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DFT studies of the adsorption and interaction of two methanol molecules on a MgO edge

A.H. Rodríguez [a,b], M.M. Branda [b,c], N.J. Castellani [b,c,*]

[a] *Facultad de Ingeniería, Universidad Nacional de la Patagonia San Juan Bosco, Comodoro Rivadavia, Argentina*
[b] *Grupo de Materiales y Sistemas Catalíticos, Departamento de Física, Universidad Nacional del Sur, Avenida Alem 1253, Bahía Blanca, 8000 Buenos Aires, Argentina*
[c] *CONICET, Argentina*

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Abstract

The adsorption of two methanol molecules on an edge along the [001] direction of MgO was studied. The calculations were carried out within the DFT formalism employing an embedded cluster model approach. From the four possible geometrical configurations of dimers, one of them shows the dissociation of a methanol molecule. In order to attain a deeper understanding of substrate influence on this process, the adsorption energy was considered as a contribution mainly due to the direct interaction with the substrate and, separately, another one coming from the methanol–methanol interactions. The results indicate that the first adsorbed methanol molecule acts like a new defect at the surface and it turns more reactive the MgO edge site.

Keywords: Adsorption; Methanol; MgO; DFT

1. Introduction

Magnesium oxide (MgO) is considered as an ideal system in order to study the catalytic properties of oxides fundamentally due to its very simple cubic crystalline structure. Alkaline earth oxides like MgO, BaO and CaO are known by their basic character [1]. This property comes from the strong Lewis basicity of surface oxygen anions. Several reactions of catalytic interest comprise primarily the rupture of a heterolytic bond where the basic character of an O^{-2} anion predominates over the acid character of a Mg^{+2} cation. This behavior can be observed in relatively simple reactions as the H_2 dissociation and the dehydrogenation of CH_4 [2], and in more complex reactions as the hydrogenation of olefins [1]. On the other hand, it is well documented that the catalytic properties of MgO are noticeably only when the MgO surface has defects [3]. Surface defects on other alkaline-earth oxides play also a fundamental role in several adsorption processes [4]. Recently, the different behavior of these sites compared to the five-coordinated terrace sites have been rationalized considering their reduced Madelung potential [5].

Different molecules (CH_3OH [6–9], H_2 [10], CH_4 [11], H_2O [12], NO_2 [13], H_2S [14], CO [15,16], CO_2 and SO_2 [17], O_2^- and CO^- [18]) have been considered regarding the adsorption equilibrium geometry and the possibility of molecular dissociation. In the adsorption of methanol, the modification of O–H and C–O bonds is essential to understand the dissociation and transformation of this molecule. Our theoretical approach to this question [6–8] and the experimental results [19,20] show that the stoichiometric and most stable (001) face of MgO is inert for the dissociation of methanol. The adsorbed molecule is linked by a hydrogen bond with the surface where the hydroxyl of methanol and an O^{-2} anion of the surface participate.

The adsorption of methanol on MgO has been studied by several experimental techniques. Thermal desorption spectroscopy (TDS) measurements performed on powered MgO [21] and on smooth and defective (001) surfaces of MgO [20] revealed that only when low coordination adsorption sites are present, methanol dissociates. Infrared spectroscopy (IR) spectra [22] indicate the presence of at least four different species. Two of them named as I and II are weakly adsorbed,

* Corresponding author. Address: Grupo de Materiales y Sistemas Catalíticos, Departamento de Física, Universidad Nacional del Sur, Avenida Alem 1253, Bahía Blanca, 8000 Buenos Aires, Argentina. Tel.: +54 291 4595141; fax: +54 291 4595142.
E-mail address: castella@criba.edu.ar (N.J. Castellani).

