450 - 500$	10^{-4}	

$$\frac{d\theta_{\text{Ti}}}{dt} = -r_1 = -\Phi K_1\theta_{\text{Ti}} + K_2\theta_{\text{H}_2\text{O}}$$
$$\frac{d\theta_{\text{H}_2\text{O}}}{dt} = r_1 - r_2 = \Phi K_1\theta_{\text{Ti}} - K_2\theta_{\text{H}_2\text{O}} - K_3\theta_{\text{H}_2\text{O}}\theta_b + K_4\theta_{\text{OH}}^2 \quad (10)$$

The sum of all the different coverage at the rutile (110) surface are $\sum\theta_i = 1$ and the variation equal

$$\sum\frac{d\theta_i}{dt} = 0 \quad (11)$$

We suppose the variation of the coverage's remains the same in duration of the reaction, setting these rates to zero in the steady state gives the system (12) as indicated bellow. The stability of the set of equations is very important because any bifurcation parameter can dramatically change it and to avoid such behavior we took the rates constants K_i have similar thermal stability.

$$-\Phi K_5\theta_v\theta_b + K_6\theta_{\text{OH}}^2 = 0$$
$$-\Phi K_5\theta_v\theta_b + K_4\theta_{\text{OH}}^2 - K_3\theta_{\text{H}_2\text{O}}\theta_b + K_6\theta_{\text{OH}}^2 = 0$$
$$\Phi K_5\theta_v\theta_b - K_4\theta_{\text{OH}}^2 + K_3\theta_{\text{H}_2\text{O}}\theta_b - K_6\theta_{\text{OH}}^2 = 0$$
$$-\Phi K_1\theta_{\text{Ti}} + K_2\theta_{\text{H}_2\text{O}} = 0$$
$$\Phi K_1\theta_{\text{Ti}} - K_2\theta_{\text{H}_2\text{O}} - K_3\theta_{\text{H}_2\text{O}}\theta_b + K_4\theta_{\text{OH}}^2 = 0 \quad (12)$$

5. Results and discussion

We use a numerical method to solve this system Eq. (12) and the corresponding solution of coverages is given by the following equations:

$$\theta_{\text{OH}} = 0.16\big(-750\,\Phi\theta_v + 2.24 \times \sqrt{1875\,\Phi\theta_v - 2237\,\Phi\theta_v^2 + 96210\,\Phi^2\theta_v^2}\big), \quad (13)$$
$$\theta_{\text{Ti}} = 0.2\theta_v, \quad (14)$$
$$\theta_{\text{H}_2\text{O}} = 8.7\,\Phi\theta_v, \quad (15)$$

$$\theta_{O_b} = \frac{5.10^{-4}\big(10^3\,\Phi\theta_{O_v} - 2.10^3\,\Phi\theta_{O_v}^2 + 2.10^5\,\Phi^2\theta_{O_v}^2 - 670.8\,\Phi\theta_{O_v}\sqrt{\Phi\theta_{O_v}(1.8.10^3 - 2.2.10^3\theta_{O_v} + 9.6.10^4\,\Phi\theta_{O_v})}\big)}{\Phi\theta_{O_v}}. \quad (16)$$

It is clear that the solutions of each surface site strongly depends on the flux of water and the surface oxygen vacancies (O_V). As indicated in Fig. 5 (a), OH hydroxyls increases and reaches a maximum for O_V = 0.04 then it decreases to the minimum for a higher value of O_V. The same behavior for OH hydroxyls is illustrated in Fig. 5 (b) when this flux changes from 0 to 1. This graph indicates that the coverage of OH hydroxyls increases at low flux values and reaches a maximum around 0.7 (for a flux value around 0.4) afterward it decreases which means that OH hydroxyls production is slightly reduced.

To illustrate theses variations of OH hydroxyls on the surface versus H_2O flux and O_V, a three dimension (3D) is shown in Fig. 6. The coverage of OH hydroxyls grows with increasing the O_V and reaches to a maximum around 0.7 ML at O_V equal 0.05 ML. At high coverage of O_V up to 10 % the production of OH hydroxyls decays and gets a small value almost zero. In

