

Hydrogen adsorption, dissociation, and spillover on Ru₁₀ clusters supported on anatase TiO₂ and tetragonal ZrO₂ (101) surfaces

Hsin-Yi Tiffany Chen, Sergio Tosoni and Gianfranco Pacchioni¹

*Dipartimento di Scienza dei Materiali,
Università di Milano-Bicocca, via Cozzi 55, 20125 Milano, Italy*

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Abstract

The scope of this work is to study at atomistic level the mechanism of hydrogen spillover promoted by metal particles on oxide surfaces. By means of Density Functional Theory calculations with Hubbard correction (DFT+U) we have analyzed the adsorption and dissociation of molecular hydrogen on anatase titania, a-TiO₂ (101), and tetragonal zirconia, t-ZrO₂ (101), surfaces in the presence of a supported Ru₁₀ nanocluster. The role of the supported metal particle is essential as it favours the spontaneous dissociation of H₂, a process which does not occur on the bare oxide surface. At low hydrogen coverage, the H atoms prefer to stay on the Ru₁₀ particle, charge accumulates on the metal cluster, and reduction of the oxide does not take place. On a hydroxylated surface, the presence of a Ru nanoparticle is expected to promote the reverse effect, i.e. hydrogen reverse spillover from the oxide to the supported metal. It is only at high hydrogen coverage, resulting in the adsorption of several H₂ molecules on the metal cluster, that it becomes thermodynamically favourable to have hydrogen transfer from the metal to the O sites of the oxide surface. In both TiO₂ and ZrO₂ surfaces the migration of an H atom from the Ru cluster to the surface is accompanied by an electron transfer to the empty states of the support with reduction of the oxide surface.

Keywords: oxide surfaces, metal clusters, hydrogen spillover, DFT, titania, zirconia

¹ Corresponding author. E-mail: gianfranco.pacchioni@unimib.it (tel. +39-2-64485219)

1. Introduction

Hydrogen plays a fundamental role in chemistry and energy applications. Its interaction with solid surfaces is relevant in hydrogen storage, catalytic hydrogenation of organic substrates, ammonia synthesis, fuel cells, passivation of defects in microelectronic industry, etc. In heterogeneous catalysis the adsorption and dissociation of hydrogen on a supported metal particle is a crucial step in many reactions.^{1,2,3,4} Hydrogen is also used to activate catalysts before their use. For instance, it has been suggested that hydrogen pretreatment results in an increased activity of oxide catalysts like TiO₂ and ZrO₂ for production of biofuels from cellulosic biomass.^{5,6} A key step in bio-oil upgrading is the ketonization of carboxylic acids,^{6,7,8} and it has been shown that the ketonization rate can be increased by adding metal particles, such as Ru, on the surface of the oxide catalyst. This may be related to the formation of coordinatively unsaturated Ti³⁺ and Zr³⁺ sites,^{9,10} although a direct confirmation of this mechanism is missing. Calculations performed on Ru and Ni clusters deposited on a-TiO₂ and t-ZrO₂ have excluded the direct reduction of the oxide by metal deposition.^{11,12} Oxide reduction can be achieved by hydrogen adsorption in the presence of the deposited metal particles, a phenomenon that has been observed long time ago.^{13,14} Hoang and Lieske showed that hydrogen pretreatment of ZrO₂ is correlated to catalytic activity at high temperature in hydrocarbon conversion, presumably due to the presence of catalytically active acid sites.¹⁵

An important question in this context is the role of the supported metal particle. The status of hydrogen spillover (interphase diffusion of adsorbed hydrogen) has been reviewed,¹⁶ also recently.¹⁷ From the original study of Khoobiar,¹⁸ where it was shown that when Pt/WO₃ is exposed to H₂ the oxide turns blue due to the chemical reduction, many studies have been dedicated to the phenomenon. There is general consensus that the metal particle facilitates the dissociation of the H₂ molecule thus providing the excess electrons that are needed in order to reduce the surface. This is of key importance in fuel cells.¹⁹ A lot of efforts have been directed at the identification of metals able to efficiently split hydrogen or, even better, of anodes able to oxidize hydrocarbons directly to allow the elimination of internal reforming, C_mH_{2m+2} + C_nH_{2n+2} → C_{m+n}H_{2(m+n)+2} + H₂. Once atomic hydrogen has been produced from H₂ dissociation, various subsequent steps can be hypothesized. One is that the hydrogen spillover occurs from metal particles (Ru in our case) to the supporting oxide surface (M = Ti or Zr):

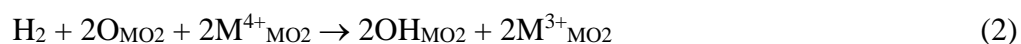


In fact, adsorbing metallic particles such as Pt and Rh on ZrO₂ aids the interaction between H and ZrO₂; it has been suggested that H spillover from Pt or Rh to ZrO₂ leads to an increased amount of H on ZrO₂ surfaces.^{15,20} The methanol synthesis promoted by Cu/ZrO₂ catalysts has

been attributed to the role of Cu in dissociatively adsorbing H₂ and promoting spillover of atomic hydrogen.²¹ Zhu reported that by preloading Pt nanoparticles on TiO₂, the hydrogen spillover from Pt to TiO₂ accounts for the raise of hydrogenation capability.²² Nonetheless, not all TiO₂ supported metal catalysts make H spillover possible. For instance, H spillover was observed for Au/TiO₂,^{23,24} and Pd/TiO₂ but not for Ni/TiO₂.²⁵ In general, it is believed that hydrogen spillover does not take place on non reducible oxides,¹⁶ although the question is still debated for certain cases.

The situation is even more complex if one considers that some reports indicate the spontaneous occurrence of the opposite phenomenon, i.e. hydrogen reverse spillover.^{26,27,28,29} Here is the hydrogen atom from an OH group of the oxide surface that, in the presence of a supported metal particle, migrates to the supported metal forming multiply hydrogenated metal species. Computational studies revealed that this process is energetically favorable for late transition metals, except for Au.^{27,30} Under operative conditions, the occurrence of the direct or reverse hydrogen spillover on reducible oxides depends on the hydrogen partial pressure. By changing this parameter one changes the hydrogen chemical potential and the direction of the equilibrium.

If direct hydrogen spillover occurs, with migration of hydrogen from the metal particle to the oxide, then the situation is formally analogous to the direct adsorption of H₂ on the oxide surface. When two H atoms are added to the bare MO₂ surface (M = Ti or Zr) they form hydroxyl groups:



The electron associated to atomic H is transferred to a metal cation that changes its oxidation state from M⁴⁺ to M³⁺ (reduction of the oxide).³¹ In the case of hydrogen spillover, however, what remains to be clarified is the nature of the species that diffuses from the metal particle: a neutral H with its valence electron, or a proton? In the first case one electron is moved from the metal cluster to the oxide, with its consequent reduction; in the second case the electron remains on the metal which assumes a negative charge, and no direct reduction of the oxide occurs.

Another possibility, at least in theory, is that once the hydrogen has been dissociatively adsorbed on the metal particle, there is a spillover of oxygen from the oxide surface to the metal; the oxygen can react with the hydrogen adsorbed on the metal and form water that then desorbs from the surface:



This latter mechanism leads to the formation of O vacancies (V_{MO2}) on the oxide, which is reduced

as the consequence of loss of oxygen, and not of addition of electrons (as in the case of direct H₂ adsorption).

This brief summary is far from being complete and exhaustive, but it illustrates the complexity of the study at atomistic level of hydrogen adsorption on oxide supported metal nanoparticles. In this work we try to address the problem and to understand the influence of a Ru nanoparticle on the interaction of H₂ with a-TiO₂ and t-ZrO₂(101) surfaces and to get an atomistic picture of the adsorption mechanism. We compare, using the same computational setup, the adsorption of a single H atom and the dissociation of one or more H₂ molecules on a Ru₁₀ cluster supported on stoichiometric anatase TiO₂ and tetragonal ZrO₂ surfaces. The properties of a Ru₁₀ cluster supported on stoichiometric and reduced TiO₂ and ZrO₂ surfaces has been reported previously.^{11,12} In this work we considered as a starting point fully dehydroxylated titania and zirconia surfaces.