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disappearing after evacuation [22]. Species I is a physisorbed methanol molecule. Species II is a methanol molecule linked by a hydrogen bond to an acidic–basic Mg/O pair, requiring a stronger evacuation. The other species observed at greater desorption temperatures, named as III and IV, are dissociated molecules [22]. Species III corresponds to a methoxy group linked to a magnesium ion and an adjacent hydrogen atom forming a hydroxyl group with an exposed oxygen ion of the surface. Species IV has been assigned to a surface methyl group linked to an oxygen ion and a hydroxyl group residing on a magnesium ion. Nuclear magnetic resonance (NMR) [23] techniques have also been used. Only species III has been observed in a NMR study performed at room temperatures [23].

The interpretation of recent TPR spectra [24] of methanol adsorbed on a, in principle, perfect MgO (100) surface shows that there is a net repulsive interaction of 0.03 eV between neighboring methanol molecules. In addition, an adsorption energy value of 0.64–0.75 eV/molecule was reported. It is 0.21–0.32 eV greater than high quality calculated values including BSSE corrections [9]. A possible reason for this discrepancy could be that the real surface is not perfect and that lower coordination sites are present [24]. Therefore, it is outstanding to study the interaction of methanol molecules adsorbed on a non-perfect MgO surface.

On the other hand, recent IR studies of the methanol/MgO (100) system show that film growth occurs by layer, with the completion of the monolayer before multilayer growth begins. At low coverage, the methanol molecules congregate into two-dimensional islands, which are strongly associated with the substrate. The properties of this sub-monolayer to monolayer thin film are similar to those of solid methanol [25].

From a theoretical point of view, the adsorption of a methanol molecule on MgO has been widely studied on perfect as well or on defective MgO surface. Taking into account the important influence that the defects have on the MgO surface reactivity, it is reasonably to think that the interactions between methanol molecules would be perturbed by the support. We guess that the first adsorbed molecule could act as a new defect in the surface, assisting the second adsorption.

In the present work, the adsorption of two methanol molecules on an edge along the [001] direction of MgO was studied. The edge site was selected considering its known reactivity like surface defect in front of molecules such as methanol as well as its relative greater abundance in the surface of real oxide surfaces (see Refs. [7–9]). Their adsorption energies and the interaction energies between them were evaluated for different possible mutual orientations on the edge.

2. Computational details

The properties of the two methanol molecules adsorbed on the edge of MgO surface were studied employing an embedded cluster model approach.

Anywhere a methanol molecule was initially placed, it evolved to acquire an adsorption configuration with its hydroxyl group residing on the bisecting plane. At the presence of a second molecule, only four symmetric configurations are possible. Indeed, taking into account the asymmetry of the methoxy group which can be either in one or the other side of the edge and the two possible orientations of the hydroxyl groups, four possible configurations were considered as initial step in geometry optimization, which were named as configurations A, B, C and D (see Figs. 1–4). More precisely,

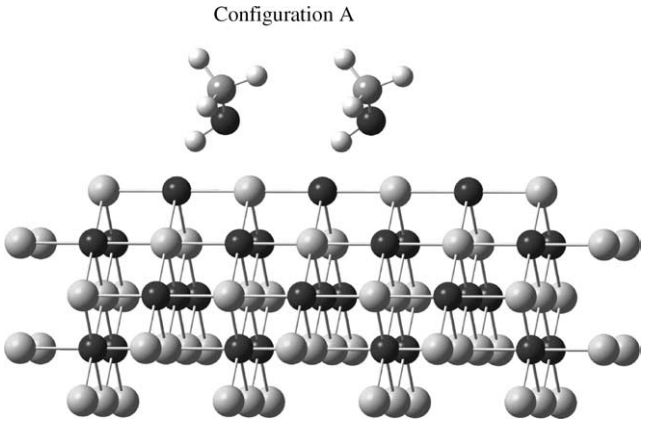

Fig. 1. Initial configuration A: the hydroxyls are both parallel and the methoxy groups are both on the same side of the edge.

