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Hartree–Fock periodic study of the chemisorption of small molecules on TiO_2 and MgO surfaces

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Abstract

We present ab initio periodic Hartree–Fock calculations (CRYSTAL program) of the adsorption of small molecules on TiO_2 and MgO. These may be molecular or dissociative, depending on the acidic and basic properties of the molecules in gas phase and of the nature of the surface oxide. For the molecular adsorption, the molecules are adsorbed as bases on Ti(+IV) sites, the adsorption energies correlate with the proton affinities. The dissociations on the surface correlate with the gas phase cleavages of the molecule; they also depend on the surface oxide; the oxygen atom of MgO, in spite of its large charge, is poorly reactive and dissociation on MgO is not favorable.

The surface hydrosyl of MgO are more basic than the O of the lattice and water is not dissociated under adsorption. As experimentally observed, NH_3 adsorbs preferentially on TiO_2 and CO_2 on MgO. However, this difference of reactivity should not be expressed in terms of acid vs basic behavior, but in terms of hard and soft acidity. MgO surface is a ''soft'' acidic surface that reacts preferentially with the soft base, CO_2.

Another important factor is the adsorbate–adsorbate interaction: favorable cases are the sequence of H-bonds for the hydroxyl groups resulting from the water dissociation and the mode of adsorption for the ammonium ions. Lateral interactions also force the adsorbed CO_2 molecules to bend over the surface, so that their mutual orientation resembles the geometry of the CO_2 dimer.

Keywords: Chemisorption; TiO_2 and MgO surfaces; Adsorption

1. Introduction

In this paper, we present Hartree–Fock periodic calculations on the adsorption of various molecules on perfect surfaces of metal oxides. The program, CRYSTAL-92 [1], is presented in [2]. We consider a slab and define a surface unit cell by two translation vectors. For MgO(1 0 0), we have used a single layer. The electron charge distribution at the surface is close to that in the bulk.

To represent the TiO_2 surfaces, we have used two models: at first, we considered the polymer that is characteristic of the rutile structure; it is a chain containing the sequence of titanium atoms and the equatorial oxygen atoms attached to them (see Fig. 1) obtained by the cleavages of all the apical Ti–O bonds. The polymer is obviously far from being a complete representation of a crystallographic face; however, as it is common feature of several faces (the top layers for the different faces of the rutile structure result from various assemblages of these polymer units), results on the polymer may be used as common references to emphasize the face specificities. The polymer model

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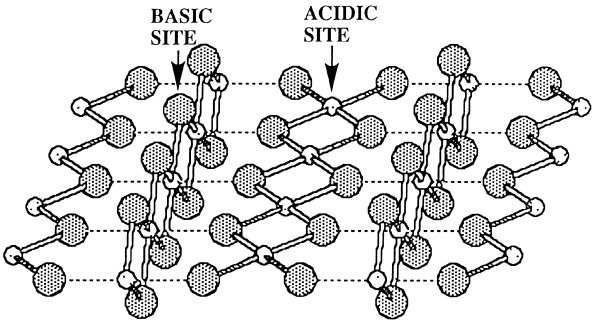

Fig. 1. The (1 1 0) face of rutile results from the coupling of TiO_2 polymers which contain the basic and acidic sites of adsorption. Small white circles are titanium atoms and large gray circles are oxygen atoms.

presents the two characteristic sites for adsorption, the cation sites (Lewis acids) and bridging oxygen sites (Lewis bases). The (1 1 0) face that is the most stable face [3,4] results from the coupling of polymers shown in Fig. 1; the axis of the polymer are parallel, but there is an alternation in their orientation: half of the polymer lies in the surface plane, whereas the other half is oriented perpendicularly. There is an electron donation from the O-atoms from the polymer in the plane to the Ti-atoms of the adjacent polymers increasing the reactivity at the surface sites. Indeed, the coordination of these two atoms remains identical to that of the polymer (see Fig. 1) and the electron transfer enhances the reactivity of the surface atoms: the Ti-atom in the plane becomes more acidic and the O out of the plane becomes more basic. Calculations have also been performed with the complete slab represented in Fig. 1. The heats of adsorption for the different adsorbates on the slab model are classified in the same order as the simple polymer model, but the values are generally larger as a consequence of the electron donation associated with the coupling of the polymers.

