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Surface reactivity of MgO oxygen vacancies

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Abstract

The interaction of gas-phase molecules (O_2, CO and H_2) with oxygen vacancies (F_s centers) on the MgO(1 0 0) surface was studied by cluster models ab initio wave functions. The F_s centers exhibit a high reactivity towards O_2, CO and H_2 at variance with the regular sites of the MgO surface. The reaction proceeds through the formation of radical anions, O_2^- and CO^-, via the transfer of one electron trapped in the surface cavity to the empty levels of the adsorbed molecule, and can lead to the heterolytic dissociation of the H_2 molecule. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

MgO powders react with CO at room temperature with the formation of complex species of general formula $C_nO_{n+x}^{2-}$ (x=0,1,2) [1,2]. On the contrary, O_2 does not react with the MgO surface unless a large number of defects is artificially created by, e.g., γ- or UV-irradiation followed by doping with alkali metals [3–7]. In this case O_2 forms adsorbed superoxide anions, O_2^-, and the reaction is accompanied by very characteristic changes in electron paramagnetic resonance (EPR) spectra [3–7]. Thus, the reactivity of the pre-irradiated MgO surface or of MgO powders is totally different from that of the (1 0 0) face of MgO single crystals. In fact, on the MgO(1 0 0) surface CO physisorbs at the Mg cations through electrostatic forces [8,9], while O_2 does not adsorb at all, at least at room temperature [3–7]. The high reactivity of thermally activated MgO originates from an high concentration of surface defects and irregularities. Particularly important is the role of the oxygen vacancies, also known as the F_s centers (the subscript 's' indicates the localization of these defects at the surface). F_s centers can be neutral or charged, depending on the number of electrons associated to the defect [10]. In neutral F centers two electrons are trapped in the cavity by the Coulomb potential of the ionic crystal. The paramagnetic centers, F_s^+, consist of a single electron localized in the surface cavity formed by removing an oxygen anion, O^- [10–12]. F_s^+ centers are particularly interesting for the characterization of oxygen vacancies because they can be detected by means of EPR spectroscopy. If no electrons are associated with the vacancy (which formally corresponds to the removal of an O^{2-} ion) the center formed is F_s^{2+}. These latter centers are very electron deficient and have the tendency to extract electrons from other

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adsorbed species, in particular metals. The deposition of alkali metals on irradiated MgO results in a large increase of the number of paramagnetic centers as the consequence of the ionization of the alkali metal and the trapping of the corresponding electron in the surface oxygen vacancy. The unusual electronic structure of the F_s and F_s^+ centers, with "free" electrons in the cavity, is the basis of their high chemical reactivity [1–7,13].

In this paper we review the interaction of CO, O_2 and H_2 gas-phase molecules with the F_s centers localized at the (1 0 0) terraces and at low-coordinated corner sites of the MgO surface. We have investigated theoretically, by means of cluster models and Hartree–Fock wave functions, the mechanism and the energetics of formation of O_2^- and CO^-, two paramagnetic molecules which have been detected spectroscopically at the surface of polycrystalline MgO interacting with the corresponding neutral counterparts [1–7]. We have also considered the possible existence of low-coordinated F centers and their capability to dissociate hydrogen molecules. We will show that the interaction of O_2 and CO with the surface F centers is dominated by electrostatic contributions. The different stability of the radical anions, O_2^- and CO^-, formed during the surface reaction is largely due to the different electron affinity of the two neutral molecules. H_2, on the other hand, dissociates over an electron deficient F_s^{2+} center at a corner site of the MgO surface with the formation of Mg^{2+}–H^- and O^{2-}–H^+ units.

2. Computational method

The interaction of CO, O_2 and H_2 with the MgO oxygen vacancies has been studied with cluster models embedded in point charges (PC) to represent the Madelung potential (cf. Fig. 1). We placed an effective core potential, ECP, at the position of the +2 PCs around the cluster to provide a representation of the finite size of the Mg^{2+} core [14–16]. The main role of the ECP [17] is to take into account the Pauli or exchange repulsion of the O^{2-} valence electrons with the surrounding.