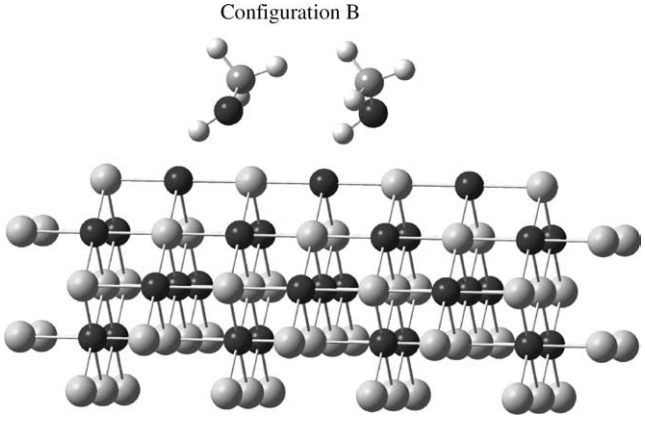

Fig. 2. Initial configuration B: the hydroxyls are both parallel and the methoxy groups are in the opposite sides of the edge.

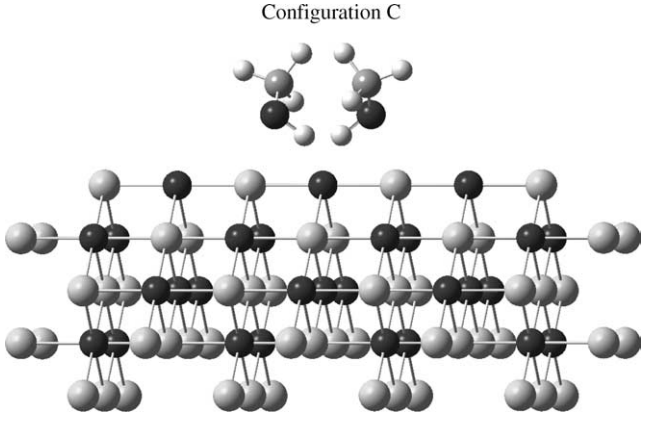

Fig. 3. Initial configuration C: the hydroxyls are in opposition and the methoxy groups are in the opposite sides of the edge.

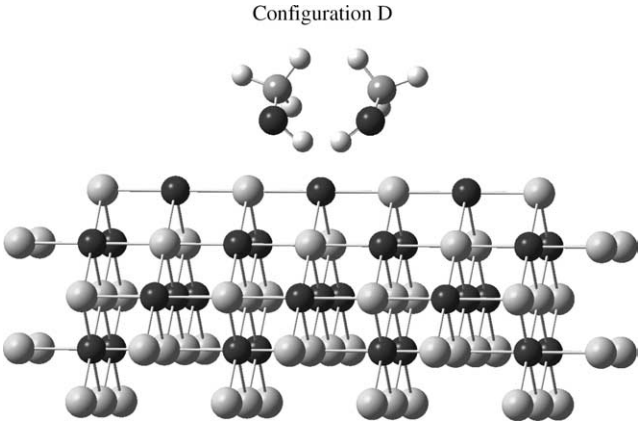

Fig. 4. Initial configuration D: the hydroxyls are in opposition and the methoxy groups are both on the same side of the edge.

in configurations A and B the hydroxyls are both parallel while in configurations C and D they are in opposition. On the other hand, the methoxy groups are both on the same side of the edge in configurations A and D while they are in opposite sides in configurations B and C.

Density functional theory (DFT) quantum–mechanical calculations were carried out using the gradient corrected Becke's three parameters hybrid exchange functional [26] in combination with the correlation functional of Lee, Yang and Parr [27] (B3LYP).

The use of a cluster to represent the interaction of small molecules with an oxide and between them is justified by the fact that normally a limited number of atoms of the substrate participates in the adsorption process. The so called 'cluster size-effects' refer to the long-range interactions, absent in the cluster, but present in the semi-infinite and periodic system. The importance of these effects (finite Madelung potential, dangling bonds of final atoms, for example) have been studied for MgO in the literature and different ways have been proposed to remedy the problem. One of them considers clusters for which the size increases up to an acceptable degree of convergence is obtained [14,28]. Another possibility is to use a relative small cluster and to mimic the influence of the rest of the solid by embedding this cluster in an array of model potentials [16,29,30].