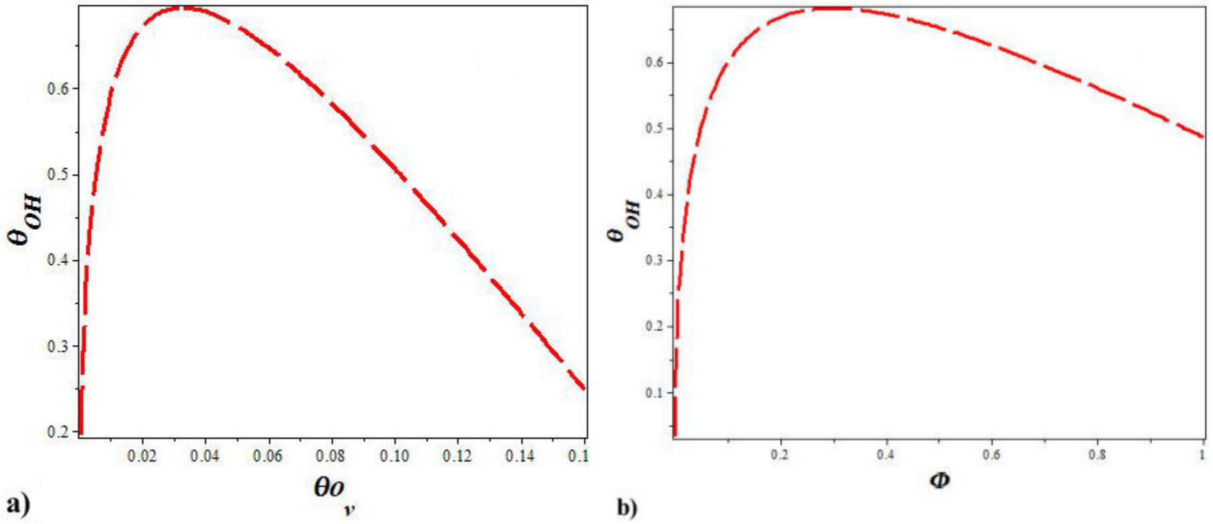

FIGURE 5. a) The effect of oxygen vacancies on the production OH hydroxyls at H_2O flux equal 0.4. b) The effect of H_2O flux on the production OH hydroxyls at O_v around 0.05 in the steady state solution.

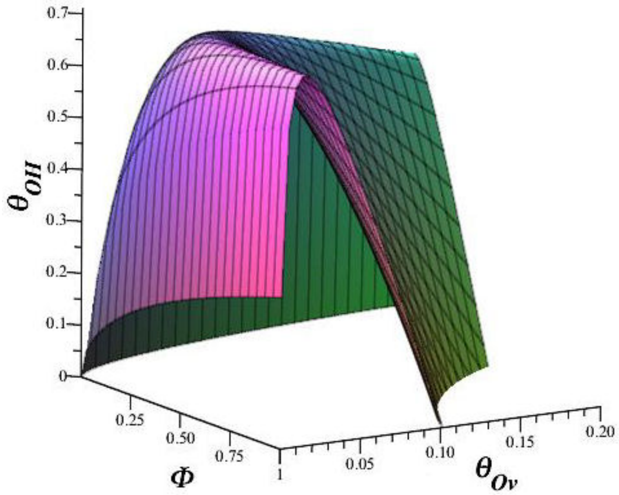

FIGURE 6. Kinetic curves for the OH hydroxyls at rutile TiO_2 (110) surface for various H_2O flux and concentration of O_V on the surface.

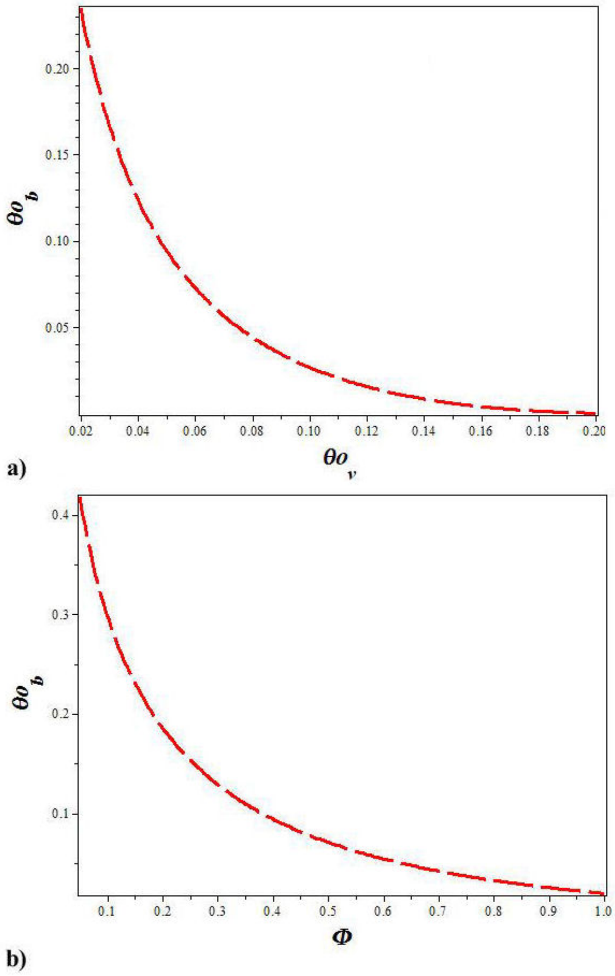

FIGURE 7. The coverage of bridging oxygen change versus: a) the coverage of O_v with the H_2O flux remains 0.4 ML, b) H_2O flux at the coverage of O_v around 0.05 ML on rutile TiO_2 (110) surface.

other hand, also the coverage of OH hydroxyls depends on the arriving H_2O molecules; when the H_2O flux arrived at surface increases, the production of OH hydroxyls increases and reaches a maximum at 0.7 ML for H_2O flux around 0.4 ML, despite, for H_2O flux takes value more than 0.4 ML and filling all the surface leading to no production of OH hydroxyls on the surface which is occupied only with H_2O molecules.