The paper is constructed as follows. After some computational details (Section 2), in Section 3.1 we discuss the adsorption of atomic hydrogen on (a) the bare a-TiO₂ and t-ZrO₂ surfaces, (b) the same surfaces in the presence of a Ru₁₀ particle, and (c) directly on the supported metal cluster. In Section 3.2 we discuss (a) dissociation of an H₂ molecule on Ru₁₀/TiO₂ and Ru₁₀/ZrO₂, (b) the spillover of one of the two hydrogens from the cluster to the surface, and (c) the effect of the adsorption of several H₂ molecules on the Ru₁₀ cluster (saturation coverage). The conclusions are reported in the last section.

2. Computational methods

The calculations are performed using the VASP 5.2 simulation package.³² The valence electrons, H(1s), O(2s, 2p), Ti(3s, 4s, 3p, 3d), Zr(4s, 5s, 4p, 4d) and Ru(5s, 4p, 4d), are expanded on a set of plane waves with a kinetic cutoff of 400 eV, while the core electrons are treated with the Projector Augmented Wave approach.^{33,34} The PBE functional is adopted to calculate the exchange and correlation energy, as formulated in the generalized gradient approximation (GGA) of the density functional theory.³⁵ The GGA+U approach is applied to the calculation of the electronic structure of TiO₂ and ZrO₂, in order to partially account for the self-interaction error.^{36,37} This method partly reduces the underestimation of the electronic band gap and the excessive tendency to delocalize the electron density.³⁸⁻⁴⁰ In this work, we set the Hubbard parameters to U-J = 3 and U-J = 4 eV for Ti and Zr, respectively, which ensures a good qualitative description of structure and electronic properties of Ti and Zr oxides. For example, the relaxed lattice parameters are in reasonable agreement with the experiment (errors on the cell volume < 5-6%).^{41,42,43}

There are several polymorphs of TiO₂ – anatase, rutile, brookite and some high pressure phases. Although rutile is the thermodynamically stable bulk phase at all temperatures,^{44,45,46}

anatase is the most common phase in catalytic applications.^{47,48,49,50,51} The (101) anatase facet is the most stable surface. ZrO₂ can exist in at least five polymorphs.^{52,53} Only monoclinic ZrO₂ could stabilize at room temperature; a transition to a tetragonal phase occurs at around 1480 K and transforms into the cubic fluorite phase by increasing the temperature to 2650 K.⁵⁴ The monoclinic polymorph has few practical applications due to the brittleness of the structure when cooling from the tetragonal phase.⁵⁵ The most stable facet of tetragonal ZrO₂, (101), is analogous to the most stable cubic ZrO₂ (111) surface.⁵⁶ We have chosen the a-TiO₂ (101) and t-ZrO₂ (101) surfaces for this present study since these are the most stable surfaces of a-TiO₂ and t-ZrO₂, in agreement with previous reports⁵⁷⁻⁶⁰

For the relaxation of lattice and internal coordinates of anatase TiO₂ and tetragonal ZrO₂ we used a cut-off of 600 eV and a Γ -centred high-density grid of K-points. Surface properties are studied by means of slab models. Convergence of the electronic structure (density of states) is reached for five-MO₂ layer models (M = Ti or Zr) by fully relaxing both sides of the slabs. For the case of zirconia also the surface energy is well converged due to the stiffness of the (101) surface.

3x1 and 3x2 supercells were used for TiO₂ and ZrO₂, respectively; the sizes of the supercells are 11.5 x 10.5 x 35.0 Å for TiO₂ and 11.0 x 12.9 x 35.0 Å for ZrO₂, respectively (see Fig. 2 in ref. 11). This corresponds to a composition Ti₆₀O₁₂₀ and Zr₆₀O₁₂₀. The sampling of the reciprocal space is set to the Γ -point, given the relatively large dimension of the supercells. In all cases, at least 10 Å of empty space above the adsorbed species is considered to avoid interactions between the replicas of the slab model.

For all models, we perform structural relaxations of all atoms with convergence criteria of 10⁻⁵ eV and 10⁻² eV/Å for the electronic and ionic loops, respectively. Atomic charges have been determined according to the Bader partition method.⁶¹

3. Results and discussion

3.1 H atom adsorption

H adsorption on TiO₂ and ZrO₂

In general, irreducible metal oxides, like MgO, induce the heterolytic splitting of H₂ with formation of Mⁿ⁺-H⁻ and O²⁻-H⁺ species,^{62,63} on the contrary, on reducible metal oxides such as TiO₂ or ZrO₂, homolytic dissociation occurs with formation of surface hydroxyls.^{64,65,66,67,68,69,70,71} In this case, two electrons are transferred from the H₂ molecule to the oxide, with direct reduction of the metal cations from Mⁿ⁺ to M⁽ⁿ⁻¹⁾⁺ (eq. 2).

Assuming that H₂ dissociation has already taken place (see below), we adsorbed the H atom on a 2-fold-coordinated O_{2c} site of a-TiO₂ and a 3-fold-coordinated O_{3c} site of t-ZrO₂ (101) surfaces; the optimal O-H bond length is 0.97 Å for both oxides. Of course, the H coverage affects the

adsorption energy,⁶⁹ but here we consider an isolated H atom (with the supercells used, the coverage is of 1/36 monolayer, ML). The H adsorption energy is defined with respect to gas-phase H₂:

$$E_{\text{ads}} = E(\text{H}/\text{MO}_2) - E(\text{MO}_2) - 1/2E(\text{H}_2) \quad (4)$$

E_{ads} , see Table 1, is positive for both oxides, indicating an endothermic reaction. In both a-TiO₂ and t-ZrO₂, one electron is transferred to Ti 3d and Zr 4d empty states with formation of an adsorbed proton, H⁺, and Ti³⁺ and Zr³⁺ ions, respectively, as shown by the spin density plots of Fig. 1. The presence of an unpaired electron trapped on the oxides is shown also by the analysis of the spin population and of the Bader charge which shows an overall negative charge of -1.0 |e| on the oxide after H adsorption, Table 1.

It should be mentioned at this point that the identification of Ti³⁺ (3d¹) and Zr³⁺ (4d¹) sites is a complex issue. It depends on the details of the computational approach used (larger U parameters result in more localized solutions) and on the polaronic distortion that accompanies the formation of reduced M³⁺ centers.⁷² Sometimes to obtain a localized solution one has to manually distort the lattice in order to favour the formation of the polaron during the geometry optimization. Of course, several possible solutions exist.⁷² These solutions are relatively close in energy, and the barriers needed to induce electron mobility are relatively low. In both rutile and anatase TiO₂ they have been estimated, and are of the order of 0.3 eV.⁷³ This means that at the temperatures relevant for the catalytic processes the trapped electrons will rapidly hop from one site to another, resulting in a considerable electron mobility. For this reason a detailed discussion of the nature of the reduced M³⁺ sites, useful to show the occurrence of a reduction of the oxide, is not relevant for the modelling of the catalytic processes following reduction by hydrogen adsorption.

Table 1. Adsorption energy, E_{ads} (in eV), and Bader charges, q , of H, oxides and Ru (in |e|) for an H atom adsorbed on a-TiO₂ and t-ZrO₂ (101) surfaces. The nature of the electron on the oxide, localized or delocalized, is also reported. The associated structures are shown in Figures 1 and 2.