We have constructed Hartree–Fock, HF, self-consistent field, SCF, wave functions using localized sets of Gaussian type orbitals. The basis sets used for the oxide and magnesium ions of the MgO clusters are [8s4p/4s2p] [18] and [13s8p/6s3p] [19], respectively. To reduce the size of the basis set, the 3s and 3p orbitals have been removed from the Mg^{2+} ions not directly interacting with the adsorbate [10]. For CO we used a [9s5p/4s3p] basis [20] augmented by a diffuse p function ($\alpha_p(C)=0.06$, $\alpha_p(O)=0.10$). The basis set for O_2 is constructed from the [8s4p/4s2p] basis used for the crystal oxygens by adding a diffuse s and a diffuse p function; the exponents of these diffuse functions have been optimized directly on O_2^- ($\alpha_s(O)=0.070$, $\alpha_p(O)=0.052$). With these basis sets the CO and O_2 electron affinities, EA, are +1.93 and −0.24 eV, respectively (in our notation the EA is negative if the radical anion is stable). The experimental EA of

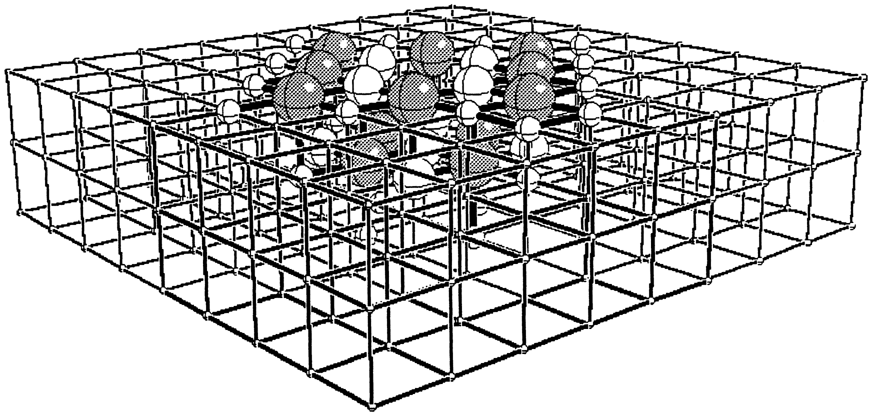

Fig. 1. $O_{12}Mg_9$ cluster model of an oxygen vacancy on the MgO surface. The cluster is embedded in a large array of point charges (only partially shown); ECPs have been used instead of +2 PCs to represent the finite size of the Mg^{2+} ions around the cluster.

O_2, −0.44 eV [21] is close to the computed value. For CO, the estimated experimental EA of +1.5 eV is somewhat smaller than computed with the present basis. The H_2 molecule has been described with a [4s1p/2s1p] basis set of double-zeta plus polarization quality.

To describe the (1 0 0) MgO surface we used a $[O_{12}Mg_9]^{n-}$ cluster (Fig. 1). This cluster is not stoichiometric, and electrons have to be added according to the notion of a fully ionic crystal. The cluster is surrounded by 654 PCs and 20 ECPs. The exact formulation is $[O_{12}Mg_9]^{8-}$+20 ECP for F_s, $[O_{12}Mg_9]^{7-}$+20 ECP for F_s^+, and $[O_{12}Mg_9]^{6-}$+20 ECP for F_s^{2+}, respectively. The geometry of adsorbed CO and O_2 has been fully optimized by means of analytical gradients. Sections of the potential energy surface have also been determined to identify the crossing of various electronic configurations, see Figs. 2–5. In this case we used smaller clusters, O_8Mg_9, with and without embedding in ECPs. CO was placed normal to the surface, the usual coordination mode for this molecule. O_2 has been adsorbed with the molecular axis parallel to the surface since EPR experiments show unambiguously the equivalence of the two oxygen nuclei in O_2^- [4,5].

The F_s^{2+} center at the corner of the MgO surface has been described by a $[O_{12}Mg_{13}]^{2+}$ cluster surrounded by 31 ECPs and a large set of PCs. An H_2 molecule has been adsorbed near the vacancy and the resulting geometry has been fully optimized, Fig. 6.

