

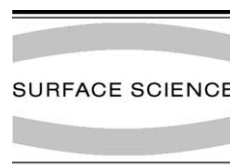


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Methanol adsorption on magnesium oxide surface with defects: a DFT study

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Abstract

The methanol adsorption on several defects of the magnesium oxide surface were studied. Structural and electronic study with geometrical optimization and natural bond orbital (NBO) analysis were performed using a density functional theory (DFT) method. Oxygen and magnesium with different coordination numbers have very different reactivity in this surface producing dissociated and non-dissociated species. These results are in agreement with infrared spectroscopy observations where CH_3OH , OCH_3 and OH species were found in defective MgO surfaces.

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Keywords: Density functional calculations; Catalysis; Physical adsorption; Magnesium oxides; Alcohols; Surface electronic phenomena (work function, surface potential, surface states, etc.); Surface structure, morphology, roughness, and topography

1. Introduction

The MgO has been considered as an ideal system in order to study the catalytic properties of oxides, due fundamentally to its very simple cubic crystalline structure. Moreover the oxides of simple metals like MgO , BaO and CaO are known by their basic properties [1]. They come mainly from the strong Lewis basicity of surface oxygen anions. It is believed that 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. In this way, MgO seems to be also an ideal system for modeling the influence of defects like terraces, steps, corners and vacancies. The oxygen vacancies are very interesting because they act as electron traps which can be detected by electronic paramagnetic resonance spectroscopy [3]. This is particularly noticeably in the case of MgO doped with Li , a highly active system for production of C_2H_4 . The experimental results have been related mainly to the density of produced vacancies than to the density of Li^+ cations [4].

A considerable deal of works has been focused to study the structural aspects as well as the

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reactive properties of surface defects of MgO. The works published by Soave and Pacchioni [5] and Nakajima and Doren [6] summarize the essential aspects of these studies. The adsorption catalytic site and its immediate environment are usually represented by a “cluster” of atoms which size requires a careful analysis. In particular the effect of the cluster size has been studied in a previous work [7] focused on the MgO(100) surface. The cluster sometimes is surrounded by an ensemble of model potentials acting as an “embedding”, in order to simulate the influence of the rest of the solid. The substrate can also be represented by a “slab” whose atoms must satisfy periodic conditions. Several molecules (CH_3OH [7], H_2 [8], CH_4 [9], H_2O [10], NO_2 [11], H_2S [12], CO [5,13], CO_2 and SO_2 [14], O_2^- and CO^- [15]) have been considered regarding the adsorption equilibrium geometry and the possibility of an eventual molecular dissociation. In the adsorption of methanol two bonds, specifically O–H and C–O, could play a role in the dissociation and transformation of this molecule. Our theoretical approach to this question [7] and the experimental results [16,17] indicate that the most stable and stoichiometric (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 techniques. Thermal desorption spectroscopy measurements performed on powdered MgO [18] and on smooth and defective (001) surfaces of MgO [17] revealed that only when low coordination adsorption sites are present, methanol dissociates. Infrared (IR) spectroscopy spectra [19], indicate the presence of at least four different species. Two species, named as I and II, are weakly adsorbed, disappearing after evacuation [19]. Species I is a physisorbed methanol molecule. Species II is a methanol molecule linked by a hydrogen bond to a acidic–basic Mg/O pair, requiring a stronger evacuation. It was suggested that the different frequencies corresponding to the OH stretching could be associated with an ensemble of different atomic configurations for the acidic–basic pairs. The other species observed at greater de-

sorption temperatures, named as III and IV, are dissociated molecules [19]. 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 Mg ion. Nuclear magnetic resonance (NMR) [20] techniques have also been used. Only species III has been observed in a NMR study performed at room temperatures [20].

The goal of the present work is to perform a more detailed study of the influence of coordination number of the adsorption site on the adsorption process itself and to analyze how this reaction is related with the electronic structure of the active site.

2. Computational details

Calculations were carried out in a model system containing a methanol molecule adsorbed on a non-perfect (100) face of MgO. The staggered rotamer was the selected conformation for the methanol because of its greater energetic stability with respect to the eclipsed rotamer [7]. A cluster consisting of 12 oxygen atoms and 12 magnesium atoms, $(\text{MgO})_{12}$, was employed to represent the local structure of the MgO surface. The cluster size was analyzed in a preceding paper finding that the $(\text{MgO})_{12}$ formula was suitable to this adsorption study [7]. Seven different sites for methanol adsorption on this cluster have been considered, selected in such a way to represent possible defects of the MgO(100) surface. They are depicted in Fig. 1. As the oxygen or magnesium ions can have different coordination number, the following seven $\text{O}_{nc}\text{Mg}_{mc}$ pairs have been considered, classified according to the ion coordination: (a) $\text{O}_{5c}\text{Mg}_{5c}$, (b) $\text{O}_{5c}\text{Mg}_{4c}$, (c) $\text{O}_{4c}\text{Mg}_{5c}$, (d) $\text{O}_{4c}\text{Mg}_{4c}$, (e) $\text{O}_{4c}\text{Mg}_{3c}$, (f) $\text{O}_{3c}\text{Mg}_{4c}$, (g) $\text{O}_{3c}\text{Mg}_{3c}$, where the subindexes “nc” and “mc” design the coordination number of O and Mg, respectively.