Both models contain titanium atoms with the oxidation number +IV and bridging oxygen atoms. The presence of tetracoordinated cations is not enough to create states in the band-gap and the electronic structure remains close to that of larger systems. Spectroscopy also supports that the reduction of the ligand coordination of cations is not sufficient to alter the surface electronic structure [5] and all-electron calculations confirm that the features of the density of states and the binding energies of the different surfaces "agree with a possible dissociation behavior of the rutile structure into TiO_2 chains, which are calculated to be stable" [4]. Titanium atoms from our polymer model are tetracoordinated. They are more reactive than the pentacoordinated surface atoms would be. To estimate the influence on the heat of adsorption of the increase in coordination, we have also used the "double polymer model" described in [6], where a vertical polymer accounts for the atoms of the first layers beneath the surface. The conclusions on the preferential adsorption modes are preserved in this model even if all the calculated heats of adsorption are decreased. The reduction of heats of adsorption is of the order 25–28% for NH_3 and CO. Based on spectroscopic observations, Heinrich also remarked that ligands coordination was "not the dominant factor affecting the surface electronic structure" by opposition to the introduction of defects and vacancies [5]. Our study concerns perfect surfaces even if some studies emphasized that experimental defects may be important, for example on MgO-surfaces [7–9] and on TiO_2 [10]. We assumed no reconstruction and optimized the position of the atoms of the adsorbates; the (1 1 0) surface of rutile is known to be stable [3,4].

The adsorption energies are defined positive for a stable adsorbate/substrate system according to the expression: $E_{ads}=E_{adsorbate}+E_{substrate}-E_{(adsorbate+substrate)}$, where $E_{(adsorbate+substrate)}$ is the energy of the adsorbate/substrate system, $E_{substrate}$ is the energy of the substrate and $E_{adsorbate}$ is the energy of the isolated adsorbate in its equilibrium geometry.

As the unit cell must remain neutral in the periodic calculations, it is not possible to study the adsorption of the charged species with the CRYSTAL program without a coupled adsorption of a species of the opposite charge. Thus, we have made cluster calculations (see Fig. 2). For that, we have used the SINDO program [11], which provides SCF values at low cost. The accuracy of this method has been tested on a large number of systems including second-row elements [12,13].

2. The acidity of the metal oxide

The acidity or basicity of active sites of solid catalysts is of crucial importance in determining

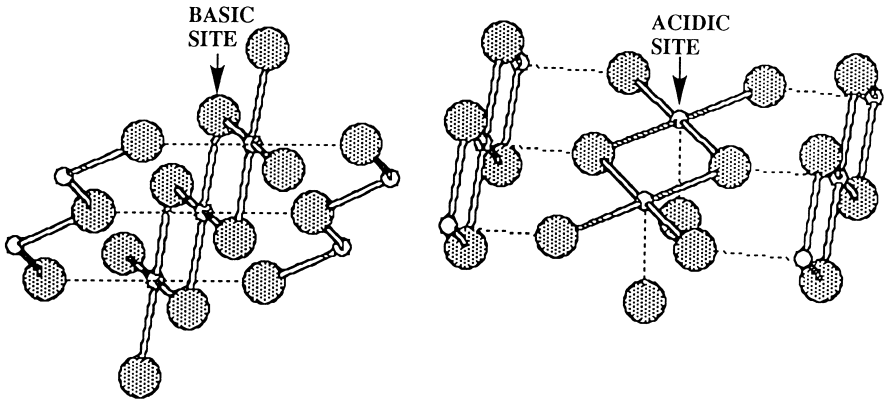

Fig. 2. The Ti_7O_{14} and Ti_8O_{16} clusters used, respectively, for the adsorption of H^+ and OH^-. Small white circles are titanium atoms and large gray circles are oxygen atoms.

their adsorption properties [14], and to control their catalytic behavior. On the surface of metal oxides, the exposed metallic cations are the acidic centers, whereas the surface oxygen ions are the basic sites.

Metal oxides are classified as acidic, amphoteric or basic [15,16]. Experimentally, this classification corresponds to the adsorption of probe molecules. NH_3 is a base probe molecule that reacts with the electron deficient metal atoms (Lewis acid) or the protons adsorbed on the hydrated surface. CO_2 is usually considered as acidic, and thus it is expected to adsorb more strongly on basic sites. According to this classification, TiO_2 belongs to an amphoteric species and MgO to a basic species.

Most of the molecules are adsorbed as bases on the metallic cations and adsorption is stronger on TiO_2 than on MgO (see Section 4). The Fermi levels for both TiO_2 and MgO are very close to each other. TiO_2 is more reactive than MgO since the peaks of unoccupied levels are lower. Magnesium is more electropositive than titanium (1.23 vs. 1.32 according to Allred and Rochow [17,18]); it follows that the LUMO (lowest unoccupied molecular orbital) of Ti^{4+} is lower than that of Mg^{2+} and that Ti cations are more acidic than Mg cations; the electron affinities of the ions are 43.2 and 15.0 eV, respectively.