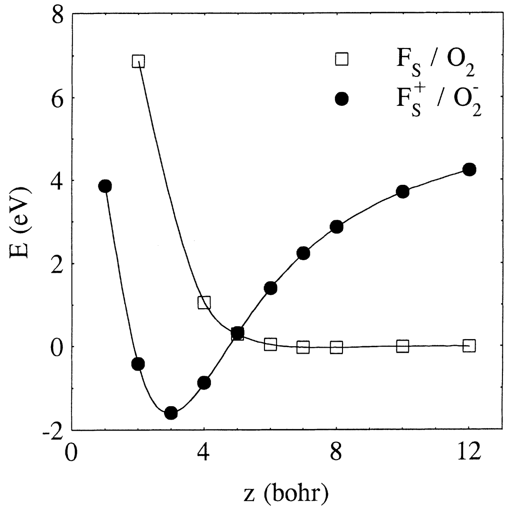

Fig. 2. Potential energy curves for the interaction of O_2 with MgO oxygen vacancies: O_2 on a F_s center (□———□); O_2^- on a F_s^+ center (●———●). The results have been obtained with a O_8Mg_9 cluster model; a positive energy indicates a repulsive interaction.

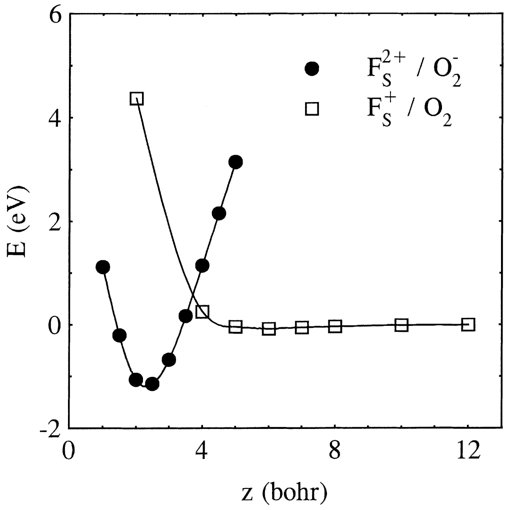

Fig. 3. Potential energy curves for the interaction of O_2 with MgO oxygen vacancies: O_2 on a F_s^+ center (□———□); O_2^- on a F_s^{2+} center (●———●). The results have been obtained with a O_8Mg_9 cluster model; a positive energy indicates a repulsive interaction.

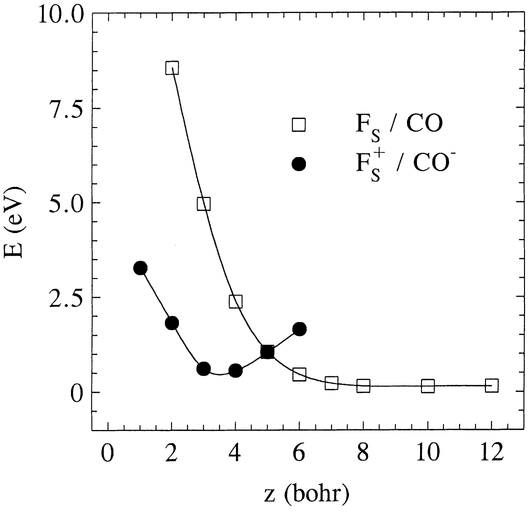

Fig. 4. Potential energy curves for the interaction of CO with MgO oxygen vacancies: CO on a F_s center (□———□); CO^- on a F_s^+ center (●———●). The results have been obtained with a O_8Mg_9+16 ECP cluster model; a positive energy indicates a repulsive interaction.

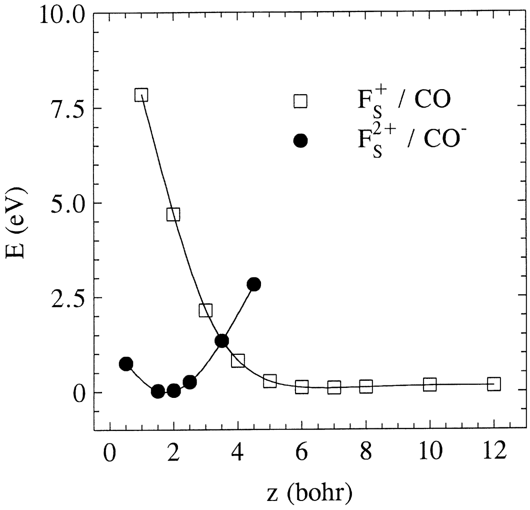

Fig. 5. Potential energy curves for the interaction of CO with MgO oxygen vacancies: CO on a F_s^+ center (□———□); CO$^-$ on a F_s^{2+} center (●———●). The results have been obtained with the O_8Mg_9+16 ECP cluster model; a positive energy indicates a repulsive interaction.

