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1 Highlights

2 **Towards H₂ Production from Water and Ethanol Interactions on** 3 **Hydrated TiO₂(101): Insights from ReaxFF Molecular Dynamics**

4 Hicham Jabraoui, Mehdi Djafari Rouhani, Carole Rossi, Alain Esteve

- 5 • Exploring liquid ethanol/water interaction with hydrated-TiO₂(101)
6 using ReaxFF molecular dynamics.
- 7 • Ethanol dissociation lowers TiO₂ hydration and hydrogen mobility through
8 permanent bonding of ethoxy radicals on Ti surface sites.
- 9 • Water dominates the surface interactions when mixed with ethanol,
10 maintaining a high level of surface hydration, i.e., lowering ethoxy fixa-
11 tion.
- 12 • Mechanisms of surface hydration (i.e., generation of surface hydroxyls)
13 via water or ethanol molecules all show activation barrier inferior to
14 0.5 eV.
- 15 • Calculation of the formation of H₂, while unlikely energetically, still
16 shows the prevalence of catalytic (molecule/surface) rather than purely
17 surfacic mechanisms.

18 Towards H₂ Production from Water and Ethanol
19 Interactions on Hydrated TiO₂(101): Insights from
20 ReaxFF Molecular Dynamics

21 Hicham Jabraoui^{a,*}, Mehdi Djafari Rouhani^a, Carole Rossi^a, Alain Esteve^{a,**}

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22 **Abstract**

23 ReaxFF molecular dynamics is employed to investigate interactions between
24 water, ethanol, their mixture, and hydrated TiO₂(101) surfaces. Water main-
25 tains hydration, while exchanging both hydrogen and oxygen atoms with
26 the surface. Ethanol dissociates, leading to the formation of ethoxy radi-
27 cals (CH₃CH₂O) permanently attached to the surface, water molecules, and
28 acetic acid (CH₃CO₂) species. Ethoxy reduces the number of hydroxyl groups
29 and hinders hydrogen migration across the surface. The mixture of water,
30 ethanol, and TiO₂(101) results in a reduction of ethoxy coverage, inhibits
31 CH₃CO₂ formation, and increases hydroxyl coverage, indicating the domi-
32 nant role of water. Potential of mean force analysis shows that hydroxyl
33 formation follows exothermic paths, with activation energy lower than 0.45
34 eV. A narrower pathway for ethanol access to its adsorbed site is a key factor
35 in the dominance of water. The formation of H₂ molecules exhibits a pro-
36 hibitive energy barrier (> 4 eV), suggesting that catalytic pathways, rather
37 than purely surface reactions, could be favored.

38 *Keywords:* Reactive force field molecular dynamics, Potential of Mean
39 Force (PMF) analysis, water-ethanol-TiO₂ interface, hydrogen production,
40 hydrated-TiO₂

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41 1. INTRODUCTION

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79 1. INTRODUCTION
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94 ? ? ?]. One such historical path is
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96 faces to achieve the photoreduction of
97 water (the so-called water splitting);
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99 (TiO₂), because of remarkable photo-
100 catalytic capabilities, made early
101 demonstrations of water splitting-induced
102 hydrogen production [? ? ? ?
103]. Since then, TiO₂(101) has imposed it-
104 self as the most studied model
105 surface to investigate the fundamentals of
106 water splitting chemistry and
107 electrochemistry both theoretically [?] and
108 experimentally [? ?]—i.e., the
109 role of surface chemistry, crystallinity,
110 grain boundaries and orientation,
111 doping, defects, charges (lifetime, localization,
112 and transport). Among
113 the various phases of TiO₂, anatase stands out for
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115 in separating electrons and holes, partly facilitated by
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119 under debate due to the multiplicity of factors influencing the
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125 studies have been limited to rather
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133 studied from a
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135 Alcohol, such as ethanol (via the photode-
136 hydrogenation of ethanol to form
137 molecular hydrogen and acetaldehyde [?
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139 as direct chemical agents for hydrogen
140 production. Ethanol is supposed to be
141 thermodynamically more efficient
142 ($G_0 = +237$ kJ·mol⁻¹ for water oxidation
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145 input required [? ?]. Note that
146 ethanol is also commonly used as an additive
147 to water solvent, acting as a
148 sacrificial agent (hole scavenger), allowing for
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151 production performances.

116 Finally, in the photocatalytic process, ethanol can78 prevent the generation
117 of O₂ species by producing carboxylic groups. All79 these characteristics
118 make it difficult to predict which process will finally80 dominate when mix-
119 ing water and ethanol, as the collective arrangement of81 these molecules
120 in contact with the surface is not known.82 Importantly, along the same
121 line, the surface hydration level in contact83 with different liquid mediums is
122 one key factor of the photocatalytic response84 and its durability (stability
123 of the surface chemistry, i.e., hydration stability)85 [?]. Despite all, this
124 aspect has never been addressed so far.86 This work employs ReaxFF molec-
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126 different liquid environments, i.e. pure water88 and ethanol phases before
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2. COMPUTATIONAL DE- 139 TAILS

101 In this study, we conducted molecular dynamics (MD) simulations
140 with102 periodic boundary conditions using the LAMMPS package [?]. The
141 temper-103 ature within the NVT ensemble was controlled using the Nosé-
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147 the anatase crystal structure, featuring a109 tetragonal unit cell with lat-
148 tice parameters $a = b = 3.78 \text{ \AA}$, $c = 9.62 \text{ \AA}$, and110 $\alpha = \beta = \gamma = 90^\circ$. The
149 space group assigned to the supercell was I41/amd111 [?]. To create the
150 (101) surface, we followed a specific procedure resulting112 in face-to-face
151 (101) planes, each with dimensions of $31.40 \text{ \AA} \times 38.03 \text{ \AA}$ and113

152 urgent search for alternative and eco-friendly solutions. Molecular hydrogen (H₂)
153 has emerged as a promising candidate, offering a clean and highly efficient

154 energy prospect. However, the natural occurrence of hydrogen atoms being
155 typically bound to other elements renders the direct sourcing of molecular
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157 pathways to produce hydrogen has been ongoing for decades [1, 2, 3, 4, 5, 6].
158 One such historical path is to make use of photocatalytic surfaces to achieve
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160 titanium dioxide (TiO_2), because of remarkable photocatalytic capabilities,
161 made early demonstrations of water splitting-induced hydrogen production
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173 Theoretically, atomistic simulation studies have been limited to rather
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175 surface, such as water [7, 13, 8, 1, 2, 3, 4, 6], or ethanol [4]. Similarly, other
176 surfaces of technological interest have been investigated, such as alumina [14]
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197 and quantify the interaction of different liquid environments, *i.e.* pure water
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202 reactivity at the interface between water, alcohol, and mineral materials,
203 including TiO₂ [20, 7, 21]. The study provides new insights into how water
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222 in face-to-face (101) planes, each with dimensions of $31.40 \text{ \AA} \times 38.03 \text{ \AA}$ and
223 a slab height of approximately 24 \AA . Before surface formation, the bulk su-
224 percell underwent relaxation in the NVT ensemble for 0.1 nanoseconds (ns)
225 using a time step of 1 femtosecond (fs). Subsequently, we constructed the
226 final supercell as depicted in Figure 1, comprising two bulk cells separated by
227 vacuum spaces of (45 and 26 \AA). We ran the relaxation process in the NVT

228 ensemble at a temperature of 300 K for an additional 0.1 ns, with a time
229 step of 1 fs. The overall $\text{TiO}_2(101)$ region contained 1662 O atoms and 831
230 Ti atoms. The smaller vacuum space was designated to be filled with liquid
231 phases. The face-to-face surfaces were chosen to increase the likelihood of
232 significant events from a statistical standpoint (see Figure 1a). This structure
233 also facilitated the breathing of the liquid phase during relaxation, preventing
234 contamination from potential molecule evaporation or pressure effects. The
235 choice of the (101) anatase plane to represent TiO_2 was based on its distinct
236 chemical reactivity and adsorption characteristics towards water and other
237 protonated molecules (e.g., ethanol, methanol). Additionally, $\text{TiO}_2(101)$ is
238 the most stable and predominant surface for nanocrystals, occupying over
239 94% of the total surface area [25].

240 With the goal of constructing hydrated $\text{TiO}_2(101)$ surfaces, we introduced
241 water molecules to protonate and hydroxylate surface sites on the two ex-
242 posed surfaces. To achieve this, the system was relaxed at 300 K in the NVT
243 ensemble, using a time step of 0.5 fs for a simulation period of 1 ns. The
244 density of the water molecules placed in the vacuum was set to 1 g/cm^3 .
245 After the relaxation process, we removed water molecules that maintained
246 their molecular form, while the dissociated water components were retained
247 on the surfaces. These resulting functional groups enhanced the hydrogen
248 bond networking with the outer surface, leading to a delicate network of in-
249 teraction dynamics. It became evident that a smaller time step than 1 fs
250 was necessary to accurately simulate the behavior of water and the hydrated
251 system [20, 26, 27, 28], and notably the Grothuss kind of mechanism [29].
252 Consequently, we successfully obtained two hydrated surfaces exposed to a
253 vacuum environment (see Figure 1b).

