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Theoretical Study of the Chemisorption of CO on Al$_2$O$_3$(0001)

Maurizio Casarin,[*,†] Chiara Maccato,[†] and Andrea Vittadini[‡]

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Padova, Italy,
and Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione del CNR,
Via Marzolo 1, Padova, Italy

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Density functional molecular cluster calculations have been used to study the adsorption of CO on the α-Al$_2$O$_3$(0001) surface. Substrate and adsorbate geometry modifications, adsorption enthalpies, and adsorbate vibrations are computed. Despite the rather small size of the employed cluster, relaxation phenomena evaluated for the clean surface agree well with experimental measurements and periodic slab calculations and mainly consist of an inward relaxation of the Lewis acid site (L_s^a). Different adsorbate arrangements, perpendicular and parallel to the surface, have been considered. Among them, the most stable CO chemisorption geometry ($\Delta H_{ads} \approx -13$ kcal/mol) is that corresponding to the adsorbate perpendicular to the surface, atop L_s^a and C-down oriented. The C−O stretching frequency (ν_{C-O}) computed for such an arrangement is 2158 cm^{-1}, i.e., blue shifted by 44 cm^{-1} with respect to the free adsorbate. The lack of experimental evidence pertaining to CO interacting with a well-defined α-Al$_2$O$_3$(0001) surface prevents the possibility of a direct check of the computed quantities. Nevertheless, low-temperature IR data for CO on alumina powders (Zecchina, A.; Escalona Platero, E.; Otero Areán, C. *J. Catal.* **1987**, *107*, 244) indicate for the chemisorbed species a $\Delta\nu = 12$ cm^{-1}. The adsorbate−substrate interaction relieves some of the L_s^a relaxation, even if the L_s^a electronic structure is only slightly affected upon chemisorption.

1. Introduction

α-Al$_2$O$_3$ is one of the most technologically important of all ceramics; nevertheless, definitive measurements concerning the atomic positions and the nature of the surface termination layer are, even for low index surfaces, quite limited and very recent.[1,2] From these investigations it results that the α-Al$_2$O$_3$(0001) surface is terminated by a single Al layer,[3] strongly inward relaxed. Such a relaxation reduces the spacing between the Al first layer and the O second layer from 0.837[4] to 0.3 ± 0.1 Å.[1,2] Recent Hartree−Fock[5a] and density functional (DF)[5b−d] calculations are in quantitative agreement with these data; however, these calculations, based on periodically repeated slabs, are often computationally demanding, and they are not very efficient, e.g., for calculating adsorbate vibrations.

The relatively limited number of studies concerning the clean α-Al$_2$O$_3$(0001) surface is mirrored by very few surface chemistry investigations conducted on well-defined, single-crystal α-Al$_2$O$_3$ surfaces.[6−8] Moreover, analogous considerations hold for theoretical work devoted to an understanding of the α-Al$_2$O$_3$(0001)−adsorbate interactions.[5c−d,7−12]

In this contribution we present the results of a theoretical study of the bonding between CO and the α-Al$_2$O$_3$(0001) surface. Our goals are (i) to provide a thorough description of the adsorbate−substrate interaction and (ii) to show that small clusters terminated with pseudo-hydrogen saturators are able, as already found for other ionic materials,[13−18] to model adequately the molecular adsorption on Al$_2$O$_3$.

2. Computational Method

2.1. Model. The clean surface was modeled by using the same stoichiometric cluster (Al$_8$O$_{12}$; see Figure 1) employed by Wittbrodt et

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[*] To whom correspondence should be addressed. Phone no.: 39-049-8275164. Fax no.: 39-049-8275161. E-mail: casarin@chim02.chin.unipd.it.

[†] Dipartimento CIMA, Università di Padova.

[‡] CSSRCC, CNR di Padova.

(1) Ahn, J.; Rabalais, J. W. *Surf. Sci.* **1997**, *388*, 121.

(2) (a) Renaud, G. *Surf. Sci. Rep.* **1998**, *32*, 1. (b) Guénard, P.; Renaud, G.; Barbier, A.; Gautier-Soyer, M. *Surf. Rev. Lett.* **1998**, *5*, 321.

(3) Each Al surface atom carries three coordinative vacancies, and it is bonded to three oxide ions, each of them missing a single ligand. The overall charge (1.5 e) occupying the three Al dangling bonds (DBs) can be thought to be transferred to the partially occupied DB of the three O surface ions of the second layer, which then result filled by two electrons. As a whole, the number of empty and filles DBs on the α-Al$_2$O$_3$(0001) is the same, and the surface is nonpolar.

(4) Lattice parameters ($a = b = 4.7570$ Å, $c = 12.9877$ Å) and internal coordinates ($x = 0.3063$, $z = 0.3522$) are taken from the following: Kirfel, A.; Eichhorn, K. *Acta Crystallogr. A* **1990**, *46*, 271.

(5) (a) Puchin, V. E.; Gale, J. D.; Shluger, A. L.; Kotomin, E. A.; Günster, J.; Brause, M.; Kempter, V. *Surf. Sci.* **1997**, *370*, 190. (b) Batirev, I. G.; Alavi, A.; Finnis, M. W.; Deutsch, T. *Phys. Rev. Lett.* **1999**, *82*, 1510. (c) Verdozzi, C.; Jennison, D. R.; Schultz, P. A.; Sears, M. P. *Phys. Rev. Lett.* **1999**, *82*, 799. (d) Di Felice, R.; Northrup, J. E. *Phys. Rev. B* **1999**, *60*, 12287.

