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Adsorption on perfect and reduced surfaces of metal oxides

M. Calatayud, A. Markovits, M. Menetrey, B. Mguig, C. Minot*

Laboratoire de Chimie Théorique, UPMC 7616 CNRS, 4, Place Jussieu, 75252 Paris Cedex 05, France

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Abstract

Two major chemical processes, acidobasic and redox, track the adsorption mechanism on metal oxides. Molecular and dissociative adsorption on stoichiometric surfaces can be understood as acid–base processes. Clean and anhydrous surfaces of metal oxides have two different active sites: cations and anions. Electron-rich molecules or fragments arising from a heterolytic bond cleavage (Lewis bases) react with M^{n+}, while electron poor ones (Lewis acids) react with O^{2-}. The MgO and TiO_2 surfaces clearly appear to be predominantly acidic and molecules that do not dissociate generally bind to the metal cation. The electronic structure, insulating character 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 is via a redox mechanism that restores the situation of an insulator and the highest oxidation states for all the atoms.

For radical adsorption a first solution occurring on irreducible oxides is to couple the electrons and form two opposite ions adsorbed on the two surface sites, as for H_2/MgO, involving an acid–base mechanism. Another possibility occurring on reducible oxide is via an electron transfer to or from the oxide (redox mechanism). The electron transfer occurs from the substrate to the adsorbate for electronegative group (Cl adsorption on O) or the other way around for an electropositive one (NO adsorption on M). The reactivity at surfaces deviating from stoichiometry differs from that on the perfect ones. The difference does not only originate from the modification of the coordination number but also from the electron counting.
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1. Introduction and general overview

In spite of many experimental and theoretical studies [1–5], many surface properties of metal oxides are not well-understood [6]. Metal oxides surfaces react with gases or solutions; they behave as catalyst or as support for catalyst. The challenge is to understand the factors controlling the adsorption and the reactivity of the moieties on the surface. Metal oxide clean and anhydrous surfaces present two different active sites: cations and anions. 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]. Sites of low coordination are in general more reactive than sites of high coordination [5,8]. Besides acid–base reactions and coordination, the redox mechanism also controls other adsorption behavior [5]. We will illustrate these interactions using the examples of MgO and TiO_2 (or V_2O_5) that have different properties, the former being irreducible whereas the latter is reducible. They should then behave differently when a redox mechanism is involved. When the oxide deviates from the stoichiometry due to the presence of defects such as vacancies or adatoms, the oxidation

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* Corresponding author. Tel.: +33-1-44-27-25-05; fax: +33-1-44-27-41-17.
E-mail address: minot@lct.jussieu.fr (C. Minot).

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state of the surface atoms varies and the electron count becomes a determining factor.

For the stoichiometric metal oxides with metals in their highest oxidation state, the metal atoms have lost all their valence electrons. Then, they can be understood as insulators. The valence band has a predominant bonding character and the crystal orbitals are mainly localized on O^{2-}. The conduction band, on the contrary, has a predominant antibonding character and the crystal orbitals are mainly localized on M^{n+}. The most stable surfaces do not show intrinsic surface states in the band gap [10,11]. Then, a large part of the reactivity emerges from an HOMO–LUMO interaction: Lewis bases (electron pairs filling the HOMO) react at the acidic site (M^{n+}) of the oxide while Lewis acids (characterized by the LUMO) adsorb on the basic site (O^{2-}). The former case is the most frequent and metal oxide surfaces are predominantly acidic surfaces when organic molecules are adsorbed without dissociation [8,12,13]. The adsorption on the surface oxygen atoms concerns only the cations resulting from a heterolytic cleavage, the metal atoms and a few specific adsorbates.

Acid–base reactions do not modify the oxidation states of the atoms. In a molecular orbital description, the occupied orbitals of the base are stabilized and the vacant orbitals of the acid are destabilized. It follows that stoichiometric oxides remain insulating after adsorption with an increased gap. The electron count for the whole system is determining. If initially the gap exists (perfect surfaces and closed-shell adsorbate) the adsorption mode through acid–base mechanism is the best solution to maintain it. If not (defective surface, open-shell adsorbate), the best adsorption mode, restoring the gap, implies a redox mechanism.

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 (and some O atoms have -1 for oxidation state instead of -2). 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. These oxygen adatoms as well as low coordinated O anions at steps and kinks are known to exhibit a pronounced basic character and to be more reactive than terrace sites via electron transfer from the surface to the adsorbate [14].

Oxygen vacancies modify the adsorption scheme by decreasing the coordination of the surface atoms and by modifying the electron count. The first factor enhances the activity of the acidic sites close to the vacancy. The second factor, the electronic factor, can operate in both ways, improving or diminishing the reactivity. When the oxide is reducible, the electrons reduce the surface metal cations, as for TiO_2. Then, an adsorption that implies the acidity of the metal sites close to the vacancy becomes more difficult; the surface acidity indeed decreases with the reduction [15,16]. This is less clear for an adsorption within the vacancy itself: the coordination number of the adsorbate is large and the final structure is close to that of the stoichiometric oxide. When the adsorption involves the oxygen sites through an acid–base mechanism, weak differences are expected for the reducible oxides since the adsorption occurs always upon unchanged O^{2-} anions. On the contrary, we expect a strong enhancement for the irreducible oxides as MgO, the adsorption taking place upon the oxygen vacancy (an F center); the electron pair, trapped in the F center, is indeed extremely basic. When the adsorption implies the oxygen sites through a redox mechanism, it becomes easier for an electron-acceptor adsorbate and more difficult for an electron-donor one.

The adsorption of radicalar species is 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, as for H_2/MgO, involving 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 it 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.

We will discuss 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 and will be briefly discussed at the end.

Finally, we should note that the reaction media plays 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 a substitution of hydroxyl groups) or it happens directly upon these groups through H-bonds.

For simplicity, we only give the method of calculation and the reference of the corresponding studies. For all of our calculations performed with the VASP method, relaxation of the uppermost layers of the substrate (one for MgO and three for TiO_2) has been taken into account together with that of the adsorbate.

2. Representative metal oxides in the highest oxidation state

In this section we will briefly describe representative bulk structures of the metal oxides and their most common surfaces. Bulk structures of MgO and TiO_2 (anatase and rutile) are shown in Fig. 1. Slabs describing the main surfaces are displayed in Fig. 2.