In this work, the MgO (100) surface was represented by a finite cluster consisting of 34 oxygen atoms and 34 magnesium atoms, $(MgO)_{34}$, embedded in ± 2 point charges (1906 PCs). The cluster size was selected in order to be able to adsorb two molecules in adjacent neighboring Mg–O sites. This cluster comprises four layers along the bisecting plane. In this way, a methanol molecule adsorbed on each edge side interacts with the atoms of at less two conventional unit cells of MgO structure. To avoid the artificial polarization of the O^{2-} anions at the cluster border induced by the PC's [16,31] the positive PCs at the interface have been replaced by effective core potentials (26 ECPs) [32] which take into account the finite size effect of the Mg^{2+} cation. No basis functions are associated to these atoms. This approach has been used in the past to study the GS properties of MgO and has been compared to periodic approaches and more elaborate embedding schemes based on Green functions [33].

A gaussian basis set was employed, specifically, locally dense 6-31G. In this basis set, the following polarization functions were added for every methanol atoms and for the substrate atoms directly involved in the adsorption process: d-type orbitals for O and Mg atoms and p orbitals for the hydroxyl H atom. The geometry of both adsorbed methanol molecules was fully optimized. The cluster geometry was taken from Ref. [34] where the Mg–O distance is 2.106 Å. Experimental studies have demonstrated a poor surface relaxation in this oxide, therefore, the substrate cluster was not relaxed in the optimization process [35].

The adsorption energies E_{ads} of two methanol molecules were computed as the difference between the energy of the $(methanol)_2$/MgO system and the sum of the energies of the separated fragments, $E_{ads} = E(meth_2/MgO) - E(MgO) - 2E(1meth)$. A similar expression was considered for one adsorbed molecule. In order to attain a deeper understanding of substrate influence on adsorption energetic, the adsorption energy was considered as the contribution of two terms: (a) one coming mainly from the direct interaction with the substrate, named as E^*_{ads}, which do not includes the direct inter-molecule interactions and, (b) a second due only to the methanol–methanol interactions, named as E'_{int}, which is the difference between the energy of both adsorbed molecules but without the presence of substrate and twice the energy of a free methanol molecule. The last term takes into account the intermolecular interaction mediated by electrostatic forces when the molecules are put together under adsorption geometrical constraints and for this reason it can be interpreted as a deformation energy. In this way, we are able to compute the first term as $E^*_{ads} = E_{ads} - E'_{int}$. Furthermore, the interaction energy between methanol molecules can be defined as follows: $E_{int} = E_{ads}(2meth) - 2E_{ads}(1meth)$. The full counterpoise procedure was applied to correct the basis set superposition error (BSSE) [36].

Electron delocalization interactions that takes place in the methanol molecules and between the methanol and MgO cluster were studied employing the natural bond orbital (NBO) [37,38] population analysis. Within this approach localized orbitals with occupation numbers close to two correspond either to core, bonds and/or lone pairs, localized orbitals with occupation numbers notably smaller than one, to antibonds and Rydberg orbitals. Their respective occupation numbers are given by the density-matrix element as calculated in the NBO basis. Since the Fock-like matrix is not diagonal in the NBO basis, it is also possible to evaluate, by means of second order perturbation theory, the delocalization energy, $\Delta E^{(2)}$, associated to the charge delocalization from a highly occupied orbital to an almost unoccupied orbital [37,38].

The calculations have been performed using the GAUSSIAN 03 program package [39].

