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Spin localization for NO adsorption on surface O atoms of metal oxides

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Abstract

The adsorption of NO on the oxygen site of several metal oxide surfaces is discussed. It is shown that the strength of the interaction and the variation of the bond lengths are not always correlated to the electron transfer from NO to the surface atoms. In cases of irreducible metal oxides, NO_2^{2-} may be strongly adsorbed. The formation of NO_2^- on reducible metal oxide is difficult unless terminal oxygen is present on the surface. Then, the reduction of the surface by transferring the unpaired electron from the NO to the surface appears in DFT calculations (VASP code).

Keywords: NO adsorption; Metal oxide; Electron transfer

1. Introduction

An important class of chemical reactions occurring on surfaces implies electron transfers. Such processes are crucial for many technological applications like gas-sensing or heterogeneous catalysis [1]. The electron transfer can take place from the adsorbed molecules to the surface, vice versa or even between two adsorbates depending on the nature of both adsorbate and metal oxide. It is then necessary to understand such phenomena on an atomic scale. We propose to investigate the electron localization in an open-shell system consisting of a radical NO adsorbed on transition metal oxide surfaces of TiO_2 and SnO_2. Adsorption on the surface can lead to a weak interaction with no electron transfer at all or it may form oxidized species like nitrites or nitrates (redox reaction). The former would involve that the unpaired electron remains on the NO molecule whereas the latter would imply a transfer to the surface cationic sites. The possibility of intermediate situations will be discussed.

In general, NO adsorption on metal oxides sites is weak. NO is both a poor Lewis acid and a poor Lewis base and over stoichiometric oxides it is not surprising to have a weak interaction (physisorption), preserving the spin localization on N and O. Adsorption on a metallic site is the most common situation occurring on low index faces of crystals [2–4]. However, adsorption on an oxygen site is also possible [2,5] (see Ref. [6] and therein) when the O atoms are reactive, for instance located at low coordination sites and clearly nucleophilic; in both cases, the orientation is N-down over the surface site. However, stronger interactions take place on surfaces implying NO dissociation [7], nitrite and nitrate formation [5,8] and references therein.

Since NO is a radical, adsorption on metal oxides should be stronger (chemisorption) when involving an electron transfer coupling electrons. The conservation of an odd number is indeed incompatible with the preservation of an energy gap in stoichiometric oxides. The electron transfer could occur between a pair of radicals, NO and another radical; alternately, it could happen between the radical and the surface. In the former case, the redox process concerns the two radicals; one is reduced and the other oxidized. The easiest solution couples the adsorption of a radical donor (NO) with that of a radical acceptor (NO_2). This ''cooperative adsorption'' leads to strongly chemisorbed products [6,9,10]. This takes place on alkali-earth oxides of MgO that are not reducible. It can also couple two identical radicals when they have amphoteric character. For NO, the disproportionation reaction of 2 NO giving NO^+ and NO^-, generates two different ions adsorbed on different sites of the surface: the former adsorbs on anionic sites O^{2-} and the latter on cationic metallic sites. This process is not strange and has been observed to occur for 2 H adsorption on MgO [11–13] or on ZnO [14,15], or 2 Cl on rutile TiO_2(110), with formation of Cl^-/Ti^{4+} and Cl^+/O^{2-} [16].

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For the exchange of electrons with the surface, the ideal situation is to start from an oxidized or reduced substrate; then, when NO loses or wins electrons, the stoichiometry may be restored. On a regular stoichiometric surface, the oxide should be reducible to be able to accommodate different oxidation states.

NO is an electrodonor radical. The nitrosonium cation NO^+ isoelectronic with the carbonyl group is the ''normal ion'' [17] and could be found as a σ donor (through the nitrogen atom in sp hybridization) in metal complexes where the nitrosyl group appears most of the time to be linear [18]. The nitrogen atom is oxidized (formal oxidation state +3) and the NO binding as NO^+ is associated with a reduction of the metal. The formation of NO^+ implies an electron transfer from the molecule, NO, to an electropositive atom, M. This is compensated by a back-donation. On metal oxide surfaces, NO^+ binds through N as a Lewis acid on the basic sites of the surface, the O^{2-}, and forms a nitrite group NO_2^-. This requires an active oxygen site at the surface. On TiO_2 anatase, the terminal oxygen atoms of irregular surfaces are then very active [5,19]. On V_2O_5, nitrites are presumably the intermediates responsible for the exchange of oxygen atoms between NO and surface vanadyl species during the SCR reaction [20,21]. They have been calculated to be the best adsorption structure [22] even though this adsorption was found only very slightly exothermic (+5.3 kcal/mol) [23].