In terms of HSBA theory [19,20], Ti^{4+}, more strongly charged, is an hard acid, while Mg^{2+} is a soft acid. According to Klopman, the hardness is measured by the E^* energy value, the energy of an

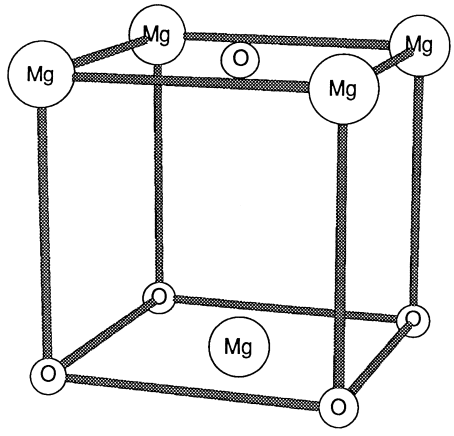

Fig. 3. The Mg_5O_5 cluster used for the adsorption of H^+ and OH^- in the SINDO calculation.

orbital under the influence of its partner; those for Ti^{4+} and Mg^{2+} are 4.35 and 2.42 eV, respectively. TiO_2 is, therefore, expected to adsorb bases more strongly than MgO and to preferentially adsorb hard bases.

We have performed cluster calculations for the case of a OH^-adsorption to measure the adsorption of the hydroxyl fragment independently of the adsorption of the counterion. We have used an Mg_5O_5 cluster with C_{4v} symmetry for the adsorption on MgO (Fig. 3) and a Ti_8O_{16} cluster with C_{2v} symmetry for the adsorption on TiO_2 (Fig. 2). TiO_2 is more reactive than MgO for OH^-, E_{ads} (OH^-/TiO_2)=6.5 eV vs. E_{ads} (OH^-/MgO)=5.6 eV. This is confirmed from tight binding

calculations [21] with an even more striking difference.

3. The basicity of the metal oxide

The adsorption on the oxygen atom of the metal oxide is less usual and it will be emphasized in Section 5 that CO_2 that is generally considered as an acidic species is adsorbed on the surface cations and not on the O-atoms. However, very acidic species are adsorbed there. Metal atoms are examples of acidic species that adsorb on the O-atoms from the metal oxides. For example, the nickel atom is adsorbed on the O-atom of TiO_2 with an adsorption energy of 137 kcal/mol. The basicity of the metal oxide also appears when the adsorbate is dissociated into acidic and basic fragments, since then the acidic fragment goes on the surface oxygen. For the Brønsted acid, the proton generated by the cleavage is the strongest acid; it is, therefore, strongly adsorbed by the O-atoms. TiO_2 appears to be more basic than MgO from the analysis of the total DOS of the occupied levels of the clean surfaces (Fig. 4); the case of TiO_2 shows a peak very close to the Fermi level at variance with that of MgO. The origin comes from a different coordination of the O-atoms. With five neighbors (four in the single-layer model), the O-levels are shifted to the lowest energies for MgO, whereas they are less dispersed and remain concentrated close to the Fermi

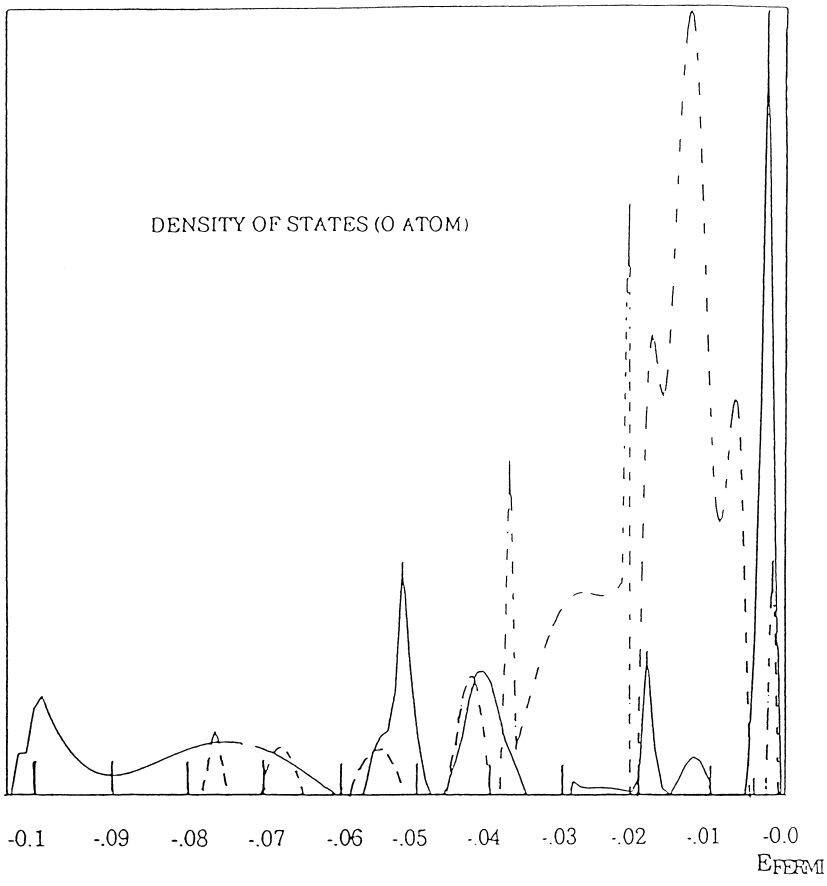

Fig. 4. The projected density of states for the p_x, p_y and p_z oxygen atoms from TiO_2 (continuous lines) and MgO (doted lines). The Fermi level is at the right-hand side. The DOS of O_{TiO_2} peak is near the Fermi level, whereas the O_{MgO} peak is shifted down and is associated with a reduced reactivity towards electrophilic species.