3. Results and discussion

The optimized geometries corresponding to the adsorbed methanol pairs A, B, C and D are shown in Figs. 5a–8a,

Configuration A

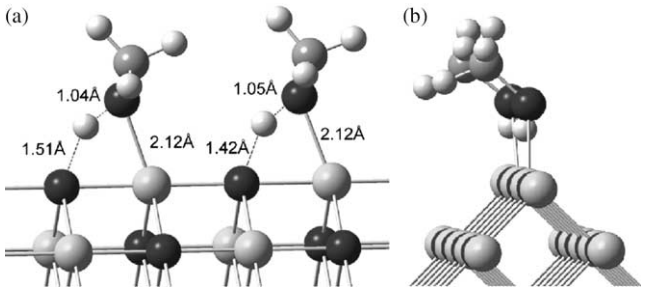

Fig. 5. (a) Optimized configuration A, (b) lateral view.

respectively. Figs. 5b–8b show their lateral views. As it can be observed from Figs. 5 and 6 (O_M–Mg) and (O_s–H) distances are very similar for cases A and B. However, in the first configuration A, where the $-CH_3$ groups are not opposed, the (O_s–H) distance is slightly smaller than in the other situation. In configuration C, both methanol molecules are more away from the oxide surface than in configurations A and B (see Fig. 7). In the case of configuration C, the same surface oxygen atom links simultaneously with the hydrogen atoms of both methanols, with the formation of two hydrogen bonds. Their lengths (∼1.8 Å) result ∼0.3 Å larger than for the former cases. However, the (O_M–Mg) distances are practically the same in configurations A, B and C. Finally, in the configuration D the substrate oxygen atom takes one of the alcohol hydrogens, producing a surface –OH group. The reacting methanol molecule becomes dissociated. This hydrogen atom keeps its link with the methoxy group by means of a strong hydrogen

Configuration B

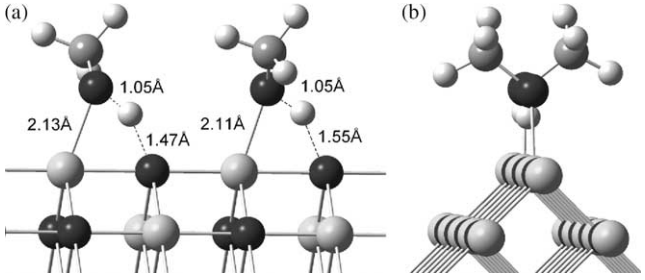

Fig. 6. (a) Optimized configuration B, (b) lateral view.

Configuration C

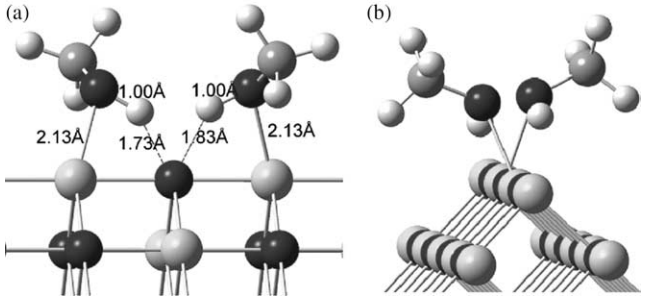

Fig. 7. (a) Optimized configuration C, (b) lateral view.

Configuration D

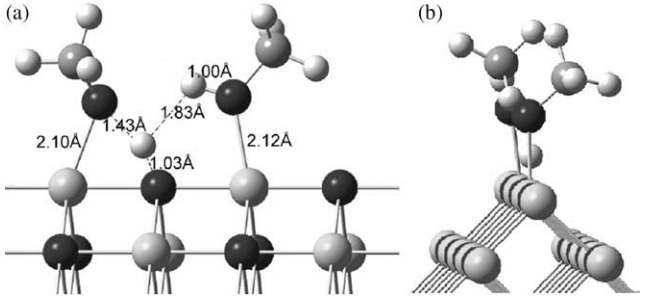

Fig. 8. (a) Optimized configuration D, (b) lateral view.

bond (see Fig. 8). The second methanol molecule preserves its identity nevertheless the hydrogen atom of alcohol is separated from the surface making a MgÔH bond equal to 117° in front of 80° in configuration C (see Figs. 7 and 8). The alcohol –OH group corresponding to the not dissociated molecules on the surface undergoes a slight stretching, going from 0.96 Å in the free methanol molecule to 1.00–1.05 Å in the adsorbed A and B ones.

