On the Need for Spin Polarization in Heterogeneously Catalyzed Reactions on Nonmagnetic Metallic Surfaces

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ABSTRACT: A series of reactions including water, oxygen, hydrogen and nitric oxide dissociation and carbon monoxide or nitric oxide oxidations catalyzed by metallic surfaces have been investigated by means of periodic density functional calculations with the main aim of establishing the importance of spin polarization when the substrate is nonmagnetic. Numerical differences in the calculated total energies and bond lengths of the breaking/forming bonds corresponding to spin restricted or spin unrestricted formalisms are usually smaller than the inherent error of density functional theory based methods. Nevertheless, it is important to insist on the fact that the spin polarized solution exists and is lower in energy than the one corresponding to the spin restricted formalism, as one would expect, and from a practical point of view, results obtained without taking spin polarization into account lead to the same description of the potential energy surface.

1. INTRODUCTION

To a large extent, chemistry can be viewed as the art of making and breaking bonds, and understanding the basic science behind this has been one of the main challenges of theoretical chemistry. From a fundamental point of view, understanding the mechanism of bond formation became one of the earliest successes of the nowadays well established molecular orbital theory, from which original ideas were formulated in a rather qualitative way by Robert Mulliken with the aim of understanding molecular spectra. The ideas of Mulliken were published initially in several quite unknown reviews[1] and reported later in a more complete manner in a nowadays classical paper.[2] From basic chemistry textbooks, one learns that, according to this theory, a chemical bond is formed when two electrons from separated units (atoms or radicals) occupy a bonding molecular orbital. The ab initio implementation of this idea resulted in the so-called (restricted) Hartree−Fock (RHF) wave function based method,[3] which allows one to compute and predict rather accurately molecular structures.

The Hartree−Fock method wave function makes use of a single Slater determinant made of molecular orbitals minimizing the ground state energy expectation value. Because of the restriction to a single Slater determinant, the RHF method incorrectly describes the potential energy curve of the hydrogen molecule and its dissociation limit. For this small molecule (and possible for other simple ones), it is possible to make use of sophisticated (almost) exact (full) configuration interaction techniques, but for reasons which will become obvious later on, it is convenient to recall that the simplest way to solve, in part, the problem of incorrect dissociation of the RHF method covalent bond breaking is to remove the spin restriction which allows α and β electrons to be described by different spatial molecular orbitals. The resulting formalism, first proposed by Pople and Nesbet,[4] has been since termed the unrestricted Hartree−Fock (UHF) method. The removal of spin symmetry

in the UHF formalism allows one, in some cases, to obtain a (spin polarized) solution with energy lower than that of RHF. This is the case for H_2 at a sufficiently large internuclear separation, leading to a physically correct situation with two well-separated H atoms, each maintaining its magnetic moment. However, it is important to point out that close to the equilibrium geometry, the UHF converges to the RHF solution, and here, spin symmetry is not a restriction. The textbook explanation is that approaching the two H atoms results in one bonding and one antibonding level which, being well separated in energy, lead to a closed shell structure with one electron pair in one bonding orbital. In this sense, chemical bonding quenches the atomic magnetic moment; we will come back to this argument later on.

In spite of these appealing features of the UHF method, its use in quantum chemistry was rather limited because of the problem of spin contamination inherent to the formalism and of the advent of efficient multiconfigurational self-consistent field (MCSCF) methods that, through appropriate configuration mixing, allow for a proper description of molecular dissociation.[5] However, the idea behind UHF is at the heart of the unrestricted, often also termed spin polarized, version[6,7] of the usual Kohn−Sham[8] implementation of density functional theory (DFT).[9] In fact, although DFT was first applied mainly to solid state problems [see refs 10 and 11 as representative earlier applications], it is broadly used at present as shown by recent reviews [see refs 12 and 13 and references therein], and this is the reason for such historical and perhaps lengthy introduction. Here, one may argue that since DFT only makes use of the density provided by the Kohn−Sham determinant, which in turn represents the density of the noninteracting reference system, it is not necessary to worry about spin

contamination. It has also been claimed that spin contamination in DFT is less severe than in UHF.[14] However, one must be aware that ignoring the effect of spin contamination can lead to misinterpretations and to severe errors.[15,16]