Most often, MgO is chosen as representative for the metal oxides. The bulk and the (1 0 0) surface structures are simple with a rock-salt structure [1,17] and an alternation of ions with opposite charges. It is an ionic oxide whose metal cation is very electropositive; Mg is more electropositive than the transition metals. The (1 0 0) surface is stable, nonpolar, classified as type I according to Tasker [18]. The clean surface is easy to prepare with well-defined stoichiometry [19]. It does not undergo large relaxations. It is an irreducible oxide and oxygen vacancies leave electrons trapped in

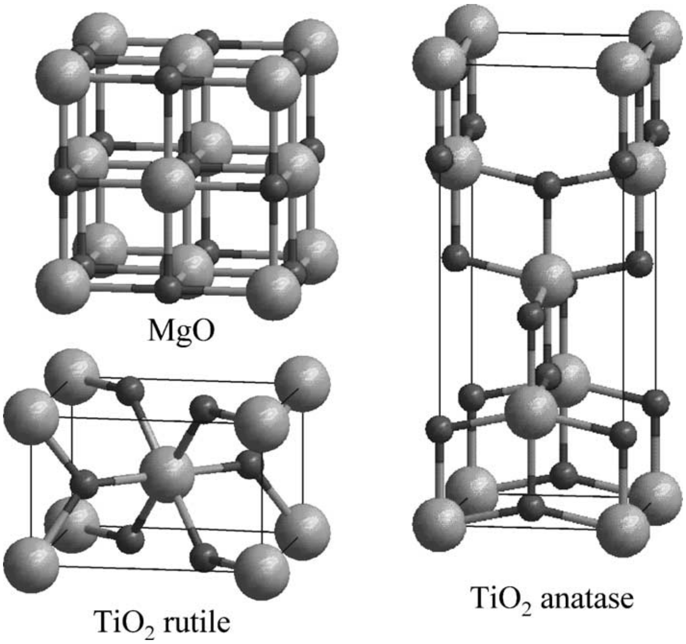

Fig. 1. The bulk structures of MgO and TiO_2. Cations are represented by large gray spheres and O^{2-} anions by small black spheres [190].

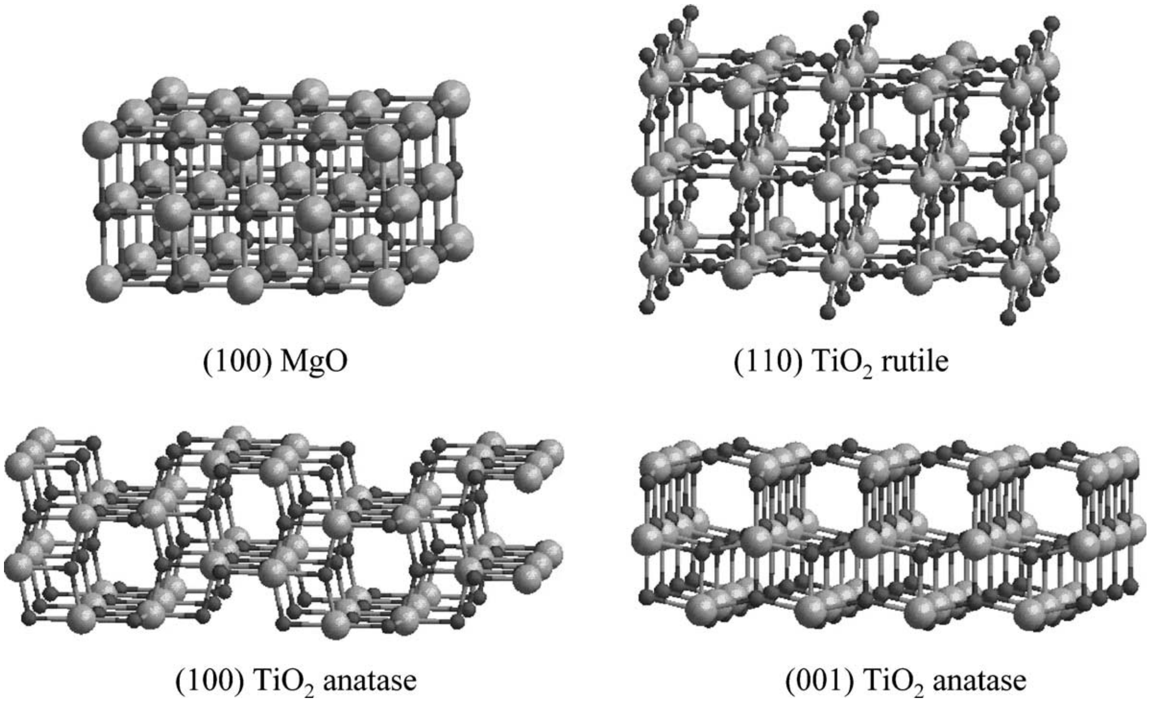

Fig. 2. The most frequent stable surfaces for MgO and TiO_2. Cations are represented by large gray spheres and O^{2-} anions by small black spheres [190].

the vacancy (a pair or a single electron for the F or F^+ center, respectively) [20–24]. The oxygen vacancies are of great importance for the properties and chemical reactivity of MgO [25]. A lot of experimental and theoretical studies have been devoted to the surface anion vacancies with trapped electrons [26–30]. Despite the fundamental role of this defect, the control of its synthesis is still a challenge.

After its first use for the photoelectrolysis of water on TiO_2 anodes [2], the interest to titanium dioxide is extending to many applications such as white pigments in paintings, coating of metals, sensor technology [31], adhesion, microelectronic devices and photovoltaic cells [32,33]. It is used for its applicability to the treatment of pollutants and the chemical conversion of solar energy [34]. TiO_2 crystallizes in three different phases: rutile (the most stable one), anatase and brookite. The rutile $TiO_2(1\,1\,0)$ surface is one of the most important surface-model for the metal oxide. The perfect rutile $TiO_2(1\,1\,0)$ surface has been extensively studied (see for instance [3,4,13,35–38]). The structure is made of alternative horizontal and vertical polymers [39]. The symmetry for the three-layer slab imposes no dipole moment in the [1 1 0] direction [3,4]. It is classified of type II according to Tasker [18]. There is an electron donation from the polymers in the surface plane to the perpendicular ones which enhances the acidic and basic properties of the surface sites. This structure makes the surface at the same time reactive and stable [13,37,38]. The reconstruction is weak contrary to other surfaces that form (1 1 0) facets upon heating [5,40,41] and restricted to a small relaxation and rumpling of the bridging oxygen atoms [36,42]. 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. An example is rutile $SnO_2(1\,1\,0)$; Cox and co-workers [43] obtained the perfect stoichiometric surface, partial reduced surface by removal of the bridging oxygen and totally reduced surface by a complete removal of the O row and reduced by removal of the in-plane oxygen atoms.

Though more difficult to grow, anatase particles are also used in industry for their high activity. It is almost exclusively used in heterogeneous catalysis [44,45]. The natural crystallographic faces are the (1 0 1) and (0 0 1) [46–48]. The (0 0 1) bulk terminated anatase reconstructs to present (1 0 1) facets [49–52]. The (0 0 1) and (1 0 0) faces are also often considered when anatase is a support because of its good match with active catalysts [53,54]. 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. The charge of the titanium cation, +4, is twice that of the magnesium cation, +2. TiO_2 is therefore more acidic. The O^{2-} ions are less stabilized by their first neighbors: in the bulk structures, each O^{2-} ion has three neighbors for TiO_2 compared with six for MgO; at the surfaces each outmost O^{2-} ion has two neighbors in rutile TiO_2 (1 1 0) 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 on the corresponding MgO surface. Let us note that comparing the scales of the heats of adsorption in a series of adsorbates necessitates a finer approach: relative scales require considering the hard and soft acids and bases (HSAB) concepts [55,56]. For the surfaces, obviously Ti^{4+}, having a localized and strong charge, is a hard acid while Mg^{2+} is a soft one. For the adsorbates, ammonia is a stronger and harder base than CO_2. Both molecules adsorb as bases at the cationic site. However, the difference in the heats of adsorption shows a preference for coupling the hard base with the hard acid and the soft base with the soft acid. NH_3 reacts better on TiO_2 (a factor 7) whereas CO_2 reacts as well on MgO as on TiO_2 [38].

