

Available online at www.sciencedirect.com



Catalysis Today 85 (2003) 153-165



www.elsevier.com/locate/cattod

Proton abstraction ability of MgO: a DFT cluster model study of the role of surface geometry

M.M. Branda*, P.G. Belelli, R.M. Ferullo, N.J. Castellani

Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

Received 12 February 2003; received in revised form 26 March 2003; accepted 5 May 2003

Abstract

Methanol and isocyanic acid adsorptions on a defective MgO surface have been studied. Equilibrium geometries, adsorption energies, atomic and molecular charges and electronic densities were obtained using a density functional theory method. Oxide surface atoms with different coordination numbers show very different reactivity giving both molecular and dissociated adsorbed species. The methanol molecule requires lower coordination numbers of the active site than the isocyanic acid molecule for dissociative adsorption. The role of the acidic and basic sites has been considered and analyzed in terms of natural bond orbital charges. The main vibration frequencies have been compared with available infrared spectroscopic data. © 2003 Elsevier B.V. All rights reserved.

Keywords: DFT; NBO; Charge transfers; Catalysis; Physical adsorption; Magnesium oxide; Methanol

1. Introduction

It has been recognized that acidic and basic properties of oxide catalysts and oxide supports play an important role in a great deal of catalytic processes such as oxidation, reduction, hydrogenation and hydrocracking. A complete description of these properties on a solid oxide surface requires the determination of the acid and base strength, and the amount and nature of the acidic and basic sites. The interpretation of chemisorption and spectroscopic data and the use of theoretical methods of investigation demonstrated the dominant role of local factors in this area of heterogeneous catalysis and revealed the presence of three principal types of active sites of oxide catalysts: (i) Brönsted acid sites usually represented by rather strongly hydroxyl groups formed due to the partial hydrolysis of oxide surface, which are involved in intermediate protonation of reactants; (ii) Lewis acid sites and/or acid–base pairs consisting of non-transition metal cations produced by dehydrogenation of oxide surfaces, which are involved in catalytic hydrogenation, dehydrogenation and hydrogen exchange interactions; (iii) transition metal ions acting as active sites both in catalytic redox reactions and in coordination-type catalysis [1]. For the determination of strength and amount of a solid acid or a solid basis site, different titration methods using gaseous base and acid molecules, respectively, are usually used [2]. On the other hand, infrared spectroscopic studies of certain molecular probes is the usual technique to distinguish between Brönsted and Lewis acid sites.

The MgO has been considered as an ideal system in order to study the catalytic properties of oxides, due to fundamentally to its very simple cubic crystalline structure with strict 1:1 stoichiometry and its electronic structure that implies only s-p electrons.

^{*} Corresponding author. Fax: +54-291-4595142.

E-mail address: cabranda@criba.edu.ar (M.M. Branda).

 $^{0920\}mathchar`sec: 0920\mathchar`sec: 0920\mathch$

Moreover, the oxides of simple metals like MgO, BaO and CaO are known by their basic properties, related mainly from the strong Lewis basicity of surface oxygen anions [2]. 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 combines with the acid character of a Mg²⁺ cation. This behavior can be observed in relatively simple reactions as the H₂ dissociation and the dehydrogenation of CH₄ [3], and in more complex reactions as the hydrogenation of olefins [2]. Nevertheless, the acidic character of Mg cations predominates in the case of molecular adsorption [4], where the molecule resides on the cationic site.

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. A considerable deal of works has been focused to study the structural aspects as well as the 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. Several molecules (CH₃OH [7–9], H₂ [10], CH₄ [11], H₂O [12], NO₂ [13], H₂S [14], CO [5,15], CO₂ and SO₂ [16], O₂⁻ and CO⁻ [17]) have been considered regarding the adsorption equilibrium geometry and the possibility of an eventual molecular dissociation.

The experimental results related to the adsorption of acid molecules like formic and acetic acid, methanol, ethanol, acetylene and water performed by Peng and Barteau [18] show that the Brönsted acid dissociates on acid-base pairs of defective MgO surfaces. The adsorption of methanol on MgO has been studied by several techniques. Thermal desorption spectroscopy (TDS) measurements performed on powered MgO [19] and on smooth and defective (001) surfaces of MgO [18] revealed that only when low coordination adsorption sites are present, methanol dissociates. Infrared spectroscopy (IR) spectra [20] indicate the presence of at least four different species. 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 previous theoretical approach to this question [7] and the experimental results [18,19] 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.