The need for spin polarization in the calculation of dissociation energy of molecules has been recognized since the earlier work of Gunnarsson et al.[17] and of Painter and Averill[18] on the first row diatomic molecules but mostly to describe the separated atoms. However, it is in the transition state structures where chemical bonds are stretched, leading to a situation resembling the one described above for H_2 at large internuclear separation with the concomitant appearance of nondynamical (near degeneracy or left-right) correlation, where one may wonder whether the calculation of the corresponding activation energy requires using a spin unrestricted formalism. This has sometimes been termed the symmetry dilemma, as initially introduced by Lowdin in the framework of Hartree–Fock theory.[19] The concept has also been addressed by several authors in the past in connection to DFT[20–22] and even led to an alternative interpretation of spin density functional theory.[23] The answer to the question above is obvious when the molecular system has an odd number of electrons,[24] but spin polarization is often a necessary requirement when a chemical reaction takes place through a concerted mechanism involving a diradical like transition state structure, the Diels–Alder reaction of butadiene and ethene being a paradigmatic example.[25] Spin-polarization was also found to play a crucial role in calculations of gas phase reactions involving radical states along the reaction path.[26–28] What happens when the situation just described above takes place above a metal surface? Metals are common components of heterogeneous catalysts, and their presence affects precisely chemical bond forming or breaking. Hence, we reach the central question of the present work. Is spin polarization playing a role also in the transition state of a chemical reaction occurring above a metal surface?

Spin polarization is obviously necessary if the metallic substrate already exhibits a magnetic character, but a less clear situation emerges when dealing with a metallic, nonmagnetic surface. The question also holds when the surface has an insulating character, as is the case of oxides widely used as supports in catalysis, although these will not be further discussed except as examples when necessary. The key question is whether the transition state structure for a given bond dissociation taking place above a nonmagnetic metallic surface maintains a diradical character with rather well localized and separated electrons, as in the gas phase reaction, or, on the contrary, the electrons from the bonding electron pair are delocalized in the metallic bands (Fermi sea in the language of solid state physics). This is a crucial question because in the first case spin polarization is mandatory, whereas in the second one it is possible to obtain physically meaningful results without needing to impose spin polarization, which implies a somewhat larger computational effort.

Inspecting the specialized literature concerning reactions taking place at nonmagnetic metallic surfaces, it appears that the argument that upon bond cleavage the otherwise unpaired electrons delocalize in the metallic bands is usually invoked and the reaction profile calculated using a non-spin-polarized scheme.[29–31] This point of view is supported by the evidence that atoms adsorbed at metallic surfaces do not maintain their high spin multiplicity,[32] and spin unrestricted seems to be a common choice[33,34] already from the very first applications of DFT to the study of atomic adsorption on metal surfaces.[35] A completely different scenario emerges when considering transition metal atoms adsorbed on oxide surfaces such as MgO(001) or Al_2O_3(0001)[36,37] where the electronic bands are narrow and, consequently, the unpaired electrons are not efficiently delocalized, the result being that, at these surfaces, the transition metal atoms maintain the high spin state. Here, Hund's rule prevails over chemical bonding and concomitant spin quenching. The interaction of NO with NiO and Ni-doped MgO offers another interesting example where spin polarization is crucial to understand the electronic structure of the adsorbed species, which indeed exhibits a strong multiconfigurational character and provides a challenge to DFT,[38–41] and CO on MgO(001) provides yet a difficult case for standard DFT approaches.[42]

Nevertheless, it must be pointed out that the DFT method, mainly with standard functionals of the generalized gradient approach (GGA) type is widely used in calculations regarding catalytic reactions on metallic surfaces providing microscopic insights in complicated mechanisms such as the water–gas shift reaction catalyzed by Cu(111) where a detailed description is obtained with agreement of theoretical and experimental turn-over rates.[43] The accuracy of the total energies may be questionable, but the resulting relative energies are much less affected by the GGA inherent errors (see refs 30, 44–46, and references therein) to the point that these techniques are already used in the industrial development of new catalysts.[47] There are still difficult cases such as CO on Pt(111) mainly due to the well-known "*gap*" problem, which has to be expected for adsorption systems where a competition occurs between the electron donation from the molecular HOMO to the surface and the electron back-donation from the surface to the molecular LUMO.[48] However, it is nowadays accepted that DFT can describe correctly reactions catalyzed by metallic surfaces.[49] Still, the question about the role of spin polarization in the resulting energy profile remains open.