In Table 1, the values of previously defined adsorption and interaction energy parameters, E_{ads}, E'_{int}, E^*_{ads} and E_{int}, are summarized for methanol molecules adsorbed in configurations A, B, C and D. Regarding the adsorption of only one molecule on the MgO edge, an adsorption energy value of 1.09 eV was obtained. Looking at the E_{int} values we note that the two methanol molecules prefer to be ensemble with respect to isolated geometries in configurations A, B and D. However, these values are very low and from them it is not possible to make a relationship with the geometrical distribution adopted by both molecules together. Moreover, in configuration C a slight repulsion is present.

A diagram in bars in order to compare E_{ads} and E^*_{ads} is presented in Fig. 9. Their values have been normalized to the energy necessary to adsorb two isolated methanol molecules taking $E_{ads}/2E_{ads}(1meth)$ and $E^*_{ads}/2E_{ads}(1meth)$. It is noteworthy that the E_{ads} values are very similar in all the cases and near to $2E_{ads}(1meth)$. However, there are noticeable differences in the E'_{int} values. All these energies are positive and correspond to a net electrostatic repulsion. In the case of configuration C, E'_{int} is very small (∼0.1 eV) giving $E^*_{ads} \approx 2E_{ads}(1meth)$. In configurations A and B, E'_{int} becomes much more positive than in the former case (by ∼0.3 eV), revealing to be less stable situations. These results agree with

Table 1
Adsorption and interacting energy parameters E_{ads}, E_{int}, E'_{int} and E^*_{int} with BSSE correction

	A	B	C	D
E_{ads} (eV)	−2.233	−2.261	−2.010	−2.215
E_{int} (eV)	−0.053	−0.081	0.170	−0.035
E'_{int} (eV)	0.348	0.298	0.098	2.454
E^*_{ads} (eV)	−2.581	−2.559	−2.108	−4.669

$E_{ads} = E(meth_2/MgO) - E(MgO) - 2E(1meth)$; $E_{int} = E_{ads}(2meth) - 2E_{ads}(1meth)$; $E'_{int} = E(2\ deformed\ methanols) - 2E(1meth)$; $E^*_{ads} = E_{ads} - E'_{int}$; $E_{ads}(1meth) = -1.09$ eV.

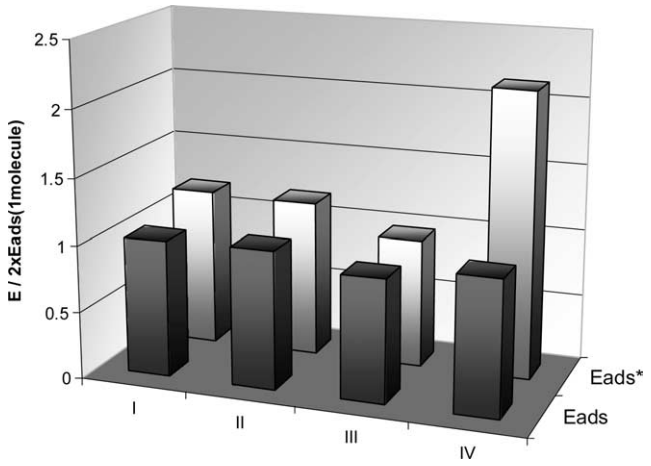

Fig. 9. $E/2E_{ads}$(1meth) where E is equal to E_{ads}(2meth) = E(meth$_2$/MgO) − E(MgO) − 2E(1meth), dark bars, and E is $E^*_{ads} = E_{ads} - E'_{int}$, light bars.