The one-electron orbitals, eigenenergies and total molecular energy for adsorbed methanol were calculated using the gradient corrected density

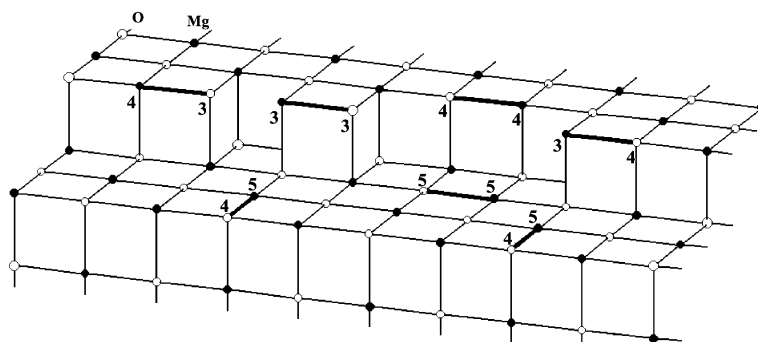


Fig. 1. Schematic graph of the MgO(100) surface with possible defects.

functional theory (DFT) with the hybrid Becke3 functional for exchange [21] and the Lee–Yang–Parr correlation functional [22], B3LYP. A Gaussian basis set was employed, specifically, the locally dense 6-31G. In this basis set the following polarization functions were added for atoms directly involved in the adsorption process: d-type orbitals for O and Mg atoms and p orbitals for the hydroxyl H atom. The adsorbed methanol geometry was fully optimized. The optimization procedure began taking as the initial configuration that of the methanol over a Mg–O pair of the substrate. The cluster geometry was taken from Ref. [23] where the Mg–O distance is 2.106 Å. The substrate cluster was not relaxed in the optimization process. The main vibrational frequencies for adsorbed (dissociated or not) methanol have also been computed and compared with experiments.

The adsorption energies were computed as the difference between the sum of the energies of the separated fragments and the energy of the methanol/MgO system. The full counterpoise procedure was applied to correct the basis set superposition error (BSSE) [24]. Due to the fact that this method is particularly suitable when the fragments do not undergo important modifications of their geometries after bond formation, the correction was applied only in some cases (see below). As a first approach, for comparison reasons only the non-corrected values were considered.

Electron delocalization interactions that takes place in the methanol molecule and between the methanol and the MgO cluster were studied employing the natural bond orbital (NBO) [25,26]

population analysis. Within this approach localized orbitals with occupation numbers close to 2 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 [25,26]. All calculations reported in this work were carried out with the Gaussian 98 package of programs [27].

3. Results and discussion

The geometrically optimized methanol adsorbed on the seven different sites of the MgO surface are showed in Figs. 2–4.

In Table 1 the main molecular properties of methanol adsorbed on these sites are summarized. They comprise: adsorption energy, E_{ads} , methanol intramolecular O–H and C–O interatomic distances, $d(\text{Oa–Ha})$ and $d(\text{Ca–Oa})$, methanol–surface Os–Ha, Mgs–Oa and H(methyl)–Os (second oxygen neighbor) interatomic distances, $d(\text{Os} \cdots \text{Ha})$, $d(\text{Mgs} \cdots \text{Oa})$ and $d(\text{Hmethyl} \cdots \text{Os})$, and methanol COH angle at equilibrium.

Looking at the E_{ads} values for $\text{Mg}_{5c}\text{O}_{5c}$, $\text{Mg}_{4c}\text{O}_{5c}$ and $\text{Mg}_{5c}\text{O}_{4c}$ cases, they can be classified as “weak

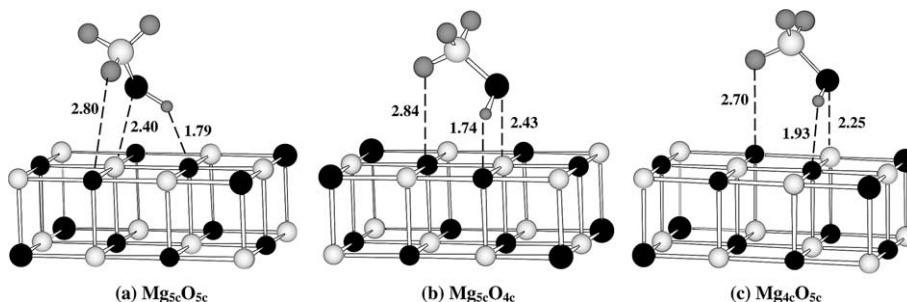


Fig. 2. “Weak methanol adsorption” on (a) $\text{Mg}_{5c}\text{O}_{5c}$, (b) $\text{Mg}_{5c}\text{O}_{4c}$ and (c) $\text{Mg}_{4c}\text{O}_{5c}$ cases.

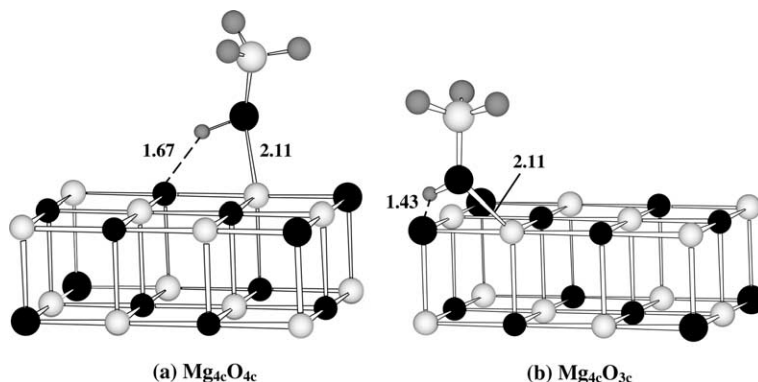


Fig. 3. “Strong associative methanol adsorption” on (a) $\text{Mg}_{4c}\text{O}_{4c}$ and (b) $\text{Mg}_{4c}\text{O}_{3c}$ cases.