Contrary to Mg (MgO), Ti (TiO_2) is reducible. Ti^{4+} can be reduced to Ti^{X+} ($X < 4$). The removal of a neutral O atom has been shown to result in two unpaired electrons on the fivefold coordinated Ti neighboring to the vacancy [57] 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 [58] and V_2O_5 are very similar to TiO_2, Sn^{4+} being able to be reduced to Sn^{2+} [43,59,60] or V^{5+} to V^{4+} [45,61]. They could also instead of TiO_2 illustrate this possibility of redox mechanism modifying the adsorption scheme occurring on reducible oxides. In vacuum environment that is intrinsically reducing, the surface metal-to-oxygen ratio of SnO_2(1 1 0) increases under simple thermal treatment [5,62]. The complete removal of the bridging O rows of the rutile TiO_2(1 1 0) forms suboxides of Ti_2O_3 stoichiometry [63–65].

The interest to V_2O_5 originates from the wide application of the vanadia-based materials as catalysts, as well for oxidation (aliphatic or aromatic hydrocarbons) [66] as for reduction (NO_x by ammonia) [45].

3. Adsorption on the metal cation

In Section 3.1, we will indicate that molecules adsorbing without dissociation always bind to one or several metal cations [8,12,13,38,67–69]. Adsorption at the O^{2-} site is the exception; on terraces, it takes place as secondary interaction in complement of a main interaction with the metal cation or it happens on very uncoordinated O sites [14,70]. We will show an example starting by a typical basic molecule, NH_3, and commenting on other molecules with less pronounced basicity such as H_2O, CO, CO_2 and SO_2. Dissociative adsorption is discussed in Section 3.2 (for the adsorption of the basic fragment on the metal cation) and in Section 4.1 (for the adsorption of the acidic fragment on the O surface atom). Any change in the stoichiometry affects the electron count of the surface atoms and modifies the acidic property of the surface cations; this will be commented in Section 3.3. Finally, adsorptions with donor-like or acceptor-like adsorbates imply a redox mechanism and an electron transfer from (to) the adsorbate to (from) the oxide. Acceptor-like moieties after accepting electrons behave like Lewis bases and bind to the metal cations; such adsorption mode will be presented in Section 3.4, while the donor-like adsorption will be presented in Section 4.

3.1. Molecular adsorption on the perfect surfaces

Molecular adsorption can be understood as an acid–base 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.

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 [8,12,38,67–69]. The larger the gas phase adsorbate's proton affinity the larger will be the heat of adsorption. Strong bases such as NH_3 adsorb on the metal cation of the surface with the lone pair oriented toward the metal [71–73]; the deviation from normality to favor a H-bond as secondary interaction is slightly destabilizing [74]. NH_3 is the usual probe for the acidic sites [75–77]; 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 [8,38] by a factor 7 (see Section 2).

Water is adsorbed without dissociation on MgO(1 0 0); it is oriented roughly parallel to the surface to benefit from H-bonds. At low coverage, these 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) [38,78,79]. Water adsorption is stronger and dissociative on clean anhydrous rutile TiO_2(1 1 0) surface [15,39].

At small coverage, CO is also adsorbed C-down on top of the metallic center though it is not usually considered as a base [63,80–83]. 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 electronegative (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, [84]. The back-donation that is predominant for the adsorption on 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 [73,85].

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 [86,87] 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 [88,89]. On rutile TiO_2(1 1 0), CO_2 is perpendicular to the surface building a OCOL $\cdots$ Ti bond. On MgO(1 0 0) CO_2 is flat and parallel to the surface bridging two adjacent Mg sites [78,89,90]; this adsorption mode involves the making of two Mg–O bonds. The adsorption energies are nearly equal, 304 meV vs. 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 HSAB concepts. CO_2 is a softer and weaker base [38].

For SO_2 that is a poor base, the best adsorption mode on MgO, flat above the surface, involves three interactions [82,91–93]: two $Mg_{lattice}$–O_{SO_2} bonds (surface acidity) and only one $O_{lattice}$–S_{SO_2} bond (surface basicity). This is consistent with a predominance of the acidic property of the surface. 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 [94–97] three adsorption modes on a three-layer 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 to 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 an adsorption.

3.2. Dissociative adsorption: adsorption of the anionic fragment on perfect surfaces

For water, dissociation does not occur on MgO(1 0 0) surface since the O atoms from the surface hydroxyl group are more basic than those from the lattice. Protons adsorbing on them recombine and form water. For the clean and anhydrous rutile TiO_2(1 1 0) surface, the situation is the reverse; the O atoms from the lattice are more basic than those from the surface hydroxyl. The protons bind to the O atoms from the lattice and dissociative adsorption is preferred. This has been supported by CRYSTAL [38,39] and VASP [15] calculations even though it is still a matter of controversy (see Section 4.1).

Brønsted acids dissociate on a variety of oxide 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 [5,98]. However, for amphoteric compound the best heterolytic cleavage is not always the acidic one. Alcohols behave as Brønsted bases. In the gas phase, the basic cleavage ROH $\rightarrow$ $R^+ + OH^-$ is easier than the acidic cleavage, ROH → $H^+ + OR^-$, and this determines the adsorption mode on the rutile $TiO_2(1\,1\,0)$, R^+ on O^{2-} and OH^- on Ti^{4+}: OR groups are bridging while OH groups are terminal [8,12,99,100]. The same has been found for rutile $SnO_2(1\,1\,0)$ [101]. It is remarkable that the opposite orientation exists for the thio-compound [99]: H^+/O^{2-} and RO^-/Ti^{4+}. This compound is indeed more acidic and in the gas phase, the acidic cleavage RSH → $H^+ + SR^-$ is the easiest [68,102–104]. H_2S can completely dissociate to S^{2-}/Ti^{4+} and H^+/O^{2-} [103,104].

$RCO_2{}^-$ groups from the dissociation of acids bind by one or two bonds to the metal cations [44,105–109]. Carboxylic acids undergo acidic cleavage when the binding mode involves the formation of two bonds. The acidic cleavage generates $RCO_2{}^-$ binding to two surface cations and H^+ binding to a surface anion (bridging OH in case of the rutile structure). The formation of two O–M bonds is necessary to favor this fragmentation mode that is not the most favorable in the gas phase. 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 [105]. Even if a surface M site is available close by, the geometry of $RCO_2{}^-$ (with one O from the $RCO_2{}^-$ originating from the lattice) is not very favorable to allow another interaction. Thus the singly coordinated $RCO_2{}^-$ is less favorable than the dicoordinated species.

3.3. Adsorption on defective surfaces

When the substrate is not stoichiometric, redox mechanisms are necessary to restore stoichiometry; this will be discussed in Sections 3.4 and 4.2–4.6. 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 present section is devoted to the comparison of the heats of adsorption of the molecules at acidic sites between perfect and defective surfaces.