From Eq. (16), the curve of the coverage of O_b for deferent concentrations of O_V and H_2O flux arrived on surface is shown in Fig. 7.

Figure 7 (a) illustrates the variation of θ_{O_b} as a function of θ_{O_v} for the H_2O flux taken 0.4 ML. The graph clearly shows that θ_{O_b} decreases when the concentration of O_V grows. Besides, in Fig. 7(b) the coverage of O_b decays exponential-like with increasing the H_2O flux for the concentration of θ_{O_v} equals 0.05 ML.

Figure 8 is plotted using Eq. (16); it is interesting to note some common relations; the coverage of O_b decreases exponential-like with increasing the coverage of O_V and

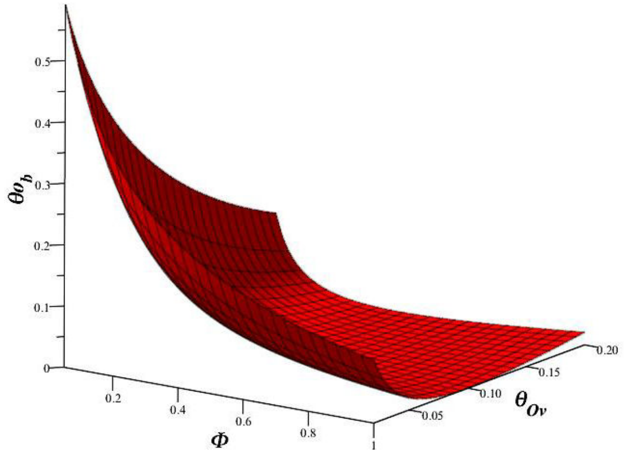

FIGURE 8. The coverage of O_b as a function of H_2O flux and O_v defects on rutile TiO_2 (110) surface.

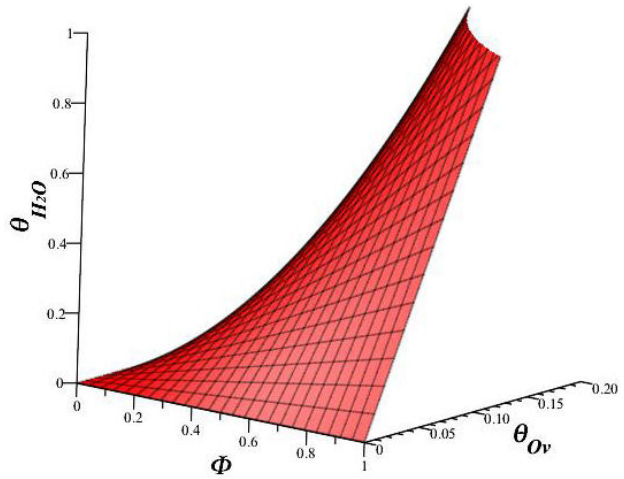

FIGURE 9. The coverage of H_2O on surface versus H_2O flux and the coverage of oxygen vacancies O_v.

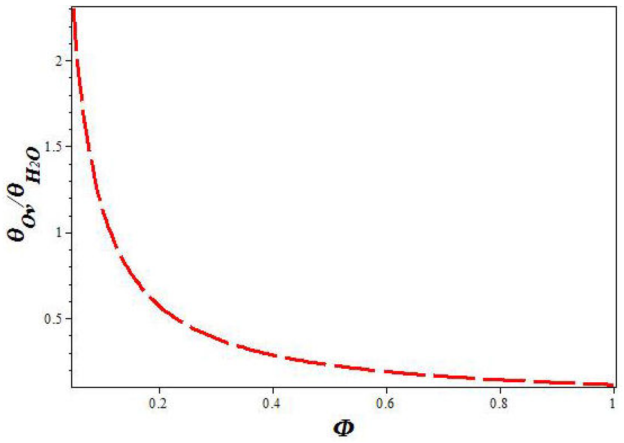

FIGURE 10. The ratio of (θ_{O_v} / θ_{H_2O}) on rutile TiO_2 (110) surface versus H_2O flux.