254 To construct the liquid medium, we introduced 882 water molecules, as
255 depicted in Figure 1c, along with 500 ethanol molecules with a density of
256 0.8 g/cm^3 , as illustrated in Figure 1d. Additionally, we created a precise
257 balanced mixture comprising 445 water molecules and 288 ethanol molecules
258 (in a 1:1 volume ratio). In this mixture, the density of water was maintained
259 at 1 g/cm^3 , while ethanol had a density of 0.8 g/cm^3 , as shown in Figure 1e.
260 This arrangement was designed to occupy the vacuum space between the two
261 hydrated surfaces. Subsequently, these liquid/surface interfaces underwent
262 relaxation at 400 K in the NVT ensemble, using a time step of 0.5 fs over 6
263 ns.

264 To gain further insights into the energetics and reaction pathways of a
265 selection of chemical reactions of interest, not necessarily occurring during

266 the elapsed simulations (such as molecular hydrogen production), we con-
267 ducted Molecular Dynamics (MD) simulations employing the Potential of
268 Mean Force (PMF) method [30]. Before commencing the PMF simulations,
269 we ensured that the system attained thermodynamic equilibrium by allow-
270 ing it to relax at room temperature. Subsequently, we applied a moving
271 harmonic potential to control the system’s behavior during the simulations
272 in a desired way.

273 For these simulations, we utilized the steered molecular dynamics (SMD)
274 algorithm, implemented within the LAMMPS software package [31, 32, 33,
275 34, 35]. In this framework, we applied a constant velocity along the negative
276 direction to one of the atoms from ethanol or water molecules involved in the
277 chemical reaction. This approach facilitated the formation of a bond between
278 the selected hydrogen atom and a targeted atom present at the surface or in
279 the solution. To achieve this, a spring constant (K) of 1×10^4 kcal/mol/Å
280 was applied to steer the selected atoms towards each other. To ensure the
281 reliability of our simulations, the pulling velocity was set to -0.00005 Å per
282 femtosecond [36, 35]. This choice enabled a smooth and controlled approach
283 of the target atom towards the surface, minimizing significant perturbations
284 to the overall system, including the local environment in contact with the
285 constrained atoms.

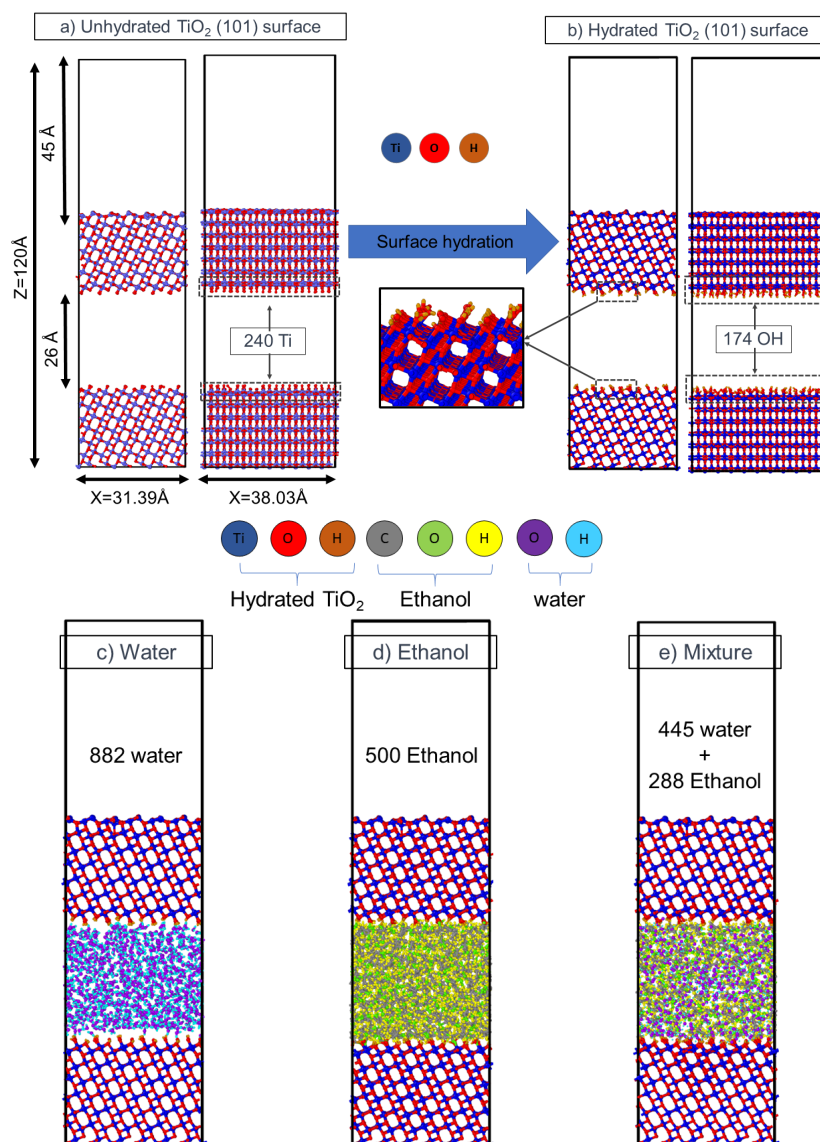


Figure 1: Side-view schematics of the initial atomic-scale model of the anatase $\text{TiO}_2(101)$ surface, depicting both the (a) unhydrated and (b) hydrated (101) surfaces. Side view schematics of the water- $\text{TiO}_2(101)$ interface (c), the ethanol- $\text{TiO}_2(101)$ interface (d), and the mixture of ethanol and water- $\text{TiO}_2(101)$ interface (e). The $\text{TiO}_2(101)$, water, and ethanol atoms are visually represented with red, blue, orange, green, grey, yellow, purple, and sky blue spheres, representing O_{TiO_2} , Ti, H_{TiO_2} , $\text{O}_{\text{Ethanol}}$, $\text{C}_{\text{Ethanol}}$, $\text{H}_{\text{Ethanol}}$, $\text{O}_{\text{H}_2\text{O}}$, and $\text{H}_{\text{H}_2\text{O}}$ atoms, respectively.

286 3. RESULTS AND DISCUSSION

287 This section is divided into two main subsections. First, a statistical anal-
288 ysis of the interaction between hydrated $\text{TiO}_2(101)$ and three liquid phases is
289 presented: monomolecular liquids, *e.g.*, water and ethanol, serving as refer-
290 ence interfaces to further investigate the more complex interaction of a mix-
291 ture of water and ethanol with hydrated titanium dioxide, see Figure 1(c-d)
292 for initial interfaces and Figure SM1(a-c) for interfaces after MD run. Note
293 that for quantifying the various radicals present on the three interfaces, we
294 use the number of top surface Ti-sites (in direct contact with the liquid
295 phases) as the reference, which amounts to 240 and remains unchanged dur-
296 ing the annealing. From this reference, the percentage of each identified
297 radical at the interface is calculated using the following equation:

$$\text{radical}(\%) = \text{Number of a radical} \times \left(\frac{100}{240} \right).$$

298 Subsequently, we proceed to a more detailed analysis of specific surface
299 chemistries (pathways and energetics) using the PMF technique. Notably, we
300 determine the OH formation pathways from the liquid phase which governs
301 the hydration level of the surface. This method also allows investigating rare
302 or even non-occurring events during the elapsed simulations.

303 3.1. Statistical Analysis of Interfacial Events

304 3.1.1. Interactions at the Water- $\text{TiO}_2(101)$ Interface

305 In this subsection, all calculations are performed at 400 K. Figure 2 fo-
306 cuses on the water/surface protonic exchange. From Figure 2a, green curve,
307 a nearly constant number of hydroxyl groups (OH) is observed throughout
308 the entire 6 ns simulation, with an average number of about 188 OHs (78%
309 coverage as referred to as the total number of Ti-adsorption sites), averaged
310 over the last ns. Note that this results in a slight increase of the number of
311 hydroxyl groups compared to the initial hydration procedure at 300 K. De-
312 spite this apparent global chemical stability of the hydrated surface, a closer
313 examination of the interactions shows substantial chemical activity at the
314 interface. A dynamic process of hydrogen exchange between water molecules
315 and the hydrated TiO_2 surface is taking place. Indeed, a vast number of
316 hydroxyl groups are generated from the decomposition of water molecules
317 that stabilizes at about 173 OHs (72% coverage). Concomitantly, a number
318 of hydrogen atoms initially associated with the hydrated TiO_2 are released

319 into the bulk water, which loss compensates the protonic gain due to protons
320 released from dissociated water. *In fine*, almost all initial surface hydrogen
321 atoms have been replaced by hydrogen emanating from the water medium
322 (surface coverage of hydrogen illustrated by blue spheres in Figure 2c). From
323 the simulation, the exchange is always local, either direct ($\text{H}_{\text{TiO}_2} \leftrightarrow \text{H}_{\text{H}_2\text{O}}$),
324 or indirect, involving nearest neighbours and Grotthuss type of mechanisms.
325 This overall exchange of hydrogen atoms between the surface and the liquid
326 water results in an equilibrium state between the two phases where occur-
327 rence of the exchange mechanisms is still but rarely observed. In Figure 2b,
328 the peak associated with the shortest surface OH bond length after reach-
329 ing interface equilibrium, in the range 0.93-1.03 Å, considering oxygen and
330 hydrogen species initially belonging to different medium (liquid or solid),
331 demonstrates that hydrogen exchange has been operated. The $\text{O}_{\text{TiO}_2}-\text{H}_{\text{H}_2\text{O}}$
332 peak at around 1.8 Å is due to the hydrogen bonding of non-dissociated water
333 molecules on surface adsorption sites. In a previous ReaxFF MD simulation
334 investigation, Raju et al. [7] studied the adsorption and dissociation dynam-
335 ics of water at 300 K on unhydrated TiO_2 surfaces. Specifically, they focused
336 on anatase (101), (100), (112), (001), and rutile (110) surfaces, considering
337 various water coverages. Their results unveiled a clear correlation between
338 the extent of water dissociation on the various surfaces and the strength of
339 hydrogen bonding between the adsorbed water molecules and those located
340 outside the adsorbed layer. In a separate study by Huang *et al.* [13], molec-
341 ular dynamics simulations using the ReaxFF force field were employed to
342 hierarchize the reactivity in term of water dissociation on different TiO_2 sur-
343 faces [rutile (011) > monoclinic crystal (100) > anatase (001) > rutile (110)],
344 with no observed water dissociation on the monoclinic crystal (001) surface.
345 Additionally, their simulations highlight changes in water dissociation and
346 TiO_2 surface chemistry, emphasizing the impact of new surface Ti-OH and
347 O-H functional groups on the orientation of nearby water molecules.

