

Chemical reactivity of oxygen vacancies on the MgO surface: Reactions with CO₂, NO₂ and metals

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Abstract

Density functional theory was used to investigate the chemical reactivity of oxygen vacancies on the MgO surface towards CO₂, NO₂ and metal atoms. The oxygen vacancies induce changes in the electronic structure of the MgO compared to that of the regular surface. The most common surface defects can have one or two electrons confined in the vacancy. The main effect of the vacancies is the reduction in the energy of the gap between the HOMO and LUMO of the MgO causing in this way a change in its reactivity towards adsorbed molecules such as CO₂ and NO₂ or atoms such as Ni, Pd, Pt, Cu and Zn. It was found that F_s centers are more reactive than F_s⁺ centers. In the case of metal atoms, the level of interaction is proportional to the degree of transfer of electron density towards the incoming atom.

Keywords: Chemical reactivity; Oxygen vacancies; Electron localization function; DFT

1. Introduction

The most important and common catalytic reactions are those that take place on metals, mainly transition metals. Nevertheless, some metal oxides have important characteristics that are very useful in catalysis, such as large surface area and special physical and electronic properties that can induce important catalytic properties in metals. Among the great variety of ionic oxides available for the application in catalytic systems, magnesium oxide has particularly been used in both experimental and theoretical basic research due to its apparent structural simplicity and facility of synthesis. In particular, MgO is one of the supports of preference in the preparation of catalysts for dry reforming of methane, due to the great catalytic activity that presents for this reaction [1–3]. The reforming reaction of methane is very important since two of the most important gases causing the greenhouse effect are converted to synthesis gas which can later be turned into liquid fuels or chemical products of high value via Fischer–Tropsch type reactions. Although the reactions involved in the methane dry reforming are of great industrial importance, relatively very

little is known of their reaction mechanisms. In general, it has been proposed that CH₄ is activated on metal-supported catalysts while CO₂ can be activated on a basic support [4,5].

It has been found that the most important properties of the MgO are directly or indirectly related to the presence of defects, particularly of defective points. These centers determine the optical [6,7], electronic and transport properties [8–13] and usually dominate the chemistry of this surface [14–20]. A detailed understanding of the nature of the defective points is therefore of fundamental importance for the synthesis of new materials with well-defined properties.

The most important defects in magnesium oxide are those created by oxygen vacancies. The oxygen vacancies are 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. In neutral F_s centers, two electrons are trapped in the cavity, while the paramagnetic centers, F_s⁺, consist of a single electron localized in the surface cavity.

In the case of films of MgO, the vacancies can be generated in ultra high vacuum condition by impact with Ar⁺ ions [21]. In polycrystalline MgO, vacancies can be formed by dehydroxylation at high temperatures [22].

Experimentally, the oxygen vacancies can be characterized by their optical spectra [23], energy electron loss spectroscopy

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(EELS), metastable impact electron spectroscopy (MIES) [24,25], scanning tunneling microscopy (STM) [26], and electron spin resonance (EPR) [27].

Experimentally and theoretically, it has been found that the generation of oxygen vacancies is associated to the generation of electronic states in the MgO band gap, between the top of the valence band (2p of O) and the bottom of the conduction band (3s and 2p of Mg). The occupied impurity states due to the MgO oxygen vacancies give rise to typical atomic orbital energies in the region of 5 eV [10,28]. Illas et al. [29] used a topological analysis method based on the electron density of the system such as the atoms-in-molecules (AIM) theory [30] and the electron localization function (ELF) [31] to study the F_s centers of the MgO surface. They found that the use of these tools provides very valuable information on the nature of the centers and of the reactivity of the investigated materials. Furthermore, several investigations of Pacchioni et al. [32–35], have shown that the neutral molecules of oxygen, carbon monoxide and nitrogen interact weakly with the regular MgO surface, that is, without defects, while the same molecules strongly interact with oxygen vacancies to form anionic radicals. It was proposed that the interaction is dominated by an electrostatic mechanism of electron transfer and that this is strictly connected to the oxygen vacancies.

In spite of the catalytic application in the dry reforming of methane that MgO has, particularly on the CO_2 activation, there are very few theoretical studies on the interaction of CO_2 with MgO, which can contribute to the understanding of the CO_2 activation mechanism in this process [36,37].

For example, Pacchioni [36,38] studied the physisorption and chemisorption of CO_2 on regular sites and defective sites of the surface of MgO. Recently, Olsbye et al. [37], studied the interaction of CO_2 with several sites of MgO and CaO. Nevertheless, the authors of the present work do not know of any study on the adsorption of CO_2 on oxygen vacancies in the surface MgO (1 0 0).