In order to bring new arguments and, perhaps, a definitive answer to the question about whether the proper description of transition state structures and corresponding energy barrier of chemical reactions taking place at a (nonmagnetic) metal surface require explicitly to account for spin polarization effects, the present work explores a representative set of heterogeneous reactions catalyzed by metallic surfaces. The reactions selected are CO and NO oxidation and NO, O_2, H_2O, and H_2 dissociation, which, in principle, may involve an open-shell electronic structure for reactants or products. The text is organized as follows: Computational methods are described in detail in section 2. Calculated results are reported and discussed in section 3, and the most important conclusions are summarized in section 4.

2. COMPUTATIONAL DETAILS

2.1. Periodic DFT Approach. All of the density functional theory (DFT) calculations described in the present work have been carried out using a periodic surface model approach as described below. The Perdew–Wang (PW91) form[50] of the generalized gradient approach (GGA) has been chosen for the exchange-correlation potential. This approach is usually employed to describe metals and metallic surfaces providing a rather accurate description of the main features of the atomic and electronic structure of these systems, such as work function and work function changes induced by adsorbates.[51] Nevertheless, it is important to point out that, in principle, this choice is important because it may affect the calculated energy profile.

Table 1. Differences in the Total Energy (eV, Absolute Values) Calculated Using Spin Restricted and Spin Unrestricted DFT Approaches for the Initial State (IS), for the Transition State (TS), and for the Final State (FS) of Several Different Heterogeneous Reactions on Model Transition Metal Surfaces[a]

reaction	surface	IS	TS	FS
$H_2O^* \rightarrow OH^* + H^*$	Cu(110)	0.000033	0.000005	0.000013
$H_2O^* \rightarrow OH^* + H^*$	Pt(111)	0.000006	0.000024	0.000016
$H_2O^* \rightarrow OH^* + H^*$	Ir(110)	0.000030	0.000019	0.003508
$H_2O^* \rightarrow OH^* + H^*$	Au(321)	0.021121	0.000013	0.000189
$OCOO^* \rightarrow CO_2 + O^*$	Au(321)	0.004823	0.002791	0.022139
$CO^* + O^* \rightarrow CO_2$	Au(321)	0.000095	0.002385	0.000078
$ONOO^* \rightarrow NO_2^* + O^*$	Au(321)	0.000137	0.000023	0.000047
$NO^* + O^* \rightarrow NO_2^*$	Au(321)	0.000027	0.000967	0.000041
$H_2^* \rightarrow H^* + H^*$	Au(321)	0.032435	0.000022	0.000027
$NO^* \rightarrow N^* + O^*$	Au(321)	0.009610	0.112225	0.000001
$O_2^* \rightarrow O^* + O^*$	Ag(110)	0.002975	0.000007	0.000010

[a]Note that IS and FS correspond to adsorbed reactants and products, respectively, whereas TS stands for the transition state for the surface reaction.

For instance, the performance of different density functional approximations on describing geometries and energies of different systems has been analyzed in a series of systematic works.[41,42,52,53,55] In the case of adsorbate−metallic substrate systems, the influence of three exchange-correlation functionals (PBE, PW91, or RevPBE) has been reported for the case of the water dissociation reaction on the Cu(111) surface.[56] The analysis of adsorption and reaction energies showed that the RevPBE values were rather far from the experimental results,[57] while the best results were those computed with the PBE and PW91 density functionals. Interestingly, the results calculated with the PBE and PW91 approaches were found to be very similar. In any case it is worth pointing out that in the present case the choice of the exchange-correlation potential is not so important because the main focus concerns the comparison of spin unpolarized versus spin polarized results, both obtained using the same density functional approach.

