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A theoretical study of CO adsorption on TiO_2

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Abstract

This paper presents a theoretical study of the interaction of CO with a model of the rutile TiO_2 structure. The calculations are performed using the periodic Hartree-Fock CRYSTAL program. The CO molecule is vertically adsorbed over a titanium atom. Using the PS-31G basis set, the binding energies for the two orientations of the CO molecule, Ti–CO and Ti–OC, do not differ by much, whereas the calculations with the 6-31G* basis set exhibit a pronounced preference for the Ti–CO adsorption. The adsorption is discussed in terms of σ and π interactions.

Key words: Titanium; Carbonyl; Adsorption; Metal oxide; Molecular orbital calculations; Surface

1. Introduction

The adsorption of CO on oxide surfaces is important since it is involved in many processes of heterogeneous catalysis [1]. Carbon monoxide can be formed by the decomposition of alcohols [2] and carboxylic acids [3] on oxide surfaces. Carbon monoxide is also used as a probe adsorbate for IR spectroscopy and other oxide surface analytical methods [4,5]. In this paper, we are concerned with the adsorption of CO on bare TiO_2 surfaces.

2. The computational features

Using the *ab initio* Hartree-Fock crystalline orbital program CRYSTAL [6], we performed effective core pseudopotential calculations. The basis sets for the oxygen and the carbon atoms are the PS-31G basis sets [7] or the standard 6-31G* basis sets. For titanium atom, the basis set consists of the d functions contracted to (4/1) basis set and a single 4sp shell with an exponent of 0.484 for polarization purposes [8]. The pseudopotentials are those from Durand-Barthelat [9]. Bulk TiO_2 calculations for both rutile [8] and anatase [10] and for the adsorption of H_2O on TiO_2 [11] have already been calculated with the PS-31G basis sets. One might think that the PS-31G basis sets are of medium quality. However, for a periodic calculation they are more appropriate than for a molecular calculation. Indeed, very diffuse orbitals are not required as in the molecular calculation because they are responsible for the basis set linear dependence [12]. When 6-31G* basis sets are used instead, the cohesive energy for the bulk rutile is increased by only 3 kcal/mol whereas the energy of CO molecule is increased by 97 kcal/mol. The choice of the basis sets induces a shift of the reference value in the calculation of the adsorption energy (a reduction when the large basis sets are used) and does not influence the comparison of the different adsorption modes on the surface.

3. The model for the rutile surfaces

Our polymer representing the rutile surface is a one-dimensional planar structure containing the tita-

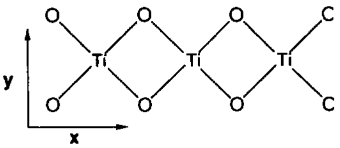

Fig. 1. The single polymer.

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nium atoms and equatorial oxygen atoms (see Fig. 1). It consists of rectangular pieces with a long edge (3.0065 Å, the c parameter from the bulk) in the direction of the chain and a short one (2.4872 Å) perpendicular to it. The TiO distances are the equatorial distances from the bulk structure.

This polymer is obviously far from being a complete representation of a crystallographic face, even if it is significantly better than a simple cluster model. The model however contains titanium atoms with the oxidation number IV and bridging oxygen atoms. The polymer can be recognized as a main feature of the (110) and (100) crystallographic faces. It contains the linearity of the sequence of titanium atoms that is specific of the rutile structure. In this model, the presence of tetracoordinate cations is not enough to create states in the gap, and the electronic structure remains close to that of larger systems.

4. The CO molecule

Experimentally, the dipole moment for carbon monoxide is very small, 0.13 D [13], and positive, C^-–O^+. The negative charge on the carbon atom corresponds to the dative bond, $:O \overset{\rightarrow}{=} C:$. The difference between the electronegativities of C and O opposes this polarization so that the charges are small (see Table 1).