On the other hand, it is well known that defects act not only as catalytic centers for chemisorption of small species but also as nucleation centers for the growing of metal islands or clusters and also that the defects can modify the catalytic activity of these adsorbed metal particles via the metal–support interaction at the interface [19,39,40]. For example, Ferrari et al. [41], have shown that Pd atoms deposited on the regular fivefold coordinated sites of the MgO surface are inert for the acetylene-to-benzene cyclization and only when the metal is bound to defect sites, either low-coordinated O anions or O vacancies (F_s center) do they become catalytically active for this reaction. They suggested that the large enhancement in the activity of supported Pd atoms is due mainly to the electron transfer from the cavity to the supported metal [19,42,43].

Based on the mentioned antecedents, the goal of this work is to study the chemical activity of MgO surface oxygen vacancies, aimed at the interaction with molecules of CO_2 , NO_2 and metallic atoms. This investigation will look for fundamental information that helps to understand the interaction CO_2 –support, NO_2 –support and metal–support.

2. Computational details

The defective MgO (1 0 0) surface is modeled by an embedded cluster approach. In this approach, a cluster of $\text{Mg}_{13}\text{O}_{12}$ is selected from the MgO (1 0 0) surface to represent an oxygen vacancy where the surface oxygen atom in the center of the cluster is removed. In the embedded cluster approach, the quantum cluster is surrounded by a set of total ion model potentials (TIMP) for all Mg^{2+} ions that are nearest to any oxygen atom and an array of point charges forming a unit cell of 1.2 nm. These TIMP's and point charges ($\text{PC} = \pm 2$) are located at the lattice positions which were taken from the experimentally determined MgO bulk structure. With these TIMP's, the artificial polarization of oxygen anions at the cluster borders can be reduced [44]. The Madelung potential of the remaining extended MgO surface is represented by a set of surface charges derived from the surface charge representation of the external embedded potential (SCREEP) method [45,46]. From a computational point of view, the treatment of point defects is particularly challenging. It has been found both experimentally and theoretically that the F_s centers are characterized by an electronic density localized in the vacancy region and that the location of this electronic density in the vacancy is due to the electrostatic stabilization by the Madelung potential of the extended crystal. In fact, the electronic properties of point defects are often determined by its local environment and require a localized description but the effect at the neighborhood should in some way be taken into account. In order to determine a good model for such systems that takes into account the point charges and TIMP's, a study was done to calculate the electron localization function. The results are shown in Fig. 1.

In Fig. 1a–c, the electron localization domains for the 0.70 isosurface of the ELF function corresponding to the F_s center simulated by a quantum cluster alone, a quantum cluster + point charges and a quantum cluster + TIMP's + point charges, respectively, can be observed. The differences between these three plots illustrate that the model has a significant effect on the location of the electron density. Note that such electron location is not observed in the quantum cluster alone (Fig. 1a) nor in the quantum cluster + point charges (Fig. 1b). Also, by

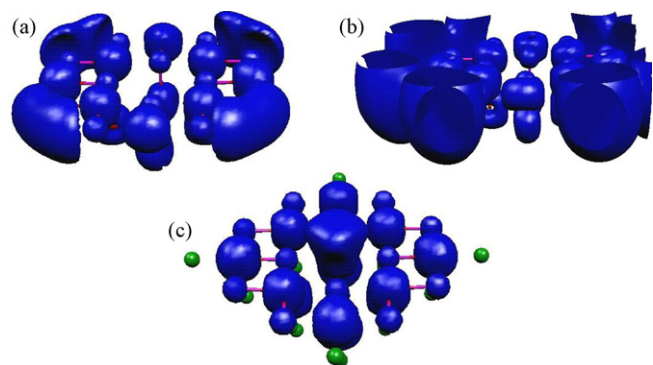


Fig. 1. Schematic representation of the localization domains of the electron localization function at an isosurface value $\eta = 0.7$ for an F_s center simulated by (a) quantum cluster, (b) quantum cluster + point charges, and (c) quantum cluster + TIMP's + charge points for an F_s of the MgO (1 0 0) surface.

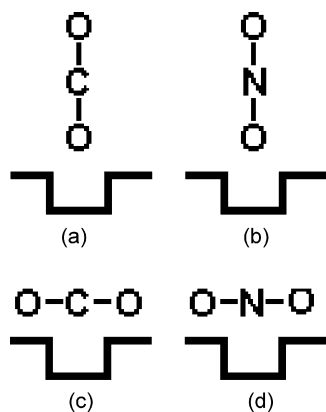


Fig. 2. Adsorption modes of CO_2 and NO_2 molecules on an F_s center: (a and b) adsorption mode $\eta^1\text{-O}$ and (c and d) adsorption mode $\eta^1\text{-C}$ and $\eta^1\text{-N}$.

comparing Fig. 1b and c, it can be observed that TIMP's completely reduce the artificial polarization of oxygen anions at the quantum cluster border.