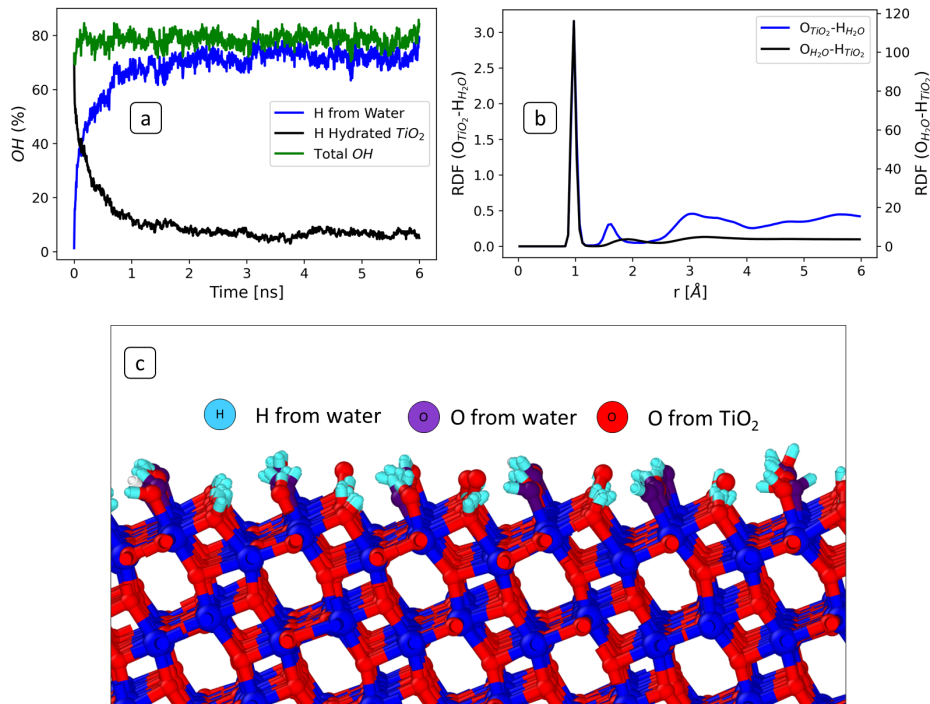


Figure 2: Water-hydrated $\text{TiO}_2(101)$ interface after 6 ns of annealing at 400 K: (a) Evolution of: the number of hydroxyl groups, number of surface hydrogen initially belonging to the water medium, and hydrogen released from the initial hydrated $\text{TiO}_2(101)$ into bulk water, (b) Radial distribution function (RDF) plots for $\text{H}_{\text{TiO}_2}\text{-O}_{\text{H}_2\text{O}}$ and $\text{H}_{\text{H}_2\text{O}}\text{-O}_{\text{TiO}_2}$, (c) Visualization of the $\text{TiO}_2(101)$ surface after 6 ns of annealing at 400K. Different colors are used to represent $\text{O}_{\text{TiO}_2(101)}$ (red), Ti (blue), $\text{O}_{\text{H}_2\text{O}}$ (purple), and $\text{H}_{\text{H}_2\text{O}}$ (sky blue) atoms. Note that no hydrogen atom from the initial bare hydrated surface is present after 6 ns, due to the exchange process with water. The number of H forming OH hydroxyl at the surface is calculated for the cutoff $\text{O-H} = 1.2 \text{ \AA}$.

348 Purple atoms representing oxygen atoms initially belonging to water molecules
 349 form more than half of the surface OH groups on the hydrated surface in Fig-
 350 ure 2c. This already suggests that, beyond hydrogen exchange, oxygen ex-
 351 change is also occurring, which is analyzed in greater detail in Figure 3. Dur-
 352 ing the relaxation process, non-dissociated water molecules occupy binding
 353 sites on the hydrated $\text{TiO}_2(101)$ surface, establishing two types of bonding:

- 354 • Hydrogen bonding on the surface bridging ($\text{H} \text{---} \text{O} \text{---} \text{H} \cdots \text{O}_{\text{TiO}_2}$,
 355 see Figure 3c).

- A dative bond between a water oxygen atom and a top surface Ti atom (Figure 3d).

From these adsorption sites, some $\text{O}_{\text{H}_2\text{O}}$ atoms involved in these interactions integrate into the surface, mostly as OH groups (Figure 2c, and Figure 3a, blue curve). This reaches an average value of 44 within the last nanosecond (18% coverage), while others remain in their molecular, non-dissociative configuration. Concurrently, but to a lesser extent, some oxygen atoms originally belonging to the hydrated $\text{TiO}_2(101)$ surface are released into the bulk water. These detached oxygen atoms combine to form new water molecules in the water phase, with the average number reaching 18 within the last nanosecond (about 6% coverage loss). Both the surface-inserted $\text{O}_{\text{H}_2\text{O}}$ atoms and the number of water-released $\text{O}_{\text{Ti}_2\text{O}}$ atoms increase during the annealing period. However, the increase in the number of oxygen atoms binding to the surface is more significant, indicating a net gain of oxygen atoms on the $\text{TiO}_2(101)$ surface after the entire relaxation process (Figure 3a). Examination of the radial distances between Ti atoms with $\text{O}_{\text{H}_2\text{O}}$ and $\text{O}_{\text{Ti}_2\text{O}}$ is another illustration of the adsorption and exchange processes taking place at the interface.

In summary, two mechanisms contribute to the enrichment of the hydration of the $\text{TiO}_2(101)$ surface through the dissociation of water molecules. The first involves the adsorption of water via one of its hydrogens on a free oxygen site, resulting in the formation of the surface structure ($\text{H} - \text{O} - \text{H} \cdots \text{O}_{\text{TiO}_2}$). Thus, an adsorbed proton from water can bind to the free oxygen site to form OH at the surface, instead of merely undergoing adsorption if the oxygen site carries an excess of negative charge, acting as a Lewis acid site [37, 38, 39]. The second mechanism occurs after water adsorption via its oxygen onto the exposed Ti-adsorption sites, which can lead to the formation of OH^- hydroxyl groups after the generation of a proton. In this case, the proton is only generated if the Ti-adsorption site exhibits an excess of positive charge, necessitating the presence of OH^- .

In this context, we compare the charge distribution of Ti in the five layers of the $\text{TiO}_2(101)$ surface exposed to water molecules between the first frame of annealing and the last frame, after 6 ns of annealing. Figure SM2 shows Ti net charges after the first frame of annealing and a given frame after 6 ns of annealing. Some surface atoms of the first layer exhibit a gain of charge, indicating their need for a positive charge to reach equilibrium (0.04 e gain), while some atoms in the subsurface show a loss of positive

393 charge (about 0.03 e loss), indicating their need for a negative charge to
394 reach equilibrium. Here, Ti atoms from the surface present O non-bridging
395 configuration, needing an H^+ as a positive charge, while subsurface Ti will
396 needs an undercoordination value, which requires OH^- as a negative charge.
397 After the dissociation of this adsorbed water, the liberated proton can either
398 return to the solution, participating in the water network or recombine with
399 a leaving surface hydroxyl. Note that water adsorption cannot be considered
400 isolated, as a collective network of hydrogen atoms is constituted within the
401 interface involving both water molecules and surface atoms [37]. Tilocca
402 and Selloni [40] used DFT-GGA and DFT+U simulations to investigate the
403 effect of a reducing subsurface Ti interstitial defect on the structure and
404 reactivity of thin water layers on reduced $TiO_2(101)$ surfaces, finding that the
405 defect enhances the surface reactivity and alters the structure of the water
406 layers. More recent investigations detailed the energetics of bonding and
407 dissociation behavior of a single water molecule on various subsurface defects
408 pointing to the influence of oxygen vacancy (shown to be unstable upon water
409 dissociation) and Ti interstitial notably [2, 41], that should be extended and
410 compared to similar surface configurations but exposed to water.

411 The formation of H—O bridges and non-bridging oxygen species indi-
412 cates the creation of surface complexes that stabilize water molecules on the
413 surface. Interaction of water with the surface via its hydrogen results in the
414 slight elongation of associated surface Ti-O bonds at about 1.9 Å, as shown
415 in Figure 3b and Figure 3c. Meanwhile, there is another type of oxygen from
416 water close to the surface, maintaining its molecular form with a distance
417 of 2.33 Å, as also illustrated in Figure 3d, representing a non-dissociative
418 adsorption of water *via* its oxygen onto the exposed Ti of the surface. Note
419 that the presence of additional oxygen atoms on the surface was shown to
420 influence the material’s reactivity, affecting its performance as a catalyst in
421 water-splitting reactions or pollutant degradation [42].