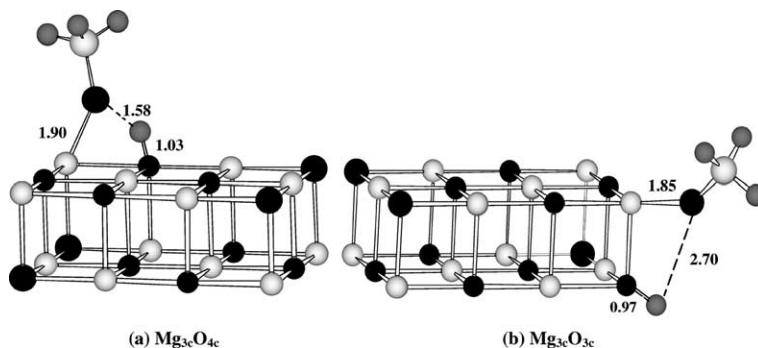


Fig. 4. “Strong dissociative methanol adsorption” on (a) $\text{Mg}_{3c}\text{O}_{4c}$ and (b) $\text{Mg}_{3c}\text{O}_{3c}$ cases.

adsorbed” methanol ($E_{\text{ads}} \sim 0.5$ eV), while for $\text{Mg}_{4c}\text{O}_{4c}$, $\text{Mg}_{3c}\text{O}_{4c}$, $\text{Mg}_{4c}\text{O}_{3c}$ and $\text{Mg}_{3c}\text{O}_{3c}$ cases they correspond to “strong adsorbed” methanol ($E_{\text{ads}} \sim 1$ eV or greater). The $d(\text{Os} \cdots \text{Ha})$, $d(\text{Mgs} \cdots \text{Oa})$ distances are longer than 1.7 and 2.1 Å, respectively, for the higher coordinations, and shorter

than 1.7 and 2.1 Å, respectively, for the lower coordinations, in relationship with the strength of the methanol–magnesia interaction. The corresponding atomic configurations are shown in Fig. 2. Notice that in all cases the hydroxyl group is oriented in such a way that the methanol O atom is

Table 1

Main molecular properties of methanol adsorbed on MgO surface: adsorption energy (E_{ads}), methanol intramolecular, $d(\text{O–H})$ and $d(\text{C–O})$, and methanol–surface, $d(\text{Os}\cdots\text{Ha})$, $d(\text{Mg}\cdots\text{Oa})$, $d(\text{Hmethyl}\cdots\text{Os})$, interatomic distances and methanol COH angle at equilibrium

	Isolat. meth.	Mg _{5c} O _{5c}	Mg _{4c} O _{5c}	Mg _{5c} O _{4c}	Mg _{4c} O _{4c}	Mg _{4c} O _{3c}	Mg _{3c} O _{4c}	Mg _{3c} O _{3c}
E_{ads} (eV) ^a	–	0.59 (0.27)	0.61 (0.31)	0.62 (0.31)	1.01 (0.73)	1.27 (0.99)	1.60	2.39
$d(\text{Os}\cdots\text{Ha})$ (Å)	–	1.79	1.93	1.74	1.67	1.43	1.03	0.97
$d(\text{Mgs}\cdots\text{Oa})$ (Å)	–	2.40	2.25	2.43	2.11	2.11	1.90	1.85
$d(\text{Oa–Ha})$ (Å)	0.96	0.99	0.98	0.99	1.01	1.07	1.58	2.70
$d(\text{Ca–Oa})$ (Å)	1.44	1.44	1.44	1.44	1.45	1.44	1.42	1.41
$d(\text{HM}\cdots\text{Os})$ (Å)	–	2.80	2.70	2.84	–	–	–	–
(COH) _a	107.2°	110.0°	110.2°	110.2°	113.3°	113.4°	129.7°	151.6°

a: adsorbate, s: substrate, HM \cdots Os: bond between the hydrogen of the methyl group and the closest Os atom (see Fig. 2).

^a $E_{\text{ads}} = E(\text{MgO cluster}) + E(\text{methanol}) - E(\text{MgO cluster and methanol})$. In parenthesis, the BSSE corrected adsorption energy. Positive values correspond to exothermic adsorption processes.

directly linked with a Mg cation while the methanol H atom is directly linked with a O anion. More specifically, the weak adsorbed methanol undergoes a slight distortion of its geometry: an elongation of 0.03 Å in O–H bond and a 3° opening of COH angle with respect to the free molecule values. Besides, the methanol molecule presents a bending toward the surface due to an electrostatic interaction between a H atom of the methyl group and an O surface atom (situated by 2.7–3.0 Å apart). This situation could, in principle, correspond to a hydrogen bond formed between the carbon atom of methyl and the oxygen anion on of MgO.

The methanol adsorption over penta-coordinated Mg_{5c}O_{5c} site was studied in a former work under Hartree–Fock formalism [7]. The $d(\text{Mgs}\cdots\text{Oa})$ distance is 0.84 Å shorter in that work in comparison with the present one using DFT. On the other hand, the E_{ads} values are only comparable if MP2 correction in the HF calculations is included. Those results, both the distance and the energy, indicate the importance of correlation effects in the description of the methanol–magnesia interaction.