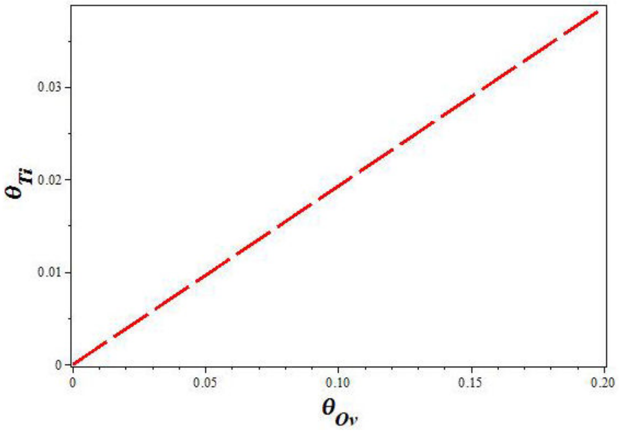

FIGURE 11. The coverage of Ti_{5c} on rutile TiO_2 (110) surface as a function of the concentration of oxygen vacancies (O_v).

tends to a small value for large value of O_V, also at high value for the H_2O flux, the coverage of O_b decreases.

This figure demonstrates that the O_b is a key factor in the dissociation and the adsorption of H_2O molecules.

The Eq. (15), variation of water coverage versus the rate of oxygen vacancies and the H_2O flux, indicating, the coverage of H_2O takes small values almost plateau when the H_2O flux and the concentration of O_V on surface is very small, afterward, the coverage of H_2O increases steadily with H_2O flux and the concentration of O_V, as illustrated in Fig. 9.

Figure 10 shows the ratio of (θ_{O_v} / θ_{H_2O}), from Eq. (15), versus the H_2O flux; indicating that the fraction of (θ_{O_v} / θ_{H_2O}) decreases with increasing the H_2O flux. This can be explained that increasing the coverage of H_2O at the surface is caused by the filling of oxygen vacancies sites.

From these results, the interactions of H_2O with rutile TiO_2 (110) surface were heavily affected by the O_V and H_2O flux. This was expected, since the H_2O flux arrived on rutile TiO_2 (110) surface, H_2O molecules take up to Ti_{5c} sites (which is positively charged) rendering its able to bind H_2O molecules via electrostatic interactions. Many authors [52, 54] have studied the effect of H_2O flux and the coverage of O_V on the behavior of H_2O molecules on rutile TiO_2 (110) surface. First, at low values of H_2O flux, is expected the mobility of H_2O molecules to be high which is helpful for the H_2O molecules to diffuse on the surface on direction [001] which dissociate at oxygen vacancies firstly to heal the vacancies and defect-free sites as well as a strong attractive of H proton to near bridging oxygen due to transfer the H proton and formed another OH hydroxyls, because dissociation at bridging oxygen vacancies is more favourable than H_2O adsorption on the Ti_{5c} sites [55], as the H_2O flux increases the OH hydroxyls continue to increase till reach the maximum at 0.7ML for 0.4 of H_2O flux, this is in good accordance with the prediction by Lindan and Zhang [56]. At a high H_2O flux, water may be adsorbed molecularly with a small fraction adsorbed dissociative on O_V because (i) at least one or two H_2O molecules uptake on Ti_{5c} sites and form a chains of H_2O molecules (ii) when the amount of H_2O molecules are large, hinders the diffusion of H_2O molecules and remains in molecular forms, therefore, H_2O molecular adsorption is more favourable at high coverage [30] . As it is seen, the coverage of O_V affects on the adsorption of water, however, the amount of OH hydroxyls formed on rutile TiO_2 (110) surface increases at low concentration of vacancies because the H_2O favourites the dissociation at oxygen vacancies [54] reach to the maximum around 0.7 ML because the repulsive interaction between the functional groups, afterward, when the coverage of O_V increases beyond to 0.05 ML, the OH groups coverage decreases, because at high concentration of O_V affects on the structure properties, which lead to (2x1) reconstruction surface [40], additionally, and we know the O_V 's created from the bridging oxygen, this implies that the coverage of O_V increases due to decrease the bridging oxygen as illustrated in Fig. 8. In noting, when ($N_{O_b} < N_{O_v}$) deficient the dissociation in O_V and the defect-free sites, this is in a good agreement with previous works reported in [57]. Exists due to the fact, the dissociation of H_2O molecules in either terminal hydroxyl or OH in vacancy need a neighbouring oxygen atoms for the H proton creates the second OH hydroxyls on O_b , besides, the coverage of bridging oxygen decreases with H_2O increases as Fig. 7(a) improved that clearly. The formation of these radical groups is active to promote the charge separation process as well as the oxidation of organic substances and several applications (self-cleaning, pharmaceutical...) [49] and references therein]. This inhibit the production of OH hydroxyls, meanwhile the molecular adsorption will be the predominant as Fig. 9 illustrates that; where the vacancies increasing the asymmetry for titanium atoms near vacancies that leads to enhance the water adsorption further the H_2O adsorbed molecular at high and low coverage [38, 53]. From the Eq. (14) it is clearly shown that the coverage of Ti_{5c} is independent to the flux, it depends only on the concentration of the surface O_V . Many authors overbalanced the increase to transfer the Ti_{6c} coordinate underneath the O_V to Ti_{5c} [52, 58]. In other hand, H_2O adsorbed molecular on Ti_{5c} meanwhile diffuses toward the vacancy site where the dissociation takes place, thus, H_2O let behind a Ti_{5c} site, however, the coverage of Ti increases as illustrated by Fig. 11. Several literature papers conclude that mixed molecular/dissociate is the most stable configuration on rutile TiO_2 (110) surface [59], besides, the behavior of the water (molecular or dissociative) can change dramatically even for the same materials as the structure and termination of the surface changes.