System	Fig.	E_{ads} (eV)	$q(\text{H})$ e	$q(\text{MO}_2)$ e	$q(\text{Ru})$ e	e ⁻ localization
TiO ₂ -OH	1(a)	+0.07	+1.00	-1.00	-	Ti _{5c}
TiO ₂ -OH	1(b)	+0.14	+1.00	-1.00	-	Ti _{6c}
ZrO ₂ -OH	1(c)	+0.79	+1.00	-1.00	-	Zr _{6c}
Ru ₁₀ (6,4)/TiO ₂		-	-	-1.28	+1.28	Delocalized
Ru ₁₀ (6,4)/TiO ₂ -OH	2(a)	+0.17	+1.00	-2.24	+1.24	Ti _{6c}
Ru ₁₀ (6,4)/TiO ₂ -OH	2(b)	+0.16	+1.00	-2.15	+1.15	Delocalized

$\text{Ru}_{10}(7,3)/\text{ZrO}_2$	-	-	-0.28	+0.28	-	
$\text{Ru}_{10}(7,3)/\text{ZrO}_2\text{-OH}$	2(c)	+0.15	+1.00	-0.91	-0.09	Delocalized
$\text{Ru}_{10}(7,3)/\text{ZrO}_2\text{-OH}$	2(d)	+0.67	+1.00	-0.93	-0.07	Delocalized

On a- TiO_2 we have been able to obtain two different solutions, one with the electron trapped on a Ti_{5c} ion and one where the electron goes to a Ti_{6c} ion. The corresponding adsorption energies are +0.07 and +0.14 eV, respectively, Table 1. This means that H_2 is not expected to spontaneously dissociate on the regular surface of a- TiO_2 , in agreement with previous work.^{70,71,74}

The reaction is even more endothermic on t- ZrO_2 where E_{ads} is +0.79 eV, Table 1. This reflects the fact that in ZrO_2 the bottom of the conduction band is much higher than in TiO_2 , by 1.5 eV according to our DFT calculations (see Fig. 1 in ref. 11), and that it is more unfavourable to transfer one electron from the H atom to the Zr 4d empty states. Notice that on ZrO_2 , a less reducible oxide than TiO_2 , previous theoretical calculations have reported the possible occurrence of an heterolytic splitting of H_2 with formation of an hydride, Zr-H, and an OH groups.⁷⁵ Of course, this process does not lead to a reduction of the zirconia.

These results show that H_2 dissociation with formation of protons adsorbed on O ions and electrons trapped at cation sites does not occur on the regular surfaces of a- TiO_2 and t- ZrO_2 . The presence of deposited metal particles is thus essential for the process as it will be discussed in the next Section.

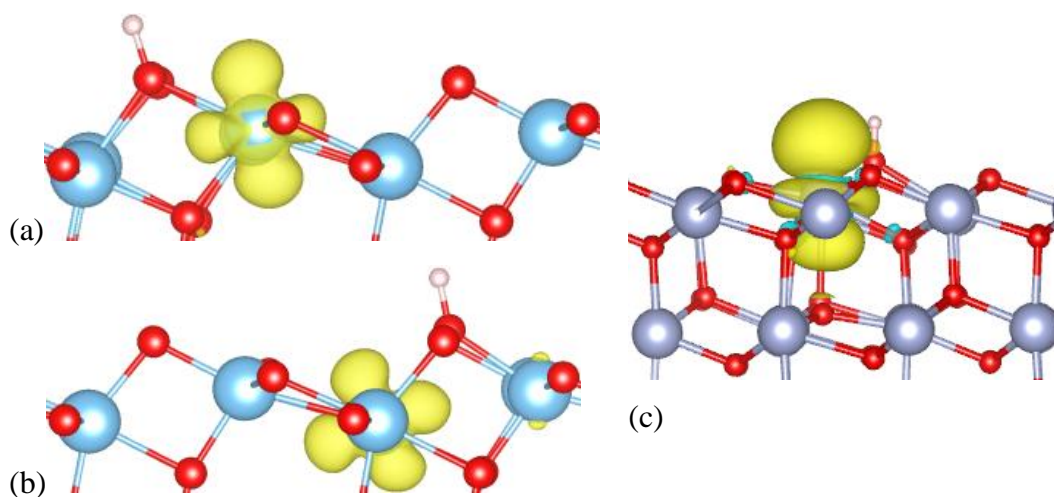


Figure 1. Spin density plot of a H atom adsorbed on a O site of (a) and (b) a- TiO_2 and (c) t- ZrO_2 (101) surfaces. The excess electron is trapped on (a) Ti_{5c} ; (b) Ti_{6c} ; (c) Zr_{6c} . See also Table 1. Blue: Ti; violet: Zr; red: O; white: H. The isosurface corresponds to $0.005 |e|/\text{\AA}^3$.

H adsorption on surface O of Ru₁₀/TiO₂ and Ru₁₀/ZrO₂

Here we consider the properties of atomic H adsorbed on the surface of a-TiO₂ and t-ZrO₂ in the presence of a Ru₁₀ nanoparticle. The question we want to address is whether the supported metal cluster has an effect on the adsorption properties and electronic structure of the oxide or not. To this end, we considered H adsorption on the same O sites of the two oxide supports with a neighboring Ru₁₀ cluster, Table 1 and Fig. 2. The Ru₁₀ cluster is at 2.7 and 4.6 Å, respectively, from the OH group (shortest Ru-H distance) for the case of TiO₂ and ZrO₂. Following our previous work,¹¹ two different isomers of Ru₁₀ have been considered, one with seven atoms at the interface and three on the top layer, Ru₁₀(7,3), and one with six interface Ru atoms and four in the top layer, Ru₁₀(6,4). Ru₁₀(6,4) is more stable on TiO₂ while Ru₁₀(7,3) is more stable on ZrO₂, so the analysis is performed with respect to these two isomers (but we checked that the results do not change if the other isomer is considered). The adsorption energy is defined with respect to each isomer:

$$E_{\text{ads}} = E(\text{H/Ru}_{10}(n,m)/\text{MO}_2) - E(\text{Ru}_{10}(n,m)/\text{MO}_2) - 1/2E(\text{H}_2) \quad (5)$$

For TiO₂ we do not observe any significant variation in the properties with respect to the case where H has been adsorbed on the clean surface (no supported Ru), Table 1. The adsorption energy remains slightly positive, 0.16 eV, and the electronic charge is transferred to the oxide. We have been able to obtain two solutions, one where the spin is entirely localized on a Ti ion (Ti³⁺), Fig. 2(a), and one where the charge is delocalized, Fig. 2(b). The difference in energy between the two solutions is negligible, Table 1, showing that the localization does not lead to an important stabilization. In both cases the Bader charge indicates an accumulation of negative charge in the oxide, $\Delta q \approx -1.0 |e|$, which is a sign of the occurrence of a chemical reduction. From these results we can conclude that there is no beneficial long range effect of the Ru₁₀ nanoparticle on the H adsorption on TiO₂.

The situation is rather different when we consider the same process on ZrO₂. In this case, in fact, the formation of an OH group in the presence of Ru₁₀, Fig. 2(c), has an adsorption energy, +0.15 eV, still endothermic, but 0.64 eV more favourable than on the bare surface, see Table 1. One electron is transferred to the oxide, as shown by the Bader charge, $\Delta q \approx -1.0 |e|$. However, no spin localization on a Zr ion is found, despite several attempts. Rather, the charge accumulates on a few Zr ions below the Ru₁₀ cluster, which also becomes slightly negatively charged, Table 1. This seems to suggest a role of the supported metal particle in inducing accumulation of the extra electron at the metal/oxide interface. Notice that if the hydrogen is adsorbed on an O atom at the metal-oxide interface, Fig. 2(d), the adsorption energy is +0.65 eV, indicating that the proton prefers to be far from the metal particle.

