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Review

Electron-count control on adsorption upon reducible and irreducible clean metal-oxide surfaces

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Abstract

Two major chemical processes, acidobasic and redox, monitor the adsorption mechanism on metal oxides. Cations and anions of surfaces can be described as acid–base pairs. Thus, electron-rich molecules (Lewis bases) or anionic fragments formally arising from a heterolytic bond cleavage of molecule interact on the metal M^{n+}, while electron-poor ones (Lewis acids) interact on the oxygen one O^{2-}. In these cases, the electronic structure, insulating for the stoichiometric surface, is preserved upon adsorption.

When the initial system does not favor an energy gap (open-shell adsorbates, defective surfaces), the best adsorption mode implies a redox mechanism and restores the situation of an insulator. In the case of open-shell adsorbates, an electron transfer to or from the oxide is a possible solution. The electron transfer occurs from the substrate to the adsorbate for an electronegative group (Cl adsorption on M^{n+}) or the other way round for an electropositive one (NO adsorption on O). The reactivity at surfaces deviating from stoichiometric differs from that on the perfect ones, since the electron count is different.

We will illustrate the previous concepts by the study of these adsorption processes on MgO and TiO_2 surfaces.

Keywords: MgO; TiO_2; Adsorption

1. Introduction

Despite many experimental and theoretical studies [1–5], many surface properties of the metal oxides are still poorly understood [6]. Metal-oxide surfaces react with gases or solutions; they behave as catalyst or support for catalyst. The challenge is to understand the factors controlling the adsorption and the reactivity of the moieties adsorbed on the surface.

Three major features control the behavior of metal-oxide surfaces. First, coordination plays an important role and sites of low coordination are in general more reactive than sites of high coordination [5,7]. A second point is the acid–base properties. Clean and anhydrous metal-oxide surfaces present two different active sites, cations and anions, which determine reactivity towards gas-phase adsorbates. Thus, electron-rich molecules (Lewis bases) will interact at the cationic site and electron-poor ones (Lewis acids) will interact at the anionic site [7–9]. Besides coordination and acid–base reactions, the redox mechanism also seems to be crucial in some adsorption processes [5]. When the oxide deviates from the stoichiometry due to the presence of defects such as vacancies or adatoms, the oxidation state of the surface atoms varies and the electron count is determining to control the adsorption. We will illustrate these aspects by using the examples of MgO and TiO_2 (or V_2O_5), which are known to behave differently when a redox mechanism is involved. This is due to the fact that the former contains an irreducible metal whereas the latter is reducible, although both of them are in their higher oxidation state.

As a general rule, the adsorption process of closed-shell adsorbates on stoichiometric perfect surfaces takes place through an acid–base mechanism. The adsorption of closed-shell adsorbates usually takes place on the metal sites, and metal-oxide surfaces are predominantly acidic surfaces. This is the case when organic molecules are adsorbed without dissociation [7,10,11]. If dissociative adsorption follows a heterolytic cleavage of the adsorbate, the same principle is valid, and the cationic fragment will adsorb on the surface oxygen atom, while the anionic fragment will bind to the metal site.

When an open-shell adsorbate is involved, the initial electron count of the surface is no longer maintained. A first solution is to couple the electrons and to form two opposite ions adsorbed on the two surface sites, as for H_2/MgO, in-

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volving an acid–base mechanism. Another possibility of adsorbing radicals is via an electron transfer to or from the oxide (redox mechanism). When the adsorbate is an electropositive group (donor-like adsorbate such as NO), the unpaired electron can be transferred to a reducible metal cation of the metal oxide. When the radical is an electronegative atom (acceptor-like adsorbate such as Cl), it can capture an electron from the metal oxide provided that the substrate is in a reduced form. Then, the first adsorption would correspond to a Lewis acid (such as NO^+) on the oxygen atom, and the second one becomes that of a Lewis base (such as Cl^-) on the metal atom. In both cases, the heat of adsorption may be analyzed as the sum of two terms: an electron transfer and the adsorption of the fragment.

When defects are responsible for a deviation from the stoichiometry, the electron count does not correspond to an insulator. All the atoms are not in their highest oxidation state. In cases of oxygen vacancies, the metal oxide is reduced, some electrons filling the bottom of the conduction band or levels in the gap. In cases of oxidation (O adatoms), the valence band is not completely filled. The most favorable adsorption scheme is the redox mechanism which restores the situation of an insulator and the highest oxidation states for all the atoms.

We will comment these different points in this paper with a special emphasize on the basic properties of the surfaces. We will focus on the electron count that monitors the stability of the clean and defective systems. The same count allows the possibility of redox reactions on surfaces. Reconstructions, stabilizing the clean surfaces or allowing a better match between the adsorbate and the substrate under adsorption can strongly influence the adsorption modes.

Finally, we should note that the reaction media play an important role in adsorption processes. Clean surfaces exist in dry conditions when the surface is exposed at low pressure of gases. In hydrated conditions, when the metal-oxide surface is covered by water, the surface sites are not available for other molecules. As a consequence, either the adsorption is strong enough to imply the desorption of the water molecules that are directly bound to the clean surface or it happens directly upon these groups through H-bonds.