As it was discussed above the sites for which one ion is penta-coordinated and the other tetra-coordinated show an adsorptive behavior similar to that observed for the Mg_{5c}O_{5c} site, both in energy and in internal methanol geometry. Notwithstanding, changes in the adsorbate–substrate interface occur when the coordination number of

one element decreases from 5 to 4 keeping the other one unchanged. Indeed, the Mgs \cdots Oa distance decreases for Mg_{4c} with respect to Mg_{5c}. The same situation takes place with the Os \cdots Ha distance when the oxygen coordination number changes from 5 to 4, although in this case the change is much less important. This indicates that the decrease of the coordination number increases the bond strength in both cases.

The stronger adsorption sites (i.e., Mg_{4c}O_{4c}, Mg_{3c}O_{4c}, Mg_{4c}O_{3c} and Mg_{3c}O_{3c} sites), are able to produce an “associative adsorption” (Mg_{4c}O_{4c} and Mg_{4c}O_{3c} sites) or a “complete dissociation” (Mg_{3c}O_{4c} and Mg_{3c}O_{3c} sites). The dissociative state is exothermic with respect to the less favourable (Mg_{5c}O_{5c}) non-dissociative one by almost 1.0 eV for the Mg_{3c}O_{4c} site and by almost 1.8 eV for the Mg_{3c}O_{3c} site. The diminution of the Mg coordination number is more important for the surface activity than the diminution of the oxygen coordination number. Indeed, the complete dissociation only happens for Mg_{3c}:Mg_{3c}O_{3c} and Mg_{3c}O_{4c}. The first one, where the coordination number of oxygen is also 3, presents the higher adsorption energy. It should be noted that the order in adsorption energies calculated in this work: Mg_{3c}O_{3c} > Mg_{3c}O_{4c} > Mg_{4c}O_{3c} is the same as it was reported in HF calculations performed to study the H₂ dissociation on MgO [8]. The dissociation of methanol molecule implies the complete scission of the O–H bond, producing a dissociated state similar to species III proposed by Tench et al. to

explain their IR results [19]. Recent theoretical studies of methanol adsorption on the stoichiometric (110) face of TiO_2 have shown that at medium coverage the methanol O–H bond breaks preferentially over the C–O bond, while the opposite is obtained at $\theta = 1$ [28].

In cases where the geometry did not undergo significant modifications, i.e., for non-dissociative methanol adsorption, the BSSE corrected E_{ads} values have also been reported. This correction can be relevant (up to 50%) for the highest coordinations, nevertheless it does not modify the classification of adsorbed methanol species above commented.

The significant influence of the coordination number on the adsorbate internal distances must be underlined. The methanol O–H distance increases, in comparison with the free methanol molecule, by 0.02–0.11 Å for the non-dissociative states and by 0.6 Å or greater when the dissociation is complete. In the last situation the $d(\text{Ha} \cdots \text{Os})$ values near 1 Å are typical distances for those of a hydroxyl group. On the other hand the methanol C–O bond length is similar in all the cases. Only for the dissociative states a small decrease of 0.2 Å is observed. The COH angle un-

dergoes, in comparison with the hydrogen bond states, a small 3° opening for the strong non-dissociative states and a very significant increase of nearly 19° and greater when the methanol molecule dissociates.

In Table 2 several NBO parameters that characterize the adsorbate–substrate charge transfer interactions are displayed. The methanol molecule is only slightly negative charged near the MgO surface for the non-dissociative adsorption, however the net charge for the dissociated fragments becomes remarkably relevant (around $-0.3e$). It suggests a basic behavior of the substrate, with more basic character in those sites with smaller coordination number.

The charge transfer interaction from the oxygen lone pairs of the substrate, Os, to the methanol (Oa–Ha) bond is similar when the oxygen have four or five coordination number and increases when this oxygen is three-coordinated. In the methanol complete dissociation (Mg_{3c}) the charge is transferred from the oxygen lone pair of the adsorbate, Oa, to the (Os–Ha) bond formed between the hydrogen of the dissociated methanol and the substrate oxygen. This interaction is almost zero when the dissociation is produced over

Table 2

Selected NBO parameters corresponding to adsorbate–substrate interactions (different adsorption sites)^a

	$\text{Mg}_{5c}\text{O}_{5c}$	$\text{Mg}_{4c}\text{O}_{5c}$	$\text{Mg}_{5c}\text{O}_{4c}$	$\text{Mg}_{4c}\text{O}_{4c}$	$\text{Mg}_{4c}\text{O}_{3c}$	$\text{Mg}_{3c}\text{O}_{4c}$	$\text{Mg}_{3c}\text{O}_{3c}$
$Q(\text{CH}_3\text{OH})^b$	−0.058	−0.039	−0.066	−0.048	−0.087	−0.267	−0.324
$\Sigma n(\text{Os}) \rightarrow (\text{Oa} - \text{Ha})^{*c}$	27.35	17.54	34.64	28.67	82.85	—	—
$\Sigma n(\text{Oa}) \rightarrow (\text{Os} - \text{Ha})^{*c}$	—	—	—	—	—	52.23	0.33
$\Sigma n(\text{Oa}) \rightarrow n^*(\text{Mg})^c$	13.68	13.77	12.50	19.82	24.35	36.40	—
$\text{Occ.}(\text{Oa} - \text{Ha})^{*d}$	0.077	0.060	0.086	0.092	0.142	—	—
$\text{Occ.}(\text{Os} - \text{Ha})^{*d}$	—	—	—	—	—	0.115	0.011
$Q(\text{Oa})^e$ (ads)	−0.826	−0.821	−0.832	−0.865	−0.899	−1.043	−1.089
$Q(\text{Ha})^e$ (ads)	0.489	0.494	0.487	0.514	0.529	0.516	0.533
$Q(\text{Os})^e$ (iso)	−1.671	−1.673	−1.604	−1.611	−1.508	−1.615	−1.513
$Q(\text{Mgs})^e$ (iso)	1.563	1.588	1.564	1.588	1.589	1.529	1.529
$Q(\text{Os})^e$ (ads)	−1.646	−1.656	−1.584	−1.586	−1.498	−1.450	−1.366
$Q(\text{Mgs})^e$ (ads)	1.576	1.613	1.578	1.611	1.621	1.628	1.647