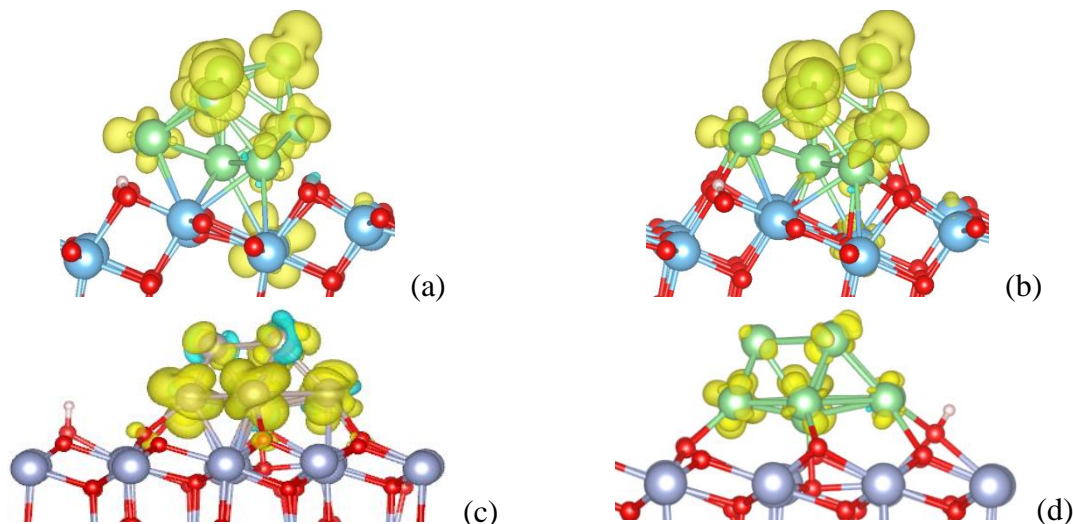


Figure 2. Spin density (in yellow) of a hydrogen atom adsorbed on (a) O_{2c} of Ru_{10}/TiO_2 with one electron localized on Ti_{6c} ; (b) O_{2c} of Ru_{10}/TiO_2 with one electron delocalized; (c) O_{3c} of Ru_{10}/ZrO_2 ; (d) interface O_{3c} of Ru_{10}/ZrO_2 . See also Table 1. Blue: Ti; violet: Zr; red: O; green: Ru; white: H. The isosurface corresponds to $0.005 |e/\text{\AA}^3$

H adsorption on Ru atoms of Ru_{10}/TiO_2 and Ru_{10}/ZrO_2

The results on the adsorption of H on O_{nc} sites of the titania and zirconia surfaces has shown that even the presence of an adsorbed Ru nanoparticle does not lead to an exothermic process, Table 1. Now we consider the direct adsorption of H on the Ru cluster. We have placed the H atom on several positions of Ru_{10} and at the Ru_{10}/MO_2 interface (see also Fig. S1 in Supporting information). For brevity we will discuss only the most stable structures, Table 2.

Table 2. Adsorption energy, E_{ads} (eV), Ru-H bond lengths (\AA), and Bader charges, q , of H, oxides and Ru (in $|e|$) for a single hydrogen atom adsorbed on Ru_{10}/TiO_2 and Ru_{10}/ZrO_2 (101) surfaces. The associated structures are shown in Figures 3.

System	Fig.	Adsorption site ^(a)	E_{ads} (eV)	$r(RuH)$ (\AA)	$q(H)$ $ e $	$q(MO_2)$ $ e $	$q(Ru)$ $ e $
$H/Ru_{10}(6,4)/TiO_2$	3(a)	Ru_{top}	-0.66	1.66	-0.26	-1.22	+1.48
$H/Ru_{10}(6,4)/TiO_2$	3(b)	Ru_{bridge}	-0.57	1.79,1.82	-0.26	-1.28	+1.53
$H/Ru_{10}(7,3)/TiO_2$	-	Ru_{top}	-0.78	1.64	-0.23	-1.15	+1.38
$H/Ru_{10}(7,3)/TiO_2$	-	Ru_{bridge}	-0.45	1.74,2.04	-0.27	-1.19	+1.46
$H/Ru_{10}(7,3)/TiO_2$	-	Interface	+0.09	1.80,1.82	-0.21	-1.18	+1.39
$H/Ru_{10}(7,3)/ZrO_2$	3(c)	Ru_{top}	-0.48	1.65	-0.26	-0.25	+0.50
$H/Ru_{10}(7,3)/ZrO_2$	3(d)	Ru_{bridge}	-0.35	1.79,1.80	-0.24	-0.24	+0.47

H/Ru ₁₀ (7,3)/ZrO ₂	-	Ru _{hollow}	-0.17	1.85,1.88	-0.16	-0.27	+0.43
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(a) Several configurations of H adsorption on a Ru hollow site were computed; however the H moves spontaneously to the bridge site.

The first observation is that when H is adsorbed on Ru₁₀ E_{ads} is always negative, indicating a favorable process. The binding of H to Ru can result in an energy gain of about 0.7 eV with respect to the free H₂ molecule, Table 2 and Fig. 3(a). This result clearly indicates the net preference for H to bind to the metal particle with respect to the oxide surface. In general, the binding of H on-top of Ru is preferred compared to the bridge sites, see e.g. Fig. 3(a) and 3(b). The Ru-H bond length is around 1.7 Å. When the H atom is placed on Ru but near the metal/titania interface, it induces a geometrical rearrangement with one O_{2c} atom that protrudes outwards the surface (not shown). The adsorption energy, however, is positive. This suggests, together with the result reported above for ZrO₂, that the interface is not a favourable region for H adsorption.

Turning to Ru₁₀/ZrO₂ structures (Fig. 3c and 3d), the H adsorption energies range from -0.48 to -0.17 eV, Table 2. Thus, the adsorption energy on TiO₂ (in absolute value) is about 0.2 eV larger than on ZrO₂, suggesting that the support has an effect on the adsorption properties of the metal particle and that hydrogen adsorption is preferred on Ru₁₀/TiO₂ compared to Ru₁₀/ZrO₂. For the case of Ru₁₀-ZrO₂, we performed some tests on the adsorption of H on a gas-phase Ru₁₀(7,3) particle. On an on-top site of Ru₁₀(7,3) the adsorption energy is -0.73 eV (fully relaxed cluster); this reduces to -0.61 eV if the Ru atoms are frozen into the positions they assume on t-ZrO₂. We also computed by an energy decomposition the relaxation energy induced by H adsorption. This turns out to be negligible in the case of Ru₁₀/TiO₂ (0.02 eV) while it is larger (0.12 eV) for Ru₁₀/ZrO₂. The lower binding energy of H to Ru₁₀/ZrO₂ is therefore due to the cost of deforming the Ru₁₀ cluster when an H atom is added.

We consider now the charge distribution. The Bader charges clearly indicate that moving the H atom from the surface (OH group) to the particle (Ru-H bond) results in the displacement of electronic charge from the oxide to the Ru₁₀H complex. Since the H atom adsorbed on a metal particle assumes an hydride character (on Ru₁₀ the H atom is negatively charged, see Table 2), it has the property to “oxidize” the metal particle (as shown by the positive charge on Ru₁₀, Table 2). This is an important result which shows that the displacement of a proton from an O_{nc} site of the oxide to a Ru atom of the particle (or viceversa) is accompanied by a corresponding electron transfer.

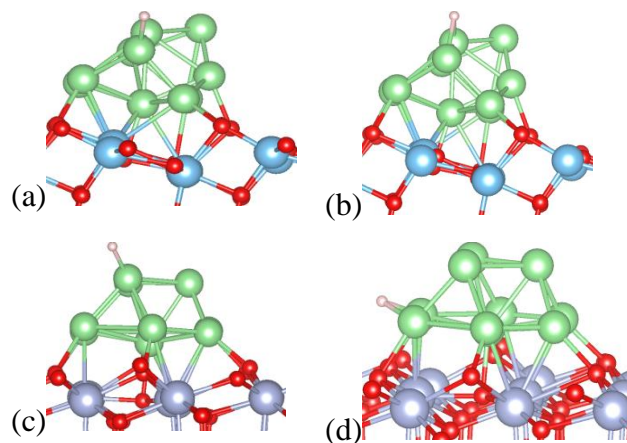


Figure 3. Structures of a hydrogen atom adsorption on different sites of Ru₁₀/TiO₂ and Ru₁₀/ZrO₂ (101) surfaces. (a) Ru₁₀/TiO₂, H on top of Ru; (b) Ru₁₀/TiO₂, H on Ru bridge site; (c) Ru₁₀/ZrO₂, H on top of Ru; (d) Ru₁₀/ZrO₂, H on Ru bridge site. See also Table 2. Blue: Ti; violet: Zr; red: O; green: Ru; white: H.