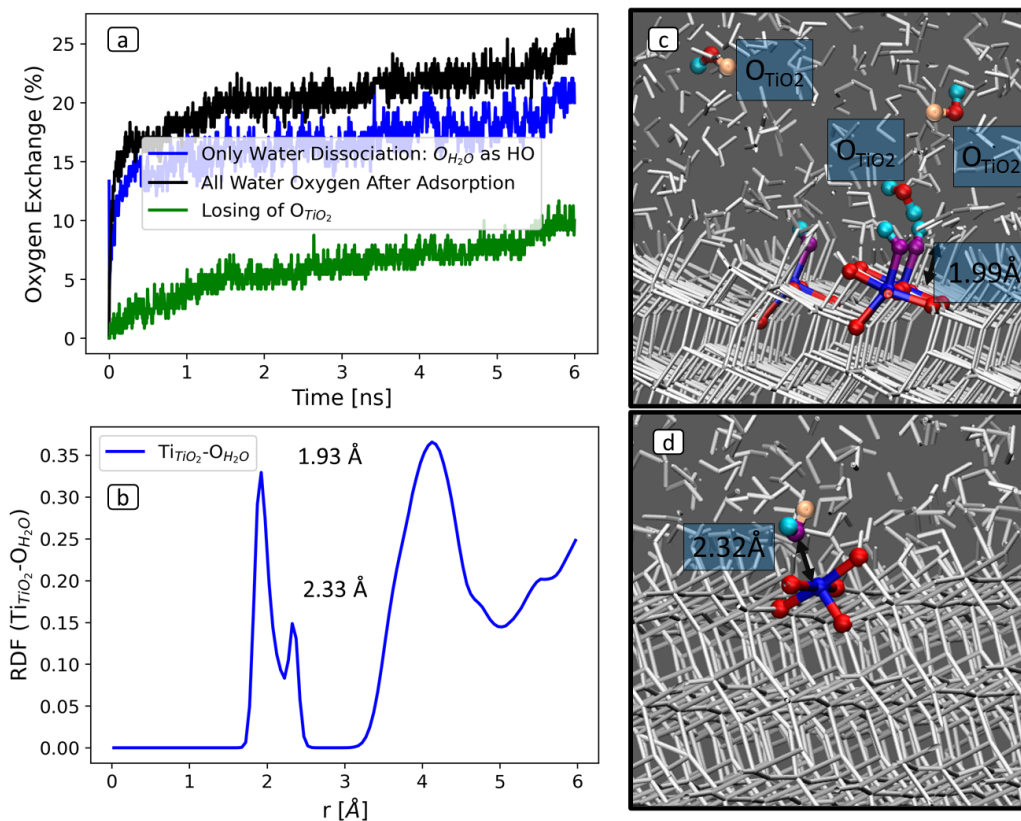


Figure 3: Water-hydrated $\text{TiO}_2(101)$ interface after 6 ns of annealing at 400 K: (a) Evolution of the insertion of $\text{O}_{\text{H}_2\text{O}}$, following water dissociation that turn into hydrated $\text{TiO}_2(101)$ surfaces (blue curve), all oxygen adsorbed (dissociative and non-dissociative adsorption) into hydrated $\text{TiO}_2(101)$ surfaces (black curve), and the release of O_{TiO_2} with the green curve, (b) Comparing the Radial Distribution Function (RDF) for $\text{Ti}_{\text{TiO}_2(101)}\text{-O}_{\text{H}_2\text{O}}$ and $\text{Ti}_{\text{TiO}_2(101)}\text{-O}_{\text{TiO}_2}$, (c) the hydration of sites in the hydrated $\text{TiO}_2(101)$ surface resulting from the dissociation of water molecules, (d) the adsorption configuration of water onto the hydrated $\text{TiO}_2(101)$ surface, where different colors are used to represent O_{TiO_2} (red), Ti (blue), H_{TiO_2} (orange), $\text{O}_{\text{H}_2\text{O}}$ (purple), and $\text{H}_{\text{H}_2\text{O}}$ (sky blue) atoms.

422 3.1.2. Interactions at the Ethanol- $\text{TiO}_2(101)$ Interface

423 Under the same conditions as before, *i.e.*, 6 ns of annealing at 400 K, the
 424 hydrated $\text{TiO}_2(101)$ surface is now exposed to pure ethanol. In contrast to
 425 water exposure, Figure 4a shows a slight decrease in the total number of OH
 426 groups present on the surface, down to 63% coverage, pointing to a lowering
 427 of the hydration level. A visual representation of the surface hydration after
 428 annealing can be seen in Figure 4c, where ethanol has been removed from

429 the structure. The figure indicates that some ethanol has dissociated, leaving
430 ethoxy radicals ($\text{CH}_3\text{CH}_2\text{O}$) bonded to surface Ti atoms with a coverage of
431 about 13.5% (about 33 ethoxy). Note that, in contrast to water exposure,
432 a great percentage of hydrogen atoms participating to the initial surface
433 hydration are still present on the surface (orange spheres), showing that
434 the exchange process is less efficient in this case, limited to the number of
435 ethanol that have dissociated. In another word, no direct exchange is taking
436 place between ethanol and the surface. Rather, exchange is taking place via
437 hydrogen from dissociated ethanol that are present on the surface, notably on
438 bridging oxygen sites. RDF is another way to picture the exchange process.
439 The Figure 4b) shows the RDF of H and O species belonging to different
440 medium (water/ or surface, see .

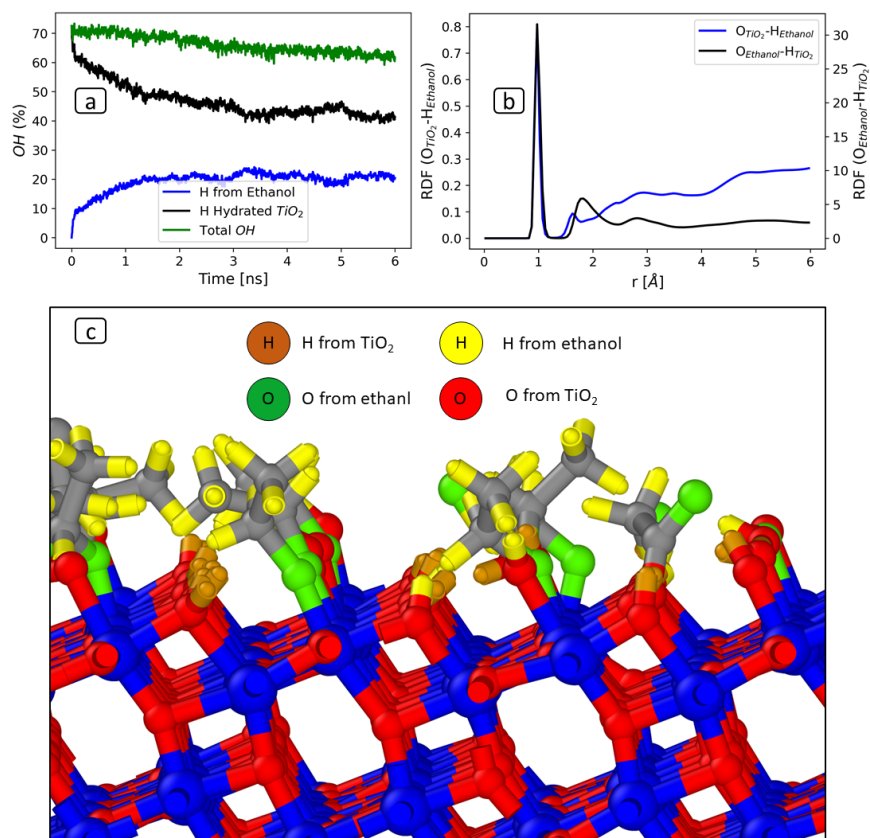


Figure 4: Ethanol-hydrated TiO₂ (101) interface after 6 ns of annealing at 400 K. (a) Time evolution of: the total number of hydroxyl groups, the number of surface hydrogen initially belonging to ethanol, and hydrogen released from the initially hydrated TiO₂ (101), (b) Radial distribution function (RDF) plots for H_{TiO₂}-O_{H₂O} and H_{H₂O}-O_{TiO₂}, (c) Visualization of the hydration structure after 6 ns of annealing at 400 K: O_{TiO₂} (red), Ti (blue), H_{TiO₂} (orange), C_{Ethanol} (gray) atoms, H_{Ethanol} (yellow) atoms, and O_{Ethanol} (green) atoms. The number of H atoms forming OH hydroxyl at the surface is calculated for the cutoff O-H= 1.2 Å.