1.1. Two representative metal oxides: MgO and TiO_2

MgO and TiO_2 are two of the most representative metal oxides. In their structure, metal atoms are in their highest oxidation state, although they present different redox properties, and this will govern their behavior. The most stable surfaces of these compounds are displayed in Fig. 1.

Most often, MgO is chosen as representative for the metal oxides. The bulk possesses a rock-salt structure with an alternation of ions with opposite charges [1,12]. It is an ionic oxide whose metal cation is very electropositive. The (1 0 0) surface is stable, non-polar, classified of type I according to Tasker [13]. The clean surface is easy to prepare with well

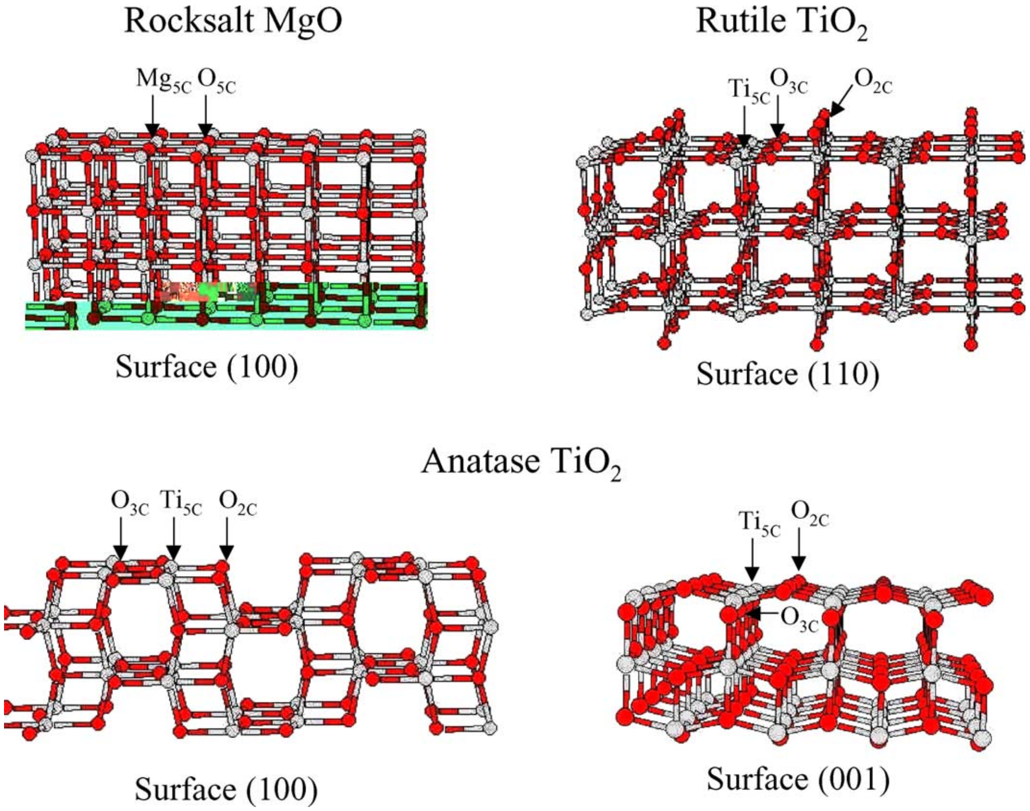

Fig. 1. The most frequent stable surfaces for MgO and TiO_2. Cations are represented by grey spheres and O^{2-} anions by dark spheres.

defined stoichiometry [14], and it does not undergo large relaxations. It is an irreducible oxide and oxygen vacancies leave electrons trapped in the vacancy (a pair or a single electron for the F or F^+ center, respectively) [15–19]. The oxygen vacancies are of great importance for the properties and chemical reactivity of MgO [20]. A lot of experimental and theoretical studies have been devoted to the surface anion vacancies with trapped electrons [21–25]. Despite the fundamental role of this defect, its control is still a challenge.

TiO_2 is becoming of great interest for electrocatalysis, sensor technology, microelectronic devices and many other technological applications [2,26–29]. The most stable TiO_2 structure is rutile. The rutile $TiO_2(1\,1\,0)$ surface is one of the most important surface models for the metal oxide. The perfect surface has been extensively studied (see for instance Refs. [3,4,11,30–33]). This structure is made of alternative horizontal and vertical polymers [34], and is classified of type II according to Tasker [13]. This surface is at the same time reactive and stable [11,32,33]. The reconstruction is weak and restricted to a small relaxation and rumpling of the bridging oxygen atoms [31,35]. The reduction of the surface mainly consists of bridging oxygen vacancies. From the experimental point of view, it is easy to control the degree of reduction of these materials, as for rutile $SnO_2(1\,1\,0)$ [36].