Fig. 2 shows adsorption modes studied for the interaction of CO_2 and NO_2 with the oxygen vacancies. The adsorption modes selected were of $\eta^1\text{-O}$ (Fig. 2a and b) where the molecule approaches by the oxygen atom in a perpendicular direction to the surface. In the case of $\eta^1\text{-C}$ or $\eta^1\text{-N}$ (Fig. 2c and d) the molecules approach to the surface by the C or N atoms in the direction of the defect.

In this work, the quantum mechanical region was treated by the hybrid B3LYP of the density functional theory. The LANL2DZ [45–47] pseudopotential with its corresponding basis set was used for transition metals. Two basis sets 6-31G(d,p) for Mg and O atoms and 6-311G(d,p) for CO_2 and NO_2 were used. The calculations for open shell molecules (NO_2) or atoms and for F_s^+ centers were done using a spin polarized approach.

All the adsorption energies were corrected by the basis set superposition error (BSSE) using the method of counterpoise of

Boy and Bernardi [48]. Electronic structure calculations were done using the GAUSSIAN 03 [49] program and the topological analysis of the electron localization function was performed using the TOP-MOD program [50].

3. Results and discussions

3.1. Characteristics of a regular surface and a surface with oxygen vacancies on MgO (1 0 0)

The oxygen vacancies are characterized by one or two electrons in the defect cavity. Thus, F_s center has two electrons (diamagnetic center) and F_s^+ center has one electron (paramagnetic center). These types of defects have been characterized experimentally and theoretically. Illas et al. [29] carried out a rigorous characterization of this defect utilizing ELF and AIM approximations. They concluded that these centers behave as quantum subsystems characterized by a high degree of electronic localization. With the methodology used in this work, the ELF analysis of the F_s and F_s^+ centers showed that the electronic population of these quantum subsystems is approximately two and one electrons, respectively, which is in agreement with the work of Illas et al. [29].

In addition, it was determined that the maximum value of the ELF for these quantum subsystems are 0.99 and 0.88 for the F_s and F_s^+ centers, respectively. This means that for both systems the electronic population is highly localized, and that the localization is greater for the F_s center than for the F_s^+ center. Fig. 3a–c shows the electron localization domains for the 0.70 isosurface of the ELF function corresponding to the regular surface, F_s , and F_s^+ centers, respectively. In a graphic way, it can be observed that the electronic density of the two (F_s) and one (F_s^+) electrons in the oxygen vacancies is highly localized in the cavity.

Our results also show that the formation of a vacancy on the MgO surface decreases the ionization potential (IP) by 3.38 eV

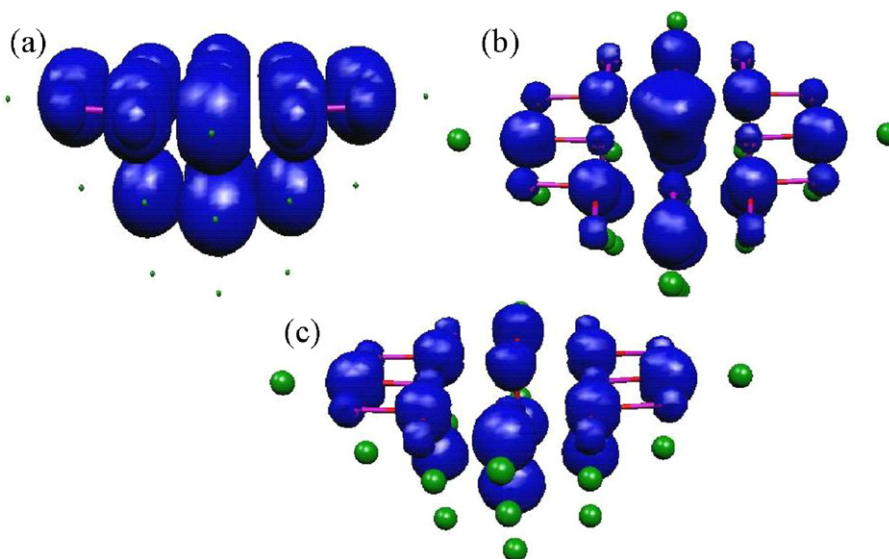


Fig. 3. Schematic representation of the localization domains of the electron localization function at an isosurface value $\eta = 0.7$ for (a) regular surface, (b) F_s center and (c) F_s^+ center of the MgO (1 0 0) surface.