level for TiO_2. In other terms, the Madelung potential of the O-anion electrons is stronger and electrons less prone to be donated resulting in a weaker basic character. Such a hypothesis conflicts with the usual claim that MgO is a very basic species and means that the basicity is mostly a property of the hydroxyl groups for the hydroxylated surface. This also contributes to explain in a greater reactivity for TiO_2 which is thus, at the same time, more acidic and more basic.

The coordination of a site is an important factor that rules the adsorption ability. The calculated atomic charges do not reveal the basicity (or acidity) at a given site. Indeed, for surface oxygens, electron density accumulates at sites of large coordination that are poorly basic since the negative charge is stabilized by the presence of many surrounding cations. Singly-coordinated O are more basic than triply-coordinated [22], in spite of their weak Mulliken charge. The overlap population is not an appropriate index of reactivity, since low values correspond to ionic bonds and not necessarily to weak bonds. The density of states of the anions, on the contrary, reveals the reactivity; the shift of the oxygen levels towards low energies associated with their coordination expresses the decrease in basicity. Similar reasoning (shift towards high energies of vacant densities of states) also applies to acidity. The charges resulting from electron counts related to the coordination such as the ''ion excess charge'' [23] are also appropriate indices.

To study the adsorption of the charged fragments *independently* with the SINDO program, we have used an Mg_5O_5 cluster with C_{4v} symmetry for the adsorption of H^+ on MgO (see Fig. 3) and a Ti_7O_{14} cluster with D_{2h} symmetry for the adsorption on TiO_2 (see Fig. 2). The heats of adsorption are extremely large since H^+ is the strongest acid. That on TiO_2, 23.9 eV, is larger than that on MgO, 11.6 eV, as expected; the Ti_{TiO_2} metal site is a stronger acid and the surface O_{TiO_2} is a stronger base. The heats of adsorption are smaller for OH^- than for H^+ (the proton deprived of any core electron is an extreme case). Counting the energy for the H_2O heterolytic cleavage, 23.1 eV, these values lead predicting the dissociative H_2O-adsorption as an exothermic process on TiO_2 (-7.3 eV), but an endothermic process on MgO ($+5.9$ eV).

4. Molecular adsorption of CO_2 and NH_3 on the clean surfaces

On TiO_2, all the molecules that we have studied are bound to the exposed metal centers when adsorbed without dissociation and the heats of adsorption correlate with the gas phase proton affinities. Therefore, adsorbates must be considered as bases and the surface appears to be acidic. The extremes cases are ammonia and carbon dioxide that are experimentally [15,16] used as probe molecules to test the surface basicity (CO_2) or acidity (NH_3).

CO_2 appears on TiO_2 and MgO as a weak base, unambiguously, since in the best adsorption modes, it interacts with the metal centers. It is perpendicular [24] on TiO_2 (1 1 0); the most favorable mode is slightly bent (see Section 8); the mode parallel to the surface, slightly less favorable, also corresponds to interactions with metal centers, Ti–OCO–Ti. The heat of adsorption for a nucleophilic attack of the carbon by a surface oxygen atom (TiO_2 would be a base and CO_2 would be an acid) is weak and would rather correspond to a physisorption. On MgO, we have found at saturation (θ=1/2), the same pattern as Girardet et al. [25,26] with molecules parallel to the surface, along the Mg-rows. Thus, even if CO_2 has been used as a probe molecule to test the surface basicity, it behaves for adsorption as a weak base.

Ammonia behaves as a base that donates its electron pair to the metal generating a dative Ti–N bond perpendicular to the surface polymer. It is strongly adsorbed on the TiO_2. There is no adsorption on the oxygen atom (the basic sites) as already calculated on clusters [27]. The heats of adsorption are weaker on MgO than on TiO_2 since Mg^{2+} is less acidic than Ti^{4+}.