^a Charges are given in a.u.; interaction energies are given in kcal/mol. ‘a’ stands for adsorbate, ‘s’ stands for substrate, ‘ads’ means adsorbed and ‘iso’ means isolated.

^b Total charge transferred from the substrate to the adsorbate.

^c ‘n’ stands for a lone pair, ‘Σ’ for both oxygen lone pairs and * means an antibond.

^d NBO occupation number.

^e Atomic NBO charge.

Table 3

Overlap populations for the methanol adsorbed on different places of magnesium oxide surface

	Mg _{5c} O _{5c}	Mg _{4c} O _{5c}	Mg _{5c} O _{4c}	Mg _{4c} O _{4c}	Mg _{4c} O _{3c}	Mg _{3c} O _{4c}	Mg _{3c} O _{3c}
OP(Ha,Os)	0.051	0.038	0.057	0.045	0.065	0.181	0.283
OP(Oa,Mg)	0.176	0.122	0.184	0.176	0.209	0.237	0.346
OP(Oa,Ha)	0.211	0.232	0.207	0.212	0.189	0.082	0.003
OP(C,Oa)	0.169	0.168	0.166	0.159	0.170	0.211	0.235

the site Mg_{3c}O_{3c} because of the long distance between the Oa atom and the (Os–Ha) bond.

The other important charge transfer interaction between the methanol and the oxide is from the oxygen of the adsorbate, Oa, to the magnesium surface atom. It can be observed that this charge transfer increases when the coordination numbers decrease, particularly for the three-coordinated Mg. This variation implies a greater Lewis acid character for the Mg when the coordination number is low.

The (Oa–Ha)* bond occupation number is in agreement with the preceding observation of the charge transfer from the Os to the (Oa–Ha)* hydroxyl bond. The non-negligible (Os–Ha)* occupation number (sixth entrance in Table 2) appears due to the charge transfer from the oxygen Oa to this bond, which is occupied only when the dissociation is complete.

The natural charges of the oxygen and the hydrogen atoms belonging to the methanol hydroxyl are showed in Table 2. It is clear that there is an important charge polarization of the (Oa–Ha) link for the stronger adsorbed methanol with respect to the weak chemisorbed methanol. The oxygen charge is about $-1e$ in the methoxide group for the dissociation cases.

The natural charges of the oxygen and magnesium atoms of pure magnesia surface are showed in the ninth and tenth entries of Table 2. Comparing the oxide oxygen charge for the different sites we observe that it is an increasing function (in absolute value) of the anion coordination number, gaining nearly $0.160e$ when the anion coordination number changes from O₃ to O₅. On the other hand, the Mg positive charge increases (by $0.025e$) when the cation coordination number changes from Mg₅ to Mg₄, but decreases more significantly (by $0.035e$) when it changes from Mg₅ to Mg₃. If

the surface with methanol adsorbed and the bare magnesia surface are compared, both the Os and Mgs atoms lose electronic charge when the molecule is adsorbed. When the methanol dissociation occurs, i.e., for Mg_{3c}O_{4c} and Mg_{3c}O_{3c} sites, the lost of the negative charge is significant. This is in agreement with the negative charge taken from the methanol molecule. It seems to be that the basic behavior of the oxide surface increases with the diminution of the coordination number.

Overlap populations calculated according to Mülliken [29] for the methanol adsorbed on different sites of magnesium oxide surface are summarized in Table 3. The OP(Ha,Os) shows the strength of the link between the methanol and the MgO surface. Notice that the adsorption energy increases (Table 1) in the same way as the (Oa–Ha) bond is weakened and the (Os···Ha) link fortifies. The OP(Os,Ha) value is more important when the dissociation is reached.