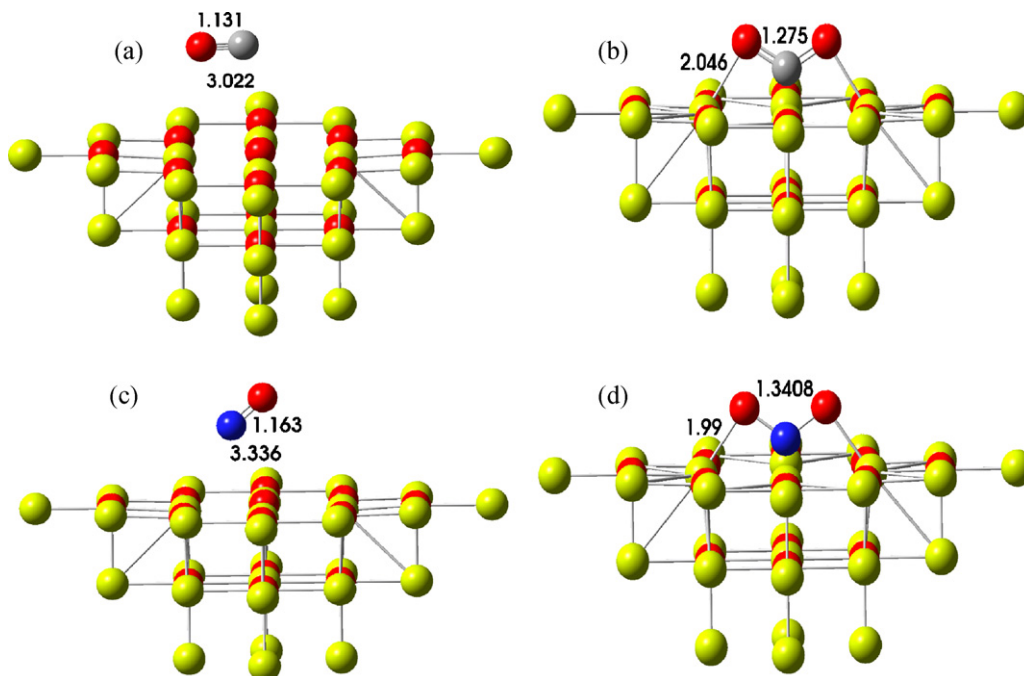


Fig. 4. Optimized structures for the interaction of CO_2 and NO_2 with an F_s center of the MgO (1 0 0) surface: (a) CO_2 , $\eta^1\text{-O}$, (b) CO_2 , $\eta^1\text{-C}$, (c) NO_2 , $\eta^1\text{-O}$, and (d) NO_2 , $\eta^1\text{-N}$.

and 2.87 eV, for F_s and F_s^+ centers, respectively, in relation to the perfect surface.

3.2. Chemical reactivity of MgO oxygen vacancies toward CO_2 and NO_2

In Figs. 4 and 5, the structures of different adsorption modes for the interaction CO_2 and NO_2 with an F_s and F_s^+ center of the MgO (1 0 0) are shown. Table 1 shows the adsorption energies for the systems described above.

For the F_s center, the results shown in Table 1 demonstrate that the interactions with CO_2 and NO_2 when the molecules approach the defect by the O atom ($\eta\text{-O}$) are highly energetic causing the dissociation of the CO_2 or NO_2 molecules to produce an oxygen atom strongly chemisorbed in the vacancy and gaseous CO or NO . The chemisorption of NO_2 approximately releases twice the energy (7.4 eV) in comparison to the one released in the chemisorption of CO_2 (3.23 eV) when adsorbed on the same type of vacancy. The so formed CO molecules have a bond length of 1.131 Å