Though more difficult to grow, anatase particles are also used in industry for their high catalytic activity [37,38]. The natural crystallographic faces are the (1 0 1) and (0 0 1) [39–41]. The (0 0 1) and (1 0 0) faces are also often considered when anatase is a support because of their good match with active catalysts [42,43]. Unfortunately, there is a lack of information on anatase systems, in particular, concerning the reducibility of its surfaces.

Compared with MgO, TiO_2 has potentially a richer reactivity toward various adsorbates. TiO_2 is more acid since the charge of the titanium cation, 4+, is twice that of the magnesium cation, 2+. In the bulk structures, each O^{2-} ion has three neighbors for TiO_2 compared with six for MgO; therefore, the O^{2-} ions are less stabilized by their first neighbors in TiO_2. The same applies for the surfaces, where each outmost O^{2-} ion has two neighbors in $TiO_2(1\,1\,0)$-rutile instead of five in MgO(1 0 0). TiO_2 is therefore also more basic than MgO. Altogether the heats of adsorption on clean and perfect TiO_2 surfaces are always larger than that on the corresponding MgO surface. Let us note that comparing the scales of the heats of adsorptions in a series of adsorbates necessitates a finer approach: relative scales require considering the hard and soft acids and bases concepts [44,45] and will be briefly discussed in Section 2.

At variance to Mg (MgO), Ti (TiO_2) is reducible. Ti^{4+} can be reduced to Ti^{3+} or Ti^{2+}. The removal of a neutral O atom has been shown to result in two unpaired electrons on the five-fold-coordinated Ti neighboring to the vacancy [46] instead of localizing them at the center of the vacancy as for MgO. Then an adsorption process can be coupled with an electron transfer. SnO_2 [47] and V_2O_5 are very similar to TiO_2, Sn^{4+} being able to be reduced to Sn^{2+} [36,48,49] or V^{5+} to V^{4+} [38,50]. They could also illustrate this possibility of redox mechanism modifying the adsorption scheme occurring on reducible oxides.

2. The acid–base mechanism

Molecular and dissociative adsorption can be understood as acid–base processes. This is the usual behavior of the adsorption process. We recall that acid–base reactions associated with frontier–orbital interactions also preserve the gap: the adsorption of a base shifts the conduction band up and the adsorption of an acid shifts the valence band down. In this section, we first consider ideal, perfect, stoichiometric and clean surfaces for which the gap of stoichiometric oxide bulks is maintained.

Molecules adsorbing without dissociation always bind to one or several metal cations [7,10,11,33,51–53]. We will show an example starting by a typical basic molecule, NH_3, and commenting next molecules whose basicity is less pronounced, H_2O, CO, CO_2 and SO_2. Note that a fine analysis of the comparison of the relative heats of adsorption in different metal oxides requires the concepts of the hard and soft acids bases. For the adsorption with dissociation, the fragments of the adsorbate adsorb each one on one site following the acid–base mechanism described before. The case of water and organic acids is discussed.

2.1. Molecular adsorption on the perfect surfaces

The MgO and TiO_2 surfaces clearly appear to be predominantly acidic. When the molecules are adsorbed without dissociation on a single site, they are always adsorbed on the metal cations. The larger the gas-phase adsorbate proton affinity is, the larger the heat of adsorption will be. Strong bases such as NH_3 adsorb on the metal cation of the surface with the lone pair oriented toward the metal [54–56]; the deviation from normality to favor a H-bond as secondary interaction is slightly destabilizing [57]. NH_3 is the usual probe for the acidic sites [58–60]; it is a hard base that strongly binds to Ti^{4+} in TiO_2. A similar adsorption also takes place on top of Mg^{2+}, but the heat of adsorption is weaker [7,33] by a factor 7 (see Section 2), since Mg is softer in the HSAB sense than Ti.

Water is adsorbed without dissociation on MgO(1 0 0); it is oriented roughly parallel to the surface to favor the frontier–orbital interaction between the surface metal and the *p* pair of the molecule, and also to benefit from H-bonds. At low coverage, these hydrogen bonds are made with the O atoms from the surface. At high coverage, they are formed between the adjacent adsorbed molecules forming a 2D net (a 2D ice layer) [33,61,62] and corresponds to a different orientation of the water molecule. The adsorption is stronger and is dissociative on clean anhydrous $TiO_2(1\,1\,0)$-rutile surface [34,63].

At small coverage, CO is also adsorbed C-down on top of the metallic center though it is not usually considered as a base [64–68]. The orientation of the adsorption mode is due to a donation to the cationic site. The heat of adsorption increases when the metal is more electropositive (a stronger acidic site): it is larger on rutile $RuO_2(1\,1\,0)$, 1.2 eV, than on rutile $TiO_2(1\,1\,0)$, 0.3 eV, [69]. The back-donation that is predominant for the adsorption on pure metal surfaces is weak for that on the metal cations. The deviations from the direction normal to the surface observed at high coverage on MgO(1 0 0) are explained by lateral interactions between the adjacent COs [56,70].