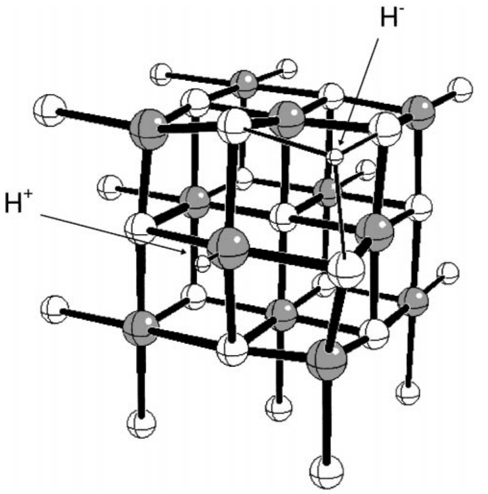

Fig. 6. Optimal structure of an H_2 molecule dissociated on a $O_{12}Mg_{13}$ cluster model of a F_s^{2+} center at a corner site of the MgO surface.

The dissociation energies, D_e, reported in this paper are defined positive for bound systems and are corrected by the basis set superposition error, BSSE [22]. Correlation effects have not been included. However, given the largely electrostatic nature of the interactions (see below), we believe that correlation is not essential for the description of the bonding mechanism. The calculations have been performed with the HONDO 8.5 program package [23].

3. Results and discussion

3.1. O_2 on MgO oxygen vacancies

In a previous study [13] we used relatively small MgO clusters embedded in PCs but without ECPs to study the interaction of O_2 with the MgO oxygen vacancies. We found that a neutral O_2 molecule forms a stable surface complex with a F_s center. This complex can be described as a charge transfer system, O_2^-/F_s^+; in a similar way, O_2 reacts with a paramagnetic F_s^+ center to form a O_2^-/F_s^{2+} surface complex. The interesting aspect is that the formation of the charge transfer complex implies necessarily a crossing of electronic states. In fact, a neutral O_2 molecule gives rise to a non-bonding interaction with a F_s or F_s^+ center. The corresponding potential energy curves are purely repulsive, see Figs. 2 and 3 (the results refer to the O_8Mg_9 cluster without BSSE) [13].

A bound state forms when one electron is transferred from the surface to O_2; the resulting surface species dissociates into ionic fragments, O_2^- and F_s^+ (or F_s^{2+}). A crossing of the "neutral" and "ionic" states occurs at about 2–2.5 Å from the surface, but for shorter distances the charge transfer complex is more stable than the neutral dissociation limit and the reaction is exothermic. An important consequence is that O_2 removes completely the trapped electrons from the MgO surface vacancies even at very low temperature, a result which perfectly fits with the experimental observation [3–5].

Since the reaction involves a net charge transfer from the surface to the adsorbate, the ionization potential of the surface center plays an important role. It is obvious that oscillations in the F_s IPs due to the use of cluster models can lead to unstable results in particular for the chemisorption energies. The use of embedding in PCs can result in too large IPs of the oxygen vacancy because of the artificial polarization of the oxygen ions at the cluster border [15,24]. Stated differently, the Coulomb potential in the cavity is too strong and the trapped electrons are more difficult to remove.