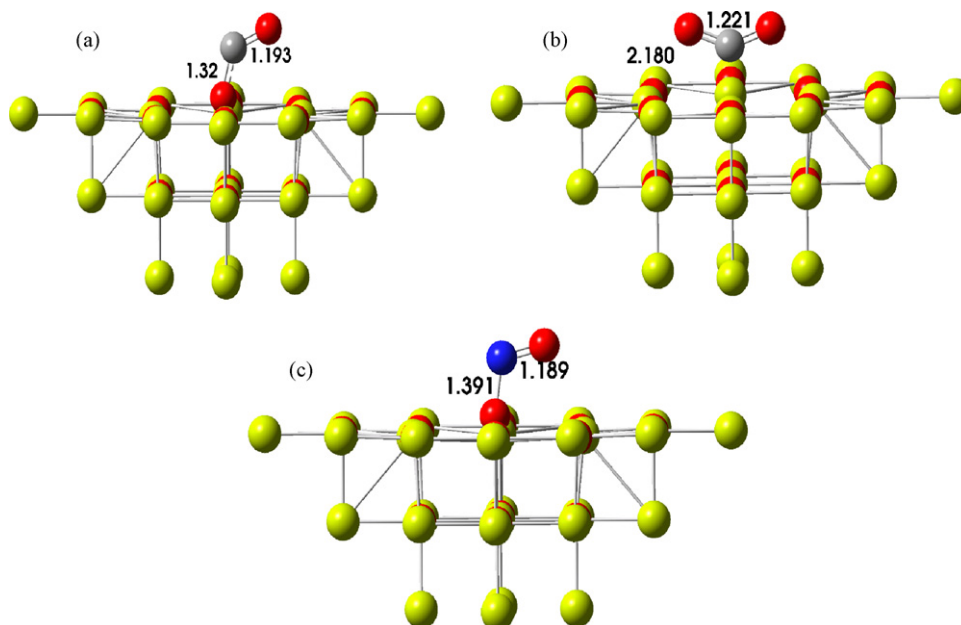


Fig. 5. Optimized structure for the interaction of CO_2 with an F_s^+ center of the MgO (1 0 0) surface: (a) CO_2 , $\eta^1\text{-O}$, (b) CO_2 , $\eta^1\text{-C}$, and (c) NO_2 $\eta^1\text{-O}$ $\eta^1\text{-N}$.

Table 1
Energetic parameters calculated for different adsorption modes of CO₂ and NO₂ on oxygen vacancies of the MgO (1 0 0) surface

Center	E_{ad} (eV)			
	CO ₂		NO ₂	
	η -O	η -C	η -O	η -N
F _s	3.23	1.85	7.42	5.43
F _s ⁺	1.039	0.23	5.69	

(see Fig. 4a) which is similar to the distance of the molecule in gas phase (1.138 Å).

For the other adsorption mode (η -C and η -N), see Fig. 4b and d, it is observed that the electron density of the vacancy has a strong influence on the geometry of molecules. For example, there is a reduction of 58° for angle O–C–O and 60° for angle O–N–O with respect to the molecules in gas phase. The bond lengths for O–C and O–N increase 0.115 Å, 0.147 Å with respect to the molecules in gas phase which are 1.198 Å and 1.16 Å for CO₂ and NO₂, respectively. For both adsorption modes, very large changes in the geometric parameters with respect to the molecule in gas phase are observed, suggesting that there was an ample charge transfer from the vacancy towards the adsorbed molecule.

In addition, in both cases, for CO₂ and NO₂, the preferred bonding mode is with one O end of the molecule filling the surface vacancy (see Fig. 4a and c). This means that the regeneration of the defect to produce a regular surface of the MgO is an energetically more stable process than the process where the whole adsorbed molecule remains unchanged on the surface.

For the interaction of CO₂ and NO₂ with the F_s⁺ center, some results are different than the ones obtained with the F_s. For example, in the adsorption mode, η -O, formation of CO or NO were not observed. It was found that the molecules remain bonded to the surface. In the case of the CO₂ adsorption through the η -C mode, small changes of the CO₂ geometry are observed, while the NO₂ molecule did not suffer any change when adsorbed in an F_s⁺ through the N atom.

The same tendency of the adsorption energy on an F_s or F_s⁺ center for both adsorption modes was observed, being the mode η -O more stable than the η -C or η -N modes in both defect sites. Also in these cases (CO₂ and NO₂) the interaction with an F_s⁺ center leads to an energy gain smaller than for F_s center.

Since the interaction is assumed to mainly be a HOMO–LUMO type [36]. The differences in the adsorption energies found for both molecules in the interaction with the F_s or F_s⁺ center can be due to the differences in energy between the HOMO of the surface and the LUMO of the CO₂ or NO₂ molecules.

In the case of a F_s center, the difference between the HOMO–LUMO for the CO₂ molecule (HOMO–LUMO = 2.27 eV) is approximately twice as big as the difference in HOMO–LUMO for the NO₂ molecule (HOMO–LUMO = 0.89 eV). As the interaction with both molecules occurs through a charge transfer from the HOMO of the surface to the LUMO of the adsorbed molecule, the smaller the value of the

HOMO–LUMO gap the easier the charge transfer, as in the case of NO₂, and consequently, the larger the adsorption energy.

In the case of the F_s⁺ center, the HOMO–LUMO energy of the gap is larger for both molecules when compared with the values of the F_s center. This is reflected in both molecules having smaller adsorption energies in this kind of defect.

On the other hand, comparison of results obtained in this study with data reported in literature [37,38] for the adsorption of CO₂ on regular sites (O_{5c}) and sites of low coordination (O_{4c} and O_{3c}) shows that the F_s centers are more reactive than those low-coordinated sites. For example, the following adsorption energy data has been published [37] for the CO₂ adsorption on regular, O_{4c} and O_{3c} sites: 0.135 eV, 1.19 eV and 1.58 eV, respectively. These energies are lower than the 3.23 eV for CO₂ adsorption energy on an F_s obtained in this work.

3.3. Chemical reactivity of the MgO oxygen vacancies towards metallic atoms

Some authors [51] have found that when a Pd atom is placed on a F_s center, there is a delocalization of the vacancy electrons over metal atoms. Considering this, we calculated the charge transfer from the defect to metallic atoms using the natural bond orbital (NBO) method and looked for the correlation that can exist between the electronic transfer and the binding energy of the M/F_s/MgO system.