6. Conclusion

The interactions H_2O / rutile TiO_2 (110) are intriguing subjects; therefore, several experimental and theoretical methods were used to understanding the reaction mechanisms. In terms of theoretical studies, the proposed model presented in this research, a system of coupled differential equations, described and solved in the steady state case taking into account the different reactions of H_2O / rutile TiO_2 (110). The findings strongly indicate that the interactions H_2O- rutile TiO_2 (110) have a crucial impact on the production of OH groups at the surface. As one might expect, the coverage of OH hydroxyls increases in the presence of O_V which can be applied to enhance the performance of the purification of waste water from organic and inorganic materials plus others applications, but when the concentration of O_V increases up to 0.05 leads to reduce the production of OH hydroxyls. This behavior is believed to be a good reason of a modification on surface structure, as well as the H_2O flux. By way of outlook for future challenge given a presence of chemically adsorbed water at rutile TiO_2 (110) interface and intriguing behavior, this shows the importance of understanding both the structure of rutile TiO_2 (110) surface and dynamics of H_2O molecules on them. Indeed, knowing the mechanism behavior of water molecules on metal oxides under deferent conditions is very important due to its applications in catalysis.

Nomenclature

variables

H_2O	Water
Ti_{5c}	Titanium five coordinate
Ti_{6c}	Titanium six coordinate
O_{2c}	Oxygen two coordinate (bridging)
O_{3c}	Oxygen three coordinate
O_V	Oxygen Vacancy
OH	Hydroxyl group
Φ	Water flux density per surface site
θ	Coverage
θ_{Ti}	Coverage of undercoordinated titanium
θ_b	Coverage of oxygen bridging
θ_v	Coverage of oxygen vacancies
$\theta_{\mathrm{H_2O}}$	Coverage of water molecules on surface
θ_{OH}	Coverage of hydroxyls groups
K_i	The rate constant (s^{-1})
K_0	Attempt frequency (s^{-1})
E_a	Activation energy (Kj/mole) or (eV)
T	Temperature (K)
R	Universal gas constant (K j/mole. K)
ML	Monolayer
n_a	The concentration of the adsorption sites
n_s	The concentration of all the atoms in the surface

Acknowledgement

We gratefully acknowledge financial support of this work from the ministry of higher education and scientific research in Algeria (MESRS).

---

1. M. Elahifard, H. Heydari, R. Behjatmanesh Ardakani, P. Bijan and S. Ahmadvand, A computational study on the effect of Ni impurty and O-vacancy on the adsorption and dissociation of water molecules on the surface of anatase (101), *J. Phys. Chem. Sol.* **136** (2020) 109176, `https://doi.org/10.1016/j.jpcs.2019.109176`.
2. U. Diebold, The surface science of titanium dioxide, *J. Surf. Sci. Rep.* **48** (2003) 53, `https://doi.org/10.1016/s0167-5729(02)00100-0`.
3. U. Diebold, Perspective: A controversial benchmark system of water-oxide interfaces: H_2O/TiO_2 (110), *J. Chem. Phys.* **147** (2017) 040901, `https://dx.doi.org/10.1063/1.4996116`.
4. B. Wei, F. Tielens, M. Calatayud, Understanding the role of rutile TiO_2 surface orientation on molecular hydrogen activation, *J. Nanomaterials (Basel).* **9** (2019) 1199, `https://doi.org/10.3390/nano9091199`.
5. M.A. Shaheed, F.H. Hussein, Preparation and applications of titanium dioxide and zinc oxide nanoparticles, *J. Environ. Anal. Chem.* **2** (2014) 1000e109, `http://dx.doi.org/10.4172/jreac.1000e109`.
6. M.L. Weichman *et al.* Dissociative water adsorption on gas-phase titanium dioxide cluster anions probed with infrared photodissociation spectroscopy, *J. Top. Catal.* **61** (2018) 92, `http://dx.doi.org/10.1007/s11244-017-0863-4`.
7. L. Jiang, Y. Wang, C. Feng, Application of photocatalytic technology in environmental safety. *Procedia Eng.* **45** (2012) 993, `https://doi.org/10.1016/j.proeng.2012.08.271`.
8. B.G. Obeid, A.S. Hameed, H.H. Alaaraji, Structural and optical properties of TiO_2, Digest *Journal of Nanomaterials and Biostructures.* **12** (2017) 1239-1246, `https://www.researchgate.net/publication/322399704`.