Auroux and Gervasini [16] emphasized that the adsorption on MgO of CO_2 was larger than that of NH_3, at variance with that on TiO_2. For, these authors, the large heat of adsorption E_{CO_2}/MgO is due to an increased surface basicity, CO_2 behaving as the acid. On the contrary, our calculations show that CO_2 behaves as a base in both cases. The heats of adsorption of CO_2 and NH_3 (see Table 1) are in agreement with the differential measures from Auroux and Gervasini [16]. However, they have to be explained by the hard and soft acid and base, HSBA, theory [19,20]. The hard base, NH_3, interacts preferentially on the

Table 1
Calculated heats of adsorption on TiO_2 (polymer model) and MgO(1 0 0) in kcal/mol

Substrate	E_{ads} (CO_2)	E_{ads} (NH_3)
TiO_2	19.0 (29.2)	47.6 (60.0)
MgO	7.0 (27.7)	6.3 (3.2)

Basis sets for the adsorbate are PS31G [41]. For Ti and Mg, the basis sets are from [22,39]. Experimental values are in parentheses (differential heats of adsorption extrapolated at zero coverage from Figures 3, 4, 7 and 9 in [15]). The heat of adsorptions vary depending on the coverage. For NH_3/MgO, slightly smaller binding energies from 4.5 to 6.4 kcal/mol have been calculated [42,43], while slightly larger values, 11/17 kcal/mol [44,45] agree with the isosteric heat of adsorptions determined on MgO powders [46,47]. For CO_2, available experimental and calculated results are in the same range: TiO_2, 15.1 kcal/mol on rutile(1 1 0) [5] and 10.8 kcal/mol on anatase [48]; MgO, 7.3 or 7.8 kcal/mol with SINDO [49] and MP2 [50] calculations on clusters.

hard acid, Ti^{4+}, more strongly charged, whereas the soft base, CO_2, interacts on the soft acid, Mg^{2+}.

5. Molecular adsorption of H_2O on the clean surfaces

Water is an amphoteric species; it is a Lewis base binding through one of its electrons pairs, σ and or p. The p-pair corresponds to the frontier orbital (orbital b_1, Fig. 5); one expects that this orbital will be involved in interaction with soft acids. The parallel orientation corresponds to this interaction. On the contrary, the σ-pair extends to increase the overlap with hard acids and leads to the perpendicular adsorption. Water is also a Brønsted acid that can interact through the protons. For the adsorption on a metal oxide, this corresponds to the formation of one or two H-bonds with the surface oxygen atoms. The heat of formation of H-bonds, ~7 kcal/mol, is small relative to the heat of adsorption on the clean surfaces. Thus, binding to surface oxygen only can be considered as a secondary interaction, when water binds to the metal site.

On MgO, the adsorption energy is 16.9 kcal/mol at θ=1/2. The best adsorption mode corresponds to the frontier orbital interaction (see above), the water behaving essentially as a base. The oxygen from H_2O is adsorbed almost on the top of Mg^{2+} center (with a small shift, 0.42 Å) and the molecular plane is nearly parallel to the surface (Fig. 6). The hydrogen atoms are oriented towards the surface oxygen atoms allowing weak H-bonds formation; the corresponding $OH\ldots O_{MgO}$ distance is large, 2.44 Å, so that obviously this interaction is not the driving force for the adsorption. At saturation (θ=1), the similar orientation is not the best; the heat of adsorption, 8.7 kcal/mol, corresponding to this mode shows a normal decrease due to saturation, whereas rotation by 45° of the H-atoms leads to 17 kcal/mol. Then, the adsorbed molecules are oriented along the Mg–Mg rows (Fig. 7). This allows a sequence of H-bonds between the adsorbates. Each molecule interacts by two hydrogen bonds with the neighboring water molecules (O...H=2.03 Å, OP=0.014). This lateral interaction between the adsorbates generates a full layer of the H_2O reminiscent of an ice-structure. This adsorption has also been found by potential energy calculations [28] and by LAUD experiments [29].

On TiO_2(1 1 0), the adsorption energy for the undissociated molecule is 74.6 kcal/mol [30] at θ=1 and 67 kcal/mol at θ=1/2. These values are large (this face is the most reactive and the three-layer slab model

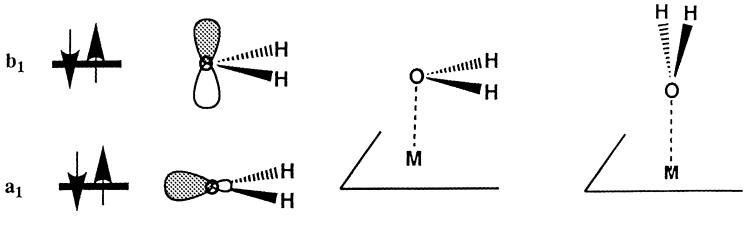

Fig. 5. The highest occupied molecular orbital has b_1 symmetry; when involved, the adsorption is flat and parallel to the surface (see middle), in terms of molecular orbital interaction, it corresponds to a frontier orbital control (soft reactants); the other pair (σ, a_1 symmetry) would correspond to a perpendicular adsorption (see at the right-hand side), to an overlap control in terms of molecular orbital interaction and to a charged controlled interaction (hard reactants).