the deformed molecules geometries. The geometry of adsorbed molecules in C (O–H = 1.00 Å) is similar to that of the free methanol (O–H = 0.96 Å), while in configurations A and B the deformation is larger (O–H = 1.05 Å) and $E^*_{ads} > 2E_{ads}$(1meth). When a methanol molecule is dissociated in case D, the E'_{int} value is very large ($\sim$2.4 eV) meaning that the first component of the adsorption energy which takes into account the direct interaction with the substrate, E^*_{ads}, is very large too ($\sim -$ 4.7 eV). The diagram in bars (Fig. 9) shows clearly all these observations, particularly that E^*_{ads}(C)/2 $\approx E_{ads}$(1meth), E^*_{ads}(A)/2 and E^*_{ads}(B)/2 $> E_{ads}$(1meth) and E^*_{ads}(D)/2 $\gg E_{ads}$(1meth). Comparing these results with an earlier work related to the adsorption of one methanol on different MgO sites [7], we observe that the adsorption cases A and B resemble the situation where one methanol molecule adsorbs on a $Mg_{4c}O_{3c}$ site. On the other hand, the adsorption case D with a dissociated methanol resembles the adsorption of one methanol on $Mg_{3c}O_{4c}$. These observations seem indicate that the first adsorbed methanol molecule acts like a new defect at the surface and it turns more reactive the MgO edge site.

In Table 2, the most relevant NBO population parameters are summarized, including NBO charges, charge transfers and occupation numbers for the atoms of adsorbates and substrate. The charge variation ΔQ corresponds to the change in NBO charge of one particular atom going from the non-interacting systems to the surface complex. Looking at the first and second rows, we notice that every molecule receive electronic charge when they are adsorbed. This charge transfer also takes place when only one molecule is adsorbed. This negative charge essentially arises from the neighbor substrate oxygen. The charge transfers and the charges taken by O_{M1} and O_{M2} in case C are smaller than those corresponding to cases A and B (see Table 2), confirming that in the former situation there is a lower interaction with the support. On the other hand, the O_M gains and the H_M loss charge increasing the O–H bond polarization in all the configurations. Notice that the O–H bond polarization in cases A and B is greater. Moreover, it is noteworthy from Table 2 that a charge transfer takes place from the O_s lone pair to the (O_M–H)* antibonding orbital, $\Sigma n(O_s) \rightarrow$ (O_M–H)*, which is in agreement with the increase of O–H distance (see Figs. 5 and 6). When a methanol molecule is dissociated (configuration D) this species takes much more charge than in other configurations (~ -0.3). Here, the charge is localized at the methoxy oxygen (see Table 2). However, this methoxy oxygen transfers charge to the new O_s–H bond, through ($n(O_{M2}) \rightarrow$ (O_s–H)*, being it stretched (= 1.03 Å). These results are in agreement with those for one methanol adsorption on a $Mg_{3c}O_{4c}$ site, reported in Ref. [7].

Table 2
Selected NBO parameters corresponding to adsorbate–substrate interactions (different adsorption sites)

	A	B	C	D
ΔQ(M1)[a]	−0.09	−0.09	−0.05	0.00
ΔQ(M2)[a]	−0.08	−0.08	−0.03	−0.26
$\Delta Q(O_{M1})$[b]	−0.15	−0.15	−0.12	−0.12
$\Delta Q(O_{M2})$[b]	−0.15	−0.15	−0.13	−0.26
$\Delta Q(H_{M1})$[c]	+0.05	+0.05	+0.04	+0.06
$\Delta Q(H_{M2})$[c]	+0.04	+0.04	+0.04	+0.03
$\Delta Q(O_{s1})$[d]	+0.04	+0.04	+0.03	+0.17
$\Delta Q(O_{s2})$[d]	+0.04	+0.04	–	–
$(n(O_{s1}) \rightarrow (O_{M1}$–H)*	67.47	69.47	10.23[e]	–
$(n(O_{s2}) \rightarrow (O_{M2}$–H)*	60.98	54.08	26.14[e]	–
$(O_s$–H)* $\rightarrow (O_{M1}$–H)*	–	–	–	23.06
$(n(O_{M2}) \rightarrow (O_s$–H)*	–	–	–	71.50
Occ.(O_{M1}–H)*	0.14	0.14	0.07	0.04
Occ.(O_{M2}–H)*	0.13	0.12	0.09	–
Occ.(O_s–H)*	–	–	–	0.14