The adsorption strength varies significantly with the coordination number 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. 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. This is the case for MgO. When the oxide is reducible, the electrons reduce the surface metal cations; the cost for the vacancy formation is decreased by a relaxation of the cavity. The metal cations are therefore less acidic than on the stoichiometric 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 adsorption of NH_3 or H_2O is 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 water adsorption next to an oxygen vacancy (molecular and dissociative respectively), by ∼38% for that of CO next to an oxygen vacancy [15] and by ∼71% for NH_3 on the hydrogenated TiO_2 surface according our VASP calculations [16].

For the vacancy site surrounded by metal cations, the decrease in the heat of adsorption is less pronounced for H, H_2, CO and molecular H_2O. 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 (see Fig. 3). Consequently, a hydration converting the defective-reduced TiO_2 to the hydrogenated nondefective-reduced surface is easy. The resulting structure possesses bridging surface hydroxyl groups.

3.4. Adsorption of radicals, the importance of redox mechanism

The adsorption of radicals involve an electron transfer to or from the surface. These processes are generally not the best for perfect surfaces of metal oxides. The adsorption indeed does not preserve the initial energy gap inducing in general a loss of the stability. On

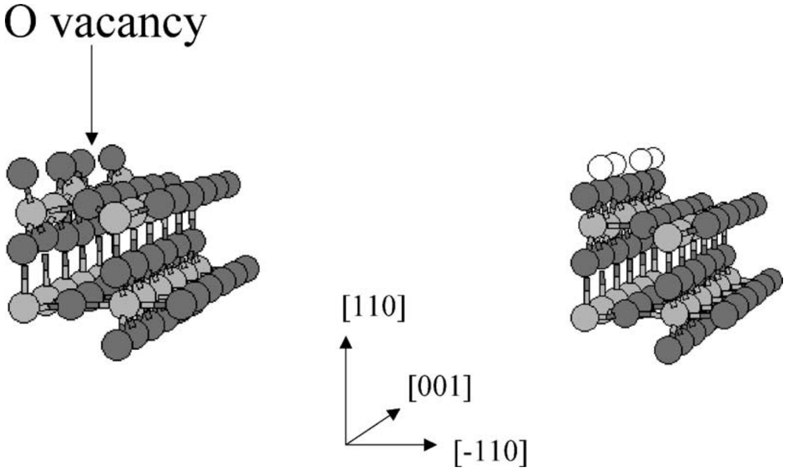

Fig. 3. The reduced rutile $TiO_2(1\,1\,0)$ surfaces: on the left-hand side, the O defective surface ($\theta = 1/3$); on the right-hand side, the hydrogenated surface ($\theta = 2/3$). The latter one may be obtained by the hydration of the former one. For both surfaces, two electrons per unit cell are transferred to the Ti surface atoms.

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.

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. An extreme example is H_2 dissociation; the symmetry of the homodinuclear molecules is not favorable to a heterolytic cleavage. However, the adsorption on MgO(1 0 0) results in the formation of H^-/Mg^{2+} and H^+/O^{2-}. This mechanism implies acid–base relation and avoids the reduction of the substrate.

Another possibility of adsorbing radicalar species is found through an electron transfer to or from the oxide (redox mechanism). When the singly occupied molecular orbital (SOMO) belongs to an electropositive atom (donor-like adsorbate), the unpaired electron might be transferred to a metal cation of the metal oxide, provided that this is possible: a reducible stoichiometric oxide or nonstoichiometric one that has been oxidized at first. Then, the adsorption is that of a Lewis acid on the oxygen atom (see next section). When the SOMO orbital is that of an electronegative atom (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).

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 $TiO_2(1\,1\,0)$ [110]. Indeed, an adsorption at the surface O^{2-} ion would require an electron transfer to the Ti atoms that is not favorable, the difference in energy of the Cl and Ti orbitals being too large. When the surface is reduced, Vogtenhuber et al. have found that the adsorption occurs preferentially on the O vacancy forming two Ti–Cl bonds ($E_{ads}(Cl) = 5.45$ eV on the vacancy better by 1.41 eV than on the pentacoordinated Ti atoms) [110–112] while according to STM measurements on the stoichiometric surface, the adsorption takes place on the pentacoordinated Ti atoms [113]. The disappearance of the defect states implies the filling of the 3p(Cl) orbitals [114] and the quenching of the defect states. Noting that the O vacancy is associated with a two electron reduction, it is natural to foresee that the adsorption of two Cl atoms (one Cl_2 molecule) per O vacancy allows restoring the stoichiometry and the electron gap. Counting these two electrons, the adsorption becomes formally that of two Cl anions, one in the vacancy the other adsorbed on the metallic site. On defective $TiO_2(1\,1\,0)$ the first one bridges two pentacoordinated Ti atoms at the vacant site and the other one binds to a pentacoordinated Ti atom from the surface rows. The reduced surface is more reactive than the clean one. The adsorption of two Cl atoms per unit cell is exothermic referred to the Cl_2 molecule whereas that of a single Cl atom on the perfect stoichiometric surface is endothermic. The heats of adsorption on the reduced surface are much larger than those on the clean stoichiometric surface up to two adsorbed Cl per vacancy (one Cl in the vacant site and the other on a fivefold coordinated Ti atom). The increase is more pronounced for MgO (a factor 3.1) than for TiO_2 (a factor 2.4) that is reducible and whose defective naked surface is relatively stabilized. On MgO(1 0 0), one Cl anion binds to the F center and the other one is above a Mg^{2+}. For MgO, there is even an enhancement for the heat of adsorption at the metallic site (second adsorption) when the vacancy is already occupied by one Cl atom (first adsorption). The second step restores the gap of an insulating system. We will comment later that electronics effects often are not always so favorable and that defective surfaces may also be less reactive than the perfect ones.

4. Adsorption on the oxygen anion

We have seen in Section 3.1 that when molecules were adsorbed on clean and anhydrous surfaces, they generally do at the cationic site. The oxygen ions, anionic sites formally charged −2, are therefore less reactive. They should adsorb Lewis acids but we have seen that CO_2 is not a enough strong Lewis acid for that. Basic properties are revealed when the molecules dissociate and when the cationic fragment adsorbs at the O surface sites. This will be commented in Section 4.1. The adsorption on O^{2-} of bases or radicals requires the electron transfer, either a pair or a single electron, to the cations of the oxide. This will be commented in Sections 4.2–4.6. Finally, the last Section 4.7 will be devoted to the metal atoms adsorption that occurs at the O^{2-} site.