9. C. Zhao, Y. Yang, L. Luo, S. Shao, Y. Zhou, Y. Shao, F. Zhan, J. Yang, Y. Zhou, γ-ray induced formation of oxygen vacancies and Ti^{3+} defects in anatase TiO_2 for efficient photocatalytic organic pollutant degradation, *J. Sci. Total Environ.* **747** (2020) 141533, `https://doi.org/10.1016/j.scitotenv.2020.141533.`

10. A. Khataee, G.A. Mansoori, Nanostructured materials titanium dioxide: properties, preparation and applications, World Scientific Publishing Company, London, 2012.

11. Y. Lan, Y. Lu, Z. Ren, Mini review on photocatalysis of titanium dioxide nanoparticles and thier solar applications, *J. Nanoen.* **2** (2013) 1031, `http://dx.doi.org/10.1016/j.nanoen.2013.04.002.`

12. H. Tributsch, T. Bak, J. Nowotny, M.K. Nowotny, L.R. Sheppard, Photoreactivity models for titanium dioxide with water, *J. Ener. Mat*. **3** (2008) 158, `https://doi.org/10.1179/174892409x435770.P.`

13. P. Krúger, J. Jupille, S. Bourgeois, B. Domenichini, A. Verdini, L. Floreano, A. Morgante, Intrinsic nature of the excess electron distribution at the $\mathrm{TiO_2}$ (110) surface, *J. Phys. Rev. Lett.* **108** (2012) 126803, `https://doi.org/10.1103/physrevlett.108.126803.`

14. T. Minato, M. Kawai, Y. Kim, Creation of single oxygen vacancy on titanium dioxide surface, *J. Mat. Res.* **27** (2012) 2237, `https://doi.org/10.1557/jmr.2012.157.`

15. C. Di Valentin, G. Pacchioni, A. Selloni, Reduced and n-type dopped TiO_2 nature of Ti^{3+} species, *J. Phys. Chem. C* **113** (2009) 20543, `https://doi.org/10.1021/jp9061797.`

16. X. Chen, S.S. Mao, Titanium dioxide nanomaterials:Nanomaterials: Synthesis, Properties, Modifications and Properties, *J. Chem. Rev.* **107** (2007) 2891, `https://doi.org/10.1021/cr0500535.`

17. S. Wendt *et al*., The role of interstitial in the Ti 3d defect state in the band gap if titanium, *J. Sci.* **320** (2008) 1755, `https://doi.org/10.1126/science.1159846.`

18. F. Han, V.S.R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu, Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment, *J. Appl. Catal. A* **359** (2009) 25, `http://dx.doi.org/10.1016/j.apcata.2009.02.043.`

19. M.A. Henderson, The interaction of water with solid surfaces: fundamental aspects revisited, *J. Surf. Sci Rep*. **46** (2002) 1, `http://dx.doi.org/10.1016/s0167-5729(01)00020-6.`

20. P.A. Thiel, T.E. Madey, The interaction of water with solid surfaces: fundamental aspects, *J. Surf. Sci. Rep.* **7** (1987) 211, `http://dx.doi.org/10.1016/0167-5729(87)90001-x.`

21. C. Sun, L.M. Liu, A. Selloni, G.Q. Lua, S.C. Smith, Titania-water interaction: a review of theorical studies, *J. Mater. Chem.* **20** (2010) 10319, `http://dx.doi.org/10.1039/c0jm01491e.`

22. L. Largitte, R. Pasquier, A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon, *J. Chem. Eng. Res. Des.* **109** (2016) 495, `http://dx.doi.org/10.1016/j.cherd.2016.02.006.`

23. N.H. Turner, Kinetics of chemisorption: An examination of the Elovich equation, *J. Catal.* **36** (1975) 262, `http://dx.doi.org/10.1016/0021-9517(75)90035-4.`

24. K.A. Connors, Chemical Kenetics: The Study of Reaction Rates in Solution, VHP Publisher, United States of America, 1990.