(6) Elam, J. W.; Nelson, C. E.; Cameron, M. A.; Tolbert, M. A.; George, S. M. *J. Phys. Chem. B* **1998**, *102*, 7008.

(7) Rodriguez, J. A.; Chaturvedi, S.; Kuhn, M.; Hrbek, J. *J. Phys. Chem. B* **1998**, *102*, 5511.

(8) Liu, P.; Kendelewicz, T.; Brown, G. E., Jr.; Nelson, E. J.; Chambers, S. A. *Surf. Sci.* **1998**, *417*, 53.

(9) Wittbrodt, J. M.; Hase, W. L.; Schlegel, H. B. *J. Phys. Chem. B* **1998**, *102*, 6539.

(10) Hass, K. C.; Schneider, W. F.; Curioni, A.; Andreoni, W. *Science* **1998**, *282*, 265.

(11) Neyman, K. M.; Nasluzov, V. A.; Zhidomirov, G. M. *Catal. Lett.* **1996**, *40*, 183.

(12) Dovesi, R.; Roetti, C.; Causà, M.; Pisani, C. In *Structure and Reactivity of Surfaces*; Elsevier Science Publishers BV: Amsterdam, 1989; p 385.

(13) Casarin, M.; Maccato, C.; Vittadini, A. *Chem. Phys. Lett.* **1997**, *280*, 53.

(14) (a) Casarin, M.; Tondello, E.; Vittadini, A. *Surf. Sci.* **1994**, *303*, 125. (b) Casarin, M.; Maccato, C.; Vittadini, A. *Inorg. Chem.* **1998**, *37*, 5482.

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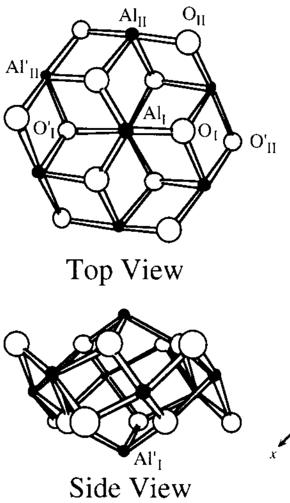

Figure 1. Top and side view of the Al_8O_{12} cluster we employed as a model of the chemisorption site on the clean $Al_2O_3(0001)$ surface. Dark and white circles represent Al and O atoms; saturators are not displayed for the sake of clarity. The adopted frawork is also sketched.

al.[9] to investigate the molecular and dissociative chemisorption of H_2O on α-$Al_2O_3(0001)$. The Al_8O_{12} bare cluster has a S_6 symmetry, it includes four types of non equivalent atoms (Al_I, Al_{II}, O_I, and O_{II} in Figure 1), and it gives rise to four aluminum and two oxygen layers. The two outermost layers of the cluster are representative of the unrelaxed, nonpolar α-$Al_2O_3(0001)$ surface. No atom of the employed cluster is chemically complete,[19] so that, to avoid the presence of spurious surface states, the dangling bonds (DBs) of all the cluster atoms except Al_I (the Lewis acid site, L_s^a) and O_I (the Lewis base sites, L_s^b) have been saturated with pseudo-hydrogen atoms carrying a fractional nuclear charge.[20] In this regard, it is worthwhile to mention that Wittbrodt et al.[9] performed their calculation either by using the bare Al_8O_{12} cluster or embedding it in a potential field due to a point charge array. Both approximations suffer from some flaws which have been thoroughly discussed elsewhere,[14,15] while the use of pseudo-hydrogen saturators has been successfully applied to model Cu_2O,[13,16-17] Ag_2O,[13] ZnO,[14] TiO_2,[15] and CuCl[18] surfaces, as well as chemisorption on them.

In the present case we proceeded as follows. The first thing to be kept in mind is that Al^{3+} and O^{2-} ions are 6-fold- and 4-fold-coordinated, respectively, in the corundum bulk structure. This means that each Al atom shares its three valence electrons with six oxygen atoms, thus contributing with 1/2 of an electron to each Al−O bond, while the O atoms participate to the same bond with 3/2 of an electron. On this basis, the Al_8O_{12} cluster is correctly saturated by providing 3/2 (1/2) of an electron to each Al (O) DB.[21] Such a result can be obtained by employing pseudo-hydrogen saturators having fractional nuclear charges (H′ with $Z = 1.5$ and H″ with $Z = 0.5$). The adopted Al−H′ (1.602 Å) and O−H″ (1.055 Å) bond lengths (BLs) have been obtained by optimizing the geometry of octahedral AlH'_6 and tetrahedral OH''_4 pseudomolecules. The next step consists of determining the correct number of electrons to fill the cluster energy levels. As already pointed out,[3] the charge of the L_s^a DBs is transferred to the DBs of the surface L_s^b. However, in our cluster we have only one surface aluminum atom with three coordinative vacancy (Al_I in Figure 1) and six surface O atoms (O_I and O_{II}) each of them carrying a single DB which needs 1/2 of an electron to result fulfilled. Thus, the filling up of the O_{II} DBs could be obtained by adding to the saturated cluster a charge equal to 3/2 of an electron. In the present case, rather than employing a charged (−3/2) cluster, we preferred to adopt a different approach. Actually, replacing the three H″ saturators of the O_{II} atoms with hydrogen atoms implies the addition of exactly 3/2 of an electron to the cluster levels without affecting the net charge of the system. We already showed in ref 15 that this procedure is preferable because no arbitrary shifts are needed to compare one-electron energy levels.