A plane-wave basis set was used to span the valence electronic states and the atomic cores represented by the projected augmented wave (PAW) formalism of Blöch[58] as implemented by Kresse and Joubert[59] in the VASP 4.6.3 computer code.[60−62] The cutoff energy for the plane waves considered here was 415 eV. Depending on the reaction studied, grids composed by $5 \times 5 \times 1$ or $7 \times 7 \times 1$ Monkhorst−Pack[63] k-points were adopted in the calculations. The conjugate-gradient algorithm was used for the relaxation of the atomic positions (atoms of the adsorbates and in the topmost layers of the metal slabs, please see below). All calculations were carried out using spin restricted and spin unrestricted formalisms.

The transition state (TS) structures were located with the *dimer* method.[64] Strict convergence criteria were used for the energies and for the forces acting on the atomic cores, with values of 10^{-6} eV and 10^{-3} eV/Å, respectively. The computation of a single imaginary frequency for the TS configurations found ensured that the structures obtained were true first order saddle points in the potential energy surfaces.

2.2. Slab Surface Models. The Cu(110), Ag(110), Pt(111), Ir(110), and Au(321) surfaces have been chosen as representative cases. Note that they include compact, open, and stepped surfaces and, hence, different types of active sites for the species involved in the set of surface reactions studied in the present work. These surfaces were modeled using the three-dimension (3D) periodic-slab approach. The slabs used in this work consist all of 2×2 supercells having four atomic layers. A

vacuum region 10-Å-thick was introduced between repeated cells in the z direction, a condition required for modeling a surface with the 3D VASP code.[60−62] The positions of the surface atoms as well as the lattice parameters were obtained in previous works.[65,66] In all of the calculations, the two topmost layers of metallic atoms with which the adsorbent(s) interact(s) were fully relaxed.

3. RESULTS AND DISCUSSION

The effect of using spin-restricted or spin-unrestricted approaches in the theoretical study of the molecular mechanisms of heterogeneously catalyzed reactions taking place at the surface of nonparamagnetic atoms is analyzed here in terms of the differences between calculated energies for the initial state (adsorbed reactants), transition state, and final state (adsorbed products). Adsorption energies are not discussed here, but they are always obtained by subtracting the energy of the isolated slab model and of the gas phase adsorbate (spin polarized when necessary) from the energy of the slab with the corresponding adsorbate and calculated using both spin restricted and spin polarized formalisms. Reaction energies involve the energy difference between adsorbed reactants and adsorbed products and have also been obtained using both spin restricted and spin polarized formalisms. Finally, activation energies are obtained from the appropriate energy difference and, again, using both formalisms. The systems under scrutiny involve water dissociation, an important step in the water gas shift (WGS) reaction, NO and CO oxidation, and also NO, O_2, and H_2 dissociation with calculated data described and discussed below. Note that, in the gas phase, these reactions involve open shell systems, either atoms or radicals, and their study at the DFT level requires no doubt to explicitly take spin polarization into account.[24] For the adsorption of open shell species such as O_2 or NO, this is also clear for the separate systems, and spin polarization is required for a correct calculation of the adsorption energy. However, for the adsorbed molecule, it is not possible to rule out spin polarization effects, although it is likely that the mixing between the molecular orbitals of the adsorbed molecule with the broad bands of the metallic substrate, indicating a string delocalization of the electron density, will result in a considerable quenching of the molecule magnetic moment. The results in Table 1 show that, in most of the studied situations, this is the case. For a chemical reaction between species adsorbed at the metallic surface and, especially, for the

corresponding transition state structure, the role of spin polarization and its effect in the potential energy surface is not so clear, and the main goal of the present work is to provide a sound answer.