It has been observed that the isocyanate species (NCO) is produced in the catalytic reduction of NO by CO or by non-saturated hydrocarbons [21] on late transition metal supported catalysts. Infrared studies indicate that isocyanate is formed on the metal and spills over onto the support (MgO, Al₂O₃, SiO₂, ZSM5, for example) where it finally resides and accumulates [22]. Very recently, some experimental studies performed over Rh/TiO₂ and Cu/Al₂O₃ systems suggested that NCO could act as an intermediate in the production of N₂O or N₂ [23]. Moreover, NCO can be the source of the formation of HCN and C₂N₂, hazardous gases which can also act as catalyst poisons. Recently, it has been suggested that the isocyanic acid (HNCO) may be a significant intermediate during the warm-up phase in catalytic converters of mixtures of NO, CO and H₂ over Pt/SiO₂ [24]. During these processes the isocyanic acid can be produced or re-adsorbed on the metallic phase or on the support [24]. From here the interest to study the adsorption of this molecule directly on different oxides. By the other hand, because it is not possible to produce NCO over oxides via the NO + CO reaction, researches use isocyanic acid directly as adsorbing species which adsorbs dissociatively yielding NCO and H [16]. Solymosi and Bánsági have studied using this procedure the NCO behavior over some dehydrated oxides usually acting as supports. They concluded that the NCO stability decreases in the following order: $SiO_2 > Al_2O_3 > MgO > Cr_2O_3 > TiO_2$ [22].

In the present work we analyze the interaction of two different molecules, methanol and isocyanic acid, with the surface of MgO. As it will be shown below these molecules show a different proton abstraction capability due to their different Brönsted acidity. Nevertheless the acid–base interaction between the broken O–H or N–H bond of the molecule and the surface ions of MgO is very similar.

The work is organized as follows. First, the theoretical method and models will be described. Second, the calculation results will be presented and discussed for each different system. Finally, the conclusions will be given.

2. Computational details

The adsorption of two different molecules, methanol and isocyanic acid, were modeled on a non-perfect (100) face of MgO. For the first one, the staggered conformation was considered due to its greater energetic stability with respect to the eclipsed rotamer [7]. In a previous work, the effect of varying the MgO cluster size on the molecular adsorption properties was analyzed concluding that the (MgO)₁₂ cluster gives satisfactory results with reasonably accuracy [7,8]. Thus, a cluster model with the $(MgO)_{12}$ formula was employed to represent the local structure of the MgO surface. Moreover some tests including charge embedding were carried out and negligible differences were found with respect to the non-embedded cluster [7]. The geometrical optimization procedure was performed considering that the molecules were initially close to the surface active site at their free optimized structures. These molecules were adsorbed on three different Mg-O pairs of the substrate acting as adsorption sites with different geometrical environment. They are pictured in Fig. 1. The following three pairs have been considered, classified according to the ion coordination: (a) $Mg_{5c}O_{5c}$; (b) $Mg_{4c}O_{4c}$; (c) Mg_{3c}O_{3c}, where the sub-indexes "mc" and "nc" design the coordination number of Mg and O, respectively.

The geometries for adsorbed methanol and isocyanic acid molecules were fully optimized. The MgO cluster geometry was taken from reference [25] where the Mg–O distance is 2.106 Å. Experiments show that the flat MgO(100) surface is close to the bulk geometry [26]. By this reason the substrate model was not relaxed in the optimization process. However, relaxation could be important for O_{3c} and Mg_{3c}.

The molecular orbitals and energies were calculated within the density functional theory (DFT) formalism, using the hybrid functional which mixes the Lee et al. functional for the correlation part and Becke's three-parameter functional for exchange (B3LYP) [27,28]. A Gaussian basis set was employed; specifically, the locally dense 6-31G. An extra basis set were added in atoms which were directly involved in the adsorption process. Thus, d-type orbitals for O, Mg, Si, C and N atoms and p-type orbitals for the H atom were incorporated. The net atomic and molecular charges were obtained with the natural bond orbital (NBO) analysis [29,30]. Besides, the overlap population (OP) values were calculated with the Mülliken population analysis [31]. All the calculations reported in this work were performed using the Gaussian'98 package [32].

The error in the adsorption energy calculation due to the basis set superposition error (BSSE) was corrected using the counterpoise method [33]. This approximation is particularly suited for systems which do not undergo a strong geometrical relaxation after bonding formation [34]. Therefore this correction was applied only for molecular adsorptions. As a first approach, for comparison reasons only the non-corrected values were considered.

3. Results and discussion

3.1. Methanol on MgO

The adsorption energies and some concerned relevant geometrical data for the three considered cases of methanol adsorption on MgO are summarized in



Fig. 1. Schematic graph of a stepped MgO(100) surface with possible positions of a pair of active sites.