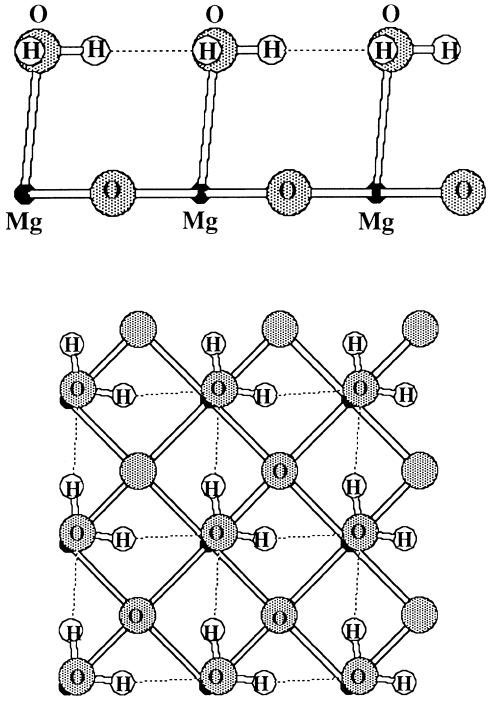

Fig. 6. Adsorption at θ=1/2. The basic adsorption mode for H_2O/MgO; the H-atoms are oriented along the Mg-O rows. The same orientation has been recently found [51] at θ=1/4.

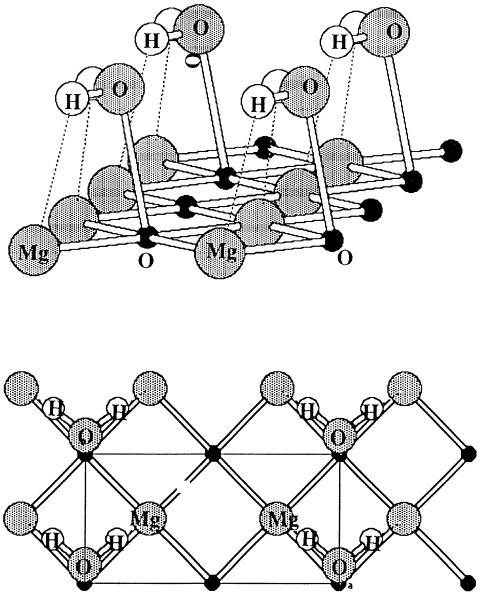

Fig. 7. Adsorption at θ=1. The sequence of the H-atoms between the adsorbed species forces the OH-bonds to orient along the Mg–Mg rows.

exaggerates the reactivity of the Ti-center, since it is tetracoordinated instead of pentacoordinated). The best orientation mode is perpendicular and corresponds to the interaction of the water with an hard acidic center. The adsorption through two protons (acidic adsorption) is weak, 13.4 kcal/mol only. The adsorption energies are large compared with that on MgO, TiO_2 is indeed more reactive oxide both as an acid and as a base. The perpendicular orientation corresponds to a charge control. The overlap between the σ-pair and the metal cation is optimal, the *p*-pair also interacts with a d_{xz} metal orbital and the protons are away from the metal center. Ti^{4+}, more strongly charged, is an hard acid, as compared with Mg^{2+} [19,20].

6. Dissociative adsorption

If the adsorption is strong enough, the adsorbate may be distorted or dissociated into fragments. The dissociation should therefore be more favorable on TiO_2 (strong adsorption) than on MgO (weak adsorption). Formally considering an heterolytic cleavage of the adsorbate, for instance H_2O, one gets both acidic and basic fragments, H^+ and OH^-. The former adsorbs on the surface oxygen and the latter on the titanium. The ionic nature of the cleavage determines the orientation of the fragment on the surface sites. For MgO(1 0 0), the dissociation is not favorable (E_{ads}=−12.9 kcal/mol at θ=1/2). The surface dissociation can be seen as the result of a competition between two basic sites on the surface. Let us consider the formal adsorption of an OH^- group as a first step. A proton can interact either with a surface oxygen, leading to a dissociative adsorption or with a surface hydroxyl group leading to the recombination of the water molecule. For TiO_2, the surface oxygens are more reactive; the coordination of the oxygen atoms at the (1 1 0) face is two and the Ti–O bond is weaker than the O–H bond. We naturally expect the surface oxygen to be a stronger base than the surface hydroxyl. For MgO, the coordination of the surface oxygen is five (four in the single layer model) and this reduces their reactivity, explaining the molecular adsorption. Such hypothesis conflicts with the usual claim that