The O^{2-} ions are sixfold coordinated in the bulk MgO and fivefold coordinated at the (1 0 0) surface. These surface atoms are not very reactive. They are less active than the surface hydroxyl groups and do not decompose water. For TiO_2 rutile bulk, the O^{2-} ions are threefold coordinated, and, in the (1 1 0) surface, the coordination decreases to 2 which still must be associated with a stable and poorly reactive ion. The rutile $TiO_2(1\,1\,0)$ surface is more active than the MgO(1 0 0) surface. Adsorption on the bridging O^{2-} ions on the stable surfaces only concerns very acidic species: metals or cations arising from a heterolytic cleavage, H^+ arising from a redox process. Low coordinated O anions at steps and kinks are known to exhibit a pronounced basic character and to be more reactive than terrace sites with incoming molecules via electron transfer from the surface to the adsorbate [14]. When terminal O atoms exist, more possibilities appear. The singly O^{2-} coordinated atoms are not frequent on stable surfaces: they could be associated with surface roughening; they also exist when the metal oxide is dispersed on a support; this is the case of V_2O_5 over TiO_2 [115–117].

Note that the reactivity of the O atom is not related to the charge of the clean surface. Large charges are obtained when the surface O^{2-} ions are stabilized by many neighboring cations. The presence of these large charge values reveals the stability of the electrons rather than their reactivity. The pentacoordinated O^{2-} ions at the MgO(1 0 0) surface are strongly charged and poorly reactive. The bridging and terminal O^{2-} ions from TiO_2 surfaces, with two or one neighbors only, have less charge whereas they are more reactive. The shifts of the projected DOS of the valence band are, contrary to net charges values, good indices for the reactivity. The most basic O atoms are those whose projected DOS is high in energy, close to the Fermi level [8].

4.1. Adsorption of cationic fragments on perfect surfaces

When a molecule dissociates heterolytically, the cation binds to O^{2-}. For Brønsted acids (H_2O, RCO_2H), the cation is always a proton that is very reactive. The pentacoordinated O^{2-} surface anion of MgO(1 0 0) is not enough basic to dissociate water. On perfect rutile $TiO_2(1\,1\,0)$ surfaces, water dissociation is still a matter of controversy. At high coverage, molecular water binds to the surface hydroxyl groups that saturate the Lewis acid sites. At low coverage, on clean and dry surfaces where the Lewis sites are supposed to be free, water should dissociate contrary to adsorption on MgO(1 0 0) [38]; hydroxyl groups detected by Henrich et al. [118] have been confirmed by synchrotron radiation studies [119]. On the other hand, some experiments conclude to minor degree of dissociation [120–122]. Defects and steps are supposed to have a minor influence [123], contrary to the case of MgO(1 0 0). However, from other experiments at low coverage, the small amount of dissociated water observed has been attributed to defects, steps or kinks [121,123,124]. Different calculations conclude that water can either be dissociated [39,79,125–129] or not [68,130,131] on rutile TiO_2(1 1 0) surfaces. From Car-Parinello simulation [130], it has been concluded that the water decomposition on partially reduced TiO_2(1 1 0) surface was not spontaneous, even if it led to stable hydroxyl groups. The VASP results conclude to a dissociative adsorption [15].

4.2. Adsorption of CO on terminal O^{2-} atoms

The adsorption requires the presence of a very reactive O atom, i.e. terminal ones. These may be found in clusters dispersed over a support. V_2O_5 on anatase remains as a V_2O_5 unit without forming a crystal surface layer [61,132]. This dispersion is the origin of the high reactivity. On stable surfaces, it is more difficult to find such singly coordinated O atom. Indeed, any increase in coordination will improve the stability. Terminal ligands can only be found in roughened surfaces or oxygenated ones. The presence of these ligands offers a possibility of adsorption at the O site that is not the usual one on a perfect surface. It has been recently suggested that CO adsorption occurred at various sites of anatase TiO_2 surface [133]. For CO, the usual adsorption mode is at the cationic site (Section 3.1). The heat of adsorption is weak. The adsorption on the many-fold coordinated O atoms (twofold for rutile TiO_2(1 1 0), fivefold for MgO(1 0 0)) that are the only existing sites for perfect surfaces is less favorable. In this section we investigate the possibility of an adsorption on terminal atoms, less frequent but when present much more reactive.

Binding CO to O^{2-} implies a redox mechanism. Two electrons are transferred to the metal oxide that has to be reducible. These electrons are paired in the TiO_2 oxide which differs from the $TiCl_n$ ($n < 4$) structures where high spin states are the most stable ones [134].

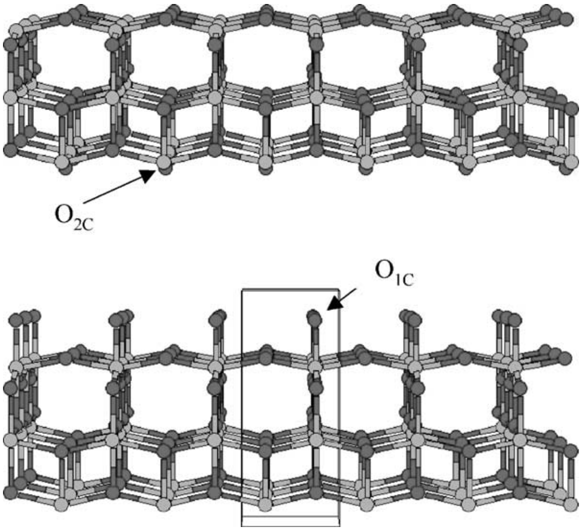

Fig. 4. Top: the perfect (0 0 1) surface of anatase TiO_2. Bottom: the “rough” surface for this orientation; the bottom layer has been transferred over the outmost layer of the “perfect” slab; thus, the bridging O_{2c} atoms become terminal atoms, O_{1c}.

We have performed VASP calculations for the CO adsorption on the “rough” (0 0 1) surface of the anatase TiO_2 [135]. In the most stable (0 0 1) slab, the outmost atoms are bridging O atoms and the surface Ti atoms, belonging to the second layer, are fivefold coordinated. The “rough” (0 0 1) slab is obtained by transferring the O atoms from the bottom layer to the top one. Then, the new top layer consists of O atoms, singly coordinated to the Ti atoms beneath that are now saturated (sixfold coordinated) in the third layer. The model is shown in Fig. 4. It remains stoichiometric and thus the change of the reactivity is not due to adsorbed O atoms.

The interaction of CO with the titanium sites is weak (0.2 eV) for the “perfect” (0 0 1) surface. As well-known on other TiO_2 surfaces, the CO binds to Ti, C-down, allowing donation and back-donation. However, recently it has been predicted by Monte-Carlo method that the adsorption occurs at various atomic sites, more easily on anatase than on rutile [133]. The adsorption of a CO molecule on a single terminal oxygen atom from the “rough” (0 0 1) anatase