In spite of the greater electronegativity of nitrogen over metal, NO is not a good electron acceptor radical. The electron transfer to NO generates a nitrosyl anion, NO^-. There are some examples of nitrosyl ligands in metal complexes. NO^- in an electron count for the stability of complexes acts similarly to other negatively charged ligands such as $C_5H_5^-$ and Cl^-. The negative ion associated with the sp^2 hybridization should lead as ligand to a bent structure. This ''anomalous structure'' has also been characterized in complexes [17]. The formation of a nitrosyl ion negatively charged requires that the metal is not in its highest oxidation state. For complexes, it is characterized on a cuprous ion. On surfaces, it must concern pure metals or reduced metal oxides. Interacting with a metal (in oxidation state 0), NO should accept electrons more easily than on the corresponding cation; adsorption on metals is stronger than on the cations of a metal oxide. In addition to the σ donation from NO^- to the metal that builds a σ_{M-NO} bond, NO behaves as ligand π acceptor and receives electrons. This results in weakened nitrogen-to-oxygen bond. With the exception of Pd, Pt and noble metals that are the least electropositive metals, the electron transfer to the antibonding NO levels induces a dissociation of the molecule [24]. The case of molecular adsorption has been studied on Pd, Rh and Pd–Mn alloys [25–30] and takes place on bridge and hollow sites. The adsorption of NO is large, 3.78 eV, on a strongly reduced TiO_2(110) rutile-surface (a complete missing row of bridging-oxygen rows) [4]. In addition to the large reduction, the large reactivity of sites of low coordination (four-fold coordinated metal atoms) contributes to this value. Similarly on SnO_2(110) surfaces with an O vacancy, the most stable adsorption sites are the defect positions where N occupies the position of a missing bridging oxygen atom [31]. More limited reduction is not always so efficient; calculations have shown that the adsorption of NO on reduced V_2O_5 was not very strong [22]. On non-transition metal oxides, the NO adsorption on a metal cation as a Lewis base is very weak [32] and the adsorbed species remain dimeric in spite of the weakness of the coupling energy of the dimer. The interaction energy with transition metal oxides is larger due to a d–π interaction, but still weak.

If the NO adsorption is wanted to initiate a reaction where the nitrogen is reduced (nitrite, nitrate or N_2 formation), it should not be adsorbed as NO^- at a metal site; the NO^+ ''normal ion'' is much more appropriate. This ion is better adsorbed on a O atom of the surface. The purpose of this paper is to investigate the spin distribution for the NO adsorption on the O surface atoms of a metal oxide. An electron transfer to the surface seems advantageous since an extra electron on NO would fill antibonding levels. The transfer represents an alternative location on the metal in a passive orbital deprived of bonding–antibonding character. However, in spite of geometry and energetics, the electron transfer has to be proved. Since the transfer is associated to relative energy levels, an abrupt electron transfer seems probable. We would expect a progressive migration if it were associated to a bond formation.

2. Computational details

We have carried out periodic calculations with the Vienna ab initio Simulation Package code [33–35] (VASP 4.4.4). In the VASP program, the Kohn–Sham equations are solved with the generalized gradient approximation (GGA) proposed by Perdew and Wang [36] and Perdew [37]. Ultrasoft pseudopotentials, USPP [38,39] or projector-augmented wave approach, PAW [40,41] have been used together with plane wave basis sets. The cutoff of plane waves is 400 eV. The integrations in the Brillouin Zone are performed on a grid of $5 \times 5 \times 1$ for rutile and anatase structures. The slab is periodically repeated to generate a 3D calculation. The c value is chosen to incorporate an empty space of 9 Å so that the NO interacts only with one face of the slab. The NO reference energies, −12.19 eV (USPP) and −12.26 eV (PAW) have been obtained in a spin polarized calculation, taking a unit cell of 10^3 Å^3. Optimizations are carried out with the conjugate gradient algorithm. The upper part of the slab has been optimized (three atomic layers in the case of the rutile structure) and the lower part (six atomic layers) has been frozen at the bulk position. The spin localization was obtained from the integration of the spin densities in spheres using the default values of the VASP code.