2.2. Computational Details. All the calculations have been run within the density functional theory (DFT) approach by using the ADF 2.3.0 package.[22,23] Geometry optimization, binding energies, and frequency calculations were obtained by using generalized gradient (GGA) corrections self-consistently included through the Becke−Perdew (BP) formula.[24] As a matter of fact, BP GGAs are able to significantly improve the agreement of metal−ligand binding energies[25] and of adsorption energies[26] with experimental data.

A triple-ζ Slater-type basis set was used for Al, O, and C atoms, while for saturators (pseudo-hydrogen and hydrogen atoms) we used a double-ζ basis. The inner cores of Al (1s2s2p), O (1s), and C (1s) atoms were treated by the frozen-core approximation.

The adsorption enthalpy (ΔH_{ads}) was analyzed in terms of the adsorbate and substrate fragment orbitals by applying Ziegler's extended transition state method[27] (ETS). According to the ETS scheme, the OC−Al_8O_{12} ΔH_{ads} can be written as

$$\Delta H_{ads} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{int} + \Delta E_{prep}$$

Here, ΔE_{elstat} is the pure electrostatic interaction, ΔE_{Pauli} is the destabilizing two-orbital−four-electron interaction between the occupied orbitals of the two fragments, and ΔE_{int} derives from the stabilizing interaction between occupied and empty orbitals of the interacting fragments, while the last term ΔE_{prep} provides information about the energy required to relax the structure of the free fragments to the geometry they assumed in the final system.

Final adsorption enthalpies were further corrected by taking into account the basis set superposition error (BSSE), which was estimated through the use of reference energies computed with ghost adsorbate and surface fragments.[28]

Rather than displaying discrete eigenvalues versus an energy axis, we preferred to plot the density of states and crystal orbital overlap population[29a] (hereafter DOS and COOP, respectively) as a function of energy by using a 0.25 eV Lorentzian broadening factor. These plots, based on the Mulliken's prescription for partitioning the overlap density,[29b] have the advantage of providing insights into the localization and the bonding/antibonding character of molecular orbitals (MOs) over a broad range of energy. The Mulliken population analysis, even though uniquely defined, is rather arbitrary; nevertheless, it results very useful

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(15) Casarin, M.; Maccato, C.; Vittadini, A. *J. Phys. Chem. B* **1998**, *102*, 10745 and references therein.

(16) Casarin, M.; Maccato, C.; Vittadini, A. *Chem. Phys. Lett.* **1999**, *300*, 403.

(17) Casarin, M.; Maccato, C.; Vigato, N.; Vittadini, A. *Appl. Surf. Sci.* **1999**, *142*, 164.

(18) Casarin, M.; Favero, G.; Tondello, E.; Vittadini, A. *Surf. Sci.* **1994**, *317*, 422.

(19) An atom carrying a complete shell of nearest neighbors is chemically complete.

(20) After saturation, the symmetry of the cluster is reduced to C_3.

(21) The atoms O_{II} carry two DBs (see Figure 1); nevertheless, only one of them has been saturated because they belong to the second layer of the α-$Al_2O_3(0001)$ surface and, analogously to O_I, they have a coordinative vacancy.

(22) *Amsterdam Density Fuctional Package*, version 2.0.1; Vrjie Universiteit: Amsterdam, 1996. *Amsterdam Density Fuctional Package*, version 2.3.0; Vrjie Universiteit: Amsterdam, 1997.

(23) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *1*, 41. (b) te Velde, G.; Baerends, E. J. *J. Comput. Chem.* **1992**, *99*, 84. (c) Fonseca Guerra, C.; Visser, O.; Snijders, J. G.; Baerends, E. J. In *Methods and Techniques in Computational Chemistry*; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, Italy, 1995; Chapter 8, p 305.

(24) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(25) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(26) (a) White, J. A.; Bird, D. M.; Payne, M. C.; Stich, I. *Phys. Rev. Lett.* **1994**, *73*, 1404. (b) Gundersen, K.; Jacobsen, K. W.; Nørskov, J. K.; Hammer, B. *Surf. Sci.* **1994**, *304*, 131. (c) Philipsen, P. T. H.; te Velde, G.; Baerends, E. J. *Chem. Phys. Lett.* **1994**, *226*, 583. (d) Hu, P.; King, D. A.; Crampin, S.; Lee, M. H.; Payne, M. C. *Chem. Phys. Lett.* **1994**, *230*, 583.

(27) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(28) Rosa, A.; Ehlers, A. W.; Baerends, E. J.; Snijders, J. G.; te Velde, G. *J. Phys. Chem.* **1996**, *100*, 5690.