Table 1
Adsorption properties of A_2 molecules on the $O_{12}Mg_9$+20 ECP cluster model of F_s and F_s^+ centers (A_2=O_2 and CO)

	O_2	CO
A_2/F_s		
r_e (A–A) (Å)	1.32	1.20
z_e (A_2) (Å)	1.69	2.05
D_e ($A_2/F_s \rightarrow A_2+F_s$) (eV)	2.85	−0.66
$D_e(A_2/F_s \rightarrow A_2^- + F_s^+)$ (eV)	4.84	3.10
A_2/F_s^+		
r_e(A–A) (Å)	1.30	1.20
z_e (A_2) (Å)	1.27	1.07
$D_e(A_2/F_s^+ \rightarrow A_2 + F_s^+)$ (eV)	2.99	−0.40
$D_e(A_2/F_s^+ \rightarrow A_2^- + F_s^{2+})$ (eV)	10.20	8.88

We have performed new calculations on the interaction of O_2 with MgO F_s centers using the properly embedded $O_{12}Mg_9$+20 ECP cluster and introducing surface relaxation effects. The results are reported in Table 1. In general, we found that by adding the ECPs to the cluster, while the IP of a F_s center goes from 7.0 to 3.7 eV, the adsorption energy of O_2 increases only by 0.9 eV [24]. The reason is that the electron is displaced but not entirely removed from the cavity as in a ionization process. Almost no effect of the embedding in ECPs is found on the geometrical parameters. As mentioned above, the change in IP going from a cluster embedded in PCs and the same cluster embedded in PCs and ECPs is large and is due to the unphysical polarization of the O ions at the cluster border when the cluster is surrounded by PCs. Of course, also correlation effects could be important for the determination of the cluster IP. It should kept in mind, therefore, that the computed interaction energies are affected by non-negligible uncertainities.

The case of O_2 interacting with a F_s^+ center closely resembles that of O_2/F_s described above. Here the inclusion of the ECPs reduces the IP of the F_s^+ center by 3 eV but increases the D_e with respect to O_2 and F_s^+ by only 0.77 eV; the resulting surface species corresponds to a O_2^-/F_s^{2+} complex and the geometrical parameters, in particular the height of the molecule from the surface, changes somewhat.

We also considered the effect of surface relaxation for both O_2^-/F_s^{2+} and O_2^-/F_s^+ complexes; we let relax the positions of the 4 Mg and 8 O surface ions as well as the O_2 molecule. The surface relaxation has a moderate effect on the geometrical parameters of adsorbed O_2 but leads also to a stronger bonding to the surface. However, the qualitative features of the bonding are the same as without surface relaxation.

To summarize, more refined calculations on the interaction of O_2 with MgO surface oxygen vacancies have confirmed the results of previous studies [13] and in particular the occurrence of a net charge transfer of one electron trapped in the cavity to O_2 with formation of a stable MgO/O_2^- surface complex.

3.2. *CO on MgO oxygen vacancies*

We first consider a neutral oxygen vacancy, F_s, described by the O_8Mg_9 cluster. This is characterized by the presence of two electrons trapped in the cavity. In molecular orbital (MO) terms, there is a doubly occupied $(a_1)^2$ level pointing out from the surface [10]. If CO is perpendicular to the surface with the C-end down, the interaction involves the diffuse CO 5σ orbital and the $(a_1)^2$ level giving rise to a strong Pauli repulsion which increases as the surface-CO distance decreases. Hence, the interaction energy curve for the $^1A_1$ state is purely repulsive, Fig. 4, and no charge transfer occurs between MgO and CO. The situation is reminiscent of that of O_2 which interacts in a repulsive way with a neutral F_s center, see Fig. 2.

In order to form a bond, one electron has to be transferred from the $F_s(a_1)^2$ orbital to the CO $2\pi^*$ MO. This corresponds to a $^3E(a_1)^1(2\pi^*)^1$ configuration in C_{4v}. At infinite distance, this state dissociates into ionic fragments, $CO^-(^2\Pi) + F_s^+(^2A_1)$. For this ^3E state we found a bound minimum, Fig. 4, which however is higher than the neutral dissociation limit (the curves have been obtained with the O_8Mg_9 cluster and have not been corrected by the BSSE). A crossing of the $^1A_1$ and ^3E states occurs at about 2.5 Å from the surface. As the surface-CO distance is increased, the ^3E curve does not dissociate into ionic fragments, CO^- and F_s^+, but leads to dissociation into ground state CO $(^1\Sigma)$ and a F_s excited state, ^3E. This dissociation limit is much lower than the dissociation in ionic fragments because of the high IP of F_s and EA of CO. At the minimum of the ^3E curve, at a distance of about 2 Å from the surface, CO^- is in a metastable state and the reaction is an activated process.