3. Results

Results are presented in Tables 1 and 2. To simplify a notation, P (physisorption), C (chemisorption) or I (intermediate) is added in Table 1 according to ratio, $d_{NO_{Surf}}/d_{NO}$, of the two NO distances: larger than 1.5, smaller than 1.3 or between these two values. Similarly, we have labeled the Table 2 according to the percentage of electron transfer: T when the spin localization on NO was below 50%, R when it was more than 75% and I for the intermediate cases.

Table 1
Adsorption energies of NO referred to the monomer

	E (eV)	$d_{M_{Surf}-O_{Surf}}$	$d_{O_{Surf}-N}$	d_{O-N}	
Rough TiO_2 anatase(0 0 1), Model 2, $NO_2^-{}_{ADS}$ [5]	2.68	2.11	1.29	1.22	C
Rough TiO_2 anatase(0 0 1), Model 1, $NO_3^-{}_{ADS}$ [5]	5.46	2.14	1.30	1.23	C
TiO_2(1 1 0) rutile, $\theta = 1/2$	0.26	1.91	2.07	1.16	P
TiO_2(1 1 0) rutile (Schottky)	0.40[a]	1.90	1.41	1.20	C
TiO_2(1 1 0) + H_2O, Ti=O	0.29	1.82	1.47	1.18	C
TiO_2(1 1 0) + H_2O, Ti–O–Ti	0.24	1.91	2.43	1.14	P
TiO_2(1 1 0) + H_2O, Ti–O–N–O–Ti	0.57	2.08	1.27	1.27	C
TiO_2(1 1 0) + OH, Ti=O	2.29	1.81	1.48	1.17	C
TiO_2(1 1 0) + OH, Ti–O–Ti	2.35	2.08	1.57	1.16	I
V_2O_5(0 1 0) on V=O (most stable structure)	0.33	1.61	2.44	1.14	P
V_2O_5(0 1 0) on V=O (metastable structure)	−0.71	2.73	1.22	1.21	C
V_2O_5(0 1 0) on V–O–V	0.19	1.80	3.01	1.15	P
SnO_2(1 1 0), $\theta = 1$ [31]	1.03	2.27	1.52	1.25	C
SnO_2(1 1 0), $\theta = 1/2$ [31]	1.23	2.23	1.38	1.25	C
SnO_2(1 1 0), $\theta = 1/3$ [31]	1.43	2.24	1.35	1.25	C
SnO_2(1 1 0), $\theta = 1/2$, USPP (most stable structure)	0.76	2.08	1.78	1.18	P
SnO_2(1 1 0), $\theta = 1/2$, USPP (metastable structure)	0.51	2.25	1.22	1.41	C
SnO_2(1 1 0), $\theta = 1/2$, PAW	0.52	2.07	1.90	1.16	P
SnO_2(1 1 0) rutile (Schottky)	3.63[a]	2.53	1.41	1.22	C
MgO(1 0 0) [6]	0.23	–	2.28	1.19	P
CaO(1 0 0) [6]	0.72	–	1.55	1.28	C
SrO(1 0 0) [6]	1.09	–	1.50	1.30	C
BaO(1 0 0) [6]	1.43	–	1.46	1.31	C

The values would be reduced by 0.2 eV referred to the dimer calculated in VASP [31]. Distances in Å for the adsorption of NO. A qualification P: physisorption; I: intermediate; C: chemisorption. The d_{NO} value for the molecule calculated with VASP is 1.17 Å.

[a] The surface in which the O atom has been displaced. The cost for the Schottky process is 1.48 and 3.12 eV for TiO_2 and SnO_2, respectively.