CO_2 is frequently considered as an acidic species. Its adsorption on MgO has been used to qualify MgO as a basic surface. CRYSTAL calculations [71,72] for the CO_2 adsorption on the naked surfaces show that CO_2 must be considered as a basic species and MgO as an acidic surface since it binds to the exposed cations of the metal oxides [73,74]. On $TiO_2(1\,1\,0)$-rutile, at low coverage, CO_2 is perpendicular to the surface building a $OCO\cdots Ti$ bond. On MgO(1 0 0) CO_2 is flat and parallel to the surface bridging two adjacent Mg sites [61,74,75]; the adsorption mode involves the construction of two Mg–O bonds and the CO_2 molecule is a basic species from both O. The adsorption energies are nearly equal, 304 meV versus 273 meV, on MgO and TiO_2, respectively. Per metal-adsorbate bond, this means a factor 2 in favor of TiO_2. Compared with the NH_3 adsorption which presents a factor 7, the difference in the ratios is explained by the HSBA concepts. CO_2 is a softer and weaker base [33].

For SO_2 that is a poor base, the best adsorption mode on MgO, flat above the surface, involves three interactions [66,76–78]. The construction of two $Mg_{lattice}$–O_{SO_2} bonds is consistent with a predominance of the acidic property of the surface while the third interaction $O_{lattice}$–S_{SO_2} is associated with the opposite interaction. The hierarchy of the stability of the adsorption modes allows telling which the most important interaction is. We have calculated using the GGA approximation with the VASP program [79–82] three adsorption modes on a three-layers slab of MgO(1 0 0) (at $\theta = 1/2$). The best adsorption mode implies the three bonds (442 meV). A weaker heat of adsorption (173 meV) is found when SO_2 is in a vertical plane only bridging two Mg atoms (formation of two Mg–O bonds with a length of 2.77 Å). Forcing the sulfur to remain on top of surface oxygen does not lead to any adsorption.

2.2. Dissociative adsorption

Dissociation can take place via either a heterolytic cleavage or a hemolytic one. As stated above, the former involves an acid–base adsorption mechanism while the latter would need a redox process to restore the initial surface electron count. When a heterolytic dissociation occurs, the resulting negative ions (Lewis bases) adsorb on the surface metal cations, and the positive ions (Lewis acids) adsorb on the surface oxygen sites.

The basicity of the surface oxygen sites determines if this adsorption mode is preferred to the molecular adsorption. An example is the water adsorption: it dissociates on rutile $TiO_2(1\,1\,0)$ but it does not on MgO(1 0 0) due to the greater basicity of the former. On rutile $TiO_2(1\,1\,0)$, water dissociation generates singly coordinated surface hydroxyls (OH^- on Ti^{4+}) and di-coordinated surface hydroxyls (H^+ on O^{2-}). On MgO(1 0 0) surface the proton recombines with the adsorbed hydroxyl and forms water. This has been supported by CRYSTAL [33,34] and VASP [63] calculations even though it is still a matter of controversy.

Brønsted acids like organic alcohols ROH and carboxylic acids RCO_2H dissociate on a variety of oxides surfaces. The result is the protonation of the surface oxygen anions and the coordination of the conjugated base of the acid to the surface cations [5,83]. However this is not always the case, and alcohols are found to behave as Brønsted bases. Thus, in the gas phase, the basic cleavage $ROH \to R^+ + OH^-$ is easier than the acidic cleavage, $ROH \to H^+ + OR^-$. This determines the adsorption mode of methanol on the $TiO_2(1\,1\,0)$-rutile: ${CH_3}^+$ on O^{2-} and OH^- on Ti^{4+}, with bridging OCH_3 groups and terminal OH groups [7,10,84]. The same has been found for methanol adsorption on rutile $SnO_2(1\,1\,0)$ [85]. It is remarkable that the opposite orientation exists for the thio-compound MeSH [86]: H^+/O^{2-} and RS^-/Ti^{4+}. This compound is indeed more acidic and in the gas phase, the acidic cleavage $RSH \to H^+ + SR^-$ is the easiest [52,86–88]. H_2S can completely dissociate to S^{2-}/Ti^{4+} and H^+/O^{2-} [87,88].

The same features apply to carboxylic acids. ${RCO_2}^-$ groups from the dissociation of acids bind by one or two bonds to the metal cations [37,89–93]. The acidic cleavage, less favorable in the gas phase, generates ${RCO_2}^-$ binding to two surface cations and H^+ binding to a surface anion. The basic cleavage that is the best in the gas phase would lead to an OH^- adsorbed on the surface cation (terminal OH in case of the rutile structure) and to a RCO^+ that binds to the surface anion, O^{2-}, forming a singly coordinated ${RCO_2}^-$ groups [89]. The geometry of this species is not very favorable, even if a surface metal site is available close by, since it involves a lattice oxygen as well as the carboxylic oxygen. Thus the singly coordinated ${RCO_2}^-$ is less favorable than the di-coordinated species.

To sum up, for clean stoichiometric surfaces and closed-shell adsorbates the acid–base mechanism governs the adsorption processes. TiO_2 show more acid and more basic sites than MgO. The difference in behavior for these two materials arises also from the electronic structure: frontier–orbitals are closer in TiO_2, and in fact it is a semiconductor whereas MgO is a typical insulator.