Table	

156

Main molecular properties of methanol adsorbed on MgO surface: adsorption energy (E_{ads}), methanol intramolecular, d(O_a -H) and d(C- O_a), and methanol-surface, d($O_s \cdots H$) and d(Mg $\cdots O_a$), interatomic distances and methanol COH angle at equilibrium and some selected OPs^a

	Isolated CH ₃ OH	Mg _{5c} O _{5c}	Mg _{4c} O _{4c}	Mg _{3c} O _{3c}
$\overline{E_{ads}}$ (eV)	_	0.59 (0.27)	1.01 (0.73)	2.39 (-)
$d(O_s \cdots H)$ (Å)	_	1.791	1.675	0.966
$d(Mg \cdots O_a)$ (Å)	_	2.396	2.114	1.847
$d(O_a-H)$ (Å)	0.966	0.990	1.006	2.695
$d(C-O_a)$ (Å)	1.437	1.443	1.446	1.406
COH (°)	107.2	110.0	113.3	_
$OP(H,O_s)$	_	0.102	0.090	0.566
$OP(O_a, Mg)$	-	0.352	0.352	0.692
$OP(O_a, H)$	0.576	0.422	0.424	_
$OP(C,O_a)$	0.394	0.338	0.318	0.470

^a $E_{ads} = E(MgO cluster) + E(methanol) - E(MgO cluster and methanol).$ In parenthesis, the BSSE corrected adsorption energy. Positive values correspond to exothermic adsorption processes. The letters a and s in the subscripts represents adsorbate and substrate, respectively.

Table 1. The data comprise: methanol intramolecular O–H and C–O interatomic distances $(d(O_a-H))$ and $d(C-O_a)$, respectively), methanol-surface O_s–H and Mg–O_a interatomic distances $(d(O_s \cdots H))$ and $d(Mg \cdots O_a)$, respectively) and methanol \angle COH angle, all at equilibrium. Notice that O_s and O_a correspond to the substrate and adsorbate oxygen atoms, respectively.

The geometrical optimization show that in all cases the hydroxyl group is oriented in such a way that the methanol O atom is directly linked with a Mg cation while the methanol H atom is directly linked with a O anion (see Figs. 2a, 3a and 4a). The adsorption energies vary from a low value to a high one, which can be classified as "weak adsorbed" methanol ($E_{ads} \sim 0.5 \text{ eV}$) for Mg_{5c}O_{5c} and "strong adsorbed" methanol ($E_{ads} \sim 1 \text{ eV}$ or greater) for Mg_{4c}O_{4c} and Mg_{3c}O_{3c}. The d(O_s ··· H) and d(Mg ··· O_a) distances for the highest coordination are longer than the same distances for the lowest coordination, in relationship with the strength of the methanol–magnesia interaction. The corresponding atomic configurations are shown in Figs. 2a, 3a and 4a. We want to notice that the weak adsorbed methanol undergoes only a slight distortion of its geometry with respect to the free molecule, as it will be shown in



Fig. 2. Optimized geometries of methanol and isocyanic acid on Mg5cO5c site of MgO cluster.



Fig. 3. Optimized geometries of methanol and isocyanic acid on $Mg_{4c}O_{4c}$ site of MgO cluster.

a subsequent paragraph. This situation can be assimilated to a hydrogen interaction where the H of hydroxyl group of methanol mediates between an oxygen of the surface and the proper oxygen of hydroxyl group.

The stronger adsorption sites, i.e., $Mg_{4c}O_{4c}$ and $Mg_{3c}O_{3c}$ sites, are able to produce an "molecular adsorption" ($Mg_{4c}O_{4c}$ site) or a "dissociative adsorption" ($Mg_{3c}O_{3c}$ site). The dissociative state, on $Mg_{3c}O_{3c}$ site, is exothermic with respect to the less favorable ($Mg_{5c}O_{5c}$) non-dissociative one by almost 1.8 eV. 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. [20] to explain their IR results. Recent theoretical studies of methanol adsorption on the stoichiometric (110) face of TiO₂ have shown that at medium coverage the methanol O–H bond breaks preferentially over the C–O bond, while the opposite is obtained at $\theta = 1$ [35].

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 0.03-0.05 Å for the non-dissociative states and by 1.74 Å when the dissociation is complete. On the other hand the methanol C–O bond length is similar in all the cases. Only for the dissociative state a small decrease of 0.03 Å is observed. The ∠COH angle shows, in comparison with the free methanol molecule, a small three degrees opening for the weak adsorption state and six degrees for the strong adsorption state.

The OP(H,O_s) overlap population gives us a measure of the occupation degree of bonding molecular orbitals formed between the methanol molecule and the MgO surface. Notice in Table 1 that the overlap populations OP(H,O_s) for the methanol adsorption in terrace (Mg_{5c}O_{5c}) and in step (Mg_{4c}O_{4c}) are similar and low in agreement with the idea that in these cases a covalent bond is not formed with the surface.



Fig. 4. Optimized geometries of methanol and isocyanic acid on Mg_{3c}O_{3c} site of MgO cluster.

Nevertheless the adsorption energy in the second case is significantly larger than for pentacoordinated site $(Mg_{5c}O_{5c})$. The reason for this particular behavior will be discussed later in this section. Conversely, the OP(H,O_s) and OP(O_a,Mg) values are remarkably large when the dissociation is reached, approximately six and two times respectively longer than the corresponding value to the non-dissociative adsorptions. The OP(O_a,H) follows the opposite trend of the OP(H,O_s). Evidently, the interaction between the surface and the molecule provokes a weakening of the O_a-H bond. It can be observed that in general the OP(C,O_a) almost do not change. Only when the molecule is dissociated this bond is stronger than the same bond for free methanol.