3.1. Rough anatase TiO_2(001) surface

Let us first consider the case of a reducible metal oxide containing reactive oxygen atom. Oxygen atoms with low coordination and low Madelung stabilization are distinctly nucleophilic. The nitrite/nitrate formation was found for models accounting for a ''rough surface'' and containing singly coordinated oxygen atoms. In Ref. [5] three layer slabs

Table 2
Adsorption energies of NO referred to the monomer and spin localization

System	E_{ads}(NO) (eV)	Spin on N (NO) (%)	Spin on O (NO) (%)	Spin on the metal oxide (%)	
NO molecule, US		64	36		
NO molecule, PAW		60	40		
Rough TiO_2 anatase(001), Model 2, $NO_2^-{}_{ADS}$	2.68	22	18	60	T
Rough TiO_2 anatase(001), Model 1, $NO_3^-{}_{ADS}$	5.46	0	0	100	T
TiO_2(110) rutile, $\theta = 1/2$	0.26	39	23	38	I
TiO_2(110) rutile (Schottky)	0.40	0.3	0.5	99	T
TiO_2(110) + H_2O, Ti=O	0.29	2	1.5	96.5	T
TiO_2(110) + H_2O, Ti–O–Ti	0.24	42	26	32	I
TiO_2(110) + H_2O, Ti–O–N–O–Ti	0.57	2.6	1.4	96	T
V_2O_5(010) on V=O (most stable structure)	0.33	42	30	28	I
V_2O_5(010) on V=O, metstable structure	−0.71	0.5	0.5	99	T
V_2O_5(010) on V–O–V	0.19	49	34	16	R
SnO_2(110), $\theta = 1/2$ [31]	1.23	57	21	22	R
SnO_2(110), $\theta = 1/2$, PAW	0.52	12	9	79	T
SnO_2(110)	0.51	14	8.4	77.6	T
SnO_2(110) rutile (Schottky)	3.63	14	2.5	83.5	T
BaO(100)	4.39	45	34	21	R

Result from [31] has been calculated using the CRYSTAL03 program.

of TiO_2 anatase(001) (9 complete atomic layers or 10 incomplete ones) were used terminated by an atomic layer (complete or half-layer) of terminal O atoms. The most stable slab is different, deprived of reactive oxygen terminated by O bridging atoms. The slabs modeling the rough surfaces correspond to less cleavages of the bulk with the same orientation, involving more M–O bonds cleavages for the three-fold coordinated O atoms; the first slab is terminated by two layers of O atoms on one side and a metal layer on the opposite side; the top O layer is made of singly coordinated O and represents a reactive surface. In the second model, the slab is terminated by half a layer of O atoms; the top half-layer consists of singly coordinated O atoms similar to those of the first layer; the bottom half-layer is made of bridging O at the bulk position. The first model may allow the interaction of an adsorbate with two adjacent nucleophilic oxygen atoms at the surface.

The reactions taking place on the terminal oxygens are the following:

$$NO + {O_{Surf}}^{2-} \rightarrow {NO_2}^{-}{}_{ADS} + e^-, \qquad Ti^{4+} + e^- \rightarrow Ti^{3+} \tag{1}$$

and

$$NO + 2{O_{Surf}}^{2-} \rightarrow {NO_3}^{-}{}_{ADS} + 3e^-,$$
$$3Ti^{4+} + 3e^- \rightarrow 3Ti^{3+} \tag{2}$$

In Ref. [5], the energetics and the optimized structures were used as proof of the redox mechanism. The adsorption of the ${NO_2}^{-}{}_{ADS}$ corresponds to a large stabilization relative to the NO desorbed, 2.68–2.96 eV; the two N–O distances were short and almost symmetrical whereas the Ti–N distance remained rather large (Table 1).

The spin distribution displayed in Table 2 shows only a partial electron transfer for reaction (1) and a total transfer for reaction (2). For the formation of the nitrite, the spin is located both on NO (40%) and on the Ti atoms (60%, predominantly on the uncovered face of the slab). In the case of the nitrate formation, the spin distribution shows a complete electron transfer.