The results of Table 3 indicate that maintaining the same coordination number for the oxygen, the overlap is lower when the coordination number of the Mg atom is higher. Moreover, the comparison between sites with the same Mg coordination number shows a greater overlap if the oxygen coordination number decreases. Our results are in agreement with previous quantum mechanical calculations performed on model MgO structures at HF level and fixed geometries [30]. These calculations revealed the effect of surface structure on the basic strength of O²⁻ ion. According to that work, the main factors generating stronger basicity are: (i) fewer Mg atoms coordinated to the central oxygen atom in the basic site and (ii) more O atoms coordinated to the Mg atoms adjacent to the central oxygen atom. It is worth commenting that the OP(Oa,Mg) increases in the same way as the OP(Ha,Os). On the other hand, the OP(Oa,Ha)

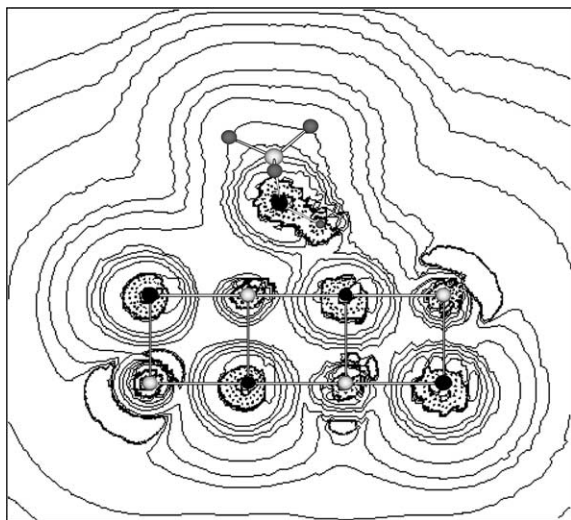


Fig. 5. Electron density Laplacian $\nabla^2\rho$ for the weak adsorption case, $\text{Mg}_{5c}\text{O}_{5c}$. The contour lines are given for a cut along the (1 0 0) plane. The short dashed lines indicate regions of electron charge accumulation and the solid lines correspond to regions of electron charge depletion.

follows the opposite trend of the $\text{OP}(\text{Ha},\text{Os})$. Evidently, the interaction between the surface and the molecule provokes a weakening of the Oa-Ha bond. It can be observed that in general the $\text{OP}(\text{C},\text{Oa})$ almost do not change. Only when the molecule is dissociated this bond is stronger than the same bond for free methanol.

The electron density Laplacian $\nabla^2\rho$ was obtained for three representative cases of the molecule–substrate interactions: (i) weak adsorption, Mg_5O_5 (see Fig. 5), (ii) strong associative adsorption, Mg_4O_3 (see Fig. 6) and (iii) strong dissociative adsorption, Mg_3O_3 (see Fig. 7). The mapping of $\nabla^2\rho$ was performed on different planes, in order to show the most important interactions above commented. To plot the $\nabla^2\rho$ contour lines, the (1 0 0) face was selected for case (i) while the (1 1 0) face was considered for cases (ii) and (iii). The dashed lines indicate regions of gain of density and the solid lines correspond to regions of loose of density. Therefore, there is a defined Ha-Oa covalent bond for case (i). On the other hand, for the case (ii) a squeezing appears along the line connecting these atoms, which is a clear evidence of the bond ionization. For the case (iii), we observe

that after the scission of Oa-Ha bond, we have a defined covalent Os-Ha bond, corresponding to a surface hydroxyl and the formation of a ionic Mg-Oa bond. Moreover, the MgOs is clearly ionic for all of these cases.

An analysis of main vibrational frequencies for adsorbed (dissociated or not) methanol merits a particular attention because they can be directly compared with experimental results of Ref. [19]. Our computed values are reported in Table 4. According to previous IR studies of Tench et al. [19] for methanol on MgO , bands about 1100 cm^{-1} were associated with the CO stretching frequencies. At low methanol coverages two strong bands at 1114 and 1068 cm^{-1} are present. Looking at our results in Table 4 the first experimental band could be related to dissociative adsorption forms on the $\text{Mg}_{3c}\text{O}_{4c}$ and $\text{Mg}_{3c}\text{O}_{3c}$ pairs and the second band to the weak and strong associative adsorptions. In the CH stretching frequency region, three bands at 2925 , 2843 and 2800 cm^{-1} were observed [19]. Moreover, these authors related two weak bands at 1458 and 1423 cm^{-1} with bending vibrations of the CH_3 groups. Our calculated frequencies are only slightly lower than the experimental values and they are not dependent on the geometry of the MgO pair. The region about 3500 cm^{-1} is characteristic of the stretching vibrations of the hydroxyl group. At low methanol coverages two strong bands were observed at 3600 – 3570 and 3330 cm^{-1} and a third small band at 3740 cm^{-1} [19]. This last band is enhanced by evacuation. Looking at Table 4, we notice that the band at 3330 cm^{-1} could be assigned to the $\nu(\text{OH})$ vibrations for methanol in the weak associative forms ($\text{Mg}_{5c}\text{O}_{5c}$, $\text{Mg}_{4c}\text{O}_{5c}$ and $\text{Mg}_{5c}\text{O}_{4c}$ pairs). On the other hand, the band at 3600 cm^{-1} could correspond to the $\nu(\text{O}_s\text{H})$ vibration of the hydroxyl formed after the complete methanol dissociation ($\text{Mg}_{3c}\text{O}_{3c}$ pair). Finally, we could rationalize the stretching frequency diminution obtained for the strong associative adsorption ($\text{Mg}_{4c}\text{O}_{3c}$ pair) and for the first dissociative adsorption ($\text{Mg}_{3c}\text{O}_{4c}$ pair) with an important OH bond lengthening. Indeed, as it can be observed in Table 1 these OH bond are all greater than 1.00 \AA . Particularly, the OH bond corresponding to the more strong associative adsorption ($\text{Mg}_{4c}\text{O}_{3c}$ pair) is very strengthened.