Self-consistent-field calculations (SCF) do not lead to a C^-–O^+ dipole moment; however the correct polarization can be obtained when correlation is properly taken into account [14]. With the PS-31G basis set, the charge on the carbon atom is +0.366; with the 6-31G* basis set, it is reduced but still positive, +0.268. When the CO distance is artificially shortened, the molecule becomes less polar and the influence of the difference in electronegativity decreases. It is then possible to reverse the dipole moment. With the 6-31G* basis set, a CO distance of 0.85 Å leads to a dipole moment with the correct sign: the charge of the carbon atom, $Q_C = -0.118$, is negative and close to the experimental value.

TABLE 1. Dissociation energy, bond length, Mulliken charge of the carbon atom and vibrational frequency of the CO molecule calculated with the PS-31G and 6-31G* basis sets. ν is derived from the force constant k that is estimated from the parabolic interpolation of $E(d_{CO})$, where E is the energy and d_{CO} varies by ±0.01 Å.

	PS-31G	6-31G*	Experimental
$E_{diss.}$ (kcal/mol)	132.4	229.3	257.3 [a]
CO (Å)	1.132	1.114	1.128
Q_C	+0.366	+0.268	−0.114 [b]
ν_{CO} (cm^{-1})	2096	2270	2169.8 [c]

[a] from ref. 26; [b] deduced from the bond distance and the dipole moment; [c] from ref. 27.

5. The two possibilities for CO orientation

In coordination chemistry, CO is both a σ-donor and a π-acceptor, that can stabilize the non-bonding d electrons of a metal. The M–CO orientation of the carbon monoxide (C toward the metal) allows favourable interactions for both the σ and π systems. A typical example is $[Cr(CO)_6]$ [15]. The σ-donation from CO is optimal when the σ pair of the carbon is involved (M–CO) since this pair is in the highest occupied molecular orbital (HOMO). The three d non-bonding orbitals of the metal are also stabilized by the π interaction. This corresponds to a donation from the metal to the π^*_{CO} orbital of the carbonyl, which is also favorable for the M–CO orientation since the π^* amplitude is larger on the carbon p orbitals than the oxygen ones. On metal surfaces, the same effects of σ-donation and π-backdonation appear for CO adsorption [16]. This is the Dewar-Chatt model [17] and has been justified by calculations on triatomic MCO species [18]. For the neutral systems, the M–CO orientation is preferred [19]. It is also the orientation found for adsorption on metal clusters [20] and on metal surfaces.

On the other hand, if the metal atom has empty π orbitals, one might think it would prefer π-donor ligands. For carbonyl, this means the M–OC orientation since the degenerate set of π_{CO} orbitals has a large amplitude on the oxygen p orbitals. This implies two immediate conclusions.

(i) The σ and π systems favouring opposite orientation, the energy difference between the two orientations will be small.

(ii) Both the σ and π interactions are donations from the CO to the metal and thus the total electron density on the CO should decrease to some degree.

Examples are found in the complexation of the carbon monoxide by an alkali cation. The M^+–OC systems are more stable than the M^+–CO systems (by 1.8 and 1.5 kcal/mol for Li^+ and Na^+ respectively with the 6-31G* basis set). The charge-transfer is small in both cases.

For the Li^+–OC orientation, 0.058 σ-electrons and 0.018 π-electrons are transferred to the lithium. The CO bond length is little changed (slightly lengthened; the overlap population (OP) is reduced; See Table 2). The bending of the Li–O–C angle is slightly destabilizing since the π_{CO} as well as the σ_C levels can interact with the empty levels of the cation.

For the Li^+–CO orientation, 0.170 σ-electrons and 0.003 π-electrons are transferred to the lithium. The

CO bond length is slightly shortened with an increased OP. The σ-donation decreases the population of the HOMO of the carbonyl. This orbital, containing mainly the σ pair of the carbon atom, has an antibonding CO character; thus its depopulation is accompanied by an increase in CO bond strength.

The CO is polarized C^+–O^- for both orientations. Thus the charges alternate in the best (Li^+–OC) orientation. While in the Li^+–CO orientation the two positive charges are adjacent.

The Lewis-acid sites (the metal cations) from metal oxide surfaces are reminiscent of the cations and the situation is expected to be similar. For the TiO_2 polymer, the charge on the titanium atom is $Q_{Ti} = +2.316$. It is obviously larger than that of the Ti^{1+} cation which, in contrast to the neutral atom, does not generate any back-donation [21]. On oxides, the two possible CO orientations have been examined by surface cluster approaches [22] and by crystalline orbital LCAO calculations [23,24].