M1, methanol molecule 1; M2, methanol molecule 2; O_{s1}, substrat oxygen atom that interacts with M1; O_{s2}, substrat oxygen atom that interacts with M2; O_s–H, O–H bond formed between the oxide oxygen and the dissociated methanol hydrogen; ΔQ, change in NBO charge on a particular atom going from the non-interacting systems to the surface complex; 'n' stands for a lone pair and '(' for both oxygen lone pair and 'occ' is the NBO occupation number.

[a] For only one adsorbed methanol ΔQ(M) = −0.08.
[b] For only one adsorbed methanol $\Delta Q(O_M) = -0.14$.
[c] For only one adsorbed methanol $\Delta Q(H_M) = +0.04$.
[d] For only one adsorbed methanol $\Delta Q(O_s) = +0.04$.
[e] In this case, $O_{s1} = O_{s2}$.

Taking into consideration the theoretical consequences above commented, a more detailed description of the dissociation process can be outlined. While the interaction between only one methanol molecule with the magnesia edge involves the OH group of methanol and one O_s atom of the edge, in the situation of two methanol molecules approaching to the same O_s atom (sites C and D), the corresponding hydroxyls compete for the interaction with O_s. Regarding site C, the methanol molecules move away symmetrically from O_s in comparison to the one methanol case. The O_s–H distance stretches from 1.51 to 1.73 Å, while the O_M–H distance shortens from 1.04 to 1.00 Å. The last result is compatible with the presence of a repulsive interaction between the alcoholic hydrogen atoms. The methyl groups also show a repulsive interaction between them, attaining more separated positions. On the other hand, on site D both methyl groups are initially place at the same edge side, undergoing an important steric repulsion. As a consequence, these methanol molecules move away, going upward from edge and rotating at the same time. This last effect is more noticeable for the second

molecule (that one which activates the dissociation). In this situation, the two alcoholic hydrogen atoms repel mutually with a greater special freedom in comparison with site C. One of them is now compelled to be linked to the oxygen atom of methanol or the surface oxygen of magnesia. This last hydrogen leaves electronic charge to O_M and simultaneously takes it from O_s. The hydrogen keeps finally bonded to O_s, with a net electron transfer between the two oxygen atoms ($\Delta Q O_{M2} = -0.26$ and $\Delta Q O_{s1} = +0.17$).

4. Conclusions

The main conclusions of this work are:

(1) When two methanol molecules are adsorbed on a MgO edge with the [001] direction four geometrical configurations are possible. For three of them, the dimers are slightly more stable than the isolated molecules. In the other configuration, the interaction energy is slightly repulsive.
(2) From the geometrical optimization, we found that a molecule dissociation occurs in one of these configurations, where initially the hydroxyl groups are in opposition and the methoxy groups are in the same edge side.
(3) In order to explain the reactivity on different sites of MgO edge, it was convenient to subtract the direct interaction between the molecules from the adsorption energies. The quantity so defined shows that in the case of molecule dissociation a relevant interaction between the molecules and the substrate is present.
(4) Comparing the geometry resulting from the dissociation process with earlier calculations for one methanol molecule adsorbed on $Mg_{4c}O_{3c}$ and $Mg_{3c}O_{4c}$ sites, it seems indicate that the first adsorbed methanol molecule acts like a new defect at the surface and it turns more reactive the MgO edge site.

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