3.2 Adsorption of H₂ molecule

Dissociative adsorption on Ru₁₀/TiO₂ and Ru₁₀/ZrO₂

So far we have considered the adsorption of a single H atom on either the oxide surface or on the supported Ru cluster. In doing this we have assumed that dissociation has occurred at some stage. In this Section we consider the dissociative adsorption of H₂ on Ru₁₀/TiO₂ and Ru₁₀/ZrO₂. The first important result is that by placing the hydrogen molecule close to the metal cluster we observe a spontaneous dissociation on both systems, indicating a non activated process. Also here we considered two different Ru₁₀ isomers, and the adsorption energies per H atom are obtained according to the following equation:

$$E_{\text{ads}} = [E(x\text{H}_2/\text{Ru}_{10}(n,m)/\text{MO}_2) - E(\text{Ru}_{10}(n,m)/\text{MO}_2) - xE(\text{H}_2)]/2x \quad (x=1\sim 15) \quad (6)$$

The most stable configurations on Ru₁₀/TiO₂ exhibit adsorption energies per H atom around -0.58 ~ -0.52 eV, see Table 3 and Figures 4 (a) and (b). With respect to a single H atom on the same Ru₁₀(6,4)/TiO₂ cluster (E_{ads} -0.66 eV, Table 2), there is a modest reduction of the adsorption energy, an effect that will be relevant for the following discussion.

On Ru₁₀/ZrO₂ the most stable configurations show an adsorption energy per atom of -0.44 eV, Table 3 and Figures 4(c) and(d). Here, the reduction of the average adsorption energy compared to the case of a single H adsorption, $E_{\text{ads}} = -0.48$ eV, is negligible.

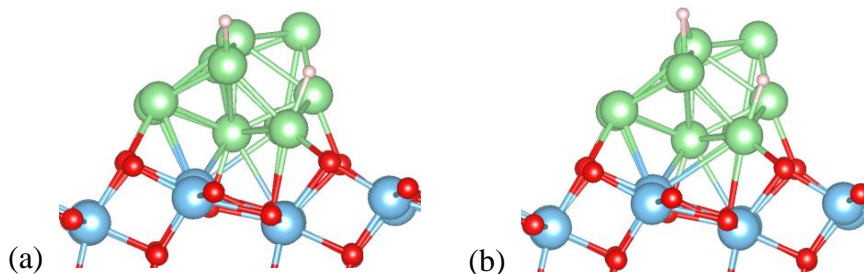
Table 3. Adsorption energy per H atom, $E_{\text{ads}/\text{H}}$, (in eV) and Bader charges, q , of Ru, H, and oxides (in $|e|$) for a H_2 molecule dissociatively adsorbed on $\text{Ru}_{10}/\text{a-TiO}_2$ and $\text{Ru}_{10}/\text{t-ZrO}_2$ (101) surfaces. The associated structures are shown in Figure 4.

System	Fig.	Adsorption site	$E_{\text{ads}/\text{H}}$ (eV)	$q(\text{Ru}), e $	$q(\text{H}), e $	$q(\text{MO}_2), e $
$2\text{H}/\text{Ru}_{10}(6,4)/\text{TiO}_2$	4(a)	$\text{Ru}_{\text{top}} + \text{Ru}_{\text{top}}$	-0.58	+1.77	-0.41	-1.36
$2\text{H}/\text{Ru}_{10}(6,4)/\text{TiO}_2$	4(b)	$\text{Ru}_{\text{top}} + \text{Ru}_{\text{bridge}}$	-0.52	+1.83	-0.44	-1.39
$1\text{H}/\text{Ru}_{10}(6,4)/\text{TiO}_2\text{-OH}^{\text{a}}$		$\text{Ru}_{\text{top}} + \text{O}_{2\text{c}}$	-0.29	+1.37	+0.73	-2.10
$1\text{H}/\text{Ru}_{10}(6,4)/\text{TiO}_2\text{-OH}^{\text{b}}$		$\text{Ru}_{\text{top}} + \text{O}_{2\text{c}}$	-0.25	+1.44	+0.73	-2.17
$2\text{H}/\text{Ru}_{10}(7,3)/\text{ZrO}_2$	4(c)	$\text{Ru}_{\text{top}} + \text{Ru}_{\text{bridge}}$	-0.44	+0.68	-0.49	-0.19
$2\text{H}/\text{Ru}_{10}(7,3)/\text{ZrO}_2$	4(d)	$\text{Ru}_{\text{top}} + \text{Ru}_{\text{top}}$	-0.44	+0.70	-0.46	-0.23
$2\text{H}/\text{Ru}_{10}(7,3)/\text{ZrO}_2$		$\text{Ru}_{\text{bridge}} + \text{Ru}_{\text{bridge}}$	-0.26	+0.85	-0.54	-0.30
$1\text{H}/\text{Ru}_{10}(7,3)/\text{ZrO}_2\text{-OH}$		$\text{Ru}_{\text{top}} + \text{O}_{3\text{c}}$	-0.06	+0.15	+0.74	-0.90

^a One excess electron delocalizes on Ti atoms

^b One excess electron localizes on one $\text{Ti}_{6\text{c}}$ atom

From an electronic point of view the addition of two H atoms to the cluster instead of one does not change the general picture. In particular, the H atoms remain negatively charged and oxidize the metal particle, Table 3, and, most important, there is no sign of an electron transfer from the metal cluster to the oxide by adsorption of a pair of H atoms. To summarize, we can conclude that the role of the supported metal nanoparticle is essentially that to adsorb and split the H_2 molecule with a non-activated and thermodynamically favourable process.



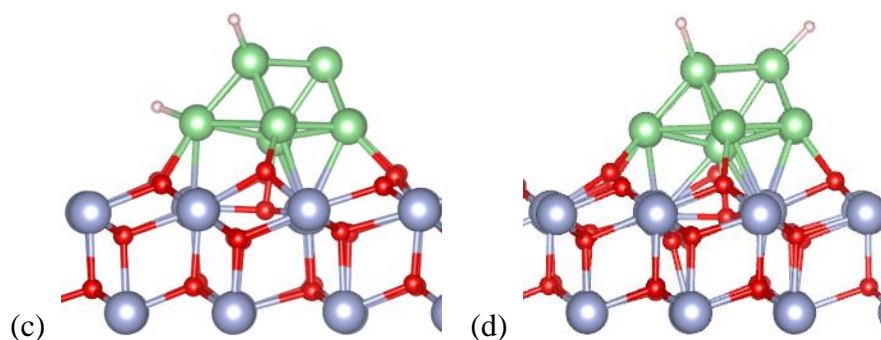


Figure 4. Structures of a H₂ molecule dissociatively adsorbed on different active sites of Ru₁₀/TiO₂ (a and b), and Ru₁₀/ZrO₂ (101) surfaces (c and d). See also Table 3. Blue: Ti; violet: Zr; red: O; green: Ru; white: H.

Hydrogen spillover on Ru₁₀/TiO₂ and Ru₁₀/ZrO₂

In this section we consider a case where, after an H₂ molecule has been dissociatively adsorbed on the Ru₁₀ supported cluster, one H atom remains on the metal cluster (top of a Ru atom) while the second one is displaced to a surface O_{2c} (TiO₂) or O_{3c} (ZrO₂) atom. This is the simplest model of H spillover and the comparison with the previous results can provide indications about (1) the energetic of the process, and (2) the electronic changes accompanying the spillover of hydrogen to the surface.