In Fig. 6a, the relation between the binding energy and charge transfer for the Pt, Pd, and Ni is shown. The tendency of the binding energy is Pt > Pd > Ni and the tendency in the charge transfer is Pt > Pd > Ni. From these results, it can be concluded that the relation between the binding energy and the charge transfer is directly proportional, meaning that when the binding energy is large the electronic transfer from the electron density of the cavity to the metal is also large. In Fig. 6b, the results obtained for the Ni, Cu and Zn period show that the trend of the binding energy is Ni > Cu > Zn and the trend for the charge transfer is Ni > Cu > Zn. This is the same relation between these two parameters as the previous one. In summary, this study suggests that the strong interaction between transition metals and vacancy sites is originated mainly from the electron transfer from the vacancy to the adsorbed metal.

On the other hand, we calculate the first ionization potential as IP = $-\epsilon_{\text{HOMO}}$, for M–F_s complexes, the result obtained were 3.16 eV, 2.65 eV, 1.78 eV and 0.78 eV for Pt/F_s/MgO, Pd/F_s/MgO, Ni/F_s/MgO, and Cu/F_s/MgO complexes, respectively. The first IP is inversely proportional to a charge transfer. Therefore, it is expected that complexes with a smaller value of the first IP are able to transfer charge more readily to another system, as in the example of a molecule that approaches the adsorbed metal atom. The above energy sequence means that the Pt/F_s/MgO complex is a less reactive one, while the Cu/F_s complex is the most reactive. These results are in agreement with previously published results [52–54] where it was found that Pt deposited on an F_s center is almost unreactive towards a Pt atom or a hydrogen atom, while the Cu deposited on an F_s is reactive towards another Cu atom, as in Cu cluster growth or towards a hydrogen atom.

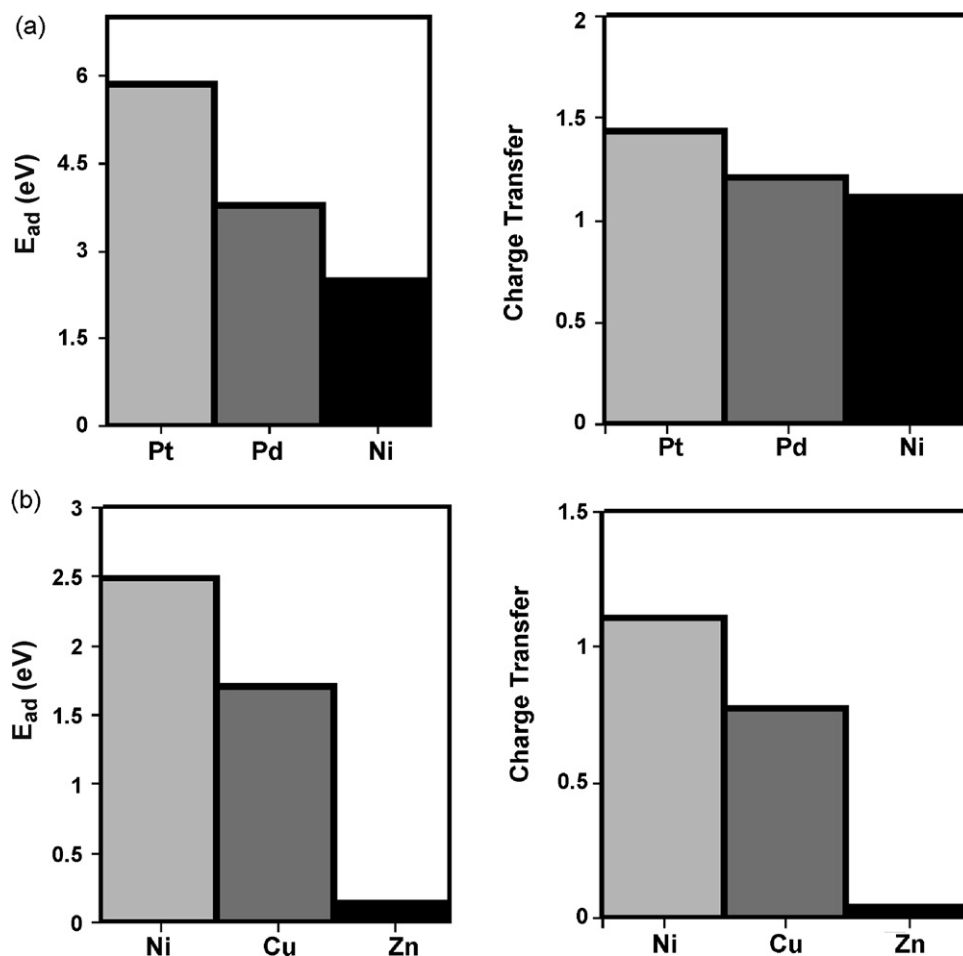


Fig. 6. Comparison of the binding energy and charge transfer of the M- F_s complexes along (a) the group Pt, Pd, Ni and (b) the period Ni, Cu Zn.

