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).
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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.