In the case of water dissociation, $H_2O^* \rightarrow OH^* + H^*$, the effect of the approach used for spin treatment was analyzed for some transition metal surfaces, namely, Au(321), Cu(110), Pt(111), and Ir(110) surfaces. It was found that the use of the spin unrestricted approach in the calculations does not significantly affect the results calculated imposing a closed shell like description of the electronic structure. Here, the unpaired electron in the H adatom and OH adsorbed radical appear to be delocalized in the substrate metallic bands, and there is no influence in the transition state. Therefore, spin polarization does not play a significant role along the water dissociation reaction path on these surfaces. In fact, the total energies calculated with these approaches for the initial state (adsorbed H_2O), the final state (coadsorbed OH + H), and the transition state structures for the reaction of water dissociation on the four metal surfaces considered differ by less than 0.03 eV (Table 1). Here, it is important to point out that this means that, in all cases, a spin polarized solution exists which is at variance with the H_2 molecule at the equilibrium geometry and similar cases, where the unrestricted formalism converge to a restricted type solution. Furthermore, the spin polarization solution exists, and its energy is lower than that provided by the spin unrestricted formalism. However, the energy difference is small and certainly smaller than the error introduced by the choice of an approximate form of the unknown universal exchange-correlation potential. The small effect in the energy profile is also encountered in the structures of the stationary points of the corresponding potential energy surface. The geometric differences obtained for the breaking or forming bonds in the configurations optimized with the two different spin polarization treatments is negligible, as can be seen in Table 2. Again, the different solutions lead to different structures, but the differences are small. In fact, the most visible geometry change was found for the adsorbate to surface distance in the case of the water molecule interaction with the Au(321) surface (this initial state is depicted in Figure 1a) very probably due to the fact that the reaction occurs in positions nearby the step and involving low coordinated Au atoms. These Au atoms have coordination numbers of 6 or 8, while in the case of planar (111) surfaces the coordination is 9. Therefore, the former are more free to move. The initial state structure in the case of water dissociation on Au(321) is the one having the largest energy difference for the energies determined with the two approximations (0.021 eV, Table 1). These results clearly indicate that the calculated energies and geometries for water dissociation on metallic surfaces of nonparamagnetic metals are not dramatically influenced by spin polarization. More details about the reaction of water dissociation on several different metal surfaces can be found in the computational study within the restricted formalism that has been reported recently.[65]

The Au(321) surface was recently used as a catalyst model for the study of the reaction of NO oxidation and provides an excellent example to test the influence of spin polarization because it has been found that it may proceed through direct reaction with gas phase NO and adsorbed molecular oxygen via an Eley−Rideal mechanism (NO + $O_2^* \rightarrow NO_2$ + O^*) or through a Langmuir−Hinshelwood mechanism involving a four-atom ONOO intermediate (NO* + $O_2^* \rightarrow ONOO^*$ + * $\rightarrow NO_2^*$ + O^*) or oxygen adatoms (NO* + $O^* \rightarrow NO_2^*$ +

Table 2. Length (Å) of the Bond Breaking/Forming in the Initial State (IS), in the Transition State (TS), and in the Final State (FS) of Several Different Heterogeneous Reactions on Model Transition Metal Surfaces Calculated with Spin Restricted or Spin Unrestricted DFT Calculations[a]

reaction	surface	bond	IS	TS	FS
$H_2O^* \rightarrow OH^* + H^*$	Cu(110)	O−H	0.98	1.43	3.11
			0.98	1.43	3.11
$H_2O^* \rightarrow OH^* + H^*$	Pt(111)	O−H	0.98	1.78	3.11
			0.98	1.78	3.11
$H_2O^* \rightarrow OH^* + H^*$	Ir(110)	O−H	0.99	1.43	2.81
			0.99	1.43	2.81
$H_2O^* \rightarrow OH^* + H^*$	Au(321)	O−H	0.98	1.86	3.74
			0.98	1.86	3.74
$OCOO^* \rightarrow CO_2 + O^*$	Au(321)	O−O	1.36	1.72	1.18
			1.43	1.72	1.18
$CO^* + O^* \rightarrow CO_2$	Au(321)	C−O	2.98	2.40	1.17
			2.98	2.43	1.17
$ONOO^* \rightarrow NO_2^* + O^*$	Au(321)	O−O	1.33	1.78	3.22
			1.34	1.78	3.22
$NO^* + O^* \rightarrow NO_2^*$	Au(321)	N−O	3.70	2.47	1.25
			3.65	2.50	1.25
$NO^* \rightarrow N^* + O^*$	Au(321)	N−O	1.18	2.30	3.14
			1.18	2.77	3.14
$H_2^* \rightarrow H^* + H^*$	Au(321)	H−H	0.76	1.33	2.69
			0.76	1.33	2.69
$O_2^* \rightarrow O^* + O^*$	Ag(110)	O−O	1.45	1.98	4.15
			1.46	1.98	4.15