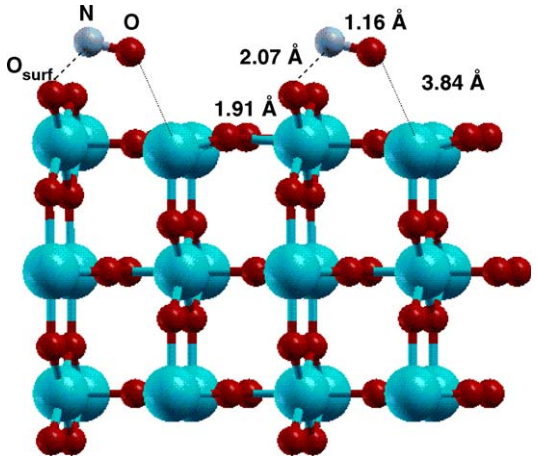

Fig. 1. Adsorption of NO on the bridging oxygen atom of TiO_2(110).

3.2. Rutile TiO_2(110) surface

The adsorption on the perfect surfaces of TiO_2 is weak. On the anatase(100) and (001) faces, it takes place on Ti (E_{ads} = 0.18–0.40 eV) and the adsorption on O is even weaker (E_{ads} = 0.07 eV) [42]. Rutile is slightly more reducible than anatase and this may facilitate the adsorption on the O site. However, on the rutile(110) surface the adsorption energy of NO on a bridging O atom is 0.26 eV and the geometry of the structure still corresponds to a physisorption (Fig. 1). The bridging O atoms are not basic enough to interact very strongly and it would cost too much energy to cleave the Ti–O bonds making a nitrite species. Consistently, the spin predominantly remains on NO. However, the delocalization on the titanium center is not negligible and the qualification in Table 2 is ''intermediate''.

3.3. Rutile TiO_2(110) with reactive oxygen atoms, Schottky defect

We have also built a rutile surface with a singly coordinated O atom, supposed to be more reactive. For that, we have moved one bridging oxygen atom out of two to a top site over a five-fold coordinated Ti_5 atom. This is a Schottky process occurring at the surface (Fig. 2). As in Section 3.1, the structure is

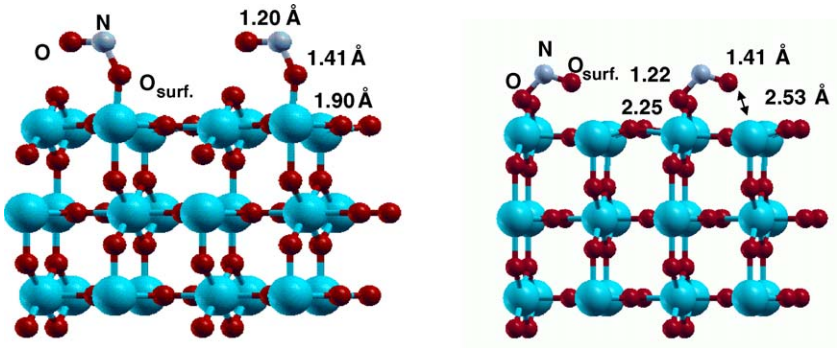

Fig. 2. Adsorption of NO on a reactive oxygen atom. The terminal atom has been created by displacing a bridging oxygen to a metal site (Schottky process). TiO_2 is presented at the left-hand side and SnO_2 at the right-hand side. Note that for the latter, the structure rearranges and should be seen as NO adsorbed on a bridging O atom of the regular surface. Starting from the regular surface, the label for the O, ''surf'', should be modified; this is done in tables.

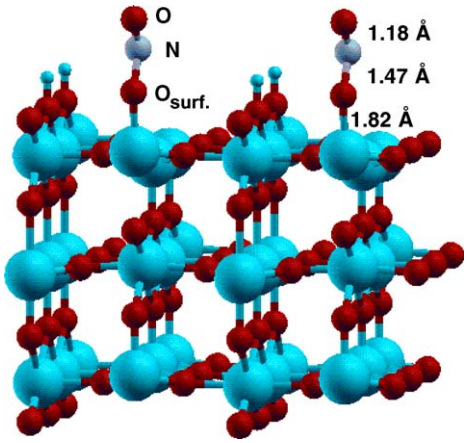

Fig. 3. Adsorption of NO on TiO_2(110) hydrated surface. The water molecule is dissociatively adsorbed: two H on two bridging oxygen atoms and one O on Ti_5. NO interacts with this latter oxygen atom.