441 Importantly, under ethanol exposure, the formation of water molecules
 442 is observed, pointing to the nature of ethanol dissociation chemistry at the
 443 surface. As the simulation progresses, we notice a steady increase in the
 444 number of water molecules, eventually reaching a count of 34 water molecules
 445 (representing 14% of coverage). From Figures 5a and c, the number of wa-
 446 ter molecules being generated coincides with the dissociative adsorption of
 447 ethanol on surface OHs. To this respect the water molecules being created

448 are composed of a hydrogen atom originating from the ethanol OH termi-
449 nation bonded to a surface hydroxyl (Figures 5a blue and black curves).
450 Figures 5c confirms that each water molecule that is created is associated
451 with a dissociative adsorption of ethanol. Analyzing the radial distribution
452 function in Figure 5b, we observe a Ti—O peak signature at 1.9 Å that
453 is slightly shifted compared to initial Ti—OH, corresponding to ethoxy
454 ($\text{CH}_3\text{CH}_2\text{O}$) radical bonded to surface Ti *via* its oxygen. The additional
455 peak at 2.3 Å is another indirect signature of ethanol reaction, as it corre-
456 sponds to the adsorption of the newly created water molecule on top of a
457 neighbouring surface Ti atom, as illustrated in Figures 5d. The resulting wa-
458 ter is confined nearby the $\text{TiO}_2(101)$ surface, forming a layer of mixed water
459 and $\text{CH}_3\text{CH}_2\text{O}$ molecules as new derivative of ethanol species. The observed
460 time-dependent formation of $\text{CH}_3\text{CH}_2\text{O}$ radical molecules exclusively occurs
461 on the Ti-adsorption site through oxygen. From the crowding of ethoxy rad-
462 icals seen in Figure 4c, despite the non saturation of the various chemical
463 processes being present, a steric hindrance is expected to play an essential
464 role in limiting the kinetics and population of grafted ethoxy's. One main
465 conclusion that may be drawn at this stage is that, in contrast to the propen-
466 sity of water to keep $\text{TiO}_2(101)$ fully hydrated, ethanol is shown to dehydrate
467 the surface, by replacing surface hydroxyl species by ethoxy radicals, with
468 potential shadowing of other surface regions due to steric hindrance. Fur-
469 ther examining surface configurations, non-dissociative ethanol adsorption is
470 quasi exclusively observed in a configuration where the interaction is driven
471 by the ethanol CH subunit. A combination of Density Functional Theory
472 (DFT) and Scanning Tunneling Microscopy (STM) images distinguished two
473 types of surface adsorbates upon ethanol exposure [43]. These adsorbates
474 can be attributed to the molecular and dissociative (in agreement with our
475 calculated configurations) modes of ethanol interacting with the surface. Fur-
476 thermore, DFT calculations demonstrated that the dissociative adsorption of
477 ethanol was the most stable configuration, with an adsorption energy of -0.89
478 eV, compared to -0.72 eV for the non-dissociative adsorption [44]. This value
479 is slightly higher than the adsorption energy of water on $\text{TiO}_2(101)$, for which
480 the calculated adsorption energy per molecule is 0.67 eV [45]. Another DFT
481 investigation explored the adsorption and dissociation of ethanol on different
482 surfaces of anatase TiO_2 [46]. Among these surfaces, the $\text{TiO}_2(101)$ sur-
483 face exhibited the most favorable product for the initial dissociation step of
484 ethanol, confirming the ethoxy formation. The energy barrier for this step
485 was calculated to be 0.96 eV [46]. In addition to these prevailing events, we

486 also observed a few instances (3 occurrences, 1.5 % equivalent coverage) of
 487 carboxylic acid radicals, namely acetic acid CH_3CO_2 formation, as commonly
 488 envisaged in the photocatalysis literature. These compounds adhere closely
 489 to the surface *via* oxygen at Ti-adsorption sites, maintaining a separation
 490 distance of about 1.4 Å, as shown in Figure 6. Interestingly, the process of
 491 converting ethanol to this newly formed radical involves the detachment of
 492 a three protons (one from the hydroxyl termination of ethanol and two from
 493 its CH_2 group).

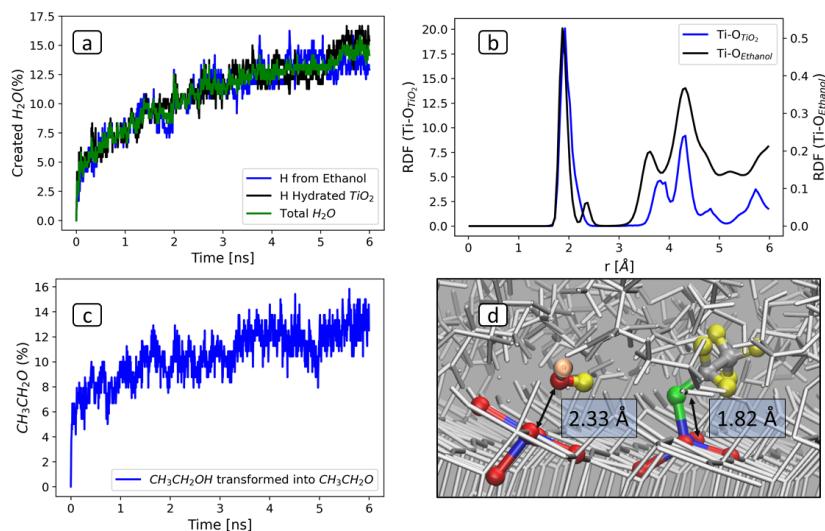


Figure 5: (a) Time evolution of the total number of H_2O , H from ethanol, and H from the initial hydration of $\text{TiO}_2(101)$ incorporated into the water medium during the 1 ns, 400 K simulation. (b) Ti-O RDF distinguishing O from $\text{TiO}_2(101)$ and O belonging to ethanol. (c) Number of newly adsorbed $\text{CH}_3\text{CH}_2\text{O}$ radicals (ethyl alcohol molecules) *via* their oxygen onto the hydrated $\text{TiO}_2(101)$ surface interface throughout the simulation. (d) Snapshot showing the local surface configuration immediately after ethanol dissociation, with the adsorption of the created water molecule and ethoxy radical bonding to titanium; O_{TiO_2} (red), Ti (blue), H_{TiO_2} (orange), $\text{C}_{\text{Ethanol}}$ (gray) atoms, $\text{H}_{\text{Ethanol}}$ (yellow) atoms, and $\text{O}_{\text{Ethanol}}$ (green) atoms. The number of oxygen atoms of the new $\text{CH}_3\text{CH}_2\text{O}$ radicals binding to the hydrated TiO_2 surface is calculated using a cutoff of $\text{Ti}-\text{O} = 2.4$ Å.

494 Furthermore, it is crucial to note that throughout the simulation, the
 495 C—C bonds in ethanol remains intact, indicating the absence of dissociation
 496 of ethanol into smaller organic carbon-based fragments, such as CO_2 or
 497 CH_4 for instance. The RDF curve shows that each carbon atom is coordi-
 498 nated by one atom at a distance of 1.58 Å. The dissociation of the C—C

499 bond is a problem encountered with some other photocatalysts. as an exam-
 500 ple, it was observed, after studying the dark catalytic reactions of ethanol
 501 over a series of catalysts based on CeO_2 , that the bottleneck of the reac-
 502 tion lies in the breaking of the carbon-carbon bond of the ethanol molecules
 503 [47, 48].

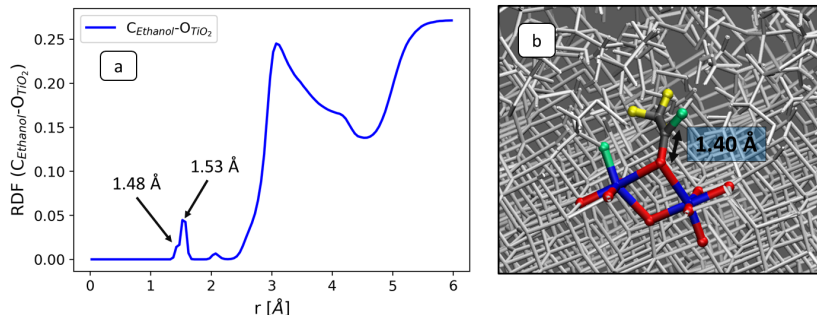


Figure 6: (a) Radial distribution function (RDF) between the carbon of ethanol and oxygen from the hydrated $\text{TiO}_2(101)$ surface, illustrating (b) the formation of acetic acid radicals at the hydrated $\text{TiO}_2(101)$ surface: O_{TiO_2} (red), Ti (blue), H_{TiO_2} (orange), $\text{C}_{\text{Ethanol}}$ (gray) atoms, $\text{H}_{\text{Ethanol}}$ (yellow) atoms, and $\text{O}_{\text{Ethanol}}$ (green) atoms.

504 3.1.3. Interactions at the water-ethanol mixture- $\text{TiO}_2(101)$ Interface

505 We finally consider a mixed water-ethanol liquid phase (half/half in vol-
 506 ume) in contact with $\text{TiO}_2(101)$. Figure 7a illustrates the time-dependent
 507 formation of surface ethoxy radicals, which serves as a signature of ethanol
 508 reaction (see the corresponding configuration in Figure 7i). It is observed
 509 that, compared to pure liquid ethanol where roughly 14% coverage of ethoxy
 510 species is reached after 6 ns of annealing, and still increasing, the water-
 511 ethanol mixture exhibits a drop in radical formation down to only 2% cov-
 512 erage, which coverage rapidly saturates within the first ns. This indicates
 513 that the presence of water inhibits surface ethoxy formation. This can be
 514 attributed to the competitive adsorption of both molecules in favour of wa-
 515 ter, which will be quantified in the next subsection. In contrast to the few
 516 instances of CH_3O_2 formation observed at the ethanol- $\text{TiO}_2(101)$ interface,
 517 this radical is not present in the case of the water-ethanol mixture.