An important effect which is missing from the calculations with the O_8Mg_9 clusters is the surface relaxation. This can be partially taken into account using the $O_{12}Mg_9$+20 ECP cluster where the 4 Mg and the 8 O ions in the first layer are free to relax. This relaxation is similar with and without CO and contributes to an additional stabilization of the CO^-/F_s^+ surface complex. When the surface relaxation is accounted for, the internal C–O distance does not change appreciably while the height of the CO molecule from the surface increases. Since the use of a larger cluster and the inclusion of surface relaxation lowers the IP of the F_s center, the D_e with respect to the ionic dissociation limit is smaller compared to the case without relaxation. However, the metastable nature of CO^- also remains after including the local surface relaxation.

In fact, the metastable nature of CO adsorbed on F_s does not depend on the model used and is found using other models and basis sets [24]. At short surface-CO distances a charge transfer from the vacancy to CO occurs, and the resulting F_s^+/CO^- complex is bound by electrostatic forces. However, at variance with the O_2 case, the large price for the charge transfer is not compensated for by the formation of the chemisorption bond and the minimum on the potential energy curve is higher than the energy of the neutral fragments.

The interaction of CO with a paramagnetic F_s^+ center is similar to that with a neutral F_s vacancy. A F_s^+ center is characterized by the presence of a single trapped electron in an orbital of a_1 symmetry pointing out from the surface. Also in this case the repulsion with the CO 5σ MO dominates the interaction and determines the repulsive shape of the interaction energy curve for the $^2A_1$ state, see Fig. 5 (the results refer to the O_8Mg_9 cluster, without BSSE). The $^2A_1$ curve dissociates into "neutral" fragments, i.e., CO $(^1\Sigma)$ and $F_s^+(^2A_1)$.

A bound state is found at short surface-CO distances, Fig. 5. This corresponds to the transfer of the trapped electron, $(a_1)^1$, to the CO $2\pi^*$ MOs giving rise to a ^2E state in C_{4v}. As for the adsorption on F_s, this state is strongly bound with respect to the asymptotic ionic dissociation limit, $CO^-(^2\Pi)$ and $F_s^{2+}(^1A_1)$, while it is weakly bound compared to the "neutral" dissociation limit, CO $(^1\Sigma)$ and $F_s^+(^2A_1)$. The small bonding is partly an artifact due to the occurrence of some BSSE. With $O_{12}Mg_9$+20 ECP, including geometrical relaxation and correcting the data by the BSSE, the CO^-/F_s^{2+} complex is 0.40 eV less stable (unbound) than the "neutral" fragments. The C–O distance, 1.17 Å, is practically the same found for the CO^-/F_s^+ complex, see Table 1.

The accurate determination of the relative stability of the charge transfer complex is rather difficult. In fact, one should consider that the actual EA of CO is slightly smaller, by about 0.4 eV, than that obtained with the present basis set and that the surface relaxation is only partially accounted for. Furthermore, correlation effects are no longer negligible to discriminate between bound and unbound states. Therefore, we conclude that the CO^-/F_s^{2+} surface complex is more or less at the same energy as the separated neutral fragments. We are unable to provide a firm conclusion about the metastable nature of the CO^-/F_s^{2+} system considered the approximations inherent to the computational approach [24].

3.3. *H_2 adsorbed on vacancies at corner sites*

An important question related to surface oxygen vacancies in MgO is if electrons trapped in the cavity left by the missing oxygen exist also on low-coordinated sites like steps, kinks, corners, etc. Recent calculations [25] support this view and indicate that the low-coordinated F centers are even more stable than the high coordinated ones. The reason is that from a thermodynamic point of view it is easier to remove an oxygen atom from a low-coordinated site of the surface than from a high-coordinated one. In other words, the energy required to form a neutral oxygen vacancy by removing an oxygen atom and bringing it to infinite distance follows the trend bulk>surface>step>corner [25].