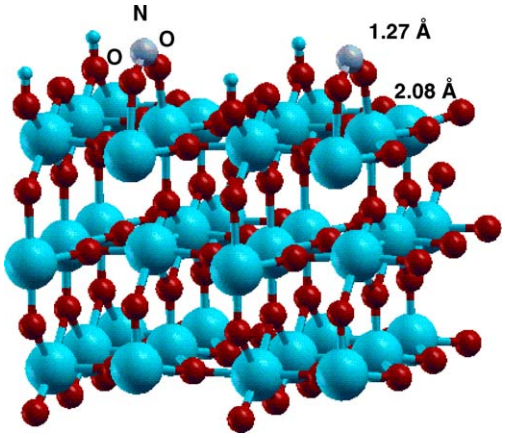

Fig. 4. Adsorption of NO on TiO_2(1 1 0) hydrated surface. NO interacts both with the terminal O via N and with Ti_5 via O; this results in a NO_2 group adsorbed on two Ti_5 atoms.

stoichiometric and the Ti_4 atoms adjacent to the defective site are not reduced. The cost of the O migration, 1.48 eV (at $\theta = 1/2$), is larger than that found at lower coverage [43]. However, the adsorption energy for NO referred to this reconstructed surface is large, 0.40 eV; this represents twice the value on the regular surface, 0.26 eV. The nitrite formation is also more pronounced than on the regular surface. The ratio $d_{NO_{Surf}}/d_{NO}$ is 1.18 instead of 1.78. The spin is completely localized on the slab which is consistent with a complete electron transfer.

3.4. Rutile TiO_2(110) hydrated surface

We have also considered another model containing an O atom over a five-fold coordinated Ti_5 atom. This oxygen arises from the complete dissociation of H_2O on the rutile(110) surface at a low coverage ($\theta = 1/3$). Two bridging O atoms are hydrogenated so that the system also remains stoichiometric. There are two adsorption sites: the terminal O atom and one uncovered bridging atom. The adsorption energy is weak, a little larger on the terminal O atom (Fig. 3) than on the bridging oxygen. In Table 1, the qualification of the structure is ''intermediate'' for the former and ''physisorption'' for the latter. The spin localization (Table 2) changes completely; for the former, the spin is completely localized on the substrate revealing a complete electron transfer; for the latter, the spin mainly remains on NO even though the transfer would represent one-third of electron.

We have also checked the case of a NO adsorption through the two atoms, the N binding to the terminal O atom and the O to an adjacent Ti_5 atom (Fig. 4). This mode is the most favorable a clearly resembles to a nitrite. For this case, the qualifications in tables are C and T that are consistent with the formation of a nitrite.

Finally we have removed one hydrogen atom of this system which corresponds to an oxidized surface. The NO adsorption then leads to a stoichiometric system with an ideal electron count (closed-shell system). The heat of adsorption is then magnified by a factor 10. The geometry for the adsorption on the terminal oxygen is however very close to that of the previous model and the qualifications are identical.

3.5. V_2O_5 surface

The vanadia is another reducible oxide. Studies on V_2O_5 cluster models have concluded that terminal O ligands are nucleophilic and that the binding to the O atom making NO_2^- corresponds to an electron transfer to the vanadium center [22]. There are two NO_2^{2-} species interacting (physisorption on O), one binding to a single V atom and the other bridging the two V atoms. The energy of the NO adsorption is 1.97 and 2.72 eV, respectively. The interaction with the (010) face of the crystal is much lower and the geometry for the adsorption on V=O or on V–O–V resembles that of a physisorption. A structure with the formation of a nitrite is metastable ($E_{ads} = -0.71$ eV), the cost to extract an O atom from a vanadyl group being not compensated by the energy gain associated with the nitrite formation. For the physisorbed states, most of the spin is localized on the NO as expected. However, the delocalization on the vanadium center reaches 28% for the interaction with the vanadyl.