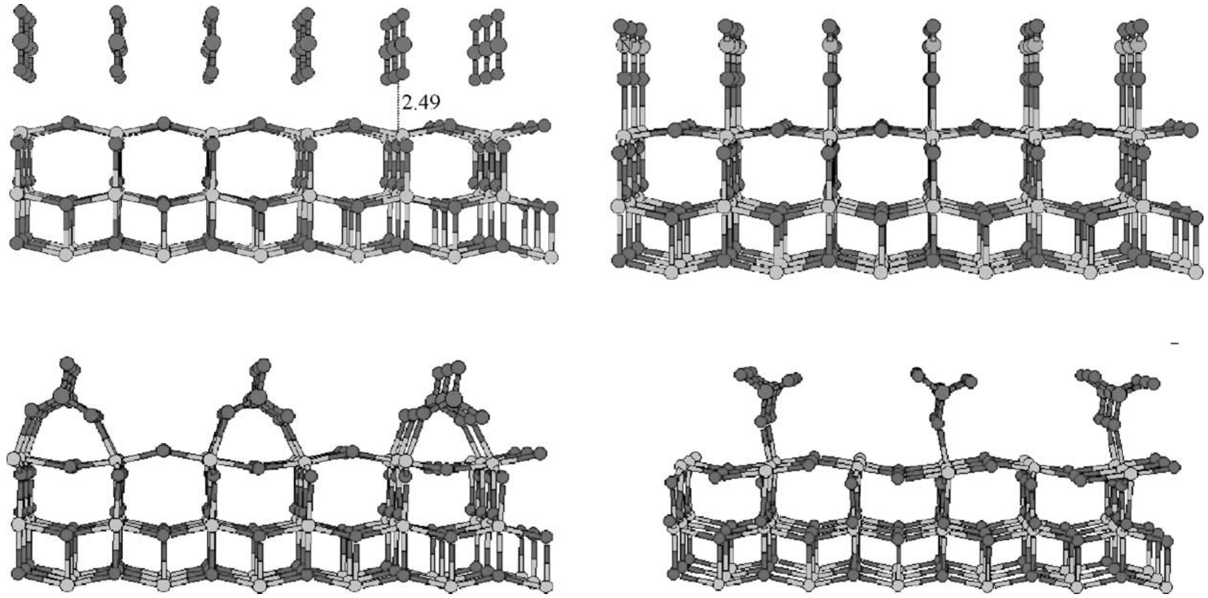

Fig. 5. Top left: result of the adsorption of CO on the "rough surface" leading to CO_2. Top right: result of the adsorption of NO on the "rough surface" leading to an adsorbed nitrite species. The NO_2 structure is bent. Bottom left: the interaction with two terminal oxygen; the topology is the same for the NO adsorption forming the twofold coordinated nitrate species and the CO adsorption forming the twofold coordinated carbonate species. Bottom right: the final structure corresponding to the previous structure. The adsorbates have rearranged from a twofold coordination to a onefold coordination. This rearrangement corresponds to a very weak stabilization in energy.

surface forms spontaneously a CO_2 by detaching the terminal oxygen atom (see Fig. 5). The calculated adsorption energy at full coverage is 4.58 eV.

When CO interacts with two terminal oxygen atoms, it forms ${CO_3}^{2-}$ species (see Fig. 5): This moiety can easily evolve from a twofold-coordination to a single coordination. The adsorption energies are large, 5.6 and 5.1 eV, respectively, for each coordination ($\theta = 1/2$), indicating a very exothermic process. Terminal oxygen ligands are thus very reactive and could be abstracted to oxidize CO. In both the formation of CO_2 and ${CO_3}^{2-}$, the redox process consists of a transfer of two electrons from the substrate to the surface. These electrons are stored by the Ti atoms at the surface that are reduced.

4.3. 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 Section 3.3 that the reduction of the oxide surface decreased the acidity of the surface cations. As a result, the effect on the basicity will also be commented in the section dedicated to the H adsorption. 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 [15]. 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. 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 [43,59,60] in sharp contrast with MoO_3 [136] and MgO [137].

4.4. Adsorption of H on perfect surfaces

The proton is the strongest acidic 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. Let us start commenting the case of irreducible oxides, such as MgO. Then, the single adsorption of an atom (a radical) is not the ideal case. The odd electron forbids reaching the optimal electronic situation with a gap. This is the main reason explaining that H_2 does not dissociate over an oxide surface; when stable, the hydrogenated surface originate from other sources (migration of atomic hydrogen from a metal, hydration of an O vacancy of a reduced surface [6,15]). The solution to stabilize atomic H on the MgO surface is to consider two atomic hydrogen atoms and couple the electrons on one of them as if they were obtained from a heterolytic cleavage of a dihydrogen molecule. 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 [138–140], or Zn^{2+} ions in ZnO [141,142]. This does not happen with alkali and noble metals that are isoelectronic to H whilst ionization potentials and electron affinities would make the heterolytic dissociation easier. A probable reason is the size of these metal atoms that would cause repulsion between the anion and the surface O^{2-} atoms from the neighboring sites of the surface cation.

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 [16]. Then, all the H atoms are adsorbed on the O atoms [16,143–145]. This adsorption mode is similar to that of alkali on metals (see Section 4.7). The VASP calculations on rutile $TiO_2(1\,1\,0)$ show that this mechanism is preferred by 1.1 eV [15]. This generates bridging surface hydroxyls. 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 (see Section 3.3). Both surfaces are then reduced [6,15]. In the case of $V_2O_5(0\,0\,1)$ the removal of a water molecule leads to an O defective surface and no OH groups are observed [146].

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. The adsorption energy decreases by 26% for rutile $TiO_2(1\,1\,0)$. On the O defective surface, the best energetic corresponds to a heterolytic cleavage avoiding a further reduction of the surface or to a molecular adsorption; the adsorption energy decrease nevertheless still represents 18%.

On MgO surface with a neutral oxygen vacancy, F center, the electron pair that is trapped in the vacancy is very basic. The heterolytic adsorption of H_2 leads to a proton over the vacancy and a hydride bound to a surface Mg atom; the heat of adsorption is larger than on the perfect surface. Calculated with the VASP program, the average atomic heat of adsorption is 2.59 eV to be compared with 1.44 eV on the perfect surface. 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 [142]. Contrary to reducible oxides, the presence of vacancies in irreducible oxides induces a higher reactivity.

On MgO surface with anion vacancy, F^{2+} center, the heterolytic adsorption leads to a hydride ion over the vacancy and a proton bound to a surface O atom; this evolves toward a H desorption oxidizing the F^{2+} center into an F^{+} one that is paramagnetic [147].

4.5. Adsorption of NO on terminal O^{2-}

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. NO interaction with TiO_2 is generally weak, and often only produces N_2O as gas product; that on a vanadia surface only occurs on reduced oxide. An alternative is the addition of the NO unit to O, forming a nitrite group ${NO_2}^{-}$. This is equivalent to say that the nitrosonium cation NO^{+}, the "normal ion" [148] is then adsorbed on O^{2-}. The nitrogen atom is oxidized (its oxidation state increases from +2 to +3) and the metal is reduced.

On the rough (0 0 1) surface of anatase TiO_2 (see Section 4.2) NO could be adsorbed similarly to CO. The NO adsorption on one terminal oxygen atom (formation of the nitrite) only necessitates a single electronic transfer to the metal instead of a pair, the formation of the nitrate as that of CO_3^{2-} inducing a further reduction of the oxide. The interaction of NO with the titanium sites is weak (the energy adsorption is 0.17 eV) for the "perfect" (0 0 1) surface in agreement with the value obtained by Sorescu et al. [63] (0.35 eV). When the molecule is placed at the twofold coordinated oxygen sites, the adsorption energy is not better.