In Table 2 NBO charges for some relevant atoms and other species that characterize the methanol–substrate interactions are reported. The methanol molecule is only slightly negatively charged near the MgO surface for the non-dissociative adsorption, however the net charge for the dissociated fragments becomes negative and noticeably high in magnitude (see Table 2), with changes of -0.385e and +0.061e for the methoxide and H fragments, respectively. It suggests a basic behavior of the substrate, with more basic character in those sites where the methanol dissociation takes place.

The NBO charges of the oxygen and magnesium atoms of pure magnesia surface are showed in the third and fourth entries of Table 2. Comparing the oxide oxygen charge for the different sites we observe

Table 2

Selected NBO charges for some relevant atoms and other species in the CH₃OH–MgO surface interactions (for comparison the first column shows the charges of the isolated methanol; charges are given in a.u.)^a

	Isolated CH ₃ OH	Mg _{5c} O _{5c}	Mg _{4c} O _{4c}	Mg _{3c} O _{3c}
Q(CH ₃ OH)	_	-0.058	-0.048	_
Q(CH ₃ O)	-0.472	-0.547	-0.562	-0.857
Q(O _s) _{isol}	-	-1.671	-1.611	-1.513
Q(Mg)isol	-	1.563	1.588	1.529
Q(O _s) _{ads}	_	-1.646	-1.586	-1.366
Q(Mg)ads	_	1.576	1.611	1.647
Q(O _a)	-0.745	-0.826	-0.865	-1.089
Q(H)	0.472	0.489	0.514	0.533

^a isol, ads, a and s in subscripts represents isolated, adsorbed, adsorbate and substrate, respectively.

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 O_{3c} to O_{5c} , suggesting the following basicity sequence: $Mg_{5c}O_{5c} < Mg_{4c}O_{4c} < Mg_{3c}O_{3c}$.

On the other hand, the Mg positive charge increases (by 0.059e) when the cation coordination number changes from Mg_{3c} to Mg_{4c}, but decreases (by 0.025e) when it changes from Mg_{4c} to Mg_{5c} . This could be related to a cluster size effect. If the surface with methanol adsorbed and the bare magnesia surface are compared (see from third to sixth entries), both the O_s and Mg atoms lose electronic charge when the molecule is adsorbed. The loss of negative charge of the MgO pair when the methanol molecule interacts with the oxide surface is 0.038e, 0.048e and 0.265e for Mg_{5c}O_{5c}, Mg_{4c}O_{4c} and Mg_{3c}O_{3c}, respectively. When the methanol dissociation occurs, i.e., for Mg_{3c}O_{3c} site, the loss of the negative charge is significant. These observations are in agreement with the negative charge taken from the methanol molecule and indicate that the basic behavior of the oxide surface increases with decreasing the coordination number. The negative charge of surface O atom and the positive charge of Mg atom decreases and increases continuously in magnitude, respectively, when the methanol molecule is adsorbed on the MgO pairs. The negative charge of surface oxygen atom follows the same trend as commented above for the bare surface.

The NBO charges of the oxygen and the hydrogen atoms belonging to the methanol hydroxyl are also reported in Table 2. It is clear that there is an important charge polarization of the (O_a-H) link for the stronger adsorbed methanol with respect to the weak chemisorbed methanol. Indeed, while the methanol molecule net charge changes by only +0.01e, the positive charge of H atom increases in magnitude by 0.025e and the negative charge of O atom increases in magnitude by 0.039e, in going from the $Mg_{5c}O_{5c}$ site to the Mg_{4c}O_{4c} site. The corresponding charge changes (in magnitude) of O and Mg ions of the oxide surface are of -0.060e and +0.035e, respectively. Moreover the net charge for the site Mg_{5c}O_{5c} is negative while that for the $Mg_{4c}O_{4c}$ site is positive. The only way to explain these important redistribution of charges for Mg_{4c}O_{4c} is the presence of dispersion electrostatic forces of more localized effect than those in the weak adsorption situation. The corresponding energy interaction is greater than for methanol on the $Mg_{5c}O_{5c}$ site.

The electron density Laplacian $\nabla^2 \rho$ was obtained for the three representative cases of the moleculesubstrate interactions: (i) weak adsorption, Mg_{5c}O_{5c} (see Fig. 5a); (ii) strong molecular adsorption, Mg_{4c}O_{4c} (see Fig. 6a); (iii) strong dissociative adsorption, Mg_{3c}O_{3c} (see Fig. 7a). 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 (100) face was selected for case (i) while the (110) 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 loss of density. Therefore, there is a defined H-O_a covalent bond for case (i). On the other hand, for case (ii) a squeezing appears along the line connecting these atoms which is a clear evidence of the bond ionization. For case (iii), we observe that after the scission of Oa-H bond a defined covalent Os-H bond is formed corresponding to a surface hydroxyl and the formation of a ionic Mg-Oa bond. Moreover, the Mg–O_s is clearly ionic for all of these cases.