4. Concluding remarks

The presence of oxygen vacancies on the MgO surface modifies its electronic structure by the generation of electronic states in the gap between the valence and conducting energy bands. The degree of alteration of the gap depends on the type of defect. Defects with one electron in the cavity of the vacancy, F_s^+ reduce the gap by 2.87 eV, and the electronic density is less localized than defects with two electrons F_s which reduce the gap by 3.38 eV. These characteristics make the defects on the MgO surface very reactive especially in systems where a charge transfer from the substrate to the adsorbate is required.

The reactivity of the MgO defects with CO_2 and NO_2 was evaluated. It was found that the F_s centers are more reactive causing the dissociation of the CO_2 and NO_2 molecules when adsorbed through an oxygen atom. In this adsorption mode, an oxygen atom of the incoming molecules is trapped in the vacancy. When the adsorption takes place through the C or N atom the molecules are not dissociated but their geometry is drastically changed. The adsorption energy of these molecules on the MgO oxygen vacancies was related to the energy of the HOMO-LUMO gap, with the case of the case of NO_2 being larger.

The reactivity of the MgO vacancies was also evaluated in their interaction with metal atoms. It was found that the binding energy of the metals is directly related to the charge transfer from the cavity to the metal atom. Therefore F_s is more reactive than the center with one electron. This strong interaction of the defect with the metal atoms has a negative behavior in this system towards other possible reactions of the metal/ F_s /MgO system as is the case of interaction with hydrogen atoms or other metals. In this work it was found that Pt strongly interacts with an F_s and therefore the complex Pt/ F_s /MgO interacts very weakly with a hydrogen atom or another Pt atom while Cu/ F_s /MgO has stronger interactions with H and Cu atoms. This tendency was correlated to the ionization potential finding that the IP in the Pt complex was 3.16 eV while in the Cu complex the IP was 0.78 eV. The larger the IP value the weaker the interaction with incoming molecules or atoms is.