(29) (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833. (b) Hoffmann, R. *Solids and Surfaces*: *A Chemist's View of Bonding in Extended Structures*; VCH: New York, 1988.

Table 1. Atomic Displacement (Å) from the Bulk Compared with Experiments and Various Cluster and Slab Calculations

			cluster					slab		
atom	this work	expt	HF[c]	B3LYP[c]	HF[d]	HF[e]	LDA[f]	LDA[g]	LDA[h]	GGA[i]
$Al_I(z)$	−0.53	−0.34[a]	−0.58	−0.54		−0.39		−0.71		
$O_I(x)$	0.05	0.07[a]						−0.03		
$O_I(y)$	0.00	0.20[a]						−0.07		
$O_I(z)$	0.03	0.09[a]	0.00	0.04				−0.01		
d[j]	0.27	0.42[a]/0.3[b]	0.25	0.25	0.27		0.11	0.12	0.11	0.15
$r_{Al_I-O_I}$	1.72	1.77[a]/1.72[b]	1.73	1.75				1.66		
$\Delta r_{Al_I-O_I}$	−0.13	−0.08[a]/−0.13[b]	−0.12	−0.10				−0.17		

[a] Reference 2. [b] Reference 1. [c] Reference 9. [d] Reference 5a. [e] Reference 12. [f] Reference 5c. [g] Reference 5d. [h] Reference 30. [i] Reference 10. [j] The *d* parameter defines the spacing between the first and second layers.

to gain at least a qualitative idea of the electron localization. Selected MO plots have been also reported to assign the character of particular MOs.

3. Results and Discussion

3.1. The Clean Surface. Our first concern was that of checking the capability of the adopted Al_8O_{12} cluster to reasonably mimic the properties of the clean surface and in particular of reproducing the strong relaxation undergone by the topmost layer of α-Al_2O_3(0001).[1,2] For this purpose, we optimized the coordinates of surface atoms (Al_I and O_I) not directly bonded to saturators. Computed quantities are reported in Table 1, where experimental[1,2] and theoretical values obtained by adopting either the cluster[9] or the slab[5,10,12,30] model are also included for comparison. The agreemet between theoretical and experimental outcomes is surprisingly good, given the limited dimensions of the adopted cluster. In particular, it deserves to stressed that all the displacements are in the right direction. Furthermore, differences between our results and those obtained by adopting the slab model appear to be of the same order as differences between different slab calculations. This might indicate that the accuracy of the local description of the potential is more important than the inclusion of long-range effects. Interestingly, also the surface relaxation energy (33.08 kcal/mol), when converted to units of J/m^2 (1.18),[31] compares rather well to the 1.98 J/m^2 DFT result recently published by Di Felice and Northrup.[5d]

Insights into the surface relaxation driving force can be gained by partitioning the surface relaxation energy in contributions due to the steric repulsion ($\Delta E_{rep} = \Delta E_{Pauli} + \Delta E_{elstat}$) and orbital interaction. As a matter of fact, when we move from the unrelaxed to the relaxed cluster, $\Delta(\Delta E_{rep})$ and $\Delta(\Delta E_{int})$ are 225.68 and −258.76 kcal/mol, respectively. This unambiguously indicates that covalency plays a very important role in determining the sp^2 rehybridization of the surface Al atoms.

In Figure 2 the DOS of the unrelaxed and relaxed saturated cluster are reported together with the PDOS of Al_I, O_I, and saturators. DOS curves in the energy region corresponding to the occupied levels consist in both cases of two bands centered at ∼ −22 and ∼ −10 eV. The former includes atomlike O 2s states, while the latter is mainly due to MOs having a significant participation of the O 2p orbitals The overall bandwidth of the O 2p band is ∼8 eV, in very good agreement with XPS measurements.[32] Its lower energy side comprises MOs having a bonding character with respect to the O−Al/O−H″/O−H interactions, while the higher energy side includes MOs nonbonding in nature. Incidentally, the three highest occupied MOs (HOMOs) of the unrelaxed and relaxed clusters are the (e + a) linear combinations of the O_I DBs (2D-contour plots of the combination of symmetry a and one component of that of symmetry e are displayed in Figure 3). The inspection of Figure 2 also testifies that the lowest unoccupied MO (LUMO), Al_I−O_I antibonding in character (see the Al_I−O_I COOP in Figure 4), undergoes a strong destabilization (2.8 eV) upon relaxation. Such an effect is perfectly in tune with an increased covalency of the Al_I−O_I bonding on passing from the unrelaxed to the relaxed surface. Incidentally, it can be useful to remind that the presence of a low-lying surface state pushed at higher energies upon surface relaxation was already indicated by Gautier-Soyer et al.[33]

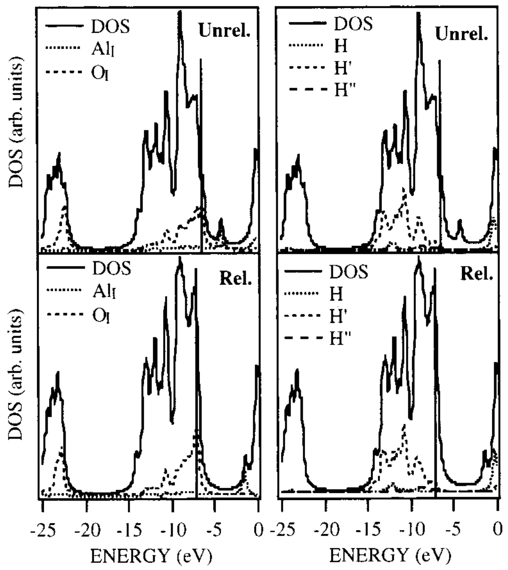

Figure 2. DOS of the unrelaxed/relaxed saturated Al_8O_{12} clusters. PDOS of Al_1, O_1, and saturators are also displayed. Vertical bars represent the energy of the highest occupied MO (HOMO).