The main vibrational frequencies for adsorbed (dissociated or not) methanol are summarized in Table 3. Following previous IR studies of Tench et al. [20] for methanol on MgO powder and theoretical and experimental IR studies of Di Valentin et al. [9] for methanol on MgO(100), bands about $1100 \,\mathrm{cm}^{-1}$ can be associated with the CO stretching frequencies. At low methanol coverages two strong bands at 1114 and $1068 \,\mathrm{cm}^{-1}$ were observed. Looking at the results in Table 3 the first experimental band could be related to dissociative adsorption species on the Mg_{3c}O_{3c} pairs and the second band to the weak and strong molecular adsorptions. In addition, in the CH stretching frequency region three bands at 2925, 2843 and $2800 \,\mathrm{cm}^{-1}$ were observed [9,20]. Our calculated values are slightly lower than the experimental ones and they are not dependent on the geometry of the MgO pair. Nevertheless, it should be noted that the theoretical frequency values often overestimate the experimental ones [32]. Finally, the region about $3500 \,\mathrm{cm}^{-1}$ 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} [9.20]. Looking



Fig. 5. Laplacian $\nabla^2 \rho(r)$ distribution of charge for methanol (a) and isocyanic acid (b) on Mg_{5c}O_{5c} site of MgO cluster. The short dashed lines indicate regions of electron charge accumulation and the solid lines correspond to regions of electron charge depletion.



Fig. 6. Laplacian $\nabla^2 \rho(r)$ distribution of charge for methanol (a) and isocyanic acid (b) on Mg_{4c}O_{4c} site of MgO cluster. Electron charge regions are same as given in Fig. 5.

at Table 3, the band at 3330 cm^{-1} could be assigned to the $\nu(OH)$ vibrations for methanol in the weak molecular form (Mg_{5c}O_{5c} pairs) while the band at 3600 cm^{-1} could correspond to the $\nu(O_sH)$ vibration of the hydroxyl formed after the complete methanol dissociation (Mg_{3c}O_{3c} pair).

3.2. Isocyanic acid on MgO

The main molecular properties of isocyanic acid adsorbed on the three considered sites of MgO surface are summarized in Table 4. They comprise: adsorption energy (E_{ads}), isocyanic acid intramolecular

Table 3

		Mg _{5c} O _{5c}	$Mg_{4c}O_{4c}$	$Mg_{3c}O_{3c}$	Experimental data	
					Isolated CH ₃ OH ^a	Adsorbed CH ₃ OH ^b
v(O-H)	3819	3358	3110	3863	3600	3330
						3600
					3740	
v(C–O) 1035 1024	1024	1032	1142	1045	1114	
					1068	
ν(C–H)	3001	3017	3022	2926	-	2800
	3052	3084	3095	2959	-	2843
	3136	3135	3164	2972	-	2925

^a Experimental data from Ref. [20].

^b Experimental data from Ref. [36].



Fig. 7. Laplacian $\nabla^2 \rho(r)$ distribution of charge for methanol (a) and isocyanic acid (b) on Mg_{3c}O_{3c} site of MgO cluster. Electron charge regions are same as given in Fig. 5.

Table 4

Main molecular properties of isocyanic acid adsorbed on MgO surface: adsorption energy (E_{ads}), isocyanic acid intramolecular, d(N–H), d(N–C) and d(C–O_a), and isocyanic acid-surface, d(O_s···H) and d(Mg···N), interatomic distances and isocyanic acid HNC and NCO angles at equilibrium and some selected OPs^a

	Isolated HNCO	Mg _{5c} O _{5c}	Mg _{4c} O _{4c}	Mg _{3c} O _{3c}
$\overline{E_{ads}}$ (eV)	_	0.45 (0.26)	1.05	3.02
$d(O_s \cdots H)$ (Å)	_	1.664	1.028	0.964
$d(Mg \cdots N)$ (Å)	_	3.191	2.116	1.950
d(N–H) (Å)	1.008	1.056	1.540	3.152
d(N–C) (Å)	1.218	1.214	1.207	1.202
d(C–O _a) (Å)	1.174	1.178	1.189	1.193
HNC (°)	124.7	131.1	_	_
NCO (°)	172.2	174.0	179.0	179.2
$OP(H,O_s)$	_	0.173	0.390	0.572
OP(N,Mg)	_	0.096	0.391	0.616
OP(N,H)	0.696	0.446	_	_
OP(N,C)	1.116	1.050	1.297	1.304
$OP(C,O_a)$	1.229	1.211	1.176	1.158

^a $E_{ads} = E(MgO cluster) + E(isocyanic acid) - E(MgO cluster and isocyanic acid). In parenthesis the BSSE corrected adsorption energy. Positive values correspond to exothermic adsorption processes. The letters a and s in the subscripts represents adsorbate and substrate, respectively.$

N–H, N–C and C–O distances (d (N–H), d(N–C) and d(C–O), respectively), interatomic isocyanic acidsurface $O_s \cdots H$ and $Mg \cdots N$ distances (d($O_s \cdots H$) and d($Mg \cdots N$), respectively), and isocyanic acid ∠HNC and ∠NCO bond angles, all at equilibrium.