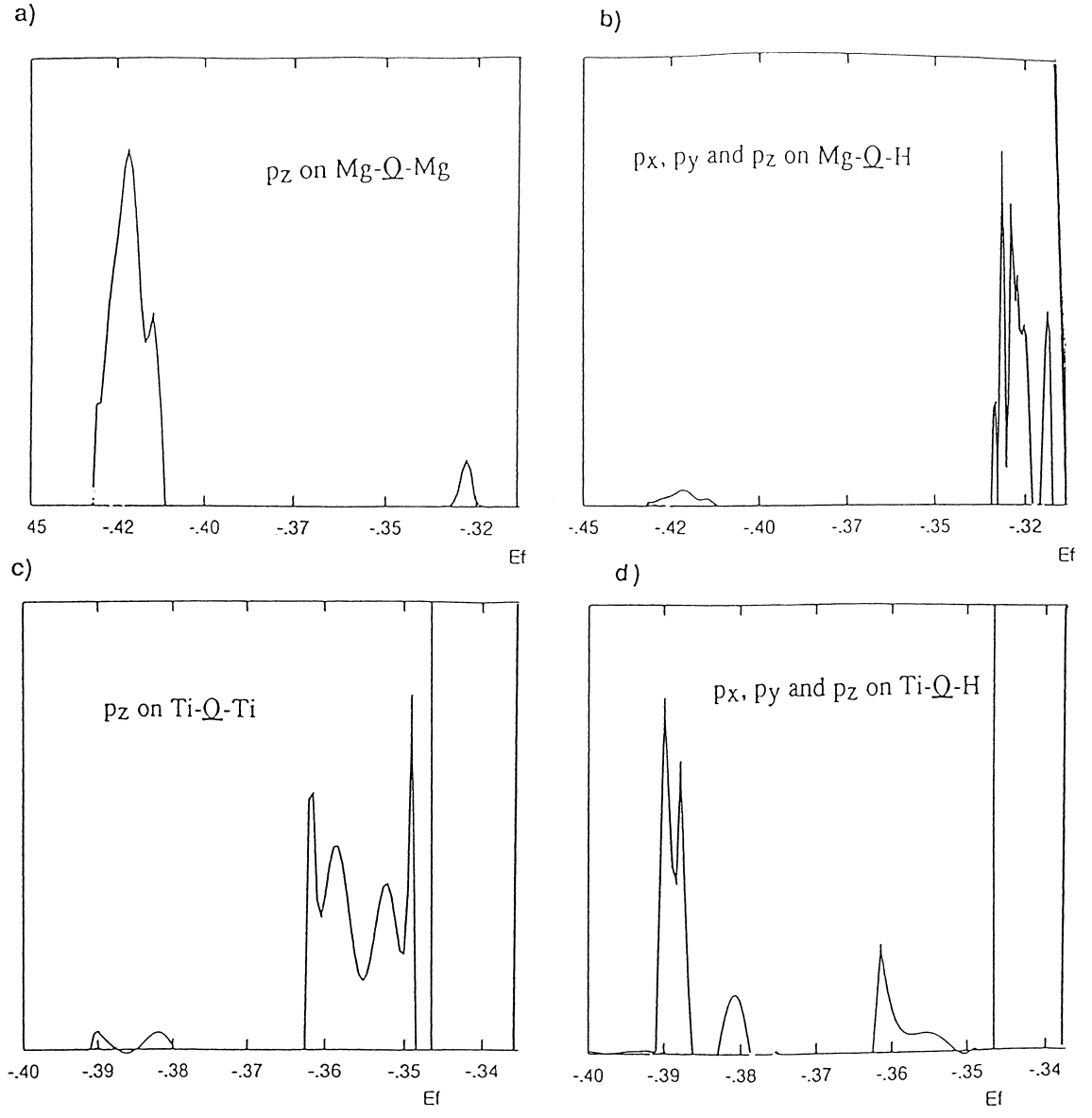

Fig. 8. The projected density of states for the p-orbitals of the oxygen atoms top: (a) from the MgOMg group; (b) from the MgOH group. Bottom: (c) from the TiOTi group; (d) from the TiOH group (P_z is normal to the surface).

MgO is a very basic species and means that the basicity is mostly a property of the hydroxyl groups for the hydroxylated surface. The projection on the reactive pairs for the two oxides are shown in Fig. 8. It is clear that for MgO, the states localized on the surface hydroxyl group are close to the Fermi level while for TiO_2 (1 1 0), we find those localized on the surface oxygen. This explains why water dissociates on TiO_2 and does not on MgO. The adsorption energy for the dissociated molecule is 121.2 kcal/mol [30] at θ=1 for TiO_2 (1 1 0), and −12.0 kcal/mol on MgO (leading to dissociation enthalpies of −51 and +29 kcal/mol, respectively). The adsorption of undissociated molecule may be observed on specific faces

of TiO_2 such as the (1 0 0) face of rutile [22] (see Section 9). It has also very recently been reported on the (1 1 0) face [31,32] in contradiction with our calculations.

Similar explanations hold in explaining that NH_3 is molecularly adsorbed and H_2S is dissociated. The adsorbed fragment NH_2 is very basic and the protons naturally prefer to recombine, whereas the HS-fragment is poorly basic and the protons rather go on the O-atom from the surface.