6. Calculations of the CO adsorption (PS-31G basis set)

The TiO_2 oxide appears formally as made of ions: $Ti^{4+}(d^0)$ cations and O^{2-} anions. Adsorptions may be seen as Lewis acid–base reactions that do not affect the oxidation number of the atoms. CO is a weak base that interacts with the Ti^{4+} centres.

The adsorption energies have been calculated according to the expression:

$$E_{ads} = E_{CO} + E_{TiO_2} - E_{(CO+TiO_2)},$$

where $E_{(CO+TiO_2)}$ is the total energy of the adsorbate/substrate system, E_{TiO_2} is the total energy of the substrate and E_{CO} is the total energy of the isolated adsorbate in its equilibrium geometry. A positive E_{ads} value corresponds to a stable adsorbate/substrate system. For simplicity, a coverage of one CO molecule per titanium atom has been assumed ($\theta = 1$).

TABLE 2. Complexation of the carbonyl by an alkali cation for the two opposite orientations. The bending is expressed in cal. mol^{-1} $degree^{-2}$. It is estimated from the parabolic interpolation of $E(\theta)$, where E is the energy and θ is the angle between the carbonyl and the direction perpendicular to the surface; θ varies by 5°.

	$Li^+ \cdots CO$	$Li^+ \cdots OC$	$Na^+ \cdots CO$	$Na^+ \cdots OC$
E_{ads} kcal/mol	14.6	16.4	9.6	11.15
MO or MC (Å)	2.267	1.955	2.647	2.307
OP (MO or MC)	0.144	0.048	0.097	0.037
CO (Å)	1.102	1.128	1.104	1.124
OP (CO)	0.703	0.592	0.678	0.602
Q_M	+0.83	+0.92	+0.89	+0.94
Q_C	+0.37	+0.46	+0.33	+0.42
Q_O	−0.20	−0.39	−0.22	−0.36
$d^2E/d\theta^2$	6.46	2.45	4.66	2.05

TABLE 3. Results for CO adsorption with the two orientations with the PS-31G basis set. The bending is expressed in cal. mol^{-1} $degree^{-2}$. For the bending, CO remains in the yz plane.

	Ti–OC $\theta = 1$	Ti–CO $\theta = 1$	Ti–OC $\theta = 1/2$	Ti–CO $\theta = 1/2$
E_{ads} (kcal/mol)	11.57	15.19	16.58	20.03
CO (Å)	1.134	1.138	1.137	1.120
TiO or TiC (Å)	2.264	2.241	2.255	2.294
$d^2E/d\theta^2$	2.8	36.9		

The CO molecule approaches the titanium atom perpendicular to the plane of the polymer. The bending of the Ti–carbonyl angle is destabilizing, and more so in the TiCO orientation. We have also investigated π adsorption (CO parallel to the surface above a titanium atom) and the di-σ orientation (CO bound to a titanium atom and to an oxygen atom). Such approaches do not lead to stable systems; optimization gives either desorption or lead to the perpendicular orientation.

With the PS-31G basis set, the two CO orientations (Ti–CO and Ti–OC) are very close in energy (a difference of 3.6 kcal/mol; see Table 3). The reasons why both orientations are possible have been discussed above. In the oxide, the titanium atoms are formally Ti^{4+} and should behave like Li^+ or Na^+. In the naked polymer, the electron density on Ti is 1.4 e instead of 0; this allows some back-donation and favours the Ti–CO orientation as long as the energy difference remains small. Similar results have already been obtained for CO adsorption on the MgO (001) [23] and (110) [24] surfaces. We believe that the main features of the adsorption process are analogous in both cases. The metal-adsorbate distance is rather large and can be ascribed to an ionic bond. The total charge-transfer is very weak: for the Ti–OC orientation, we calculate a back-donation that nearly compensates the σ-donation (σ-donation: 0.015 e *vs.* π back-donation: 0.012 e) whereas for the Ti–CO orientation the back-donation dominates (π back-donation: 0.073 e *vs.* σ-donation: 0.060 e). This lack of appreciable charge-transfer has been used to support the idea that the adsorption process is essentially due to electrostatic interactions [23]. Since Ti^{4+} is a stronger Lewis acid than Mg^{2+}, the chemisorption energy on TiO_2 is expected to be larger than that on MgO.