The intermolecular distances clearly show that the isocyanic acid is dissociated on the $Mg_{4c}O_{4c}$ and $Mg_{3c}O_{3c}$ pairs (see Figs. 3b and 4b). However, the adsorption energies on these sites are very different. While the energy value for the tetracoordinated site is similar to that of methanol (~1 eV), the corresponding value to the tricoordinated site is quite large (~3 eV). Conversely, the molecular adsorption energy (~0.5 eV) on the terrace site ($Mg_{5c}O_{5c}$ pairs) and the respective geometrical data correspond to a weak adsorption situation. The geometrical optimization on this site shows that a hydrogen bond is formed between the oxygen of the oxide surface and the isocyanate group (see Fig. 2b).

Notice that the kind of adsorption process on the tri- and pentacoordinated sites is analogous for both studied molecules, corresponding to a dissociative adsorption and weak molecular adsorption, respectively. On the other hand, while the adsorption process on the tetracoordinated site for the isocyanic acid is a dissociative adsorption without activation barrier, for the methanol molecule we have a strong molecular adsorbed species (see above). This important difference could be related with the greater acidic character of the isocyanic acid in comparison with the methanol molecule, resulting in a stronger interaction with the basic oxygen ions of the surface and an easier proton abstraction. This property also affects the adsorption on the other sites. Looking at Tables 1 and 4 we observe that the H-Os distance for methanol on the pentacoordinated site is greater (by ~ 0.13 Å) than the H–Os distance for isocyanic acid on the same terrace site (Mg_{5c}O_{5c}). In addition, the intramolecular N-H bond of the acid undergoes a stretching with respect to the free molecule that is greater than the stretching of the intramolecular O-H bond of methanol (0.048 Å versus 0.024 Å). We observe that in the case of total abstraction of the H cation on the tricoordinated sites, the higher E_{ads} for isocyanic acid with respect to that of methanol can be related also to the higher acidity of HCNO. Besides, the (N-C) distance decreases and the (C-O) distance increases when the dissociation occurs (see Table 4).

The intramolecular \angle HNC and \angle NCO angles increase slightly when the acid is adsorbed, although the NCO group practically retains its linear geometry in all the cases considered.

The main OPs corresponding to the isocyanic acid-oxide interaction are summarized in Table 4. The hydrogen bond formed between the acid and the MgO is stronger than the respective bond between the methanol and the same oxide in terrace site (compare the $OP(H,O_s)$ for both molecules in this site) in line with the shorter H-O_s distance. As expected, the OP(H,O_s) for the tetra- and tricoordinated sites increases noticeably with respect to the pentacoordinated site (two and three times, respectively), due to the O_s-H bond formation after complete H⁺ abstraction. The OP(N.Mg) in the pentacoordinated site is almost negligible and increases four and six times respectively for tetra- and tricoordinated sites, due to the N–Mg bond formation after this H⁺ abstraction. The same behavior is observed for the methanol-MgO interaction on the tricoordinated site. Looking at the OP(N,C) and OP(C,O) overlap populations, we observe that the N-C bond strength increases as the coordination number of the MgO oxide site decreases while the C–O bond exhibits the opposite trend. Both observations are in agreement with the corresponding shortening and stretching for these bonds, above discussed.

NBO charges for some relevant atoms and other species in the adsorbate–substrate interactions are displayed in Table 5. As it can be observed at the first row of Table 5 the isocyanic acid takes negative charge from the $Mg_{5c}O_{5c}$ site when it is adsorbed. These charge transfer is greater than that of methanol adsorbed on $Mg_{5c}O_{5c}$ and $Mg_{4c}O_{4c}$ sites (see Table 2). The NCO group of HNCO takes an important negative charge after H⁺ abstraction on tetra-and tricoordinated sites (by ~0.4e) in comparison with the free molecule.