We have investigated, using the VASP program, the possibility to form nitrites from the interaction of NO with a terminal O surface atom using the "rough" surface defined in Section 4.2 [70]. The results are very similar to those for the CO adsorption. The adsorption of the NO molecule on the terminal oxygen atoms of the "rough" (0 0 1) surface takes place by adopting an angular arrangement on the ONO unit (see Fig. 5). This model involves full coverage, and the calculated adsorption energy is 2.96 eV. The geometry of the ONO moiety agrees with that of the nitrous acid HNO_2.

A lower coverage has been taken in order to check the formation of nitrate species. NO reacting with two available terminal oxygen atoms forms a twofold coordinated NO_3^- species. The adsorption energy is large, 5.46 eV, indicating again a very exothermic process. An athermic reaction converts this species to monocoordinated NO_3^- one analogous to the CO_3^{2-}.

Experimental studies have reported the presence of such species: from IR and Raman spectra Dines et al. [149] conclude to the formation of bridging, monodentate and bidentate nitrate species NO_3^-. These species, together with nitrite NO_2^- species, are also detected by Hadjiivanov et al. [150] when exposing an anatase sample to NO_2.

On a V_2O_5 cluster, the formation of a nitrite is the best adsorption mode for NO. According to our Gaussian calculations, it leads with a heat of adsorption of 1.97 eV to a structure where NO_2 bridges the two V atoms forming of a six-member ring [VOVONO]: we can analyze the adsorption in two steps (i) at first, NO^+ binds to an O^{2-} of the cluster forming a NO_2^- ligand and one V atom is reduced; (ii) the NO_2^- bound to one V atom is stabilized by the interaction of the terminal O with the second V atom forming a bridging nitrite and a cycle. Similar cycles are found for the adsorption of nitrites on TiO_2(1 1 0) [151]. Similar structures are also obtained when the vanadium oxide is already reduced. On the dimer structure of the reduced oxide, V_2O_4, NO also binds to O forming a six-member ring with two bridging oxygen atoms. The formation of a ring increases the coordination of one V atom and is energetically very favorable.

In Sections 4.2 and 4.5, we have shown that singly coordinated oxygen atoms were very reactive. Our model remains stoichiometric, but requires a roughening of the surface. Perfect surfaces where the coordination of the O atoms is two or more are more stable and consequently less reactive.

4.6. Adsorption of O atoms on perfect surfaces

According to the partial pressure of O_2 and H_2, and according to the chemical potential of the surface, we have oxidative or reductive conditions [32,152–154]. O_2 is normally not reactive unless vacancies are present [155–158]. The atomic adsorption of O on a stoichiometric surface which is equivalent to that of O_2 on an O defective surface, requires some O atoms to be in oxidation state −1. This imposes a restructuring of the surface and the presence of O–O bonds. The formal O_2^{2-} moiety on the surface is a peroxo group as confirmed by the calculated O–O distance, 1.43 Å on rutile TiO_2(1 1 0) [15]. 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 [$\bar{1}$ 1 0] direction of rutile TiO_2(1 1 0), as shown in Fig. 6. This gives a low spin state and preserves the gap of an insulating system. The perpendicular orientation (high spin state) found by de Lara-Castells and Krause [159] is higher in energy by 1 eV. A shift of the O_2 along the row of half a cell vector is not favorable. This shift would translate the O_2 from the middle of the bridge to a top position of the fourfold Ti atoms, those that have lost the bridging ligands. It is remarkable that the O_{ads} does not 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

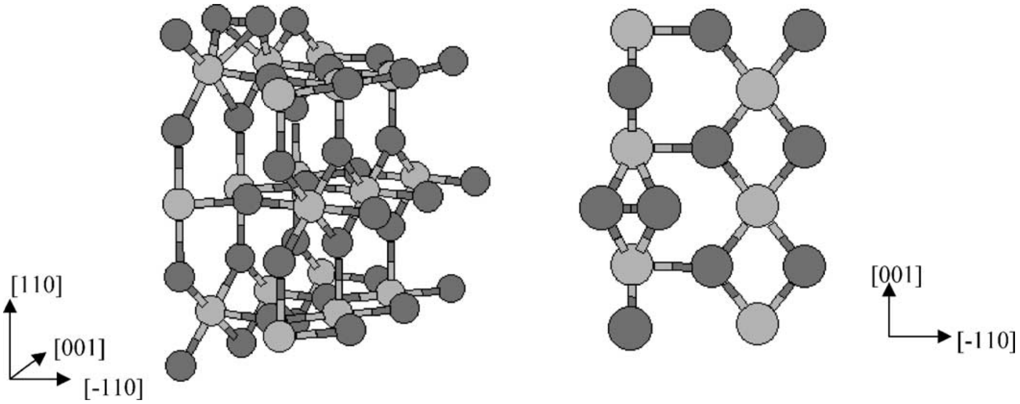

Fig. 6. Two views of the O_2 adsorption on the defective rutile TiO_2(1 1 0) surface; this is also the O atomic adsorption on the stoichiometric surface. On the left-hand side a perspective view of the adsorption mode is shown. On the right-hand side, a top view is displayed.

analogous adsorption has been proposed excepting the shift [48].

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

The metal/oxide interface has been extensively studied from both experimental [160] and theoretical point of view [161–164]. It plays a dominant role in many areas from coating, white pigmentation of paintings, microelectronic and sensors [31] to supported metal catalysts [160,165–172]. 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* [33,173–177].

All the metal atoms bind to the O^{2-} site of the MgO surface. If a metal would bind to Mg^{2+}, it would transfer an electron to Mg^{2+} leading to dissociation into M^+ and Mg^+ and desorption. Relative to the adsorption of cations, the adsorption of neutral metal atoms is weak. The charge transfer from the metal to the cations that would equilibrate the charges is not very important. Indeed, the stoichiometric oxide is made of two classes of alternating ions each one interacting with those of opposite charge; within each symmetry, this topology is that of alternate systems known for polyenes [178,179]. The addition of a metal on top of an O^{2-} ion preserves the classification in two sets, the metal adsorbed together with the Mg^{2+} ions forming the class of starred atoms (that containing the largest number of atoms). This comparison monitors the mode of delocalization of the electrons from the neutral metal: the electrons of highest energy belong to a nonbonding orbital that is localized on the starred class of atoms, i.e. on the metal and the Mg^{2+} ions; they should be predominantly localized on the least coordinated starred atom (the metal). It follows that the electrons mainly remain on the metal. The charge transfer from the metal to the cations that also depends on the differences in electronegativities is thus weak in first approximation. We have found that electron transfers were negligible for reduced and perfect surfaces; they are only significant for K and Ca when the metal oxide is oxidized. The adsorption of alkali metals is very similar to that of H on reducible oxides [180–186].