[a]Data in the top of the cells correspond to lengths obtained through spin unrestricted DFT calculations, and data in the bottom of the cells correspond to lengths obtained through spin restricted calculations.
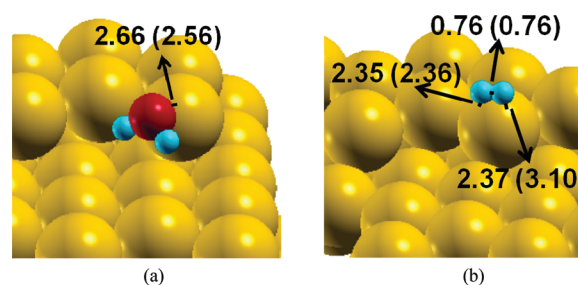

2.66 (2.56)   0.76 (0.76)   2.35 (2.36)   2.37 (3.10)

(a)   (b)

Figure 1. Variation in some selected distances for the configurations of (a) H_2O and (b) H_2 adsorbed on the Au(321) surface optimized with spin-restricted or spin-unrestricted approaches (values in parentheses).

), which are formed on the surface by previous dissociation of the molecular oxygen.[67] The reaction energy barriers calculated for these oxidation reactions are smaller than 0.3 eV.[67] Herewith, we will focus on the ONOO + * $\rightarrow NO_2^*$ + O^* and NO* + $O^* \rightarrow NO_2^*$ + * elementary steps. The calculated energy and geometry differences for the initial, transition, and final state structures are also reported in Tables 1 and 2. As can be seen, the energy differences for the initial, transition, and final states calculated with the restricted or the unrestricted approaches differ by less than 1 meV, while the maximum difference for the length of the bond being broken or formed is 0.05 Å. Again, both solutions exist, but differences in either energy or structure are almost negligible. In the following, we will show that this is indeed a general behavior. In fact, a similar situation is found for the reaction of CO oxidation also on the

Au(321) surface considering the same elementary steps discussed above for the case of NO oxidation; these are OCOO* → CO_2 + O* and CO* + O* → CO_2 + 2*, but with formed carbon dioxide desorbed from the surface since the interaction energy calculated for this molecule on the Au(321) surface is smaller than that calculated for nitrogen dioxide.[67,68] In the case of CO oxidation, the maximum energy difference (0.022 eV) was calculated for the final state of the former reaction, i.e., a configuration with an oxygen adatom interacting with the Au(321) surface and a CO_2 molecule far from the metal substrate. Minimal variations were calculated for the lengths of the C−O cleaving or forming bonds (Table 2).

Let us now consider the case of NO dissociation, which in the gas phase involves a doublet potential energy surface but where the products involve three (N, ^4S) and two (O, ^3P) unpaired electrons, respectively. Not surprisingly, this is the case where the effect of spin polarization is the largest among those studied in the present work. Thus, for NO on the Au(321) model, the explicit inclusion of spin polarization has a noticeable influence on the calculated energy for the transition state (difference of 0.11 eV between the energies calculated with the restricted or unrestricted approaches), while differences smaller than 10 meV are calculated for the reactants and for the products of the reaction. The rather large energy difference found for the optimized transition state structure is a result of a breaking N−O bond length that is 0.47 Å (Table 2) shorter in the case of the transition state search with the unrestricted approach than when located with the spin restricted formalism. Here, the larger energy difference at the TS is connected to a rather large structural difference. The origin for such a difference is the displacement of the outermost Au atom in the step line of the Au(321) surface, which is a 6-coordinated Au atom, that is more pronounced in the case of the unrestricted approach (Figure 2). The Au−Au distance in
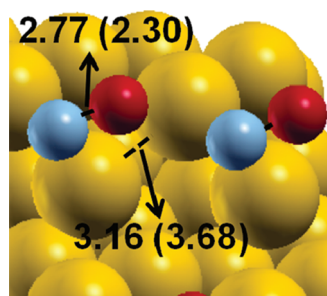

Figure 2. Variation in some selected distances for the transition state structure of the NO dissociation reaction (NO* → N* + O*) on the Au(321) surface optimized with spin-restricted or spin-unrestricted approaches (values in parentheses).

the case of the clean Au(321) surface is 2.85 Å,[69] and it is increased to 3.16 in the TS structure shown in Figure 2 (spin restricted calculations). Taking spin polarization into account increases the Au−Au distance to 3.68 Å, suggesting that, for reactions occurring above undercoordinated surface atoms, a spin-unrestricted approach is necessary. Interestingly enough, the need for spin polarization arises already from the substrate and more precisely from the presence of low coordinated metal atoms and not from the stretching of the NO bond at the transition state.