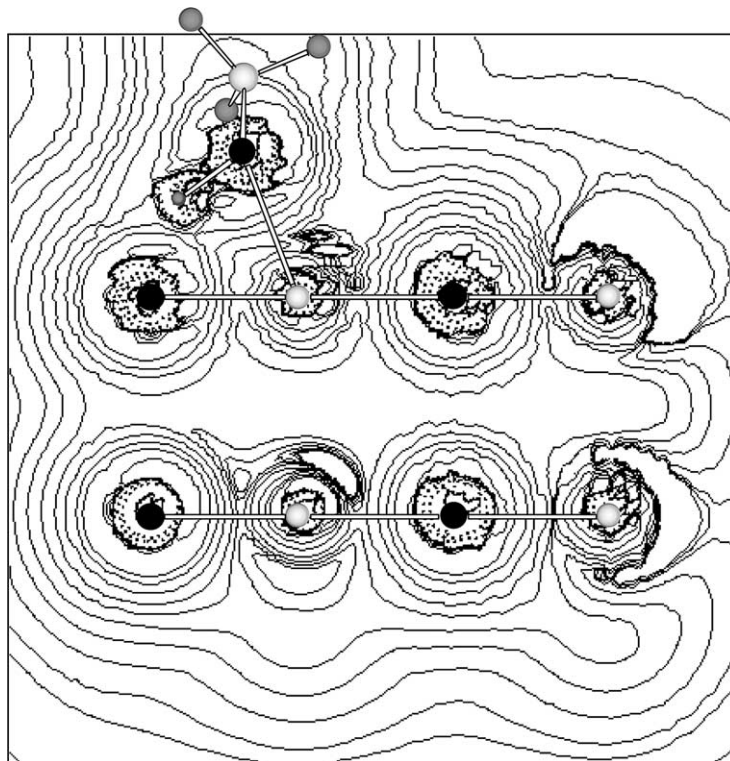


Fig. 6. Electron density Laplacian $\nabla^2\rho$ for the strong associative adsorption case, $\text{Mg}_{4c}\text{O}_{3c}$. The contour lines are given for a cut along the (110) plane. The short dashed lines indicate regions of electron charge accumulation and the solid lines correspond to regions of electron charge depletion.

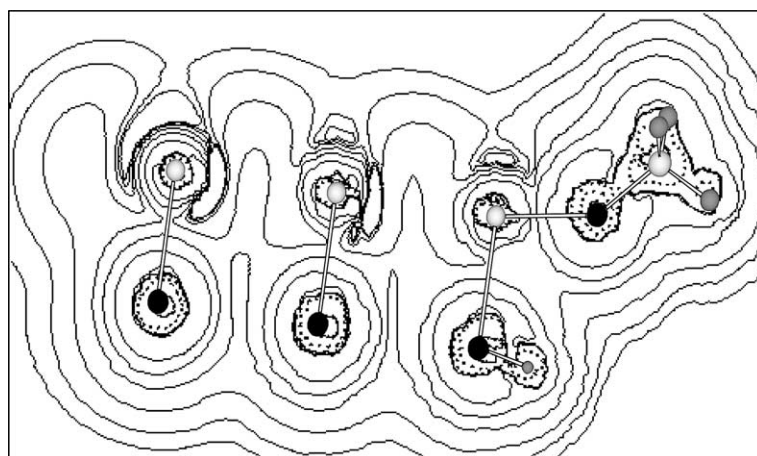


Fig. 7. Electron density Laplacian $\nabla^2\rho$ for the strong dissociative adsorption case, $\text{Mg}_{3c}\text{O}_{3c}$. The contour lines are given for a cut along the (110) plane. The short dashed lines indicate regions of electron charge accumulation and the solid lines correspond to regions of electron charge depletion.

Table 4

Selected frequency modes corresponding to the main bending and stretching vibrations found for the isolated and adsorbed methanol (in cm^{-1})

	Isolat. meth.	Mg _{5c} O _{5c}	Mg _{4c} O _{5c}	Mg _{5c} O _{4c}	Mg _{4c} O _{4c}	Mg _{4c} O _{3c}	Mg _{3c} O _{4c}	Mg _{3c} O _{3c}	Exp. data ^a
$\nu(\text{O-H})$	3819	3358	3484	3270	3110	2231	2660	3863	3330 3600 3740
$\nu(\text{C-O})$	1035	1024	1023	1023	1032	1035	1108	1142	1114 1068
$\nu(\text{C-H})$	3001 3052 3136	3017 3084 3135	3031 3102 3150	3017 3082 3139	3022 3095 3164	3008 3073 3119	2962 3014 3032	2926 2959 2972	2800 2843 2925
$\delta(\text{O-H})$	1392	1454	1422	1462	1390	1414	1388	–	–
$\delta(\text{C-H})$	1513 1541 1554	1496 1536 1552	1490 1530 1550	1499 1537 1548	1500 1541 1547	1511 1538 1550	1525 1544 1547	1527 1541 1546	1423 1458 –

^a Experimental data from Ref. [19].

4. Conclusions

The surface reactivity of the magnesium oxide strongly depends to the site selected for the molecule adsorption. The (100) face without defects has a low reactivity producing a weak adsorption but the adsorption on steps, edges and kinks is stronger. The reactivity increases when the coordination number of the surface atoms decreases. The calculated adsorption energy varies from typical hydrogen bond values (~ 0.6 eV) to chemical adsorption ones (~ 2.4 eV). The methanol molecule is dissociated on pairs with three-coordinated magnesium. In all studied cases the adsorbed molecule has negative charge which is very small for the non-dissociated species and much more significant for the dissociated species. Our theoretical results show the existence of different species on the MgO surface when the methanol molecule is adsorbed. This is in agreement with previous IR spectroscopy observations, where CH_3OH , OCH_3 and OH species were found.