518 Focusing on water reaction, the Figure 7b provides a quantification of
 519 oxygen exchange between water molecules and the substrate (configuration
 520 shown in Figure 7g). The proportion of oxygen atoms initially belonging
 521 to water molecules at the interface and binding to $\text{TiO}_2(101)$ surface as hy-

522 droxyl groups amounts to approximately 20% coverage. In comparison, this
523 quantity is decreased to 12% when water and ethanol are mixed, indicating
524 that the presence of ethanol affects the surface binding behavior of water
525 partly because of the permanent surface bonding of ethoxy radicals.

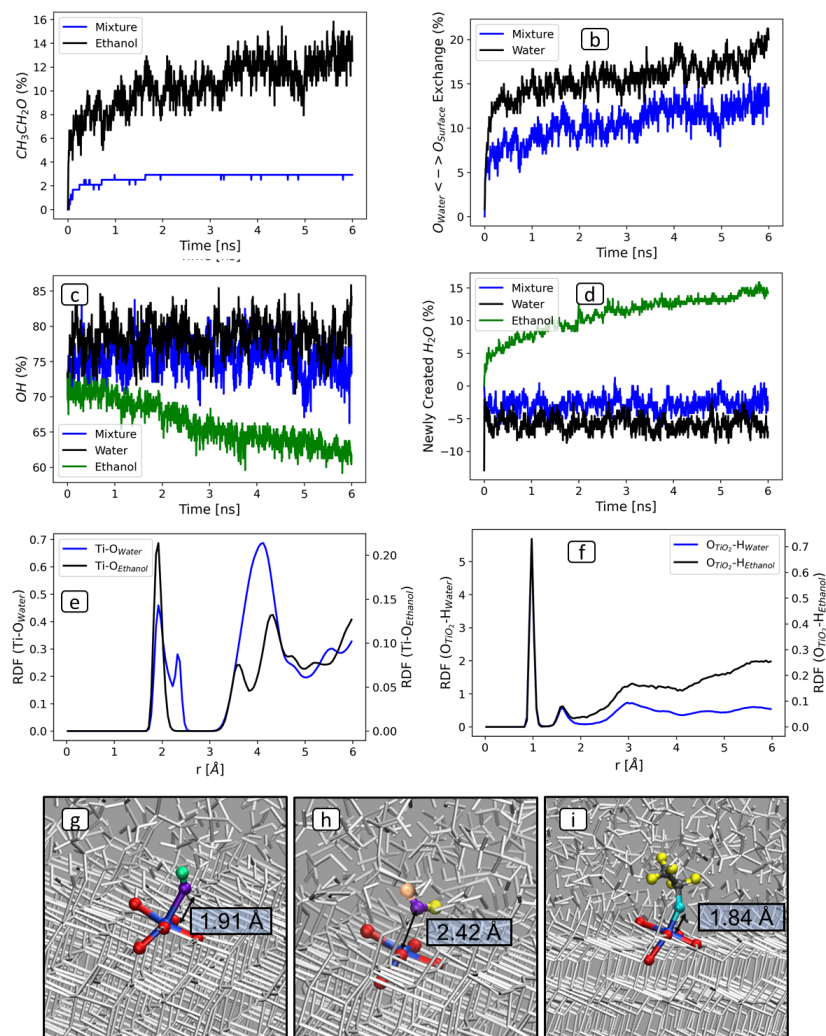


Figure 7: Comparison of water, ethanol, ethanol/water mixture interacting with hydrated TiO₂(101). Panels show: (a) temporal evolution of ethoxy coverage onto ceTiO₂(101) exposed to ethanol and ethanol/water mixture, (b) temporal evolution of liquid to surface oxygen exchange in both water and ethanol/water mixture based systems, (c) temporal evolution of the total surface OH content in the three considered systems, (d) counts the quantity of water molecules being created/annihilated over time in the three considered systems. Panels (e,f) show the Radial Distribution Functions (RDFs) of Ti with respect to oxygen and hydrogen atoms from both water and ethanol, respectively. (g-i) depict snapshots of a selection of adsorbates onto TiO₂, respectively a OH that forms after water dissociation, an adsorbed water molecule being generated after ethanol dissociation, and an ethoxy radical

526 Figure 7e illustrates the radial distribution function (RDF) of surface Ti
527 adsorption sites, distinguishing the bonding with oxygen initially belonging
528 to water molecules with oxygen atoms, distinguishing their origin, i.e., water
529 (blue curve) and ethanol (black curve). The latter exhibits a single peak
530 at around 1.9 Å, suggesting a single form of bonding, corresponding to the
531 ethoxy binding. Considering the RDF signature associated to oxygen from
532 water, the resulting formation of OH gets a similar RDF signature (the Ti-O
533 bond being approximately identical). But one additional peak is now present,
534 at 2.4 Å), which is attributed to the non dissociative adsorption of water on
535 surface Ti, at a distance of 2.4 Å (Figure 7h).

536 Notably, similarly to water and ethanol interfaces, the ethanol/water
537 based system shows H-exchanges between the molecules and the hydrated
538 surface. This exchange is clearly evidenced by the RDF signatures as shown
539 in Figure 7f, where a peak at 0.98 Å is observed, assigned to surface oxygen
540 atoms forming hydroxyls and H initially belonging to water molecules.

541 Comparing the three investigated interfaces in terms of the quantity of
542 OH in Figure 7c, pure water and mixed ethanol/water cases show almost
543 equivalent OH coverages, reaching approximately 78% and 72% coverage,
544 respectively. Again, this indicates a dominance of water behaviour, while
545 ethanol is responsible for the lowering of hydroxyl coverage. Note that the
546 hydration level remains constant over the annealing. In contrast, in the case
547 of pure ethanol, the quantity decreases gradually down to 64% coverage,
548 as more and more ethoxy are being attached to the surface. Counting the
549 number of water molecule as a function of time in Figure 7d shows that,
550 while a pure ethanol exposure will lead to an increase of water molecules
551 in the liquid phase (plus roughly 15 water molecules), water alone and the
552 ethanol/water mixture cases experience a slight decrease in number, pointing
553 again to the dominant role of water when competing with ethanol.

554 3.2. Mechanisms of Hydration and Molecular Hydrogen Production

555 The following subsection is dedicated to the energetics and pathways of
556 hydration mechanisms, specifically on the interface capability to produce
557 surface hydroxyl groups. These have been demonstrated to play an essen-
558 tial role in promoting hydrogen production during the photoreduction of
559 water [41, 49], which chemical processes will be addressed next. From the
560 previous sections, hydroxyl groups can be produced through the release of
561 protons from the dissociation of both ethanol and water molecules. Poten-
562 tial pathways and associated energetic signatures of these mechanisms are

563 investigated using PMF calculations. All following pathways were evaluated
 564 at the ethanol/water-TiO₂(101) interface, at 300 K.

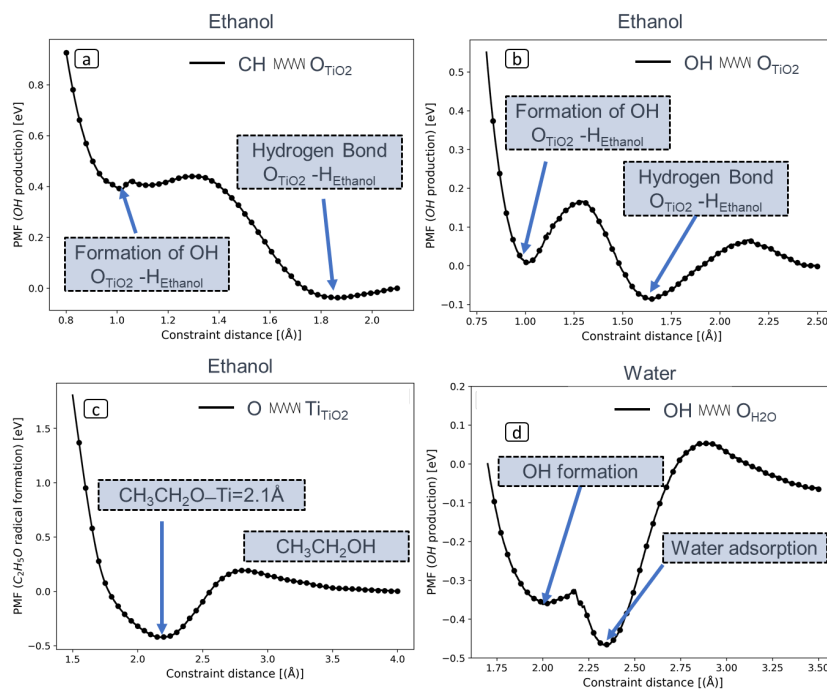


Figure 8: PMF energy profiles along reaction pathways for the generation of surface OH species through: (a) bonding of H from CH ethanol subunit onto a surface oxygen atom, (b) bonding of H of OH ethanol subunit onto a surface oxygen atom, (c) bonding of CH₃CH₂O onto a surface Ti atom, OH being created subsequently via the released H atom (d) bonding of H from H₂O onto a surface oxygen atom. Calculations were performed at the ethanol/water-TiO₂(101) interface at 300 K.