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References

- [1] K. Tomishige, O. Yamazaki, C. Yangguang, K. Yokoyama, X. Li, K. Fujimoto, *Catal. Today* 45 (1998) 35.
- [2] B.-Q. Xu, J.-M. Wei, H.-Y. Wang, K.-Q. Sun, Q.-M. Zhu, *Catal. Today* 68 (2001) 217.
- [3] E. Ruckenstein, Y.H. Hu, *Appl. Catal. A* 154 (1997) 185.
- [4] S.-B. Tang, F.-L. Qiu, S.-J. Lu, *Catal. Today* 24 (1995) 253.
- [5] S. Wang, G.Q.M. Lu, *Appl. Catal. B* 16 (1998) 269.
- [6] C. Sousa, G.I.F. Pacchioni, *Surf. Sci.* 429 (1999) 217.
- [7] E.A. Kotomin, M.M. Kukulja, R.I. Eglitis, A.I. Popov, *Mater. Sci. Eng. B* 37 (1996) 212.
- [8] A.M. Ferrari, G. Pacchioni, *J. Phys. Chem.* 99 (1995) 17010.
- [9] P.V. Sushko, J.L. Gavartin, A.L. Shluger, *J. Phys. Chem. B* 106 (2002) 2269.
- [10] G. Pacchioni, *Solid State Sci.* 2 (2000) 161.
- [11] G. Pacchioni, P. Pescarmona, *Surf. Sci.* 412/413 (1998) 657.
- [12] P.V. Sushko, A.L. Shluger, R.A. Catlow, *Surf. Sci.* 450 (2000) 153.
- [13] Q.S. Wang, N.A.W. Holswarth, *Phys. Rev. B* 41 (1990) 3211.
- [14] A. D'Ercole, E. Giamello, C. Pisani, *J. Phys. Chem. B* 103 (1999) 3872.
- [15] G. Pacchioni, A.M. Ferrari, *Catal. Today* 50 (1999) 533.
- [16] R. Orlando, R. Millini, G. Perego, R. Doveci, *J. Mol. Catal. A* 119 (1997) 253.
- [17] L. Giordano, J. Goniakowski, G. Pacchioni, *Phys. Rev. B* 64 (2001) 075417.
- [18] G. Haas, A. Menck, H. Brune, J.V. Barth, J.A. Venables, K. Kern, *Phys. Rev. B* 61 (2000) 11105.
- [19] S. Abbet, A. Sanchez, U. Heiz, W.-D. Schneider, A.M. Ferrari, G. Pacchioni, N. Rosch, *J. Am. Chem. Soc.* 122 (2000) 3453.
- [20] S. Abbet, U. Heiz, A.M. Ferrari, L. Giordano, C. Di Valentin, G. Pacchioni, *Thin Solid Films* 400 (2001) 37.
- [21] V.E. Henrich, P.A. Cox, *The Surface Science of Metal Oxides*, Cambridge University Press, Cambridge, 1994.
- [22] S. Coluccia, S. Lavagnino, L. Marchese, *Mater. Chem. Phys.* 18 (1988) 445.
- [23] Y.Y. Chen, R.T. Williams, W.A. Sibley, *Phys. Rev.* 182 (1969) 960.
- [24] J. Kramer, W. Ernst, C. Tegenkamp, H. Pfnür, *Surf. Sci.* 517 (2002) 87.
- [25] J. Kramer, C. Tegenkamp, H. Pfnür, *Phys. Rev. B* 67 (2003) 235401.
- [26] M. Sterrer, E. Fischbach, M. Heyde, N. Nilius, H.-P. Rust, T. Risse, H.-J. Freund, *J. Phys. Chem. B* 110 (2006) 8665.
- [27] M. Sterrer, E. Fischbach, T. Risse, H.-J. Freund, *Phys. Rev. Lett.* 94 (2005) 186101.
- [28] B. Henderson, R.D. King, *Phil. Mag.* 13 (1966) 1149.
- [29] P. Mori-Sanchez, J.M. Recio, B. Silvi, C. Sousa, A.M. Pendas, V. Luaña, F. Illas, *Phys. Rev. B* 66 (2002) 075103.
- [30] R.F.W. Bader, *Chem. Rev. (Washington, D.C.)* 91 (1991) 893.
- [31] A.D. Becke, K.E. Edgecombe, *J. Chem. Phys.* 92 (1990) 5397.
- [32] G. Pacchioni, A.M. Ferrari, E. Giamello, *Chem. Phys. Lett.* 255 (1996) 58.
- [33] A.M. Ferrari, G. Pacchioni, *J. Chem. Phys.* 107 (1997) 2066.
- [34] A.M. Ferrari, R. Soave, A. D'Ercole, C. Pisani, E. Giamello, G. Pacchioni, *Surf. Sci.* 479 (2001) 83.
- [35] D. Ricci, G. Pacchioni, P.V. Suchko, A.L. Shluger, *Surf. Sci.* 542 (2003) 293.
- [36] G. Pacchioni, *Surf. Sci.* 281 (1993) 207.
- [37] M.B. Jensen, L.G.M. Pettersson, O. Swang, U. Olsbye, *J. Phys. Chem. B* 109 (2005) 16774.
- [38] G. Pacchioni, J.M. Ricart, F. Illas, *J. Am. Chem. Soc.* 116 (1994) 10152.
- [39] A.D. Vitto, G. Pacchioni, F. Delbecq, P. Sautet, *J. Phys. Chem. B* 109 (2005) 8040.
- [40] A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Hakkinen, R.N. Barnett, U. Landmann, *J. Phys. Chem. A* 103 (1999) 9573.
- [41] A.M. Ferrari, L. Giordano, G. Pacchioni, S. Abbet, U. Heiz, *J. Phys. Chem. B* 106 (2002) 3173.
- [42] S. Abbet, A. Sanchez, U. Heiz, W.-D. Schneider, *J. Catal.* 198 (2001) 122.
- [43] A.M. Ferrari, L. Giordano, N. Rösch, U. Heiz, S. Abbet, A. Sanchez, G. Pacchioni, *J. Phys. Chem. B* 104 (2000) 10612.
- [44] I.V. Yudanov, S. Vent, K. Neyman, G. Pacchioni, N. Rösch, *Chem. Phys. Lett.* 275 (1997) 245.
- [45] E.V. Stefanovich, T.N. Truong, *J. Chem. Phys.* 104 (1996) 2946.
- [46] E.V. Stefanovich, T.N. Truong, *J. Phys. Chem. B* 102 (1998) 3018.
- [47] J.P. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [48] S.F. Boy, F. Bernardi, *Mol. Phys.* 19 (1970) 553.
- [49] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, R.C. Gaussian 03, Gaussian Inc., Wallingford, CT, 2004.
- [50] S. Noury, X. Krokidis, F. Fuster, B. Silvi, *Top-Mod Package*, Universitè P.M. Curie, Paris, 1997.
- [51] L. DiValentin, L. Giordano, G. Pacchioni, N. Rösch, *Surf. Sci.* 522 (2003) 175.
- [52] A. Bogicevic, D.R. Jennison, *Surf. Sci.* 437 (1999) L741.
- [53] A. Del Vitto, C. Sousa, F. Illas, G. Pacchioni, *J. Chem. Phys.* 121 (2004) 7427.
- [54] E. Florez, F. Mondragón, T.N. Truong, P. Fuentealba, *Phys. Rev. B* 73 (2006) 115423.