25. A.G. Makeev, M.M. Slinko, D. Luss, Mathematical modeling of oscillating CO oxidation on Pt group metals at near atmospheric pressure: activity of metallic and oxidized surfaces, *J. Appl. Catal. A: Genaral* **571** (2018) 127, `http://dx.doi.org/10.1016/j.apcata.2018.11.015.`

26. M. Ohman, D. Persson, C. Leygraf, In situ ATR-FTIR studies of the aluminium/polymer interface upon exposure to water and electrolyte, *J. Prog. Org. Coat.* **57** (2006) 78, `https://doi.org/10.1016/j.porgcoat.2006.07.002.`

27. E.D. Revellame, D.L. Fortela, W. Sharp, R. Hernandez, M.E. Zappi, Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws, *J. Clean. Engin. Tech.* **1** (2020) 100032, `https://doi.org/10.1016/j.clet.2020.100032.`

28. S. Wendt *et al*., Oxygen vacancies on TiO_2 and their interaction with H_2O and O_2: A combined high- resolution STM and DFT study, *J. Surf .Sci.* **598** (2005) 226, `https://doi.org/10.1016/j.susc.2005.08.041.`

29. D. Brinkley *et al.* A modulated molecular beem study of the extent of H_2O dissociation on TiO_2 (110), *J. Surf. Sci.* **395** (1998) 292, `https://doi.org/10.1016/s.0039-6028(97)00633-x.`

30. R. Mu, Z. Zhao, Z. Dohnálek, J. Gong, Structural motifs of water on metal oxide surfaces, *J. Chem. Soc. Rev.* **46** (2017) 1785, `https://doi.org/10.1039/c6cs00864j.`

31. N. kumar *et al.* Hydrogen bonds and vibrations of water interaction on (110) rutile, *J. Phys. Chem. C* **113** (2009) 13732, `https://doi.org/10.1020/jp901665e.`

32. A. Fahmi, C.A. Minot, Theorical investigation of water adsorption on titanium dioxide surfaces, *J. Surf. Sci.* **304** (1994) 343, `https://doi.org/10.1016/0039-6028(94)91345-5.`

33. J. Zhang, R. Zhang, B. Wang, L. Ling, Insight into the adsorption and dissociation of water over deferent C_uO(111) surfaces: the effect of surface structures, *J. Appl. Surf. Sci*. **364** (2016) 758, `https://doi.org/10.1016/j.apsusc.2015.12.211.`

34. P. Scheiber *et al.* (Sub) Surface mobility of oxygen vacancies at the $\mathrm{TiO_2}$ anatase (101) surface, *J. Phys. Rev. Lett.* **109** (2012) 136103, `https://doi.org/10.1103/PhysRevLett.109.136103.`

35. O. Dulub, C.D. Valentin, A. Selloni, U. Diebold, Structure, defects, and impurities at the rutile TiO_2 (011)-(2 x 1) surface: A scanning tunnelling microscopy study, *J. Surf. Sci.* **600** (2006) 4407, `https://doi.org/10.1016/j.susc.2006.06.042.`

36. Z. Zhang, O. Bondarchuk, B.D. Kay, J.M. White, and Z. Dohnalek, Imaging water dissociation on TiO_2 (110): Evidence for inequivalent geminate OH groups, *J. Phys. Chem. B* **110** (2006) 21840, `https://doi.org/10.1021/jp063619h.`

37. H. Heydari, M.R. Elahifard, R. Behjatmanesh-Ardakania, Role of oxygen vacancy in the adsorption and dissociation of the water molecules on the surfaces of pure and N_i doped rutile (110): A periodic full- potential DFT study, *J. Surf. Sci.* **679** (2019) 218, `https://doi.org/10.1016/j.susc.2018.09.014`.

38. S. Malali, M. Foroutan, Dissociative behavior of water molecules on defect free and defective rutile TiO_2 (101) surfaces, *J. Appl. Surf. Sci*. **457** (2018) 295, `https://doi.org/10.1016/j.apsusc.2018.06.275`.

39. F. Bouzidi, M. Tadjine, A. Berbri, A. Bouhekka, The impact of temperature and H_2O flux on the adsorption of water on rutile (110), *Inter Conf*. **95** (2022) 652, `https://doi.org/10.51582/interconf.19-20.01.2022.073`.

40. N. Bundaleski, A.G. Silva, U. Schröder, A.M.C. Moutinho, O. Teodoro, Adsorption dynamics of water on the surface of TiO_2 (110), *J. Phys. Conf. Ser.* **257** (2010) 012008, `https://doi.org/10.1088/1742-6596/257/1/012008`.

41. K. Sebbari *et al.*, Investigation of hydrogen bonds and temperature effects on the water monolayer adsorption on rutile TiO_2 (110) by first- principles molecular dynamics simulations, *J. Surf. Sci.* **605** (2011) 1275, `https://doi.org/10.1016/j.susc.2011.04.015`.

42. M.B. Hugenschmidt, L. Gamble, C.T. Campbell, The interaction of H_2O with a TiO_2 Surface, *J. Surf. Sci*. **302** (1994) 329, `https://doi.org/10.1016/0039-6028(94)90837-0`.