3.2. Molecular Adsorption of CO. The bonding between CO and α-Al_2O_3(0001) has been investigated by allowing the interaction of the adsorbate C-down (C_D) or O-down (O_D) oriented atop L_s^a (see Figure 5) and completely optimizing the coordinates of the adsorbate, L_s^a, and L_s^b. The possibility of flat (F) chemisorption geometries has been also taken into account (see Figure 5). Structural and vibrational properties of CO in the free and adsorbed states are reported in Table 2 together with ΔH_{ads} pertaining to the different adsorbate arrangements[34] (see also Table 3).

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(30) (a) Manassidis, L.; De Vita, A.; Gillan, M. J. *Surf. Sci.* **1993**, *285*, L517. (b) Manassidis, L.; Gillan, M. J. *J. Am. Ceram. Soc.* **1994**, *77*, 335.

(31) To convert kcal/mol in J/m^2 we used the same surface area adopted by Wittbrodt et al.[9] (19.55 Å^2).

(32) Henrich, V. E.; Cox, P. A. *The Surface Science of Metal Oxides*; Cambridge University Press: Cambridge, England, 1996.

(33) Gautier-Soyer, M.; Jollet, F.; Noguera, C. *Surf. Sci.* **1996**, *352−354*, 755.

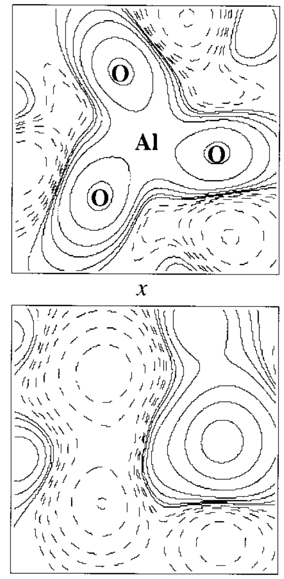

Figure 3. 2D contour plot (*xy* section) of one component of the e (lower) and a (upper) combinations of the O_I DBs pertaining to the relaxed Al_8O_{12} cluster. Both plots represent a slice 2 au above the plane of the O_I atoms. Negative values correspond to dashed contours. Contour levels are $\pm 2 \times 10^{-4}$, $\pm 4 \times 10^{-4}$, $\pm 8 \times 10^{-4}$, ..., $\pm 1.28 \times 10^{-2}$ $e^{1/2}/bohr^{3/2}$.

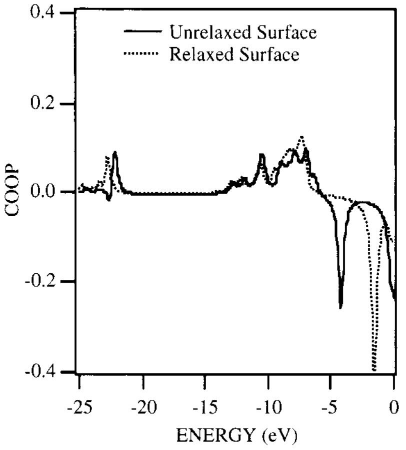

Figure 4. COOP between the Al_I and O_I atoms. Bonding (antibonding) states correspond to positive (negative) peaks.

Starting with the C_D geometry, we remark that the optimized L_s^a–C BL is quite similar to the one (2.17 Å) reported by Neyman et al.[11] and significantly shorter than that (2.41 Å) computed by Dovesi et al.[12] Furthermore, the C–O stretching frequency is blue shifted by 44 cm^{-1} with respect to the free molecule (absolute ν values computed for the free and adsorbate CO are 2114 and 2158 cm^{-1}, respectively). As far as the ΔH_{ads} is concerned, our estimate of −13.36 kcal/mol is quite different from values reported by Neyman et al.[11] (−17.99 kcal/mol) and Dovesi et al.[12] (−6.2 kcal/mol). In this regard, it has to be pointed out that the cluster adopted by Neyman et al.[11] ($Al(OH)_3$) as representative of the α-$Al_2O_3(0001)$ surface is definitely small and that, besides the neglect of correlation in HF calculations, the qualitity of the basis set employed for substrate atoms by Dovesi et al.[12] (minimal STO-3G) is rather poor.