In what concerns the hydrogen dissociation (H_2* → H* + H*) on the same stepped Au(321) surface, consideration of the

spin polarization in the calculations leads to results that are similar to those obtained using the restricted DFT approach, with differences in the total energy of the initial, transition state, and products lower than 0.04 eV. The maximum difference corresponds to the interaction energy of the H_2 molecule with the Au(321) surface (optimized configurations and selected distances are depicted in Figure 1b) again caused by some structural differences between the adsorption configurations optimized with the restricted (H_2 is coplanar with the Au(111) terrace) or unrestricted (H_2 is almost normal to the Au(111) terrace) formalisms, in regions close to the steps of the Au(321) surface. The differences in the calculated adsorption energies with the restricted or unrestricted formalisms for the hydrogen molecule are large in percentages since the calculated interaction energy for the H_2 molecule on this gold model surface is only −0.06 eV (with zero point energy).

Finally, we consider the effect of using spin polarization in the reaction of O_2 dissociation on a Ag(110) model surface as a representative example. This is also an interesting case because the isolated O_2 molecule has a triplet state ground state, and therefore, O_2 chemisorption is likely to involve a potential energy crossing. In addition, each dissociation product exhibits an O(^3P) state. Again, the interaction with the metallic surface is likely to quench the magnetic moment of these species once adsorbed. This is favored by the charge transfer from the metal to the adsorbate especially at the final state where there is strong evidence already from the days of Hartree−Fock cluster model calculations[70] that O becomes strongly negatively charged in this and other metallic surfaces.[66,71] The present results for O_2 dissociation on Ag(110) reported in Tables 1 and 2 indicate that this is indeed the case, and one may guess that other metallic surfaces will exhibit a similar behavior. Here, the difference in the energy profile obtained from spin unpolarized or spin polarized approaches is almost negligible, and differences on the optimized structures for the reactant and product states are minor and are also negligible for the transition state structure, thus confirming the trends described above for other reactions at different surfaces. It is likely that in most practical cases this general trend will also hold.

4. CONCLUSIONS

A series of surface reactions have been investigated by means of periodic density functional calculations with the main aim of establishing the degree of multiconfigurational character of the transition state and the open-shell character of the adsorbed reactants and/or products, which in gas phase will involve radical species. To this end, the calculations were carried out using standard (spin unpolarized) and spin polarized formalisms.

The present work clearly shows that spin polarization effects in the calculated energies and geometries for heterogeneous catalytic reactions on metal surfaces of nonparamagnetic elements are much less important than when the same reactions take place in the gas phase. The use of an unrestricted approach seems to be more relevant in the cases of catalytic models involving low coordinated atoms such as in the Au(321) surface. The analysis of the complete set of results reported in this work shows that the numerical differences in the calculated total energies and bond lengths of the breaking/forming bonds corresponding to spin restricted or spin unrestricted formalisms are smaller than 0.04 eV and 0.05 Å, respectively, except in the case of the transition state structure of the NO* → N* + O* reaction where the number of

unpaired electrons for the gas phase reaction changes from one in NO (double state) to five in N + O (triplet and quartet coupled to doublet).

In spite of the small numerical difference between the two types of calculations, it is important to insist on the fact that the spin polarized solution exists and is lower in energy, as one would expect. This is at variance from the situation found for gas phase chemistry, where at equilibrium geometry the spin polarized solution for nonradicalary species usually converges to the spin restricted closed shell. Nevertheless, the small energy difference between the two types of calculations implies that, from a practical point of view, results obtained without taking spin polarization lead to the same description of the potential energy surface, and the computational cost is almost halved.

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Notes

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