43. M.F. Calegari Andrade, H.Y. Ko, L. Zhang, R. Car, A. Selloni, Free energy of proton transfer at the water -TiO$_2$ interface from Ab initio deep potential molecular dynamics, *J. Chem. Sci.* **9** (2020) 2335, `https://doi.org/10.1039/c9sc05116c`

44. Z.T. Wang *et al*., Probing equilibrium of molecular and deprotonated water on TiO_2 (110), *J. Proc. Nat. Acad. Sci*. **114** (2017) 1801, `https://doi.org/10.1073/pnas.1613756114`.

45. G. Fazio, D. Selli, L. Ferraro, G. Seifert, C. Di Valentin, Curved TiO_2 nanoparticles in water: Short (chemical) and long (physical) range interfacial effects. *J. ACS Appl. Mater. Interfaces.* **35** (2018) 29943, `https://doi.org/10.1021/acsami.8b08172`.

46. R. Schaub, N. Lopez, E. Laegsgaard, J.K. Norskov, F. Besenbacher, Oxygen vacancies as active sites for water dissociation on rutile TiO_2 (110), *J. Phys. Rev. Lett.* **87** (2001) 266104, `https://doi.org/10.1103/PhysRevLett.87.266104`.

47. J.V. Barth, H. Brune, B. Fischer, J. Weckesser, K. Kern, Dynamics of surface migration in the weak corrugation regime, *J. Phys. Rev. Lett*. **84** (2000) 1732, `https://doi.org/10.1103/PhysRevLett.84.1732`.

48. U. Aschauer *et al.*, Influence of subsurface defects on the surface reactivity of TiO_2 : water on anatase (101), *J. Phys. Chem. C* **114** (2010) 1278, `https://doi.org/10.1021/jp910492b`.

49. X. Pan, M.Q. Yang, X. fu, N. Zhang, Y.J. Xu, Defective TiO_2 with oxygen vacancies: Synthesis, properties and photocatalytic applications, *J. Nanoscale* **5** (2013) 3601, `https://doi.org/10.1063/1.4967520`.

50. S. Banerjee, D.D. Dioysiou, S.C. Pillai, Self-cleaning applications of TiO_2 by photo- induced hydrophylicity and photocatalysis, *J. Appl. Catal. B: Environ.* **176** (2015) 396, `https://doi.org/10.1039/c2ee03390a`.

51. Z. Futera, N.J. English, Oscillating electric-field effects on adsorbed-water at rutile- and anatase-TiO_2 surfaces, *J. Chem. Phys.* **145** (2016) 204706, `https://doi.org/10.1063/1.4967520`.

52. M. Menetrey, A. Markovits, and C. Minot, Reactivity of a reduced metal oxide surface: hydrogen, water and carbon monoxide adsorption on oxygen defective rutile TiO_2 (110), *J. Surf. Sci.* **524** (2003) 49, `https://doi.org/10.1016/s0039-6028(02)02464-0`.

53. L. Huang, K. Gubbins, L. Li, X. Lu, Water on titanium dioxide surface: A revisit by reactive molecular dynamics simulations, *J. Langmuir.* **30** (2014) 14832, `https://doi.org/10.1021/la5037426`.

54. A.V. Bandura *et al.* Adsorption of water on the TiO_2 rutile (110) surface: a comparison of periodic and embedded cluster calculations, *J. Phys. Chem. B* **108** (2004) 7844, `https://doi.org/10.1021/jp037141i`.

55. L.-Q. Wang *et al.*, Interactions of liquid and vapor water with stoichiometric and defective TiO_2 (100) surfaces, *J. Surf. Sci*. **440** (1999) 60, `https://doi.org/10.1016/S0039-6028(99)00677-9`.

56. P.J.D. Lindan and C. Zhang, Comment on molecular chemisorption as the theoretically preferred pathway for water adsorption on ideal rutile TiO_2 (110). *Phys. Rev. Lett.* **95** (2005) 029601, `https://doi.org/10.1103/PhysRevLett.95.029601`.

57. Z. Dohnálek, I. Lyubinetsky, R. Rousseau, Thermally-driven processes on rutile TiO_2 (1 1 0)-(1x 1): A direct view at the atomic scale, *J. Prog. Surf. Sci*. **85** (2010) 161, `https://doi.org/10.1016/j.progsurf.2010.03.001`.

58. K.P. Gopinath, N.V. Madhav, A. Krishnan, R. Malolan, G. Rangarajan, Present application of titanium dioxide for the photocatalytic removal of pollutants from water: *A review, J. Environ. Manag.* **270** (2020) 110906, `https://doi.org/10.1016/j.jenvman.2020.1110906`.

59. L.J.D. Lindan, N.M. Harrison, M.J. Gillan, Mixed dissociative and molecular adsorption of water on the rutile (110) surface, *J. Phys. Rev. Lett.* **80** (1998) 762, `https://doi.org/10.1016/j.susc.2005.06.021`.