The above mentioned increase of basicity of MgO surface with the diminution of the anion–cation pair coordination number can also be observed in the case of HNCO adsorption. Indeed, the loss of negative charge of the MgO pair when the isocyanic acid reacts with the oxide surface is of 0.062e, 0.197e and 0.291e on Mg_{5c}O_{5c}, Mg_{4c}O_{4c} and Mg_{3c}O_{3c} sites, respectively. The individual atomic charges of O and Mg atoms of MgO pairs over which reside the adsorbed

Table 5

Selected NBO charges for some relevant atoms and other species in the HNCO–MgO surface interactions (for comparison the first column shows the charges of the isolated isocyanic acid; charges are given in a.u.)^a

	Isolated	Mg _{5c} O _{5c}	$Mg_{4c}O_{4c}$	Mg _{3c} O _{3c}
	HNCO			
Q(HNCO)	0.000	-0.113	_	_
Q(NCO)	-0.433	-0.525	-0.801	-0.894
Q(O _s) _{isol}	_	-1.671	-1.611	-1.513
Q(Mg)isol	_	1.563	1.588	1.529
$Q(O_s)_{ads}$	_	-1.626	-1.449	-1.358
Q(Mg)ads	_	1.580	1.623	1.665
Q(H)	0.433	0.412	0.505	0.528
Q(N)	-0.781	-0.846	-1.042	-1.084
Q(C)	0.841	0.832	0.807	0.775
Q(O _a)	-0.494	-0.511	-0.566	-0.585

^a isol, ads, a and s in subscripts represents isolated, adsorbed, adsorbate and substrate, respectively.

acid molecule (as a whole entity or fragmented) follow the same trends as those observed for methanol. Notice, nevertheless, that the charge transfer from the MgO pairs to the acid is more significant than the respective transfer to the methanol.

The last four entries of Table 5 belong to the atomic charge values of the atoms of adsorbed species (isocyanic acid or dissociated fragments). Here, the change undergone by the nitrogen atom is remarkable, which increases its negative charge by near 0.3e with respect to the free molecule when it is dissociated on the tetra- and tricoordinated sites. This is an indication of a N–Mg bond with a strong ionic character.

The electron density Laplacian $\nabla^2 \rho$ was obtained for the three representative cases of the molecule– substrate interactions: (i) weak adsorption, Mg_{5c}O_{5c} (see Fig. 5b) and (ii) and (iii) strong dissociative adsorptions, Mg_{4c}O_{4c} and Mg_{3c}O_{3c} (see Figs. 6b and 7b, respectively). The (100) face was selected for case (i) while the (1 1 0) face was considered for cases (ii) and (iii) to plot the $\nabla^2 \rho$ contour lines.

Looking at Fig. 5b, it can be observed that there is a H–N covalent bond in HNCO molecule adsorbed on the $Mg_{5c}O_{5c}$ site, which turns to a ionic bond on the tetracoordinated site and disappears on the tricoordinated one (see Figs. 6b and 7b). Practically the opposite occurs for the O_s–H bond. There is a hydrogen bond on the terrace site and a covalent bond on lower coordination sites.

The frequency modes corresponding to the main stretching vibrations calculated for the isolated and adsorbed isocyanic acid are summarized in Table 6. Contrary to the experimental data reported in the literature for methanol on MgO, only the NCO asymmetric stretching vibration frequency has been measured and published [22]. As it can be observed the calculated values of this vibrational mode are in general smaller, at least 15 cm⁻¹, when compared to the free molecule. Nevertheless they are similar in all the studied species, varying by about 45 cm⁻¹. The experimental value is in mean a 5% lower than the calculated values [32]. The NCO symmetric stretching vibration frequency undergoes a higher variation (by ~80 cm⁻¹) increasing with the H⁺ abstraction.

The important shift to lower wave numbers found for the ν (NH) (~1000 cm⁻¹) when the acid is weakly adsorbed can be understood in terms of the stretching undergone by the N–H bond (~0.05 Å). This is a consequence of the hydrogen bond interaction produced with the oxide surface. Similar phenomena were observed on the ν (OH) of the methanol molecule when it is adsorbed on the penta- and tetracoordinated sites.

The last frequency mode shown in Table 6 is $\nu(O_sH)$. As it could be seen before, the OH stretching typical value is around 3800 cm^{-1} . Notice that the O_sH stretching value obtained on the Mg_{4c}O_{4c} site is much lower (by 1251 cm^{-1}) than the respective

Table 6

Selected frequency modes corresponding to the main stretching vibrations found for the isolated and adsorbed isocyanic acid (cm⁻¹)

	Isolated HNCO	Mg _{5c} O _{5c}	Mg _{4c} O _{4c}	Mg _{3c} O _{3c}	Experimental data ^a
$\overline{\nu_{\rm sym}(\rm NCO)}$	1339	1328	1399	1410	_
$v_{\rm asym}(\rm NCO)$	2357	2339	2311	2342	2223
v(NH)	3701	2787	_	_	_
ν(OH)	_	_	2630	3881	-

^a Assigned to Mg-NCO species, from Ref. [22].

value on the $Mg_{3c}O_{3c}$ site. This remarkably difference together with the O_s -H bond stretching on the tetracoordinated site with respect to the tricoordinated site (0.064 Å) can be attributed to the electrostatic interaction between H and NCO.