Another important conclusion is that the removal of a neutral oxygen or of an O^- ion from a low-coordinated surface sites leads to the formation of trapped electrons exactly as occurs in the bulk of the material. This means that the thermal treatment of an alkaline-earth oxide should result in the migration of the surface vacancies from the high- to the low-coordinated sites. Vacancies located in these positions should give rise to a very high reactivity.

To show that this is indeed the case, we have added a neutral H_2 molecule to a corner F_s^{2+} vacancy and we have determined the minimum structure of the resulting surface complex, Fig. 6. We found that the H_2

molecule dissociates into a proton H^+ and an hydride ion H^-. The H^- species is located at the center of the vacancy forming three bonds with the Mg^{2+} ions of the vacancy; in this respect the H^- ion replaces the missing O ion of the regular MgO structure, Fig. 6. The proton, on the other hand, is bound to a four-coordinated O ion near the vacancy with formation of an OH species. The reaction is exothermic by 1.5 eV and the different character of the two hydrogens is clearly shown by the data of the Mulliken analysis. These results show that the low-coordinated F centers exhibit a very high reactivity which probably determines most of the chemical behavior of the surface.

4. Conclusions

We have studied the interaction of O_2, CO and H_2 molecules with paramagnetic and diamagnetic MgO oxygen vacancies by means of cluster models embedded in point charges and ECPs. We found some analogies in the interaction modes of the O_2 and CO but also substantial differences.

A neutral O_2 molecule forms a stable surface complex with a F_s center. This complex can be described as a charge transfer system, O_2^-/F_s^+; in a similar way, O_2 reacts with a paramagnetic F_s^+ center to form a O_2^-/F_s^{2+} surface complex. The formation of the charge transfer complex implies a crossing of electronic states. In fact, a neutral O_2 molecule gives rise to a non-bonding interaction with a F_s or F_s^+ center. The reaction is exothermic and is probably accompanied by a low activation barrier.

CO interacts in a repulsive way with the F_s and F_s^+ centers of the MgO surface. However, at short distances from the surface, a bound state is found which corresponds to a charge transfer complex of the type CO^-/F_s^+ or CO^-/F_s^{2+}. When CO interacts with a neutral F_s center the bound state, CO^-/F_s^+, is definitely higher in energy than the neutral dissociation limit ($CO+F_s$) and the charge transfer complex represents only a local minimum on the potential energy surface. The resulting CO^- species is therefore metastable. When CO interacts with a paramagnetic F_s^+ center, the charge transfer state, CO^-/F_s^{2+}, is energetically close to the corresponding "neutral" dissociation limit ($CO + F_s^+$) and it is not possible to establish in a conclusive way if the global reaction is exothermic or endothermic. In any case, the process is activated and the transformation of the weakly stable or metastable CO^- into thermodynamically more stable chemical compounds is expected as other CO molecules impinge on the surface. Therefore, the charge transfer complexes should form only at finite temperatures and should easily evolve into more stable species. This is indeed what has been experimentally observed. The CO^- radical is seen to form at about 100 K and is a transient, unstable, species [1,2].

The analogy with the O_2 bonding mechanism is that also in this case the formation of a chemisorbed species is due to a net charge transfer from the F center to the adsorbed molecule; the stability of the complex is due to the electrostatic interaction between a negatively charged adsorbate, CO^- or O_2^-, and the underlying electron deficient center, F_s^+ or F_s^{2+}. The difference with the O_2 case is in the energetics of the process. In fact, O_2 reacts spontaneously with F_s and F_s^+ centers to form the surface complex even at very low temperature. The reaction is exothermic and the charge transfer complex is stable also with respect to neutral fragments. The primary reason for the different behavior of O_2 compared to CO is the different electron affinity of the two molecules: the fact that the EA of CO is large and positive increases the cost for the charge transfer and makes the surface complex unbound or weakly bound.

Finally, we have shown that the low-coordinated F centers exhibit a very high reactivity towards adsorbed species. Even an electron deficient F_s^{2+} center, when located at a corner site, is able to dissociate H_2 with an exothermic reaction. The resulting fragments are bound at the center of the vacancy (H^-) or to a neighboring O ion (H^+) giving rise to new reactive species on the surface.

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