The potential curve associated with the bending of the Ti–C–O angle show a large angular constraint for the TiCO orientation. Such a constraint reveals that the two interactions (π back-donation and σ-donation) nearly compensate one another. Indeed, the π^*_{CO} and the σ_C levels should interact with filled and empty levels, respectively, thus imposing linearity on the system.

In contrast to the Li^+/CO and Na^+/CO systems, the Ti–OC distance is as long as the Ti–CO distance. This is due to the repulsion between the oxygen of the carbonyl and those of the surface.

In Table 3, we also present results for a coverage of one half ($\theta = 1/2$). The adsorption energies are increased; the difference is mostly due to the decrease of the adsorbate–adsorbate repulsion. This repulsion represents 3.7 kcal/mol as it results from a calculation of the chain of adsorbate with no substrate. The adsorption energy for the two orientations does not differ by much (3.45 *vs.* 3.60 kcal/mol).

7. The influence of the dipole moment

The small preference for the Ti–OC orientation (Table 3) can result from the initial polarization of the carbonyl, C^+–O^-. With the opposite dipole C^-–O^+, electrostatics should favour the opposite orientation, Ti–CO. This led us to investigate further the influence of the dipole.

When the CO distance is shortened (0.85 Å) the calculation with the 6-31G* basis set leads to a charge polarization that is close to the experimental dipole moment, with a negative charge on the carbon atom. Therefore we have performed a new calculation with fixed geometries (Ti/CO = 2.25 Å, CO = 0.85 Å) for the two orientations. The basis set used here is the 6-31G*, and is also used for the oxygen atoms of the substrate.

TABLE 4. Results for CO adsorption in the two orientations with the 6-31G* basis set. The bending is expressed in cal. mol^{-1} $degree^{-2}$.

	Ti-OC	Ti-CO	Isolated CO
E_{ads} (kcal/mol)	6.47	14.72	–
CO (Å)	1.116	1.105	1.114
TiO or TiC (Å)	2.362	2.349	–
ν_{CO} (cm^{-1})	2278	2299	2162
OP (CO)	0.570	0.661	0.624
OP (Ti-carbonyl)	0.017	0.053	–
Q_C	+0.360	+0.264	+0.268
Q_O	−0.354	−0.260	−0.268
σ-donation	0.042	0.054	
π back-donation	0.036	0.050	
$d^2E/d\theta^2$	0.54	11.3	

If the polarity C^-–O^+ is important, we would expect a preferential adsorption with the carbon interacting with the metal. The result of the calculation is very revealing. The adsorption energy for the Ti–CO orientation is 22.69 kcal/mol, whereas for the Ti–OC orientation it is only 3.94 kcal/mol.

Once adsorbed, the polarity is C^+–O^-. Two atoms that bear positive charges (C and Ti) become adjacent. This suggests that the inversion of orientation with the basis set is not a simple electrostatic effect. Furthermore, the MCO orientation can also be explained by molecular-orbital arguments: the shortening of the CO distance destabilizes the σ_C lone pair (a shift of 0.042 a.u.) and stabilizes the σ_O lone pair.

8. Calculations with the 6-31G* basis set

As mentioned previously, the CO dipole moment is inaccurate at the SCF level. The 6-31G* basis set does not provide the correct dipole moment but the CO polarization is smaller than that obtained with the PS-31G basis set. When d orbitals are added to the carbon and oxygen basis sets, the Ti–CO orientation is favoured as was already seen for the Mg^{2+}/CO system [22]. This is why we have repeated the optimization for the two orientations with the 6-31G* basis set. The results are presented in Table 4.

Compared with the calculations with the PS-31G basis set, the adsorption energy for the Ti–CO orientation does not change whereas that for the Ti–OC orientation drops. The Ti–CO orientation is favoured by 8.3 kcal/mol.