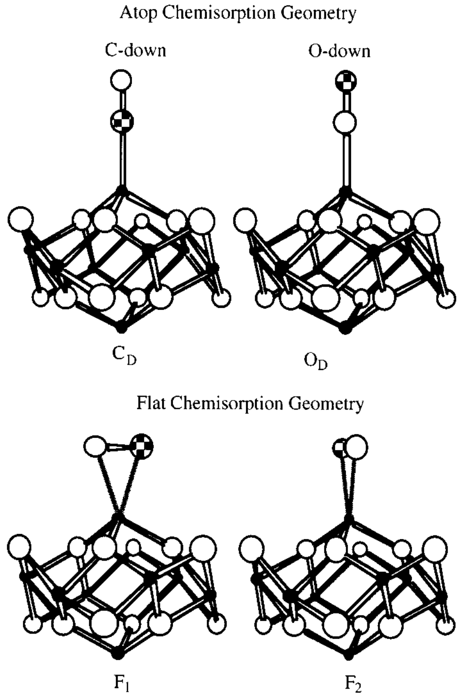

Figure 5. Schematic representation of the clusters we adopted to model the molecular chemisorption of CO on the α-$Al_2O_3(0001)$ surface.

Table 2. Structural and Vibrational Properties of the Free and Adsorbed CO as Obtained from GGA Calculations

^{free}CO

	theor	exptl
r_{C-O} (Å)	1.140	1.127
ν_{C-O} (cm^{-1})	2114	2143

^{ads}CO

	C_D	O_D	F_1	F_2	F_3[a]	exptl
r_{C-O} (Å)	1.134	1.143	1.146	1.144	1.144	
r_{Al-C} (Å)	2.224	3.494	3.041	3.097	3.100	
r_{Al-O} (Å)	3.358	2.351	2.133	2.102	2.091	
∠Al−X−Y (deg)	179.6	180.0	133.8	143.5	145.0	
d (Å)	0.397	0.336	0.270	0.272	0.269[b]	
$r_{L_s^a-L_s^b}$ (Å)	1.740	1.729	1.719[b]	1.718[b]	1.717[b]	
ΔH_{ads} (kcal/mol)	−13.36	−2.76	0.70	0.89	0.86	
ν_{Al-CO} (cm^{-1})	345	258				
ν_{C-O} (cm^{-1})	2158	2080				2165

[a] F_3 derives from F_1 by rotating the adsorbate of 180° with respect to the substrate (see Figure 5). [b] Mean value.

Table 3. Theoretical CO Adsorption Energies (kcal/mol) Decomposed by Means of the Ziegler's ETS Scheme with 1−3 Corresponding to Different Starting Geometries

	CO		CO_F		
	C_D	O_D	F_1	F_2	F_3
ΔE_{Pauli}	32.86	12.00	25.62	27.38	28.22
ΔE_{elstat}	−26.45	−7.25	−11.77	−13.07	−13.50
ΔE_{int}	−22.86	−8.91	−15.32	−16.17	−16.50
$\Delta E_{prep,CO}$	0.04	0.02	0.05	0.03	0.03
$\Delta E_{prep,surf}$	1.77	0.44	0.90	1.47	1.34
BSSE	1.28	0.94	1.22	1.25	1.27
tot. BE	−13.36	−2.76	0.70	0.89	0.86

To our knowledge, two estimates of the chemisorption enthalpy of CO on Al_2O_3 (~5[35] and ~4 kcal/mol[36]) are reported in the literature. The agreement with our estimate is actually

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(34) The calculations of vibrational frequencies are highly time-consuming, so they have been limited to chemisorption geometries corresponding to negative ΔH_{ads} (C_D and O_D).

(35) Zecchina, A.; Escalona Platero, E.; Otero Areán, C. *J. Catal.* **1987**, *107*, 244.

Table 4. C_{CO}, O_{CO}, and L_s^a Orbital Populations before and after Chemisorption[a]

orbital	C	O	L_s^a
s	1.78	1.85	0.25
	1.56/1.77	1.89/1.84	0.06/0.16
p_σ	0.86	1.47	0.18
	0.91/0.87	1.43/1.42	0.24/0.18
p_π	0.99	2.91	0.22
	1.05/0.94	2.89/2.97	0.16/0.16
d	0.08	0.06	0.55
	0.07/0.08	0.06/0.05	0.63/0.60
tot.	3.71	6.29	1.20
	3.59/3.66	6.27/6.28	1.10/1.10

[a] First/second values refer to C_D and O_D arrangements, respectively.

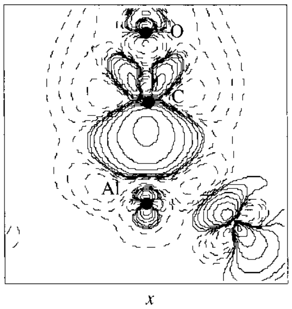

Figure 6. Plot in the *xz* plane of the difference between the SCF electron density and the sum of the electron charge of the costituent fragments for the CO$-$Al$_8$O$_{12}$ model cluster. Contour levels are the same as in Figure 3.

poor; however, it deserves to be stressed that the former value has been indirectly obtained from IR measurements on powder samples,[35] and the latter refers to O-terminated epitaxially grown Al$_2$O$_3$ layers.[36,37] Actually, low-temperature IR data[35] for CO on alumina powders confirm the ν_{C-O} blue shift (12 cm^{-1}) upon chemisorption.