3. The redox mechanism

This process is generally not the best for perfect surfaces of the metal oxides in the highest oxidation state, as shown previously. The adsorption of radicals or the presence of surface defects, such as oxygen vacancies or adatoms, induce in general a loss of stability because the initial energy gap is not preserved. On perfect surfaces, the redox adsorption mode may however occur when the metal of the oxide is reducible. When the surfaces are reduced or oxidized, the redox mechanism that recovers the energy gap may become very favorable.

3.1. Adsorption of radicals

Radicals are incompatible with an electron count maintaining an energy gap for the stoichiometric oxide. A first solution is to couple the electrons and form two opposite ions adsorbed on the two surface sites. Thus the adsorption modes can be more easily explained by referring to a heterolytic cleavage than to a homolytic cleavage of the molecule. An extreme example is the formal H_2 dissociation; the symmetry of the homodinuclear molecules is not favorable to a heterolytic cleavage. However, the adsorption on MgO(1 0 0) is that resulting from the formation of H^-/Mg^{2+} and H^+/O^{2-}. This mechanism implies acid–base relation and avoids the reduction of the substrate. In some way, the redox process has taken place before adsorption. Another example is the formal Cl_2 dissociation on rutile TiO_2(1 1 0), with formation of Cl^-/Ti^{4+} and Cl^+/O^{2-} [94].

Another possibility of adsorbing radical species is found through an electron transfer to or from the oxide (redox mechanism). When it is an electropositive group (donor-like adsorbate), the unpaired electron might be transferred to a metal cation of the surface, provided that this is possible: a reducible stoichiometric oxide or a pre-oxidized one. Then, the adsorption is that of a Lewis acid on the oxygen atom. When it is an electronegative group (acceptor-like adsorbate), it can capture an electron from the metal oxide provided that it is in a reduced form. Then, the adsorption becomes that of a Lewis base on the metal atom. In both cases, the heat of adsorption may be then analyzed as the sum of two terms: an electron transfer (to or from the adsorbate) and the adsorption of the fragment (acidic or basic).

3.1.1. Adsorption of Cl on perfect surfaces

The Cl atom is such an example of electronegative radical (acceptor-like adsorbate). The heat of adsorption for the Cl atom on the perfect surface is weak. The adsorption takes place at the metal center of rutile TiO_2(1 1 0). Indeed, an adsorption at the surface O^{2-} ion would require an electron transfer to the Ti atoms that is not favorable, since the difference in electronegativity of Cl and Ti is too large. Experiments show that on the stoichiometric surface, the adsorption takes place on the penta-coordinated Ti atoms [95], while on the reduced surface adsorption occurs preferentially at the O vacancy forming two Ti–Cl bonds [96–98]. Remarking that the O vacancy is associated with a two electron reduction, it is natural to foresee that the adsorption of two Cl atoms (formally one Cl_2 molecule) per O vacancy allows restoring the stoichiometry and the electron gap. According to our VASP calculations [94], the reduced surface is more reactive than the clean one. We will comment later that electronic effects often are not always so favorable and that defective surfaces may also be less reactive than the perfect ones.

3.1.2. Adsorption of H on perfect surfaces

The proton is the strongest acidic species. It is an example of electropositive (electron donor) species. This remarkable property allows some specific adsorption mode on the reducible oxides, where the H adsorption on the surface O^{2-} ions is accompanied by a reduction of the surface atom. We have already pointed out the case of irreducible oxides like MgO, where the solution is to stabilize two atomic H by coupling the electrons on one of them, exactly as if they were obtained from a heterolytic cleavage of a dihydrogen molecule. Thus, one of them (proton-like) is adsorbed on the O^{2-} ion and the other (hydride-like) is adsorbed on surface Mg^{2+} ions in MgO [99–101], or Zn^{2+} ions in ZnO [102,103].

On a reducible oxide, like TiO_2 or V_2O_5, a Ti^{4+} can be reduced to Ti^{3+} or Ti^{2+} (a V^{5+} to V^{4+}), the adsorption process being coupled with an electron transfer [104]. Then, all the H atoms are adsorbed on the O atoms [104–107]. The VASP calculations on rutile TiO_2(1 1 0) show that this mechanism is preferred by 1.1 eV [63]. This generates bridging surface hydroxyls (see Fig. 2). The surface is different from that obtained by hydration of clean surface where there are equivalent amounts of terminal and bridging OH groups. On the other hand, the hydration of a defective surface with O vacancies leads to the same surface but with another mechanism. Both surfaces are then reduced surfaces [6,63]. In the case of V_2O_5(0 0 1), upon exposure to a hydrogen environment no OH groups are observed, but a removal of a water molecule leading to the O defective surface instead [108].

Since the H atomic adsorption on reducible metal oxides is accompanied by a reduction, a further H adsorption on a reduced surface (hydrogenated or O defective) becomes more difficult, when it takes place again at the O site. It corresponds to a decrease in the adorption energy of 26% for rutile TiO_2(1 1 0).