In both TiO₂ and ZrO₂ the system with two H atoms adsorbed on the metal cluster is considerably more stable compared to the case where one H has migrated to the oxide (compare 2H/Ru₁₀/MO₂ with 1H/Ru₁₀/MO₂-OH in Table 3). In particular, $E_{\text{ads/H}}$ goes from -0.58 eV to -0.29 eV on TiO₂ and from -0.44 eV to -0.06 eV on ZrO₂, reflecting the unfavourable binding to O compared to Ru. The displacement of the H atom from Ru₁₀ to the TiO₂ or ZrO₂ surfaces is accompanied by an electron transfer and by the consequent reduction of the surface. On TiO₂, by displacing the H atom the charge on the oxide goes from -1.36 |e| to -2.10 |e| with a $\Delta q = -0.74$ |e|; on ZrO₂ the charge goes from -0.19 |e| to -0.90 |e| with $\Delta q = -0.71$ |e|, Table 3. This confirms that the diffusing species is an H atom and not a proton (in this latter case the extra electron would remain on the metal cluster). For TiO₂, we also observe that the extra electron localizes on a Ti_{6c} atom near the OH group; the delocalized solution is very close in energy (Table 3).

Multiple adsorption of H₂ molecules on Ru₁₀/TiO₂ and Ru₁₀/ZrO₂

In the previous sections we have shown that direct spontaneous spillover of hydrogen from the metal to the oxide does not occur, at least for low hydrogen coverage where the relative energy state

for hydrogen on the metal is lower than for hydrogen on the oxide. However, the energy states available for hydrogen will depend on the degree of saturation (or substrate coverage) which, in turns, depends on the hydrogen partial pressure.

At high hydrogen exposure the supported particle can adsorb hydrogen until saturation is reached. At that point, hydrogen will spillover to the oxide. Metal particles can adsorb large quantities of hydrogen before to reach saturation. Calculations performed on a gas-phase Pt_6 cluster have shown that the average dissociative chemisorption energy of H_2 decreases regularly by adding more molecules to the cluster, but after addition of 13 H_2 molecules the cluster can still adsorb hydrogen and is not saturated.⁷⁶ In a similar recent study, it was shown that a Pd_4 cluster can adsorb up to 9 H_2 molecules. When supported on a graphitic support, the spillover from Pd_4 to the support is thermodynamically favourable after the catalyst has adsorbed 12 H atoms, i.e. 3 H atoms per metal atom in the cluster.⁷⁷ Assuming a similar hydrogen adsorption capability of Ru as for Pd, we can expect that H spillover can occur on our $\text{Ru}_{10}/\text{TiO}_2$ and $\text{Ru}_{10}/\text{ZrO}_2$ systems only after about 30 hydrogen atoms have been adsorbed on the catalyst. Notice however that for other metals, e.g. Pt, it has been suggested that a Pt/H ratio 1:4 is necessary to reach saturation.⁷⁶

We have tested the adsorption capability of $\text{Ru}_{10}/\text{TiO}_2$ by adding an increasing number of H atoms, Table 4 and Fig. 5. Of course, by adding increasing amounts of hydrogen the structure of the cluster changes and a large number of isomers exists in principle. This has been shown in a careful study of Pt clusters supported on $\gamma\text{-Al}_2\text{O}_3$. Using a combination of X-ray adsorption near edge structure (XANES) and DFT Molecular Dynamics simulations it has been possible to show that the Pt cluster undergoes substantial reconstruction by increasing the hydrogen coverage.^{78,79} Here, while we considered a few possible structures, we did not attempt a complete search of the optimal structure. The various isomers have been constructed following some guiding principles. Hydrogen has been preferentially added on the second layer of the Ru_{10} cluster as these sites appeared to be preferred with respect to adsorption at interface Ru atoms. Once the top Ru layer has been saturated, hydrogen has been added also to the interface Ru atoms. Formation of hydride structures, with H atoms inside the Ru_{10} cluster, has also been considered for zirconia but resulted in less stable configurations or in the spontaneous displacement of hydrogen towards the surface of the cluster. In general, we found that the general trends are similar for different Ru structures and, in particular, the average hydrogen adsorption energy is similar for different Ru_{10} isomers.

We start from a single H atom. As discussed above, H is bound to $\text{Ru}_{10}(6,4)/\text{TiO}_2$ with $E_{\text{ads}} = -0.66$ eV, Table 2; if H is displaced to an O atom of the oxide surface the system becomes unbound (with respect to H_2) by +0.07 eV, Table 1. The adsorption of two H atoms, one on the cluster and one on the oxide, leads to a reduced $E_{\text{ads}/\text{H}} = -0.58$ eV/atom, Table 3, i.e. 0.08 eV smaller than for the case of single H adsorption. Next we added 12 H atoms. The total energy release is much lower

than in the previous cases; $E_{\text{ads}/\text{H}}$ becomes -0.37 eV/atom, about 0.2 eV/atom smaller than for 2H atoms adsorption, Table 4. Once 12 H atoms have been added, the displacement of one H atom from Ru to the oxide is still unfavorable by 0.54 eV, Table 4. With respect to the displacement of a single H atom from the cluster to the oxide (see Table 1 and 2) the thermodynamic energy cost is decreased by 0.35 eV. With 16 H atoms the average adsorption energy when the Ru particle is involved is 0.39 eV/atom; the displacement of one H to the oxide has a cost of 0.4 eV, Table 4. Next we have considered the addition of 24 H atoms to $\text{Ru}_{10}/\text{TiO}_2$. Also in this case we have considered different Ru_{10} structures but the final value of $E_{\text{ads}/\text{H}}$ is very similar, about -0.3 eV/atom, Table 4. Thus, there is a slow but not monotone decrease in adsorption energy as the amount of hydrogen increases, Fig. 5. Also in this case we have considered the displacement of an H atom from the Ru_{10} cluster to the TiO_2 surface and we found that the energy cost for the spillover has reduced to 0.13 eV only, Table 4. Thus, even after addition of 24 H atoms on Ru_{10} direct spillover is not spontaneous. The turnover occurs when we adsorb 30 H atoms. $E_{\text{ads}/\text{H}}$ is still negative, -0.29 eV/atom. However, the structure where all the H atoms are adsorbed on the metal particle is 0.23 eV less stable than that where an OH group has been formed, see Table 4 and Fig. 5. These results clearly show that H spillover becomes thermodynamically favourable only at high H loading, when around 3 H atoms adsorbed for Ru atom in the cluster.

We also tried to estimate the barrier for diffusion of one H atom from the Ru_{10} cluster to the TiO_2 surface. To this end we have considered one H atom bound to the bottom layer of Ru_{10} in the $30\text{H}/\text{Ru}_{10}/\text{TiO}_2$ structure. Using the Nudged elastic band (NEB) method⁸⁰ we have calculated the barrier for diffusion of this atom from the supported metal cluster to the TiO_2 surface, where it forms a surface OH group. The final structure is 0.23 eV more stable than the initial one (see above), and the barrier is 0.4 eV (see Fig. S2 in the Supporting Information). This relatively low barrier is consistent with the occurrence of hydrogen spillover at the operating temperatures of real catalytic processes.

We notice that by increasing the hydrogen coverage, not all the H_2 molecules are fully dissociated. Taking 1.2 Å as criterion for complete H-H dissociation, we found that for the highest coverage about one half of the adsorbed molecules are still in an activated molecular adsorption form (see Table S1 in the Supporting Information).

In terms of electronic properties, we notice that the subsequent addition of H on the Ru_{10} cluster on TiO_2 has two effects: (1) the H atoms bound to Ru have hydride character and lead to a the partial oxidation of the metal particle; (2) the cluster magnetic moment is progressively quenched by the addition of H until, for the 30 H atoms case a zero magnetic moment is reached.