Before moving to the analysis of the CO$-$substrate bonding scheme, we point out that recent high-quality ab initio studies[38] concerning the different stability of aluminum monocarbonyl species (AlCO and AlOC) computed an Al$-$CO dissociation energy of 8.5 kcal/mol. Furthermore, the Al$-$OC isomer was found to be 20.8 kcal/mol less stable than Al$-$CO and 11.4 kcal/mol higher in energy than a cyclic isomer.

On passing from the free CO to the chemisorbed one, the adsorbate is characterized by (i) a slightly shorter BL$_{C-O}$ ($\Delta BL_{C-O} = -0.006$ Å), (ii) a net positive charge ($Q = 0.14$),[39] and (iii) a blue shift of the C$-$O stretching frequency ($\Delta\nu_{C-O} = 44$ cm^{-1}). Furthermore, the adsorbate$-$substrate interaction partially relieves the relaxation of L_s^a (the *d* parameter increases from 0.27 to 0.40 Å),[40] even though its electronic structure is only slightly perturbed upon chemisorption (see Table 4).

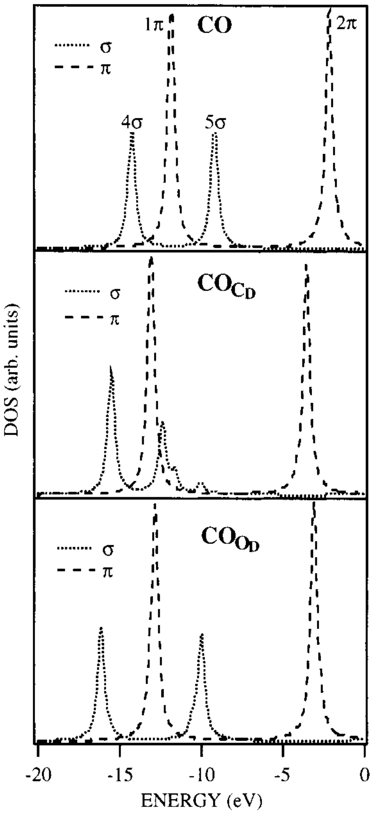

Figure 7. PDOS of the CO molecule: free (top); atop L_s^a, C-down oriented (middle); atop L_s^a, O-down oriented (bottom). σ and π PDOS are also displayed.

The use of the Ziegler's ETS scheme[27] (see Table 3) allows us to look into the nature of the adsorbate$-$substrate bonding. Data reported in Table 3 indicate that the most relevant contribution to the Al$-$C bond comes from the electrostatic term. However, the Pauli repulsion completely offsets this term, thus making determinative, as we found for CO on TiO$_2$(110),[15] the orbital contribution. In relation to that, the inspection of Table 4, where the orbital population of the C_{CO}, O_{CO}, and L_s^a atoms before/after chemisorption is reported, clearly testifies that the σ C population is the most affected upon chemisorption as a consequence of the CO → L_s^a donation. The presence of such an interaction can be further appreciated by looking at Figure 6, where a map of the difference between the charge density of the whole CO$-$Al$_8$O$_{12}$ model cluster and that of the noninteracting fragments is reported.

Further insights into the adsorbate$-$substrate bonding mechanism can be gained by referring to DOS and COOP curves reported in Figures 7 and 8, respectively. The analysis of the DOS curves reveals that the CO-based levels (the ones reminiscent of the adsorbate 4σ, 1π, and 5σ MOs) undergo an energy stabilization on passing from the free molecule to the adsorbed one. Both the 1π and the 4σ orbitals are stabilized by $\sim$1.2 eV, while the 5σ level moves down in energy by $\sim$3.2 eV upon chemisorption. Such a difference can be confidently ascribed to the CO → L_s^a donation which mainly involves the CO 5σ HOMO and the L_s^a 3p$_z$ and 3d$_{z^2}$ empty AOs (see Table 4 and Figure 8).

According to data reported by Dovesi et al.[12] concerning the bonding of CO to α-Al$_2$O$_3$(0001) through the O atom, as well as to theoretical results of Wesolowski et al.[38] pertaining to the aluminum isocarbonyl, the ΔH_{ads} corresponding to the O_D geometry is definitely less negative (see Table 2) than that

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(36) Jaeger, R. M.; Homann, K.; Kuhlenbeck, H.; Freund, H.-J. *Chem. Phys. Lett.* **1993**, *203*, 41.

(37) Jaeger et al.[36] pointed out that the topmost layer of their Al$_2$O$_3$ substrate consists of oxide ions. Moreover, their data were interpreted by assuming a flat orientation of the molecule with respect to the surface and a large ($\sim$4 Å) surface$-$adsorbate distance.

(38) (a) Wesolowski, S. S.; Crawford, T. D.; Fermann, J. T.; Schaefer, H. F., III. *J. Chem. Phys.* **1996**, *104*, 3672. (b) Wesolowski, S. S.; Galbraith, J. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1998**, *108*, 9398.

(39) The effective atomic charge of the C (O) atom passes from 0.29 ($-$0.29) in the free molecule to 0.41 ($-$0.27) in the adsorbed one.

(40) It is worth of note that the L_s^b (L_s^a) *z* coordinate decreases (increases) by 0.010 Å (0.113 Å).