3.1.3. Adsorption of NO and CO on terminal O^{2-} atoms

The interaction of NO and CO with metal oxides is found to be weak, as discussed in Section 2.1, and takes place on the metal site. However, it has been recently reported in the literature the presence of oxidized NO and CO species like nitrites, nitrates, CO_2 and carbonates, on rutile and anatase TiO_2 surfaces [109–111]. Their formation can only be explained by reaction of these molecules with oxygen atoms provided either by the reaction media or by the surface. The latter involves adsorption on surface oxygen atoms and in any case implies a redox mechanism. In order to occur, adsorption on a surface O atom requires the presence of very reactive O atoms. It takes place by oxidation of the adsorbate and reduction of the surface. These reactive oxygen

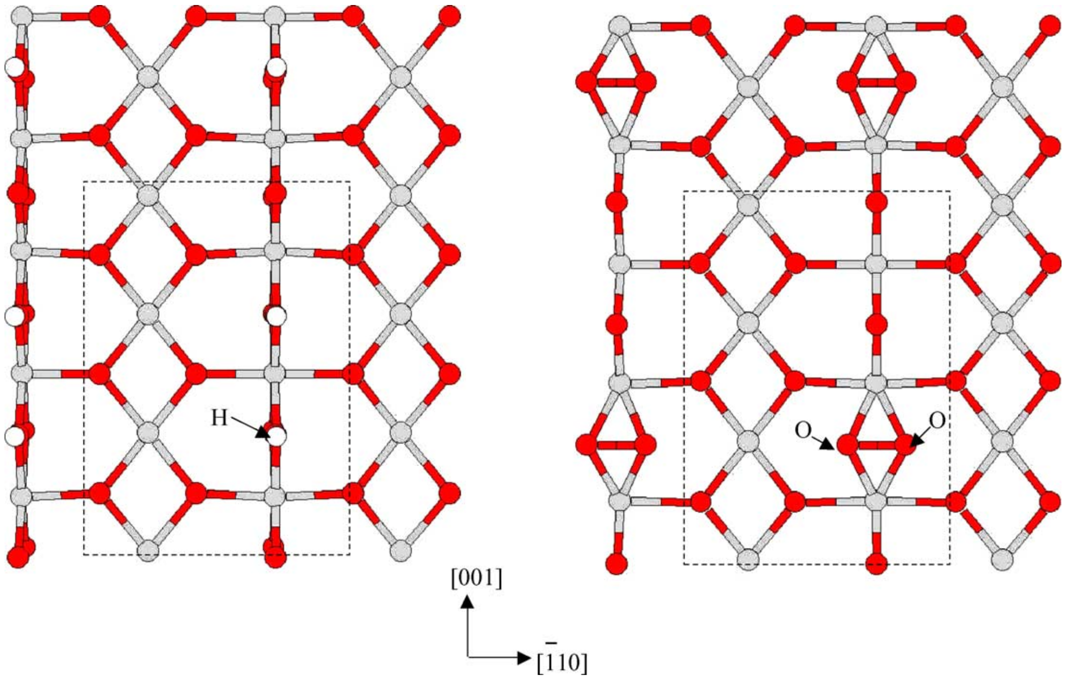

Fig. 2. Adsorption on rutile TiO_2(1 1 0) surface. A triple unit cell is used. Top view is shown, only the first layers are displayed for simplicity. On the left-hand side, hydrogen adsorbed on the stoichiometric surface. Two hydrogen atoms adsorb on the surface bridging oxygen atoms per unit cell. This picture is equivalent to the dissociative adsorption of water on a defective surface: an oxygen vacancy is filled by the hydroxyl fragment, while the proton goes to the next bridging oxygen. On the right-hand side, O_2 adsorption on a defective surface. The molecule does not fill the vacancy but is placed parallel to the surface plane, perpendicular to the bridging oxygen row.

atoms may be found as terminal ones in roughened surfaces, as well as in clusters dispersed over support, like V_2O_5 on anatase [50,112] or in oxidizing conditions.

NO is an electronegative species with an odd electron. Interacting with a metal site, it should take one electron and become negatively charged, NO^- (nitrosyl anion), N being formally reduced relative to the neutral species from the gas phase. This adsorption is clearly not very favorable when the metal in the metal oxide is in the highest oxidation state and deprived of any available electron. Thus, NO interaction with TiO_2 is generally weak. An alternative to this adsorption mode consists of the addition of the NO unit to an oxygen atom. Upon adsorption, the nitrogen atom is oxidized and there is an electron transfer from NO to the surface, thus becoming NO^+. We recall that this is the “normal ion” [113]. The adsorption process can then be seen as NO^+ adsorption on O^{2-} thus forming $NO_2{}^-$. This adsorption mode is confirmed by the recent detection of nitrites and nitrates, and is also found for CO forming CO_2 and carbonates, on rutile and anatase TiO_2 surfaces [109–111]. Thus, NO corresponds also to an electropositive adsorbate (electron donor). Upon adsorption on an oxygen site, there is an electron transfer to the surface and the nitrogen atom is oxidized.