4. Conclusions

The adsorption studies performed in this work show that the importance of basicity properties of the magnesium oxide surface depend both on the oxide site geometry and on the acidity of molecule interacting with the MgO. The terrace site (pentacoordinated atoms of regular MgO(111) surface) has the low reactivity producing associative adsorption for methanol and isocyanic acid. The kink site (tricoordinated atoms) is the more reactive one and it activates complete H abstraction of these molecules without activation barrier. On the other hand, on the step site (tetracoordinated atoms) only the isocyanic acid undergoes complete H abstraction. This higher catalytic reactivity shown by lower coordination oxygen basic sites is in agreement with experimental and theoretical results for other molecule/substrate systems.

These two adsorbed molecules both in the nondissociative and dissociative states show a negative net charge, which is very small for the first kind of species and much more significant for the dissociated ones. The calculated adsorption energies vary from typical hydrogen bond ($\sim 0.5 \text{ eV}$) to chemical adsorption ($\sim 3 \text{ eV}$) values. Moreover, the adsorption energies are similar for both molecules adsorbed on O_{4c} and O_{5c}. The isocyanic acid dissociates more easily on O_{4c} due to its intrinsic acidic character.

Acknowledgements

Financial support from CONICET and UNS (Departamento de Física) are gratefully acknowledged.

References

- [1] G.M. Zhidomirov, V.B. Kazansky, Adv. Catal. 34 (1986) 131.
- [2] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New solid acids and bases: their catalytic properties, in: B. Delmom, J.T.

Yates (Eds.), Studies in Surface Science and Catalysis, vol. 51, Kodansha/Elsevier, Tokyo/Amsterdam, 1989.

- [3] 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.
- 1. 10, 1. Tashiro, M. Kawasaki, 1. watanabe, K. 101, H. Kobayashi, J. Phys. Chem. 95 (1991) 4476.
- [4] A. Markovits, J. Ahdjoudj, C. Minot, Mol. Eng. 7 (1997) 245.
- [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] M.M. Branda, R.M. Ferullo, P.G. Belelli, N.J. Castellani, Surf. Sci. 527 (1–3) (2003) 89.
- [9] C. Di Valentin, A. Del Vitto, G. Pacchioni, S. Abbet, A.S. Wörz, K. Judai, U. Heiz, J. Phys. Chem. B 106 (46) (2002) 11961.
- [10] J.L. Anchell, K. Morokuma, J. Chem. Phys. 99 (1993) 6004.
- [11] 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.
- [12] 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. Quant. Chem. 71 (1999) 153;
 B. Ahlswede, T. Homann, K. Jug, Surf. Sci. 445 (2000) 49.
- [13] J.A. Rodriguez, T. Jirsak, S. Sambasivan, D. Fischer, A. Maiti, J. Chem. Phys. 112 (22) (2000) 9929.
- [14] 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.
 [15] C. Minot, M.A. Van Hove, J.-P. Biberian, Surf. Sci. 346 (1996) 283;

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.

- [16] G. Pacchioni, J.M. Ricart, F. Illas, J. Am. Chem. Soc. 116 (1994) 10152.
- [17] A.M. Ferrari, G. Pacchioni, J. Chem. Phys. 107 (6) (1997) 2066.
- [18] X.D. Peng, M.A. Barteau, Langmuir 7 (1991) 1426.
- [19] J. Günster, G. Liu, J. Stultz, S. Krischok, D.W. Goodman, J. Phys. Chem. B 104 (2000) 5738.
- [20] A.J. Tench, D. Giles, J.F.J. Kibblewhite, Trans. Faraday Soc. 67 (1971) 854.
- [21] K. Shimizu, H. Kawabata, H. Maeshima, A. Satsuma, T. Hattori, J. Phys. Chem. B 104 (2000) 2885.
- [22] F. Solymosi, T. Bánsági, J. Catal. 156 (1995) 75.
- [23] D. Kondarides, T. Chafik, X. Verykios, J. Catal. 193 (2000) 303.
- [24] R. Dümpelman, N.W. Cant, D.L. Trimm, J. Catal. 162 (1996) 96.
- [25] A.F. Wells, Structural Inorganic Chemistry, 5th ed., Clarendon Press, Oxford, 1984, p. 1004.
- [26] C. Duriez, C. Chapon, C.R. Henry, J.M. Rickard, Surf. Sci. 230 (1990) 123.

- [27] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [28] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [29] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
- [30] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO, Version 3.1.
- [31] R.S. Mülliken, J. Chem. Phys. 23 (1955) 1833.
- [32] 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.

- [33] N.R. Kestner, J.E. Combariza, in: K.B. Lipkowitz, D.B. Boyd (Eds.), Reviews in Computational Chemistry, vol. 13, Wiley/VCH, New York, 1999.
- [34] N. Lopez, F. Illas, G. Pacchioni, J. Am. Chem. Soc. 121 (1999) 813.
- [35] S.P. Bates, M.J. Gillan, G. Kresse, J. Phys. Chem. B 102 (1998) 2017.
- [36] A.V. Stuart, G.B.B.M. Sutherland, J. Chem. Phys. 24 (1956) 559;
 - H. Zeiss, M. Tsutsui, J. Am. Chem. Soc. 75 (1953) 897.