Note added in proof

Very recently, in a work of C. Di Valentin, A. Del Vitto and G. Pacchioni; S. Abbet, A.S. Wörz, K. Judai and U. Heiz, published in J. Phys. Chem.

B, vol. 106 (46) (2002) 11961–11969, the chemisorption and reactivity of methanol on MgO thin film has been also studied. Their results are in general agreement with those reported here.

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References

- [1] K. Tanabe, M. Misono, Y. Ono, H. Hattori, in: New Solid Acids and Bases. Their Catalytic Properties, in: B. Delmon, J.T. Yates (Eds.), Studies in Surface Science and Catalysis, vol. 51, Kodansha and Elsevier, Tokyo and Amsterdam, 1989.
- [2] T. Ito, M. Kuramoto, M. Yoshioka, T. Tokuda, J. Phys. Chem. 87 (1983) 4411;
T. Ito, T. Tashiro, M. Kawasaki, T. Watanabe, K. Toi, H. Kobayashi, J. Phys. Chem. 95 (1991) 4476.
- [3] E. Giamello, M.C. Paganini, D. Murphy, A.M. Ferrari, G. Pacchioni, J. Phys. Chem. 101 (1997) 971.
- [4] M.-C. Wu, C.M. Truong, K. Coulter, D.W. Goodman, J. Am. Chem. Soc. 114 (1992) 7565.
- [5] R. Soave, G. Pacchioni, Chem. Phys. Lett. 320 (2000) 345.
- [6] Y. Nakajima, D.J. Doren, J. Chem. Phys. 105 (1996) 7753.
- [7] M.M. Branda, J.E. Peralta, N.J. Castellani, R.H. Contreras, Surf. Sci. 504 (2002) 235.
- [8] J.L. Anchell, K. Morokuma, J. Chem. Phys. 99 (1993) 6004.

- [9] A.M. Ferrari, S. Huber, H. Knözinger, K.M. Neyman, N. Rösch, *J. Phys. Chem. B* 102 (1998) 4548;
K. Todnem, K.J. Børve, M. Nygren, *Surf. Sci.* 421 (1999) 296.
- [10] J.L. Anchell, A.C. Hess, *J. Phys. Chem.* 100 (1996) 18317;
A.L. Almeida, J.B.L. Martins, C.A. Taft, E. Longo, W.A. Lester Jr., *Int. J. Quantum Chem.* 71 (1999) 153;
B. Ahlswede, T. Homann, K. Jug, *Surf. Sci.* 445 (2000) 49.
- [11] J.A. Rodriguez, T. Jirsak, S. Sambasivan, D. Fischer, A. Maiti, *J. Chem. Phys.* 112 (22) (2000) 9929.
- [12] J.A. Rodriguez, T. Jirsak, S. Chaturvedi, *J. Chem. Phys.* 111 (17) (1999) 8077;
J.A. Rodriguez, A. Maiti, *J. Phys. Chem. B* 104 (2000) 3630.
- [13] J.A. Mejías, A.M. Márquez, J. Fernández Sanz, M. Fernández García, J.M. Ricart, C. Sousa, F. Illas, *Surf. Sci.* 327 (1995) 59;
J.A. Snyder, D.R. Alfonso, J.E. Jaffe, Z. Lin, A.C. Hess, M. Gutowski, *J. Phys. Chem. B* 104 (2000) 4717;
C. Minot, M.A. Van Hove, J.-P. Biberian, *Surf. Sci.* 346 (1996) 283.
- [14] G. Pacchioni, J.M. Ricart, F. Illas, *J. Am. Chem. Soc.* 116 (1994) 10152.
- [15] A.M. Ferrari, G. Pacchioni, *J. Chem. Phys.* 107 (6) (1997) 2066.
- [16] J. Günster, G. Liu, J. Stultz, S. Krischok, D.W. Goodman, *J. Phys. Chem. B* 104 (2000) 5738.
- [17] X.D. Peng, M.A. Barteau, *Langmuir* 7 (1991) 1426.
- [18] D.C. Foyt, J.M. White, *J. Catal.* 47 (1977) 260.
- [19] A.J. Tench, D. Giles, J.F.J. Kibblewhite, *Trans. Faraday Soc.* 67 (1971) 854.
- [20] S.H.C. Liang, I.D. Gay, *Langmuir* 1 (1985) 593.
- [21] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [22] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [23] A.F. Wells, *Structural Inorganic Chemistry*, fifth ed., Clarendon Press, Oxford, 1984, 1004.
- [24] N.R. Kestner, J.E. Combariza, in: K.B. Lipkowitz, D.B. Boyd (Eds.), *Reviews in Computational Chemistry*, vol. 13, Wiley-VCH, John Wiley and Sons Inc., New York, 1999.
- [25] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 88 (1988) 899.
- [26] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, *NBO Version 3.1*.
- [27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *Gaussian 98*, Revision D.4, Gaussian Inc., Pittsburgh PA, 1998.
- [28] S.P. Bates, M.J. Gillan, G. Kresse, *J. Phys. Chem. B* 102 (1998) 2017.
- [29] R.S. Mülliken, *J. Chem. Phys.* 23 (1955) 1833.
- [30] H. Kawakami, S. Yoshida, *J. Chem. Soc. Faraday Trans. 2* (80) (1984) 921.