We have investigated the possibility of an adsorption of NO and CO on terminal oxygen atoms on a roughened (0 0 1) surface of anatase TiO_2 [114,115]. The surface model is shown Fig. 3. Nitrite formation implies interaction of NO with one terminal oxygen, with a transfer of one electron to the surface. Nitrates involve two terminal oxygen atoms with a charge transfer of three electrons to the surface. The formation of such species was highly exothermic in contrast with the adsorption on titanium or two-fold oxygen atoms [114]. Several approaches of the molecule to the surface are possible; Fig. 3 shows a bidentate and a monodentate nitrate formed on the rough surface model. The same features apply for the CO adsorption, with formation of CO_2 and carbonates [114]. Therefore, a redox process allows to stabilize the less frequent adsorption on a reactive oxygen atom.

3.1.4. *Adsorption of O atoms on perfect surfaces*

O_2 is normally not reactive unless vacancies are present [116–119]. The atomic adsorption of O on a stoichiometric surface is equivalent to that of O_2 on an O defective surface. It requires some O atoms to be in oxidation state −1, and this imposes a rearrangement of the surface and the presence of O–O bonds. The formal $O_2{}^{2-}$moiety on the surface is a peroxo group as found in rutile TiO_2(1 1 0) [94]. The oxidized surface is hence different from the one expected by layer growth leading to the bulk structure. The best geometry is an O_2 parallel to the surface, oriented along the [−1,1,0] direction of TiO_2(1 1 0)-rutile (see Fig. 2). This gives a low spin state and preserves the gap of an insulating system. Adsorption parallel to the surface, on the top position of the four-fold Ti atoms, is not favorable. It is remarkable that O_2 adsorption in a defective surface does not

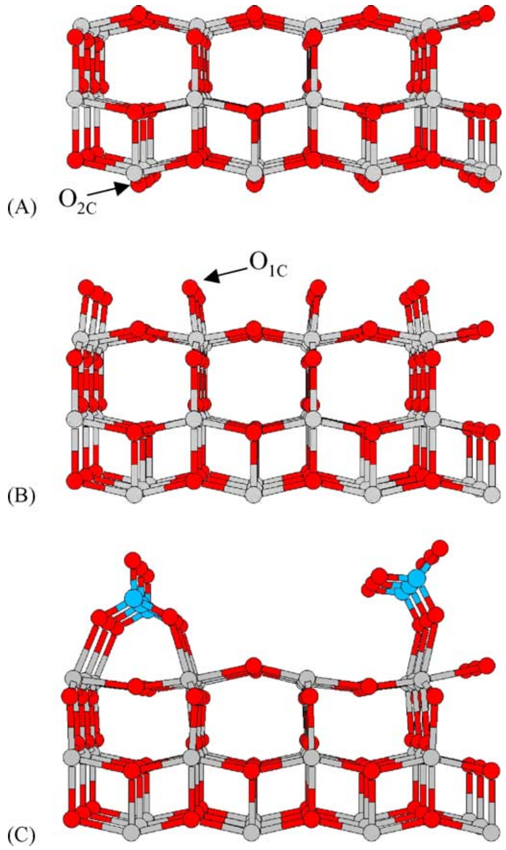

Fig. 3. (A) Perfect (0 0 1) anatase TiO_2 surface; the bottom layer is composed of two-fold-coordinated oxygen atoms. (B) The “rough” surface model obtained by transfer of the bottom oxygen layer on top. The new surface is stoichiometric and is terminated by singly coordinated oxygen atoms. (C) The NO (CO) molecule interacts with the surface terminal oxygen atoms to give the oxidized species. In this figure, bidentate and monodentate nitrate (NO_3^-) (carbonate CO_3^{2-}) species are shown.

correspond to the normal growth of the bulk structure which would imply the formation of a Ti–O bond. On SnO_2(1 1 0), for a complete missing row of bridging O, an analogous adsorption has been proposed [41]. The perpendicular orientation (high spin state) found by de Lara-Castells [120] in TiO_2(1 1 0)-rutile is higher in energy.

3.1.5. *Adsorption of metal atoms at the O^{2-} site of perfect surfaces*

The metal/oxide interface has been extensively studied from both experimental [121] and theoretical point of view [122–125]. The large enhancement of the reaction rates (for instance CO hydrogenation) by transition-metal catalysts when supported (on TiO_2) is referred as *strong metal–support interaction* [28,126–128]. We will focus on the adsorption of transition metals on MgO(1 0 0).

All the metal atoms bind to the O^{2-} site of the MgO surface, otherwise they would transfer an electron to Mg^{2+} leading to dissociation into M^+ and Mg^+ and desorption. The charge transfer from the metal to the surface cations that would equilibrate the charges is very weak, the electrons mainly remain on the metal. We have found that electron transfers were negligible for reduced and perfect surfaces. The adsorption of alkali metals is very similar to that of H on reducible oxides [129–133]. Considering the first row of the transition metals, the curve of the heats of adsorption as a function of the atomic number resembles that of the cohesive energies and corresponds to the curve of the interaction between the metal and a base. It seems that the ability for a metal atom to bind is an intrinsic property whatever the interacting species is. The spin state of the atom is preserved upon adsorption whereas a stronger adsorption would quench the spin [134,135]. Contrary to the adsorption of a metal atom, with the repulsion due to more electrons, a metal cation has acidic properties and strongly binds to the O anions of the surface.