Considering the first row of the transition metals, the curve of the heats of adsorption as a function of the atomic number (Fig. 7) resembles that of the cohesive energies. They are small for the alkali and the noble metals. They are larger for the transition metals with a depression for Cr due to the large stability of the atom in the high spin state. The comparison with cohesive energies is natural at high coverage [187], when the adsorbed metal atoms interact with each other. The distance between the metal atoms is small under epitaxy; it is remarkable that the distance between the closest cations in a metal oxide is larger than that between the corresponding metal atoms in a pure-metal bulk. This comparison loses signification at low coverage. Moreover, the same figure is obtained for the interaction

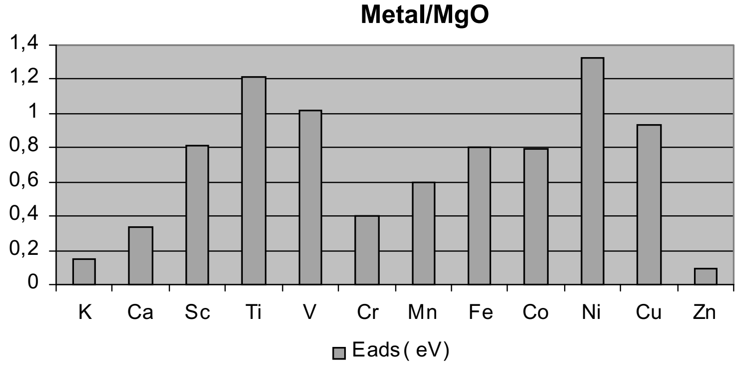

Fig. 7. Binding energies of the transition metals at low coverage ($\theta = 1/8$) on MgO(1 0 0) as a function of their atomic numbers.

between a metal and a base (NH_3 or OH^-) and corresponds to 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.

A metal cation has acidic properties and strongly binds to the O anions of the surface. The adsorption of a metal atom, with the repulsion due to more electrons, is much weaker, resembling a physisorption. The spin state of the atom is preserved upon adsorption whereas a stronger adsorption would quench the spin [188,189]. Even though the interaction with the O^{2-} atom is weak, it splits the metal atomic levels. The σ levels, 4s and $3d_{z^2}$ (or $4p_z$) are mainly a nonbonding and an antibonding M–O orbitals; it is important that the latter remains unoccupied. When it is occupied by two electrons (Zn) the heat of adsorption is negligible. When it is occupied by one electron (V, Cr, Mn, Co, Cu) the heat of adsorption is weak. The π ($3d_{xz}$, $3d_{yz}$) levels are also destabilized whereas the δ levels ($3d_{x^2-y^2}$, $3d_{xy}$) remain low in energy. The heat of interaction is large for Ti ($\sigma^2\delta^2$) since there are no antibonding occupied orbital (σ or π) while the π levels are occupied for V–Co (high spin state). The trend from K to Ti is due to the variation of electronegativity. The lower the metal atomic levels the stronger the interaction with the oxygen orbitals. This also explains the high heat of adsorption for Ni (the $3d_{z^2}$ orbital is vacant in the low spin state obtained in GGA and very low in energy) and Cu (the $3d_{z^2}$ orbital is singly occupied, leading to a 3e interaction).

When the MgO surface is oxidized (by the addition of OH or O far from the adsorption site) electrons from the metal can formally be transferred to the oxide (leading to OH^- or O^{2-}) and the metal adsorption is reminiscent of that of a metal cation (M^+ or M^{2+}). For K and Ca (electropositive atoms), the heats of adsorption are magnified by a huge factor (9 and 3, respectively). For other atoms, less electropositive than Mg, there is a modest increase. The oxidation of the surface induces an overall increase in the basicity of the surface atoms that increases the heats of adsorption without modifying the adsorption mode. Since we qualified the metal adsorption as a physisorption, the effect is of small amplitude.

When the MgO surface is reduced (F center), on the one hand, the adsorption on the O atom of the lattice is not very affected. The perturbation is small for this atom that remains in oxidation state +2; the two electrons in the vacancy replacing the missing anion. On the other hand, the adsorption in the vacancy is larger (except Sc and Mn); this site is more basic than the surface oxygen. The metal atomic configuration once again remains in general unaffected by the adsorption and the two electrons remain localized in the vacancy. As the energy level for these two-electron orbital is high, the frontier orbital control increase and the increase of the heat of adsorption is especially large at right of the periodic table (Co, Ni, Cu).

5. Surface relaxations and their influence on the adsorption on defective surfaces

Relaxations influence the heats of adsorption, E_{ads}, by two terms: they stabilize the clean surfaces (reference energies for E_{ads}) and thus tend to decrease E_{ads};

they could also allow an adaptation between the surface and the adsorbate and doing so increase E_{ads}.

The relaxation of the most stable surfaces is always the weakest. The cleavage leading to the most stable surfaces minimizes the loss of coordination. On the contrary, the O vacancies may generate large relaxations. Calculations give very large relaxations for the O vacancy in the bridging rows of the rutile TiO_2 (1 1 0). The Ti atoms at the vacant site move away from each other by 0.2 Å each; this is accompanied by a stabilization of 1.4 eV. By comparison, the relaxation of an F center for MgO is negligible. When an atom is inserted in the cavity of the vacancy, it contributes to restore the coordination of the perfect surface and the stabilization observed in the clean system is annihilated under adsorption. It follows that the heats of adsorption in the defective TiO_2 surface are weak, quite often weaker than on the perfect surface. The opposite is true for the F centers in defective MgO, even if the variations of energies are very weak.

Most often, outermost atoms distort from their original bulk positions when the surface is bare to diminish the surface energy. They tend to restore the bulk positions when a molecule is adsorbed. This is not always the case: it is also possible that surfaces exhibit important reconstruction *after* adsorption. We will illustrate this with the example of V_2O_5 adsorption on anatase TiO_2. As mentioned in Section 1, V_2O_5/TiO_2 is an active catalyst widely used in industry. Its high performance has been attributed to a synergetic effect between the V_2O_5 overlayer and the anatase substrate. We have performed VASP calculations to study the interaction of a V_2O_5 moiety and the (1 0 0) and (0 0 1) anatase TiO_2 surfaces [115]. The adsorption energy for V_2O_5 on these surfaces is always exothermic. However, we find an increase in the value when considering relaxation of the substrate upper layers. In the most favorable case, an increase of more than 50% is found for the heat of adsorption when allowing the surface to relax. Moreover, an important rearrangement is observed in the (0 0 1) surface when the surface atoms are permitted to move upon V_2O_5 adsorption; this did not happen for the bare surface. The substrate seems to adapt to the V_2O_5 unit and the adsorption energy value reaches 5.5 eV. This could be a proof of the synergetic effect between catalyst and support.

6. Conclusions

Adsorption on metal oxides involves a rich chemistry. Acid and base concepts are obviously predominant because of the alternation of charge in the metal oxide. The modification of an electron count with the presence of defect introduces the role of redox concepts. Then, the best adsorption modes contribute to restore the ideal electron count of clean and stoichiometric surfaces. This may overcome the effect of the decrease in coordination due to a vacancy: a reduction of the surface metal cation decreases its acidity. The reactivity of nonacidic species (radicals, bases) to O is weak and should be accompanied by a reduction of a surface metal cation. It could only occur by interacting with very reactive terminal oxygen atoms found in rough surfaces or dispersed catalysts. The surface relaxations are important on the least stable surface. Since the effect can be large either on the naked surface or under adsorption, the effect of the surface relaxation must be considered with care.

Acknowledgements

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