3.6. Rutile SnO_2(110) surface

On SnO_2(110), Bredow and Pacchioni [31] have calculated that NO mainly interacts via the nitrogen atom with the bridging oxygen atoms of the stoichiometric oxide. The geometry of the system varies with the coverage (Table 1). At the lowest coverage, 1/2 and 1/3, the ratio $d_{NO_{Surf}}/d_{NO}$ is close to unity, 1.10 and 1.08, which is in very good agreement with a picture of a nitrite formation; this sounds reasonable since SnO_2 is a reducible oxide. Compared with TiO_2 (rutile) we have found that SnO_2 is more reducible, not only for the formation of O vacancies but also relative to the atomic adsorption of the hydrogen that takes place with reduction [42]. The H atom is a strong electrodonor radical and the electron transfer is not ambiguous; the same hydrogenation mode (on the O atom with electron transfer) is also observed on other reducible oxides

such as V_2O_5 [44–46]. For the hydrogenation of SnO_2 and TiO_2 (rutile), an O–H bond is made [16,47] and the difference in the adsorption energies mainly arises from the ease of the electron transfer. Since it is easier on SnO_2 than on TiO_2, the adsorption energy is larger (3.1 eV versus 2.6 eV). Concerning the spin localization Bredow and Pacchioni commented that the unpaired electron remains mainly located on the NO molecule. This surprising result was part of the motivation of the present study. If the adsorption at the O site with nitrite formation were associated with an electron transfer, the spin should be on the metal oxide. Moreover, they find that a NO adsorption on a defective surface is easier than that on the regular oxide. The defective surface is reduced! If the NO adsorption were accompanied by a reduction of the surface, one would expect that a further reduction would be difficult.

We have repeated the adsorption on SnO_2 using spin-polarized GGA with the VASP code, US pseudopotential or PAW. Results are displayed in Tables 1 and 2 and essentially confirmed those obtained by Bredow and Pacchioni. The energy of adsorption referred to spin polarized NO molecule is weaker. Since the system has an odd number of electrons, we should expect that the spin polarized calculation would give a lower energy for the system where a single NO is adsorbed. This is not verified; however we report the value for the high spin state. The electron transfer calculated for the high spin state (Table 2) is very limited. It is however larger than that on TiO_2 (rutile) which is consistent with the easier reducibility of SnO_2. Using criteria of energy and geometry, the notation of Table 1 is C for the results calculated without spin polarization and P when spin polarization is included. On the contrary, the present VASP calculation finds more electron transfer (Table 2) than determined using the CRYSTAL code [31]. It is also important to note that the conclusions drawn from the two tables (P in Table 1 and T in Table 2) diverge. We have also found another adsorbed structure which better matches a nitrite formation (see next section); however, it is higher in energy by 0.25 eV.

3.7. Rutile SnO_2(110) with reactive oxygen atoms, Schottky defect

As for the analogue structure of TiO_2, the surface presenting a Schottky defect is reactive. Relative to the structure obtained after the O migration, the adsorption energy for NO is 3.63 eV and is associated to a nitrite formation considering both the geometry (Table 1) and the spin localization (Table 2). Compared with TiO_2, the formation of the Schottky defect costs more, 3.12 eV instead of 1.48 eV. This is because the adsorption energy of O is weak [43]. When NO is adsorbed (Fig. 2); the final structure is the same than one obtained by the NO adsorption on a regular surface except that it involves an exchange of the O atoms; starting by the former the bridging O atom originates from the NO. This structure is metastable relative to the structure obtained by physisorption on the regular surface (previous section).

3.8. BaO surface

Schneider [6] have calculated the NO adsorption on a series of alkali-earth metal oxides: MgO, CaO, SrO and BaO. Since the metal cations are not reducible, one should expect a physisorption. The weakness of the adsorption energy and the variations of the bond distances support this analysis for MgO. On the contrary for the other compounds, the heats of adsorption are larger and the ratio of the two N–O distances is closer to unity, 1.11 for BaO representing the extreme case. The evolution correlates with the width of the band gap; for BaO, the band gap is weak making easy an electron transfer to the bottom of the conduction band. We have calculated the spin distribution which tempers this interpretation. The spin remains localized on the metal oxide (see Table 2). There is a conflict between the qualifications C and R displayed in the two tables.