Table 4. Adsorption energy, E_{ads} , (in eV); adsorption energy per H atom, $E_{\text{ads}/\text{H}}$, (in eV); Bader

charge, q , of Ru, H, and oxides (in $|e|$) for multiple H atom adsorption on Ru₁₀/a-TiO₂ and Ru₁₀/t-ZrO₂ (101) surfaces.

System	E_{ads} (eV)	$E_{\text{ads/H}}$ (eV)	$q(\text{Ru}), e $	$q(\text{H}), e $	$q(\text{MO}_2), e $
12H/Ru ₁₀ (6,4)/TiO ₂	-4.40	-0.37	+3.09	-1.76	-1.33
11H/Ru ₁₀ (6,4)/TiO ₂ -OH	-3.86	-0.32	+2.82	-0.70	-2.12
16H/Ru ₁₀ (5,5)/TiO ₂	-6.19	-0.39	+3.13	-1.95	-1.18
15H/Ru ₁₀ (5,5)/TiO ₂ -OH	-5.79	-0.36	+2.99	-1.02	-1.97
24H/Ru ₁₀ (6,4)/TiO ₂	-7.27	-0.30	+3.26	-2.52	-0.74
23H/Ru ₁₀ (6,4)/TiO ₂ -OH	-7.14	-0.30	+3.16	-1.52	-1.64
30H/Ru ₁₀ (5,5)/TiO ₂	-8.72	-0.29	+3.42	-2.47	-0.95
29H/Ru ₁₀ (5,5)/TiO ₂ -OH	-8.95	-0.30	+3.54	-2.12	-1.42
12H/Ru ₁₀ (7,3)/ZrO ₂	-5.23	-0.44	+2.88	-2.97	+0.10
11H/Ru ₁₀ (7,3)/ZrO ₂ -OH	-3.87	-0.32	+2.06	-1.48	-0.58
16H/Ru ₁₀ (7,3)/ZrO ₂	-5.99	-0.37	+2.31	-2.28	-0.03
15H/Ru ₁₀ (7,3)/ZrO ₂ -OH	-5.20	-0.33	+2.20	-1.56	-0.65
24H/Ru ₁₀ (7,3)/ZrO ₂	-9.10	-0.38	+3.14	-3.23	+0.09
23H/Ru ₁₀ (7,3)/ZrO ₂ -OH	-9.38	-0.39	+2.87	-2.34	-0.53
30H/Ru ₁₀ (7,3)/ZrO ₂	-9.38	-0.31	+3.23	-3.49	+0.26
29H/Ru ₁₀ (7,3)/ZrO ₂ -OH	-9.49	-0.32	+3.02	-2.58	-0.44

At low loading of hydrogen, Ru₁₀(7,3)/ZrO₂ displays a rather different behaviour compared to what reported for titania. In particular, we observe almost no decrease in adsorption energy passing from 2 to 12 H. Also at loadings of 16 H and 24 H, the adsorption energy per H atom remains close to -0.4 eV, Table 4. Saturation effects start to be visible at 30 H atoms, where the adsorption energy eventually decreases to -0.31 eV. A further decrease is observed for 40 H (-0.29 eV) and 45 H (-0.23 eV). The spillover cost remarkably decreases from 1.4 eV at 12 H to 0.8 eV at 16 H, and becomes thermodynamically favourable at 24 H coverage, Table 4. Also in this case the analysis of the Bader charges reveals that there is no relevant charge transfer to the oxide as long as all H atoms remain on the metal particle. H spillover, on the contrary, always implies a remarkable electron transfer to the surface.

The metal particle on zirconia is remarkably rigid compared to what observed on titania: no isomerization nor major distortion is observed up to H₃₀. This may be a key to understand the different behaviour of Ru₁₀ on the two considered supports. We also notice that H atoms prefer in general to stay adsorbed on the surface of the cluster, and only for high H coverage (> 30 H atoms) some atoms go inside the cluster and form a kind of hydride species. Differently from titania, on

Ru₁₀/ZrO₂ even at high coverage almost all the H₂ molecules are fully dissociated. For the highest loading we find at most two-three molecules in molecular adsorption form (see Table S1 in the Supporting Information).

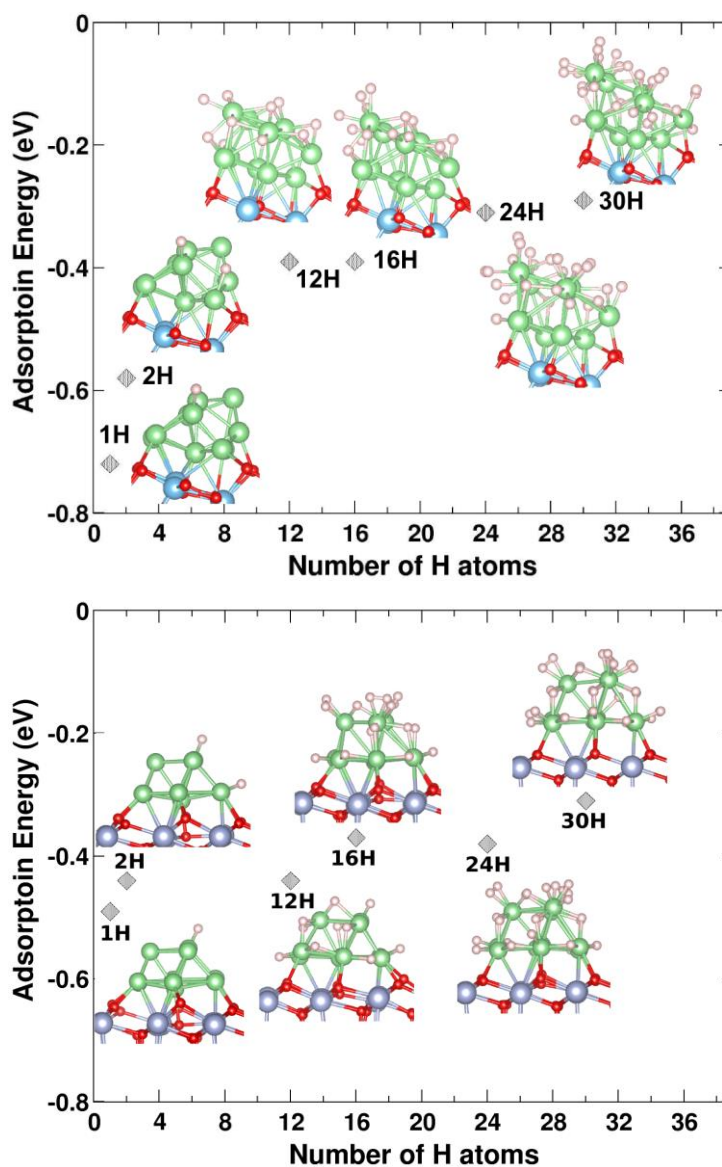


Figure 5. Calculated average adsorption energy per H atom against number of H atoms on Ru₁₀/TiO₂ (top) and Ru₁₀/ZrO₂ (bottom). The structure of the hydrogenated clusters is shown in the insets.

The results reported above show that only at high partial pressures hydrogen can spillover from the cluster and diffuse to the oxide surface. The results also show that the migration of H is

accompanied by the reduction of the oxide. The evidence of the reduction comes from the analysis of the Bader charges (the negative charge on the oxide increases as a consequence of the spillover); in some cases we have also been able to observe the formation of Ti^{3+} or Zr^{3+} species. Also in this case, at high hydrogen coverage, we notice that the H displacement is accompanied by a regular increase of the negative charge on the oxide, an effect which is basically independent of the total hydrogen coverage. In particular, the negative charge on the $\text{Ru}_{10}/\text{TiO}_2$ clusters is $\Delta q = -0.79 |e|$ (12H atoms), $\Delta q = -0.79 |e|$ (16H atoms), $\Delta q = -0.90 |e|$ (24H atoms), $\Delta q = -0.47 |e|$ (30H atoms), Table 4. A similar trend is found for ZrO_2 , see Table 4.