565 Figure 8a depicts the potential of mean force (PMF) energy curve along
 566 the reaction pathway relative to the formation of one specific OH hydroxyl at
 567 the TiO₂(101) surface, *via* a proton transfer from ethanol, initially located at
 568 its CH subunit. This process unfolds into two discernible stages. The initial
 569 stage involves the non dissociative adsorption of ethanol *via* a hydrogen bond
 570 formation, as CH₃OH-HCH...O_{TiO₂} = 1.8 Å. Importantly, this stage does
 571 not necessitate overcoming any energy barrier. Transitioning to the second
 572 stage, the creation of a TiO—H bond requires an energy barrier of 0.45
 573 eV, which falls into the room temperature class of mechanisms. Note that
 574 after dissociation, the under-coordinated carbon spontaneously react with a

575 neighboring H_2O to create an acetic acid molecule. In Figure 8b and c, we ex-
 576 amine the surface OH formation from the release of the proton from the OH
 577 alcohol termination. Two paths are envisaged by directing the bond creation
 578 either between the hydrogen of the alcohol termination and a surface oxy-
 579 gen atom ($\text{CH}_3\text{CH}_2\text{-OH}\cdots\text{O}_{\text{TiO}_2}$, Figure 8b), or between the oxygen atom
 580 from the alcohol termination and a surface Ti atom ($\text{CH}_3\text{CH}_2\text{-HO}\cdots\text{Ti}_{\text{TiO}_2}$,
 581 Figure 8c). In the first case, a non dissociative adsorption of ethanol is es-
 582 tablished first via a hydrogen bond, $\text{CH}_3\text{CH}_2\text{-OH}\cdots\text{O}_{\text{TiO}_2}$ at a distance of
 583 1.65\AA , which shows an exothermic profile. Interestingly, while a more stable
 584 state is observed (roughly -0.1 eV) compared with the adsorption through
 585 the CH group, a small energy barrier is now to be overcome (0.07 eV).
 586 While this barrier is not significant at room temperature, it might be the rea-
 587 son for a configurational adaptation associated to a narrower pathway ex-
 588 plaining the prevalence of the CH-based ethanol adsorption configuration
 589 observed in the simulations, for which no barrier is seen. Further decreas-
 590 ing the $\text{OH}_{\text{Ethanol}}\cdots\text{O}_{\text{TiO}_2}$ bond distance, ethanol dissociates with an energy
 591 barrier of 0.25 eV . The dissociation is slightly endothermic because of the
 592 strong collective stabilization (solvation) of the non dissociative adsorbate.
 593 In the second path, the formation of the ethoxy is realized first, leading to
 594 the release of a proton that in turn forms a surface hydroxyl. As pictured
 595 in Figure 8c, the pathway presents an exothermic profile, with an activation
 596 barrier of 0.2 eV and a better energy stabilization of -0.4 eV after dissocia-
 597 tion. In a comparable vein, Density Functional Theory (DFT) was used to
 598 investigate the adsorption and dissociation of a single ethanol molecule on
 599 various surfaces of anatase [46]. The $\text{TiO}_2(101)$ surface emerged as the most
 600 favorable substrate for the initial dissociation step of ethanol, leading to the
 601 creation of the $\text{CH}_3\text{CH}_2\text{O}$ species. The calculated barrier activation energy
 602 for this step was established to be of 0.9 eV , at 0 K (with almost no gain in
 603 energy after dissociation). [46]

604 We now explore the formation of surface hydroxyl *via* water molecules.
 605 Two pathways are investigated depending on the water adsorption configura-
 606 tion, forming either a hydrogen bond through one of its H atom, or forming
 607 a dative bond via its O atom, with respectively their surface O and Ti atoms
 608 counterparts. The non dissociative adsorption of water via its hydrogen
 609 atoms and surface oxygen atom is unlikely as shown in Figure SM3, with
 610 an endothermic path and a positive energy for the adsorption state. In Fig-
 611 ure 8d, the hydration through the direct formation of OH *via* after water
 612 dissociation onto surface Ti atom shows first a non dissociative adsorption

613 state which stabilizes at a distance of 2.34 Å with an energy of -0.4 eV (neg-
614 ligible activation barrier of 0.05 eV). Dissociation is calculated to be slightly
615 endothermic, with a barrier of 0.13 eV, to form a Ti—OH group with a Ti-
616 O bond length of 2.00 Å. The overall profile is similar to previous publication
617 using *ab initio* deep potential molecular dynamics [1].

618 In summary, all calculated pathways are characterized by energy barriers
619 below 0.5 eV making these events feasible at room temperature as well as ob-
620 servable in most of our molecular dynamics simulations. In this frame, PMF
621 profiles allows interpreting their occurrence and statistics in terms of: the ac-
622 cess to the adsorption sites, which is particularly true for ethanol dissociation
623 through its OH termination; and the local arrangement of chemical species
624 that is needed to stabilize the system during and after the biased reaction. In
625 this latter case, dissociation of ethanol via its CH subunit appears unlikely,
626 as for the adsorption of water through a OH—H \cdots O_{TiO₂}. Results indicate
627 that water, more than ethanol can stick to the surface (better adsorption)
628 while ethanol needs also to adapt its configuration due to steric hindrance.
629 It is worth noting that the results obtained for the interaction of ethanol
630 and water with the hydrated TiO₂(101) surface differ from what would be
631 obtained under vacuum (Figure SM4). Solvation generally lowers adsorption
632 energies by further stabilizing adsorbates, which is a collective stabilization
633 process varying from case to case as illustrated in our simulations. This is
634 particularly illustrated in comparing the energies of the O \cdots O_H hydrogen
635 bond versus the O-H chemical bond in Figure 8b, in favour of the hydrogen
636 type of bonding, which hierarchy is inverted in vacuum, where the chemical
637 bond show superior binding energy, as expected (Figure SM4).

638 The PMF technique is particularly suitable to investigate rare events,
639 i.e., necessitating extended or even unreachable duration of simulated exper-
640 iments. The generation of hydrogen molecules from the hydrated surface,
641 which is a crucial step of the photocatalysis process, is one such rare event
642 that has not been observed across any of the analyzed interfaces. Our pur-
643 pose is to investigate potential pathways either exclusively emanating from
644 the surface, or being generated at the exact molecule-surface frontier. This
645 latter type of mechanism is illustrated in Figure 9a and b, giving the PMF
646 energy profiles of the selected reactions respectively under solvent exposure
647 or in vacuum (a single molecule is then considered in contact to the surface).
648 Three different mechanisms are investigated, with H₂ resulting from the re-
649 combination: (i) a H atom from a water molecule with a surface H atom
650 (Figure 9a, blue curve), (ii) a H atom from the OH ethanol termination with

651 a surface H atom (Figure 9a, black curve), (iii) a H atom from the CH ethanol
652 subunit with a surface H atom (Figure 9a, green curve). The analogous Fig-
653 ure 9b considers the same mechanisms, under vacuum. All energy profiles
654 show high barrier in the range 4 to 5 eV, making hydrogen generation un-
655 likely at reasonable temperature. However, simulation results indicate that
656 the catalytic reaction either *via* the ethanol CH subunit or water (only when
657 solvated) show lower activation (4.5 and 4.4 eV, respectively) compare to all
658 other cases.

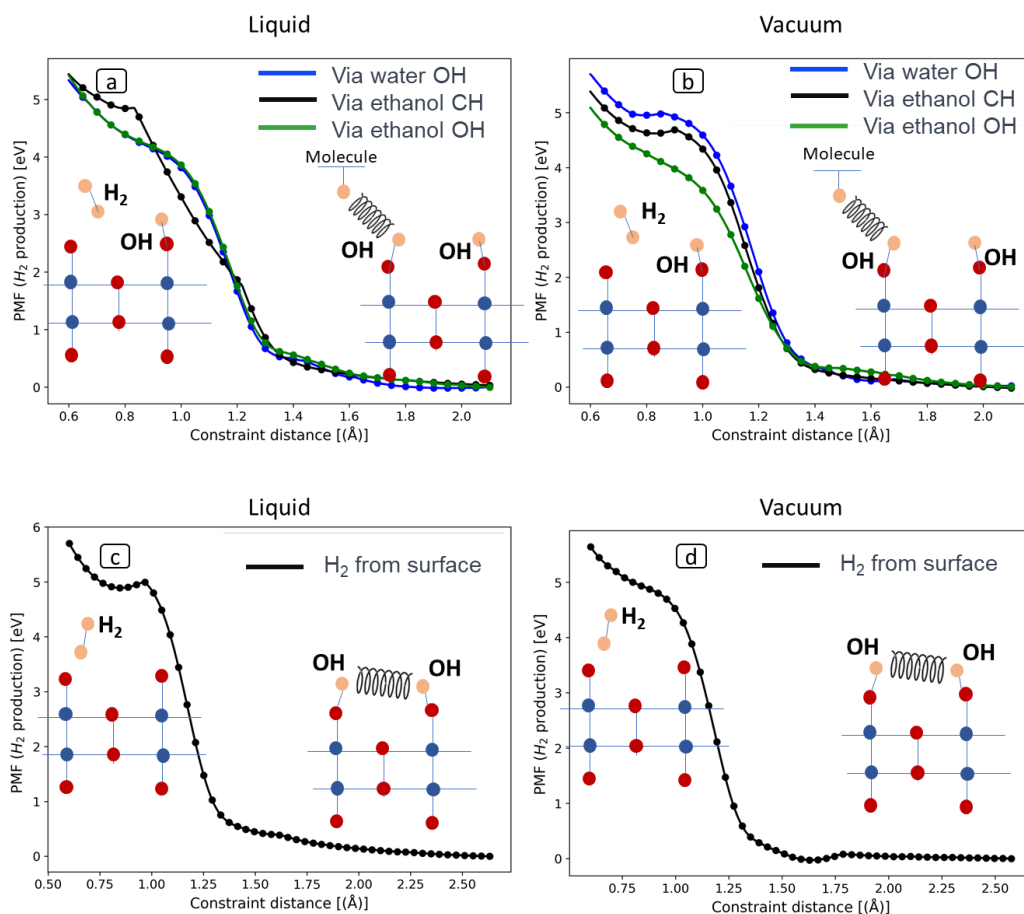


Figure 9: PMF energy profiles along reaction pathways for the generation of H₂: (a) via molecule/surface interaction under liquid exposure, (b) via single molecule/surface interaction under vacuum conditions, (c) through interacting surface hydroxyl species under solvent exposure, (d) similar case as (c), but under vacuum. These calculations were performed at 300 K, the liquid phase being composed of a mixture of ethanol and water.