4. Discussion

In the cases studied, the orientation on the O site and the variation of the bond lengths indicate a more or less pronounced formation of nitrites that the analysis of the spin localization does not corroborate with the same extend. Spin delocalization has been found important even in the cases of physisorption. For BaO, the absence of delocalization does not match the strong interaction given by Table 1. Comparing the two tables, it is obvious that the association P = R, C = T is not general.

In the extreme cases of irreducible oxide, NO is found to bind to O^{2-} forming ONO^{2-} [48–50] without electron transfer to the metal. ONO^{2-} remains a radical. The earth alkali metals are unable to welcome an extra electron and the magnitude of the interaction only reflects the nucleophilicity of the surface oxygen, O_{Surf}. On MgO(100), NO physisorbs, N-down over a surface oxygen. It is more strongly adsorbed on CaO, SrO and BaO. The comparison of the strengths (easier when the electron gap is smaller) and the structures suggest the formation of surface nitrites. However, the spin remains on the NO molecule with a rebalanced distribution in favor of the O atom. The transfer to the metal therefore may not be the driving force for the O adsorption as expected and we must involve the electronic redistribution in the adsorption mechanism.

Let us analyze the adsorption process at the O site. The interaction starts between the odd electron from NO and the electron pair of the O surface atom (the O^{2-} of the surface). The low lying SOMO of NO makes a 3e-interaction with a low lying filled orbital that is at least competitive with an alternative 1e-interaction with an empty orbital high in energy (case of an adsorption with a metal cation). The excess of electrons however is not a sign of stability and the interaction remains limited as long as the $\sigma^*_{N-O_{Surf}}$ is occupied by one electron. When this orbital rises in energy, it cannot remain filled and the odd electron has to be transferred either on a metal atom if this one is reducible or on a π^*_{N-O} orbital if there is no alternative. It follows that NO distance increases while the N–O_{Surf} distance decreases, a real dative bond being formed (donation from the O^{2-} to an empty sp^2 orbital of the N atom). This is the reason why the geometry resembles a nitrite species in every case.

The strength of the binding mostly reflects the basicity of the oxide. We have checked that the basicity of BaO was larger than that on MgO by adsorbing $AlCl_3$ on two three-layer slabs representing the oxides surfaces. The adsorption energies are 2.52 and 1.11 eV, respectively. The formation ONO^{2-} does not reduce the metal. As it depends on the basicity of the O surface site, it is easier on a reduced oxide, more basic, than on an oxidized one, less basic. It is not surprising that the ONO^{2-} formation is more energetic on a defective SnO_2 surface than on a regular one as found in Ref. [51].

5. Conclusions

NO cannot bind very strongly on the cations of metal oxides when they are in their highest oxidation state since donation from the metal to the molecule is not possible. Strong binding possibilities should then be searched at the basic sites, when O atoms are enough nucleophilic. NO adsorption on oxide sites of TiO_2 and SnO_2 is weak unless reactive oxygen sites are present. When reactive oxygens are present, ONO^{2-} is first formed allowing elongating the NO distance when the $N–O_{Surf}$ distance shortens. Nitrite and nitrate species are formed by transferring the electron to the cation metallic sites. This transfer is progressive and is facilitated by a conjugation of the π^*_{NO} orbital with d orbitals of adjacent transition-metal cations. In the case or earth-alkali metals, deprived of d orbital, this transfer does not occur. The cases of ONO^{2-} do not involve any spin transfer. However, when O atoms are nucleophilic, the variations of geometry associated with the formation of these dianions is large. The spin transfer is observed with the formation of NO_2^- on the surface; it is mainly found in cases of terminal oxygen atoms, this atom arising either from a migration of a surface O atom or by the complete dissociation of H_2O. We also found a spin transfer for the regular $SnO_2(110)$ surface qualified as a physisorption on the basis of geometry and binding energy. The correspondence between electron transfer, geometry distortion and heat of adsorption is not straightforward.

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