One should mention at this point that we considered in our models fully dehydroxylated titania and zirconia surfaces. Under working catalytic conditions the surface can become hydroxylated and the process of hydrogen spillover can be affected by the level of hydroxylation of the surface.^{81,82}

In principle, another reduction mechanism is also possible. At high hydrogen partial pressure, when the metal particle is covered by hydrogen, O atoms from the surface can diffuse to the metal (O reverse spillover). Oxygen can react with hydrogen and form water, that can then leave the surface. The process results in the removal of O from the oxide and in the release of water, facilitated by the presence of hydrogen. This provides another channel for the chemical reduction of the oxide indirectly related to the addition of hydrogen. We have considered this mechanism for two systems: $12\text{H}/\text{Ru}_{10}/\text{TiO}_2$ and $30\text{H}/\text{Ru}_{10}/\text{TiO}_2$. In both cases, the desorption of a H_2O molecule with formation of an O vacancy on the surface of the oxide is an uphill process, unfavorable by 1.9 eV. Even considering entropic effects, it is unlikely that the process will take place. Since the O vacancy formation energy is higher in ZrO_2 than in TiO_2 , this conclusion applies to zirconia as well.

4. Conclusions

In this study we have considered the energetic of adsorption, dissociation, and migration of hydrogen on models of Ru nanoparticles supported on titania and zirconia surfaces. We have found, in agreement with previous studies, that neither TiO_2 nor ZrO_2 surfaces are able to split H_2 . On titania the cost is rather small, 0.07 eV, while on zirconia it is considerably higher, 0.79 eV. This is due to the fact that the formation of an hydroxyl group is accompanied by a transfer of the H valence electron to a Ti 3d or Zr 4d empty state at the bottom of the oxide conduction band. Since the conduction band in ZrO_2 is considerably higher than on TiO_2 , the process is energetically less favorable. The presence of a Ru nanoparticle has no effect on the H adsorption properties of TiO_2 (both the adsorption energy and charge distribution are essentially unaffected) while it has some effect on ZrO_2 . Here in fact once the OH group is formed, the excess charge goes preferentially at the metal/oxide interface, lowering the cost for the dissociative adsorption.

Adsorption of H on the O sites of the surfaces is not competitive with adsorption on the metal nanoparticle. H adsorbs on Ru₁₀, preferentially on top of Ru atoms, forming a strong Ru-H bond with hydride character. The interaction is such that spontaneous non-activated dissociation of an H₂ molecule occurs on the Ru cluster which has the effect to split hydrogen and to bind a large amount of H atoms.

Therefore, the adsorption of an H atom on the surface of TiO₂ or ZrO₂ is endothermic if one takes as a reference the H₂ molecule. It is exothermic if it is referred to an H atom. The role of the Ru₁₀ cluster is to split the H₂ molecule in a barrierless process and to generate isolated H atoms that can diffuse to the oxide surface once saturation coverage on the cluster has been reached.

Direct spillover from the metal particle to the oxide surface is not favorable at low hydrogen coverage. For the hypothetical case of the dissociation of a single H₂ molecule on the Ru cluster, with one H atom that remains bound to the metal and the other one that diffuses to the oxide, the cost is of about 0.3~0.4 eV, Table 3. This cost, however, decreases gradually as more hydrogen is adsorbed on the metal cluster. At a coverage of 30 H atoms on Ru₁₀/TiO₂ i.e. a Ru:H ratio of 1:3, it becomes thermodynamically favorable to move one H from the metal to the oxide. On zirconia the effects appears already for a coverage of 24 H atoms. In this study we did not consider in detail the kinetic aspects of the problem. However, we estimated the cost of the diffusion of the H atom from the metal particle to the TiO₂ surface and we found a process where this barrier is of 0.4 eV. Since many other paths are possible, this value represents an overestimate. Previous detailed studies on hydrogen diffusion on the anatase TiO₂ (101) surface have shown that hydrogen preferentially diffuses into the bulk compared to the surface, and that the smallest barrier for surface-to-bulk diffusion is of about 0.7 eV.⁷¹ A higher barrier, 1.4 eV, has been found for diffusion on the surface. These barriers, in particular the second one, are larger than that required to diffuse an H atom from the Ru cluster to the oxide surface. In this case, the kinetic of the process would be dominated by H surface diffusion and not by metal/oxide interface diffusion. Further work is planned to specifically address this point and to extend the analysis also to ZrO₂.

From an electronic point of view, the addition of one H atom to TiO₂ or ZrO₂ leads to the reduction of the oxides with formation of localized Ti³⁺ 3d¹ and Zr³⁺ 4d¹ centers. We have been able to find localized solutions for these systems. In the presence of a deposited metal particle the tendency to localize the charge on a single transition metal atom is more pronounced for TiO₂ than for ZrO₂ surfaces. This, however, is a delicate issue where the results clearly depend on the DFT+U approach (using an hybrid functional approach or a larger U parameter could produce slightly different results). However, the occurrence of a chemical reduction of the oxide by hydrogen addition of by hydrogen spillover is clearly shown by the net atomic charges. In particular, when an H atom migrates from the Ru₁₀ particle to the TiO₂ or ZrO₂ surfaces the nuclear motion is

accompanied by an electronic redistribution which results in charge flow from the metal to the oxide. Other potential reduction mechanisms, like the reaction of hydrogen with surface oxygen to form water that desorbs leaving behind an oxygen vacancy does not seem to be competitive with the hydrogen spillover mechanism.

These theoretical results shed light on the atomistic mechanism of hydrogen spillover and are fully consistent with experimental observations. For instance, in a study of hydrogen spillover over Au/TiO₂ Panayotov and Yates⁸³ demonstrated that the rate of the spillover process is proportional to $P_{\text{H}_2}^{1/2}$, indicating that the mobile H atoms originate from the equilibrium dissociative adsorption of adsorbed H₂ on the Au particle (the main difference is that a barrier of 0.5 eV has been found for H₂ dissociation on the supported Au particles, while the reaction is barrierless on Ru₁₀). In the experiment, the diffusion of H atoms into the oxide is accompanied by the formation of trapped electrons in shallow trap states near the bottom of the conduction band edge. All these features are in line with the computational results presented in this study which provides therefore a microscopic view of this complex phenomenon.

ASSOCIATED CONTENT

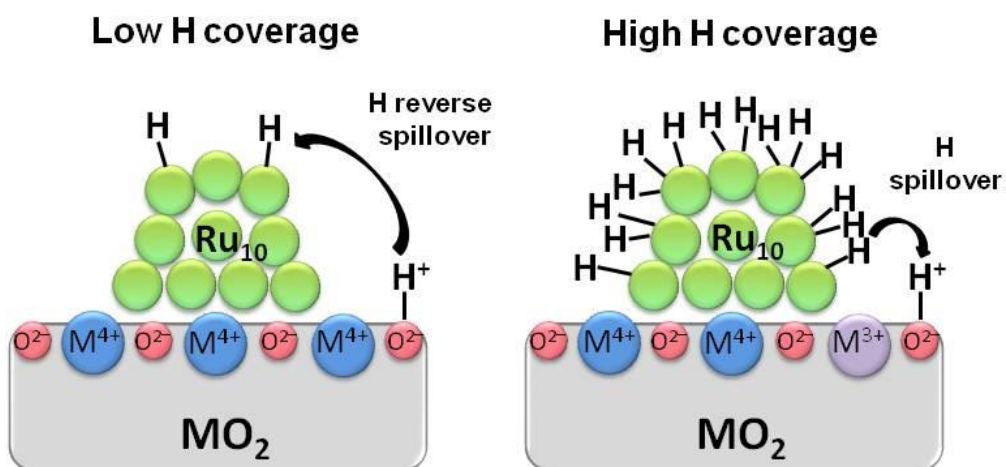
Supporting Information

Supporting Information Available: further analysis on the dissociation of H₂ at high loading and coordinates of a few representative structures. This material is available free of charge via the Internet at <http://pubs.acs.org>

Acknowledgments

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Table of content graphics



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