659 It is now considered the generation of H₂ exclusively driven by sur-
 660 face mechanisms, through the hopping of surface H atoms belonging to hy-
 661 droxyl species. The energy profile show similar trend as in the case of
 662 molecule/surface interactions but fail to produce barriers inferior to 5 eV
 663 range. Overall, these tentative mechanisms pleads for the prevalence of hy-
 664 drogen generation through the molecule/surface complexes rather than be-
 665 ing exclusively surface driven mechanisms. The relatively high value dispels

666 the likelihood of spontaneous H₂ formation across the considered interfaces,
667 which is expected since optical or electrical excitation is required experimen-
668 tally, at room temperature. One other potential perspective is to consider
669 higher degree of chemical cooperativity at around reaction sites.

670 An alternative perspective on the surface’s capacity to generate hydrogen
671 is to assess its aptitude for transporting hydrogen species across its struc-
672 ture, a crucial step in orchestrating the configuration of catalytic species
673 within a practical timeframe. This evaluation involves the computation of the
674 Mean Square Displacement (MSD) in the time window of the last nanosec-
675 ond of simulation. In our molecular dynamics (MD) simulations, we deter-
676 mine self-diffusion coefficients (D) utilizing Einstein’s relation and a three-
677 dimensional material model based on the mean square displacement (MSD).
678 The MSD equation is defined as $\text{MSD} = \langle \delta r^2 \rangle = \frac{1}{N} \sum_i [r_i(t + t_0) - r_i(t_0)]^2$.
679 Following the MSD computation, the self-diffusion coefficient (D) is ascer-
680 tained as $D = \lim_{t \rightarrow \infty} \frac{\langle \delta r^2 \rangle}{6t} = \lim_{t \rightarrow \infty} \frac{\langle \text{MSD} \rangle}{6t}$ [50, 51, 52]. These displace-
681 ments are calculated at each iteration of the last nanosecond of the molecu-
682 lar dynamics simulations, where the steady state is reached with almost no
683 chemical exchange between the liquid and solid phases. These MSD values
684 are reported in Figure 10 for the three considered liquid phase e.g., water,
685 ethanol and water/ethanol mixture. Results clearly show that ethanol in-
686 hibits surface migration of hydrogen. The calculated diffusion coefficient
687 D are $8.45 \times 10^{-5} (\pm 1 \times 10^{-7})$ cm²/s, $1.91 \times 10^{-5} (\pm 5 \times 10^{-8})$ cm²/s, and
688 $1.40 \times 10^{-7} (\pm 3 \times 10^{-9})$ cm²/s for water, ethanol/water mixture, and ethanol-
689 exposed hydrated surfaces, respectively. This confirms the major role of wa-
690 ter, at the steady state of our simulations. Examination of the simulation
691 trajectories indicate that Grotthuss mechanisms are driving the transport of
692 hydrogen, which necessitates high OH coverage.

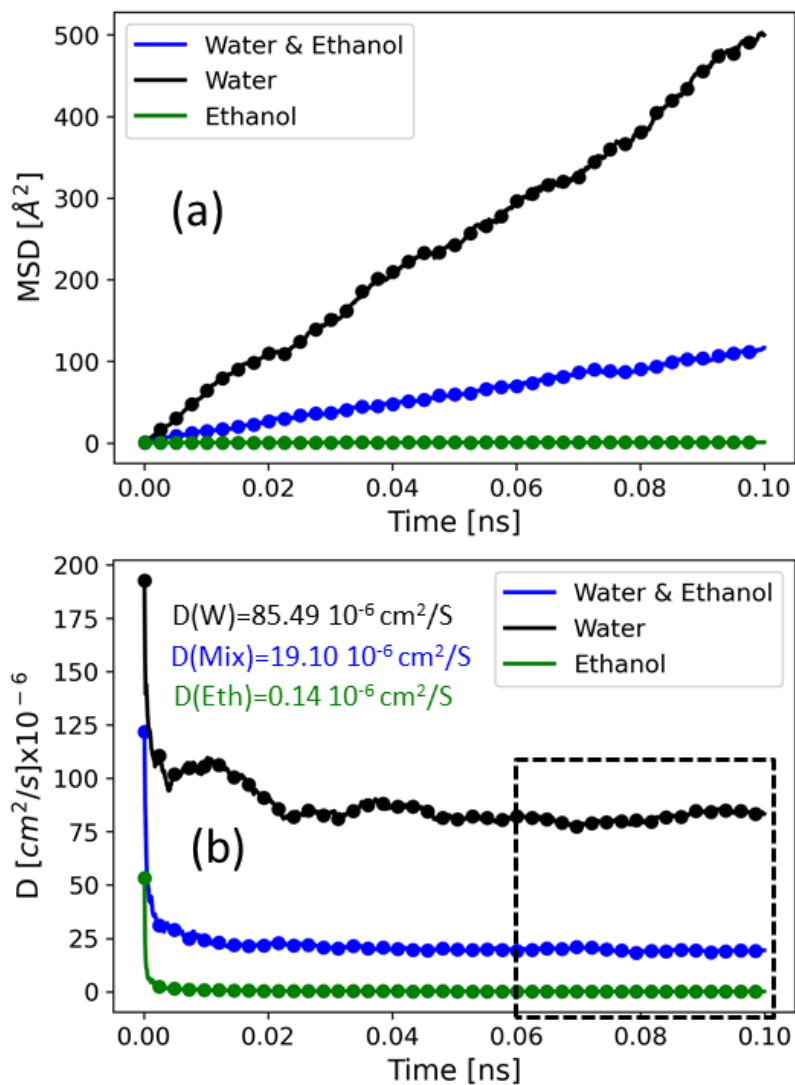


Figure 10: (a) Mean Square Displacement (MSD) and (b) Diffusion Coefficient (D) calculated over the last nanosecond of H formation in the hydration region of the $TiO_2(101)$ surface, observed at three distinct surfaces: the mixture (water/ethanol)-hydrated $TiO_2(101)$ surface, the water-hydrated $TiO_2(101)$ surface, and the ethanol-hydrated $TiO_2(101)$ surface.

693 4. CONCLUSION

694 In this study, we employed ReaxFF molecular dynamics simulations to
 695 delve deeper insights into the intricate dynamics of interactions involving

696 water, ethanol, their mixture onto hydrated $\text{TiO}_2(101)$ surfaces. At the
697 water- $\text{TiO}_2(101)$ interface, surface hydrogen atoms catalyze the formation
698 of hydroxyl groups, while surface hydrogen and oxygen atoms (to a lesser
699 extent), exchange with the surrounding liquid phase. Moving to the ethanol-
700 $\text{TiO}_2(101)$ interface, the emergence of ethoxy radicals ($\text{CH}_3\text{CH}_2\text{O}$) species
701 getting permanently bonded to surface Ti atoms, are shown to shadow the
702 surface, slightly lowering hydroxyl surface density, but affecting much the
703 hydrogen transport at the surface by three order of magnitude in their diffu-
704 sion coefficient. More anecdotally, calculation reveals instances of CH_3CO_2
705 species adorning surface Ti sites *via* their oxygen atoms. The mixed water-
706 ethanol- $\text{TiO}_2(101)$ interface exhibits reduced ethoxy radicals and CH_3CO_2
707 suppression, which allows keeping a high ratio of hydroxyl groups, pointing
708 also to the dominant and competing role of water when mixed to alcohol.
709 PMF calculations offer insights into the underlying mechanisms of hydra-
710 tion. Both the dissociation of ethanol and water orchestrate the formation of
711 hydroxyl groups on the $\text{TiO}_2(101)$ surface through protonation, overcoming
712 barriers below 0.45 eV. Notably, non-dissociative adsorption of these entities
713 exhibits lower free energy than their dissociative counterparts due to efficient
714 solvation of the non-dissociative adsorbates. Water shows the lowest adsorp-
715 tion energy, which is key to the water superior reactivity with the surface,
716 tuning the overall surface interactions. Finally molecular hydrogen formation
717 is discussed using the PMF technique, differentiating catalytic mechanisms,
718 i.e., involving molecule (water or ethanol) surface interactions, from purely
719 surfacic interactions (between adjacent surface hydroxyl groups). All calcu-
720 lated barrier are greater than 4 eV, making all tested mechanisms unlikely at
721 reasonable temperature, which is expected since external excitations (optical,
722 electrical) are known to be indispensable to achieve hydrogen recombination.
723 Anyhow, our results suggest a prevalence (by 0.6 eV) of catalytic, versus
724 purely surfacic mechanisms for generating molecular hydrogen.

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730 6. Competing Interests

731 The authors declare that there are no conflicts of interest, encompassing
732 both personal relationships and financial factors, which could have influenced
733 the publication of the study presented in this article.

734 7. Supplementary Material

735 Here we present additional analyses, configuration snapshots, radial dis-
736 tribution functions (RDFs), and mean force potential (PMF) calculations to
737 reinforce the conclusions advanced in the main content of this article.

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