For ROH and RSH, two cleavages, acidic or basic, may be distinguished. On the surface, they imply different orientations of the fragments. When ROH gives a basic cleavage, the fragment R is adsorbed on the bridging oxygen atom and the titanium center is hydroxylated (singly coordinated hydroxyl). On the contrary, for an acidic cleavage, the OR-fragment goes on the titanium center and a bridging hydroxyl group is formed. These dissociations match the relative ease of cleavage in the gas phase of the isolated molecules. For MeOH, the basic cleavage is obtained on the surface since, in the gas phase, it corresponds to the least endothermic cleavage. For MeSH, it is the reverse, but in that case, the acidic cleavage is easier [33] than the basic cleavage in the gas phase.

7. Adsorption of polyfunctional groups

The best adsorption mode for carboxylic acids involves two adsorbed oxygen atoms. For the formic acid, two O from the same carboxyl group (formate) are adsorbed on adjacent metal centers. The adsorption of the two oxygen atoms is necessary to promote the acidic cleavage of the formic acid [34]. If only one O is adsorbed, the heat of adsorption remains small and weaker than that resulting from the basic cleavage. For the oxalic acid [35], the adsorption also implies two O, one from each carboxyl group. When ammonia is adsorbed on a hydroxylated surface, ammonium ions may be formed. This only happens when they are bound to three surface oxygens by three H-bonds [30].

8. Lateral and secondary interactions

At high coverages, the adsorbates molecules interact with each other. The main interactions are H-bonds and electrostatic interactions. On TiO_2, the adsorption of H_2O at $\theta=1$ allows a sequence of H-bonds [22]. The heat of adsorption for $\theta=1/2\rightarrow1$ is, therefore, larger than that for $\theta=0\rightarrow1/2$. On MgO, the water molecules interact together to generate an ice-layer. Similar effect explains a co-adsorption effect between H_2O and NH_3. The molecular adsorption of NH_3 on a hydroxylated surface ($\theta=1/2$) is more favorable than the adsorption on a bare surface [30]. Here again, there is a sequence of H-bonds between the NH_3 and the adjacent OH^-. Electrostatic interactions influence the adsorption of CO_2 on TiO_2. At saturation ($\theta=1$), the optimization of the lateral interactions forces the adsorbed molecule to bend over the surface. The relative orientation of adjacent CO_2 are then close to the optimal geometry of the dimer. Similar effects are also found for CO_2/MgO ($\theta=1/2$); we calculated the interaction between the adsorbates in the ordered CO_2 monolayers; for the perpendicular mode the $CO_2\ldots CO_2$ interactions are repulsive, whereas they become attractive for the parallel mode. The lateral interactions between the adsorbates thus contribute to favor the parallel mode. At saturation the distribution proposed by Girardet et al. [25] should be the best.

The adsorption of CO on MgO is another example of the importance of lateral interactions between adsorbates. At low coverages, the COs are vertical above the surface [36] and parallel to each other. At $\theta=3/4$, the molecules move to decrease their mutual repulsion. In the most favorable mode, two-thirds of the CO-molecules are tilted over the surface to decrease the repulsion between the adsorbates [37–39]. They are above the Mg-rows; the adsorption therefore still involves uniquely the cations sites of the surface.

9. Face specificity

The adsorption process varies with the crystallographic face. We have emphasized (introduction) that the (1 1 0) surface of the TiO_2 rutile structure was very reactive, due to electronic effects. The geometry is also favorable to the water dissociation due to the formation of H-bonds. The (0 0 1) surface of the anatase is, on the contrary, the least reactive face due to the poor accessibility of the active acidic site. Molecular adsorption is favored on the rutile (1 0 0)

surface relative to dissociation, since the molecule can insert in the space between two polymers and be stabilized by H-bonds [22]. A non-dissociative water adsorption has been also been found on anatase (1 0 1) surface, and is due to the formation of H-bonds [40]. These examples show that the adsorption strength and the adsorption mode vary with the surface as a result of several effects: electronic, steric and lateral effects. Larger differences are to be expected when defects modify the pattern of the adsorption site.

10. Conclusion

The adsorption modes result from an interplay of several factors; acidity and basicity being the dominant factors. The hardness (softness) of the adsorbate have to be taken into account to understand the comparison between the adsorption on different metal oxides. Molecular adsorptions on the clean TiO_2 and MgO surfaces imply the exposed metal centers (acidic sites). The cleavage of the molecules corresponds to the easiest cleavage in the gas phase and involves the acidic and the basic sites from the surface. When the fragment adsorbed has several functional groups, the adsorption may be determined by secondary interactions. At high coverage, lateral effects between adsorbates are important. Stabilization through H-bonds favors the vicinity of adsorbates on the surface (islands of adsorbates, high coverage and coadsorption). Electrostatic interactions explain the change of orientation between low and high coverages.

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