In both cases, the adsorbed CO is polarized C^+–O^-. The charge-transfer from the CO to the metal oxide is negligible and results from a compensation of small donations and back-donations, as seen in Table 4.

The Ti/CO bond, and the C–O bond on the surface are stronger in the Ti–CO orientation than in the Ti–OC orientation. For the Ti–CO orientation, as for the M^+/CO triatomic system, the depopulation of the HOMO σ level removes an antibonding contribution from the C–O bond, which should strengthen it. This is indeed what happens, even if the effect is very small. The CO overlap population is larger than that of the isolated molecule (an increase of 0.037) and the bond length is smaller by 0.009 Å.

For the Ti–OC orientation, the Ti–O overlap population is very small (a third of that of the Ti–C bond for the opposite orientation). The Ti–OC and C–O distances are long compared to those for the other orientation; they are associated with an increased bond polarity. For this reason also, the CO overlap population is smaller than that of the isolated molecule (a decrease of 0.054) and the bond length is larger by

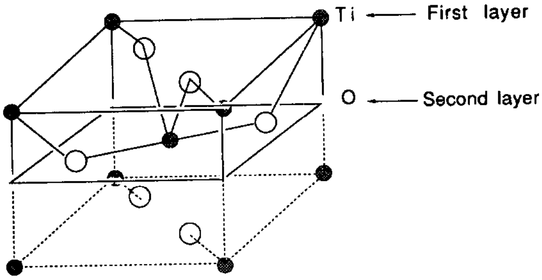

Fig. 2. The (001) rutile face.

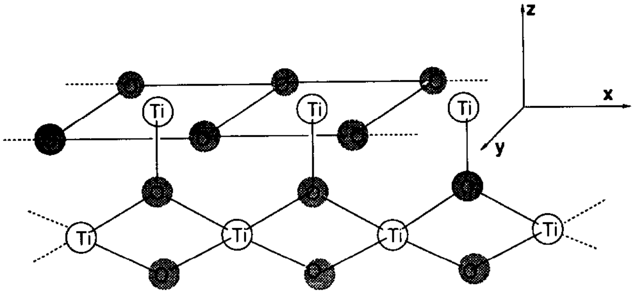

Fig. 3. The double polymer with the pentacoordinated sites.

0.002 Å. The negatively-charged oxygen atom is between two atoms with a positive charge and this is electrostatically more favourable.

9. Adsorption on a pentacoordinate titanium atom (PS-31G basis set)

Although tetracoordinate titanium atoms have been postulated in surfaces with defects, the coordination of the atoms in the linear polymer is clearly insufficient to represent a titanium atom on clean surfaces. These are generally pentacoordinate.

Four-coordinate titanium atoms may be found on the (001) face of rutile (see Fig. 2). The local environment then differs from that of the polymer because it is not planar. The adsorption energies corresponding to the two orientations are similar (see Table 5) and they differ by less than 3.7 kcal/mol. This result is essentially similar to that already obtained for the linear polymer.

We investigated the double polymer shown in Fig. 3 to evaluate the influence of a fifth ligand when the titanium atoms at the surface are pentacoordinate. The difference between the adsorption energies for the two orientations is again comparable to that for the single polymer, 4.1 kcal/mol. In conclusion, with the PS-31G basis set, the difference between the binding energies for the two orientations remains constant for the different models we have used.

The stability of this double polymer is large [11] in spite of the small overlap population (OP) value, 0.02, of the TiO bonds that couple the two polymers. The donation from the second polymer to the surface polymer is weak, 0.068 e. This should make the surface less acidic and less reactive. The calculation shows this trend (see Table 6). The adsorption energies decrease. The electronic density in the d_{xz} and d_{yz} orbitals is smaller for the double polymer than for the single (0.507 e *vs.* 0.636 e) and this explains the reduction of the back-donation. The density in the d_{z^2} orbital is larger (0.270 e *vs.* 0.123 e) and this explains the reduction of the σ-donation to the metal. The interaction of the occupied level that has a d_{z^2} contribution (a bonding level between the titanium and the oxygen atom from the layer beneath) is repulsive with the CO and is larger for the M–OC orientation since the oxygen electron pair is lower and closer in energy to that level. Thus, the observed difference of 4.1 kcal/mol is slightly greater than that obtained with the single polymer.