3.2. *Adsorption on defective surfaces*

When the substrate is not stoichiometric, redox mechanisms are necessary to bring back to stoichiometry. Acid–base mechanisms of adsorption are nevertheless still possible. The deviation from the stoichiometry in that case modifies the acidic and basic properties of the surface atoms.

The adsorption strength varies significantly with the coordination of the atom at the adsorption site [5]. It is thus generally believed that the presence of defects, adatoms or O vacancies, creates active sites and enhances the surface activity. However, there are cases in which defects decrease surface reactivity. The final situation depends on many factors like reducibility of the cation, adsorption site, nature of the adsorbate, relaxation of the surface, etc.

3.2.1. *Molecular adsorption on reduced surfaces*

The general trend is to consider that reduction activates reactivity [5]. This is not always the case. The present section is devoted to the comparison of the heats of adsorption of the molecules at acidic sites between perfect and reduced surfaces.

The formation of an oxygen vacancy does not only create sites of low coordination; it also modifies the electron count by two electrons. When the oxide is irreducible, the electron pair is trapped in an F center that is extremely basic. The geometry of the oxide does not change extensively, the electron pair replacing the anion and preserving the structure of alternated charges. When the oxide is reducible, the electrons reduce the surface metal cations; a relaxation of the cavity decreases the cost for the vacancy formation. The metal cations are therefore less acidic than on the clean surface and less active toward the adsorption of basic molecules. Thus, the general trend is a decrease of the heat of adsorption on the metal cations. Molecular NH_3 or H_2O adsorptions are less exothermic on defective rutile TiO_2 surfaces than on perfect ones. The same naturally also occurs on the hydrogenated TiO_2 surface that is also reduced. Compared with the heat of adsorption on the perfect clean surface, those at Ti sites in the vicinity of these defects diminish by ∼15 and

∼39% for the water adsorption (molecular or dissociative) and by ∼18% for that of CO. In the case of CO adsorption in a vacancy, the presence of the electron of reduction is a prerequisite: otherwise, no adsorption takes place [63].

3.2.2. Dissociative adsorption on reduced surfaces

The energy of an adsorption with dissociation depends on three factors: the cost for a heterolytic cleavage in the gas phase, the heat of adsorption of the basic fragment and that of the acidic fragment. The difference between the energies of adsorption for the same dissociative adsorption on two surfaces (a stoichiometric slab and a reduced slab) only depends on the two last ones. We have thus to examine the combined effect of a modification of the acidic and basic property under reduction. It has been shown in the previous section that the reduction of the surface oxide decreased the acidity of the surface cations. On a reducible oxide like TiO_2, the heat of adsorption was found *smaller* on the reduced surface than on the perfect one, except for H_2O in the vacancy [63]. In the particular case of the H_2O dissociative adsorption on reduced rutile TiO_2(1 1 0), the defect site is *more* reactive than the perfect surface. An O atom again occupies the site of the vacancy, and then, the topology of the clean surface is restored. This is also the case for Cl adsorption. Consequently, a hydration converting the defective-reduced TiO_2 to the hydrogenated non-defective-reduced surface is easy. The resulting structure possesses bridging surface hydroxyl groups. It is probably the easiest way to form the hydrogenated non-defective surface since molecular hydrogen does not adsorb [27,136]. For TiO_2, the defective surface requires very anhydrous conditions.

On the contrary, since the basicity of the F center was larger than that of the surface oxygen atoms, for MgO the heat of adsorption was found *larger* on the reduced surface than on the perfect one. The heterolytic dissociation of H_2 leads to a proton over the vacancy and a hydride bound to a surface Mg atom; the heat of adsorption increases from 1.44 eV on the prefect surface to 2.59 eV [63]. On ZnO(0 0 0 1), the binding energy of H_2 relative to the gas-phase molecule becomes exothermic whereas it is endothermic on saturated surfaces [103]. From this, it is not surprising that reducible oxides in their reduced form are less active toward the dissociation of Brønsted acids while irreducible ones could be more active. This is the tendency as emphasized by Barteau [5]. Reduced SnO_2(1 1 0) surfaces are far less active than stoichiometric ones [36,48,49] in sharp contrast with MoO_3 [137] and MgO [138].

4. Conclusions

Adsorption on metal oxides involves a rich chemistry. The best adsorption modes contribute to restore the ideal electron count of clean and stoichiometric surfaces. An acid–base mechanism is predominant because of the alternation of cations and anions in the metal oxide. On the other hand, the adsorption of radicals or the presence of defects introduces the role of redox mechanisms. Reducibility of the metal atom also plays an important role in determining the preferred adsorption mode.

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