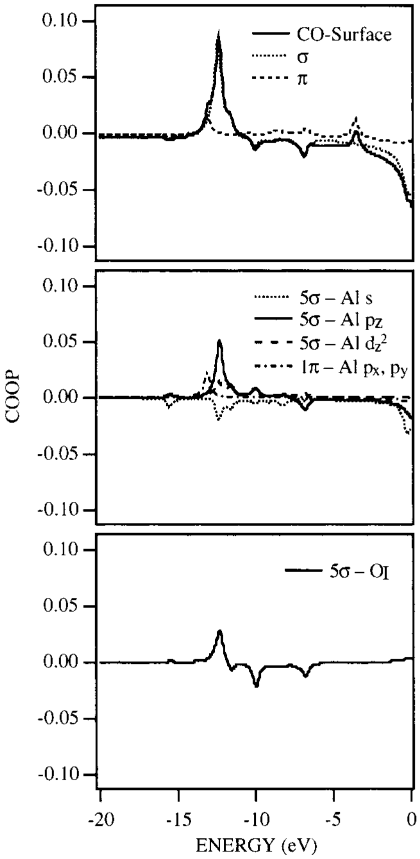

Figure 8. COOP between CO, atop L_s^a, C-down oriented and the surface (top), COOP between the 5σ CO MO and the L_s^a (middle), and COOP between the 5σ CO MO and the L_s^b (bottom).

computed for the C_D one. Furthermore, the gross atomic charge values of O_{CO} and C (−0.28 and 0.34, respectively) reveal a weaker charge transfer from the adsorbate (which again behaves as an donor) to the substrate. Finally, in contrast to IR data,[35] the ν_{C-O} results as red shifted by 38 cm^{-1}.

It is known that CO bonds in a nonclassical way on a $Cr_2O_3(0001)$ support layer.[41] Actually, angle-resolved photoelectron spectra are indicative of CO molecules flatly oriented to this substrate with C and O atoms interacting with a single Cr ion.[42] To investigate the energetics of a similar arrangement on the α-$Al_2O_3(0001)$ surface, isomorphous to the $Cr_2O_3(0001)$ one, a further series of numerical experiments with different starting geometries (see Figure 5) have been performed. Positive ΔH_{ads} values (see Table 2) were always obtained, allowing us to rule out the possibility of a flat chemisorption of CO on α-$Al_2O_3(0001)$. Furthermore, besides minor differences, final geometries always correspond to an O-down-oriented bent CO. The CO PDOS corresponding to the F_1, F_2, and F_3 starting geometries are very similar (see Figure 9), and analogously to the O_D arrangement, they are characterized by a quite pronounced shift (2.2/2.3 eV) of the O-based 4σ level.

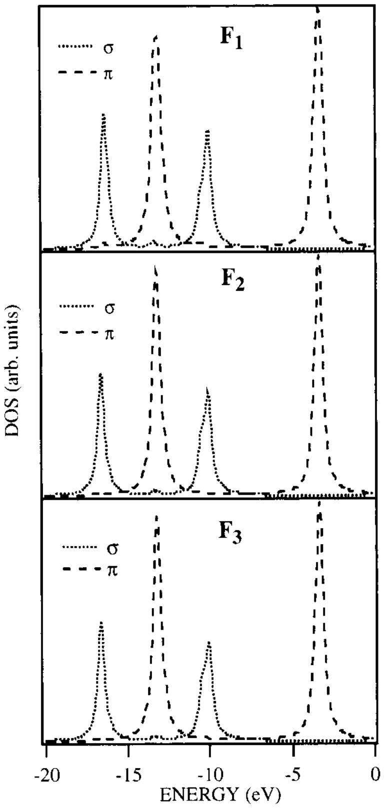

Figure 9. PDOS of the CO molecule parallel to the surface and with different starting geometries: F_1 (top); F_2 (middle); F_3 (bottom). σ and π PDOS are also displayed.

4. Conclusion

Nonlocal density functional calculations herein reported further confirm that small saturated clusters are able to realistically model the L_s^a available on clean surfaces of ionic materials, as well as molecular adsorption processes taking place on them. The present data indicate that, among the chemisorption geometries we took into account for CO on α-$Al_2O_3(0001)$, the C_D coordination is the most favored. Such a result is hardly surprising because it is well-known that, on low index faces of oxide, CO is always adsorbed through the carbon end down on surface cations.[43] On the other hand, the unusual coordination of CO on $Cr_2O_3(0001)$[41] and theoretical evidence of an unexpected cyclic minimum in the isomerization pathway between AlOC and AlCO[38b] spurred the need of a first principle investigation of the adsorption of CO on $Al_2O_3(0001)$. As a whole, the electronic structure of the adsorbate is significantly perturbed upon chemisorption, with the 1π and 5σ levels becoming almost degenerate, while L_s^a is only slightly affected by the interaction with the adsorbate. A reasonable agreement between theory and available infrared measurements is obtained.

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[41] Freund, H.-J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 452 and references therein.

[42] It is noteworthy that the chemisorption geometry proposed by Freund[41] for CO on $Cr_2O_3(0001)$ is very similar to that pertaining the cyclic AlCO isomer.[38]

[43] Zecchina, A.; Scarano, D.; Bordiga, S.; Ricciardi, G.; Geobaldo, F. *Catal. Today* **1996**, *27*, 403.