TABLE 5. CO Adsorption on the (001) face of rutile (PS-31G).

	Ti-OC	Ti-CO
E_{ads} (kcal/mol)	12.24	15.94
CO (Å)	1.131	1.105
TiO or TiC (Å)	2.275	2.425
ν_{CO} (cm^{-1})	2271	2177

Note that a purely electrostatic model would imply a larger reactivity of the pentacoordinate Ti. According to the crystal calculations for the five layers of the double polymer with the PS-31G basis set, the top layer becomes more ionic and the positive charge of the pentacoordinate titanium atom slightly increases with respect to that of the single layer (an increase by +0.058). Electrostatic interactions should then increase the acidity of the titanium atoms and lead to larger adsorption and to the M–OC orientation.

10. Comparison between the adsorption on pentacoordinate and tetracoordinate titanium atoms, (6-31G* basis set)

Experimentally [5], two σ-coordination CO sites have been found on anatase. They have been attributed to two species of coordinatively unsaturated Ti^{4+}. One of them (site B) has four oxygen ligands while the other

TABLE 6. Results for CO adsorption on the double polymer (PS-31G).

	Ti-OC	Ti-CO
E_{ads} (kcal/mol)	6.73	10.87
CO (Å)	1.132	1.123
TiO or TiC (Å)	2.340	2.379
ν_{CO} (cm^{-1})	2235	2171

TABLE 7. Results with the 6-31G* basis set for the pentacoordinated titanium atom.

	(H2O)Ti–CO	$(TiO_2)_2$–CO
E_{ads} (kcal/mol)	10.02	9.13
CO (Å)	1.107	1.107
OP (CO)	0.630	0.613
OP (Ti–C)	0.057	0.058
TiC (Å)	2.423	2.448
ν_{CO} (cm^{-1})	2301	2274
QC	+0.280	+0.282
QO	−0.274	−0.274

(site A) has five oxygen ligands. The value of ν_{CO} depends on the adsorption site. There is a shift of $\Delta\nu = 15\ cm^{-1}$ between site A and site B. For instance, on the sample TS473 the frequencies are 2188 and 2203 cm^{-1}, and on the sample TS693 they are 2191 and 2206 cm^{-1}.

To determine the influence of a fifth ligand, we have used two models, the first is the double polymer and for the second we have assumed adsorption of the carbonyl on one face of the single polymer and water on the other. The water represents the fifth ligand. Results of calculations are shown in Table 7. The carbonyl group on the pentacoordinate Ti has a lower vibrational frequency, by $\Delta\nu = 25\ cm^{-1}$.

This is the assignment of sites made by Garrone *et al.* [5] who postulate that CO adsorbed on the A sites has a lower ν_{CO} than CO adsorbed on B sites. A sites have water molecules adsorbed whereas B sites carry hydroxyls. They also suggest that the A sites were five-coordinate cations and that the B sites were four-coordinate cations. We checked this assignment by considering competition between OH and H_2O adsorptions on our single polymer model. One face of the polymer was covered with H_2O ($\theta = 1/2$) in order to generate the two kinds of cations and we saturated the other face with hydroxyl and water. The hydroxyl, being the stronger base, bonds preferentially to the four-coordinate cation whereas the water binds to the five-coordinate cation. The difference between the two adsorption energies is 5.8 kcal/mol.

11. Conclusion

CO is oriented on TiO_2 perpendicularly to the surface with the carbon atom toward a Ti^{4+} cation. Using the PS-31G basis set, the two orientations of the CO molecule, Ti–CO and Ti–OC, exhibit very similar binding energies (a difference of 3.6 kcal/mol). This is explained in terms of σ and π interactions. However, the results can overemphasise the Ti–OC orientation because of the wrong dipole moment of the CO molecule. The calculations with the 6-31G* basis set exhibit a pronounced preference for the Ti–CO adsorption. The adsorption energy is larger for a four-coordinate cation than for a five-coordinate cation. The total electron transfer is negligible, but corresponds to two small and opposite transfers, as in the Chatt-Dewar model.

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