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A DFT study of CO adsorbed on the clean and hydroxylated anatase TiO₂ (001) surfaces.

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SUMMARY

The adsorbate-substrate interaction between carbon monoxide and the clean and hydroxylated surfaces of anatase (001) has been simulated by periodic DFT calculations. For the clean surface, different periodicities have been taken into account in order to investigate the influence due to the lateral effects. The obtained results show that the molecule interacts only with the penta-coordinated titanium ion when high surface coverages are employed while it interacts with both the titanium and the di-coordinated oxygen ions when the smallest surface coverage is considered. The adsorption on the hydroxylated surface, which has been carried out for the first time, has been studied by considering the largest used periodicity and focusing the attention on the influence of both the terminal and bridging OH groups. The resulting data show that in the case of the adsorption on the hydroxylated surface, no additional bond between the surface oxygen and the carbon atom is present. Therefore, in a regime of very low surface coverage, the molecule behaves in a very different way when it interacts with the clean or the hydroxylated surface.

KEYWORDS

Adsorption; Carbon monoxide; Anatase (001); Hydroxyl group; Density functional simulations.

Introduction

Anatase, which is a polymorph of TiO_2 , is very important in the industrial field because of the wide use in heterogeneous catalysis [1]. In particular, there has been in the last years an increasing interest in its application on heterogeneous photocatalysis [2]. In this context, the hydroxyl groups deriving from the dissociative adsorption of water play a key role in the decomposition of the pollutants. Since the OH groups can also strongly affect the initial adsorption of the compound on the surface, a comparison between the behaviour of the clean and hydroxylated surface provides useful information to better elucidate this influence. One of the most important probe molecules allowing to obtain this kind of information is represented by the carbon monoxide since it is involved in many industrial processes [3] and its behaviour is well known. In fact, CO adsorbs on the surface of a metal oxide interacting by a σ -bond with the metal cations which have no d electrons, e.g. Ti^{4+} : the adsorption leads to a shift of the CO stretching frequency toward higher wavenumbers with respect to the value in gas-phase (i.e. 2143 cm^{-1}). The stretching frequency of the adsorbed CO is strictly connected with the electrophilicity of the surface Lewis acid site and it moves towards higher wavenumbers with the increasing of the electrophilicity itself [4]. In general, the blue-shift is originated mainly from the following effects: the increase of the C-O bond strength, the wall effect coming from the molecule vibrating against the rigid surface [5] and the Stark effect represented by the interaction between the CO dipole moment and the electric field [5].

The aim of this work is to carry out a quantum-mechanical simulation on CO adsorbed on the clean and hydroxylated anatase (001) representing one of the most exposed surfaces of TiO_2 [1]. A similar kind of study has been already carried out on the rutile (110) surface [6]. From the theoretical point of view, the adsorption of H_2O on the anatase (001) surface has been widely investigated: when both the molecular and dissociative interactions are taken into account, the latter mode is usually found to be favored with respect to the former one [7-13]. Unlike the water and to our best knowledge, the

interaction of CO on anatase (001) has been considered only in a work concerning the oxidation of the molecule on the stoichiometric surface [14]: the simulation of the adsorption on the metal cation, which has been carried out using a full surface coverage, showed that the molecule weakly interacts with the titanium ion. However, the simulation of the adsorption of carbon monoxide on clean, reduced and doped metal oxides represents a widely investigated topic [e.g. 6, 15-30 and references therein] because of the simplicity of the molecule and the possibility to easily evaluate the changes in the surface properties with respect to the variations of the environmental conditions: in fact, CO can adsorb on the metal cations in a weaker or stronger way depending on the kind of metal oxide considered and the related surface, as well as the presence of oxygen vacancy or doping atoms.

In the current work, before beginning the adsorption studies, a preliminary investigation on the slab thickness has been carried out. Then, in order to evaluate the influence of the neighbouring adsorbed molecules (i.e. the lateral effects), the adsorption on the clean surface has been performed using different periodicities and considering all the possible kinds of interaction energy. Besides, in order to make negligible the lateral effects, the adsorption on the hydroxylated surface has been carried out by adopting the largest used periodicity.

Computational details

The computational conditions employed in the current work are the result of a previous detailed investigation of vinyl fluoride adsorbed on the rutile (110) surface [31] and have been also used for previous works concerning the adsorption of CO on other kinds of TiO_2 surfaces, i.e. the rutile (110) [6, 32-33] and the anatase (101) [32] surfaces. In practice, the calculations have been carried out at DFT/B3LYP level employing the CRYSTAL06 software package [34].

The Ti and O atoms have been described by using a basis set properly developed for TiO_2 and consisting of a 86-51G* and a 8-411G contraction, respectively [35]. For water and carbon monoxide the standard 6-311G* contraction has been adopted [36].

In order to take into account the anharmonicity, the calculated CO stretching frequency has been scaled by using a scaling factor equal to 0.966 which has been suggested by NIST for the method and basis set adopted in the current work [37].

Results and discussion

Optimization of the clean and hydroxylated surface

The anatase phase belongs to the $I4_1/amd$ (D_{4h}^{19}) tetragonal space group and the unit cell is defined by the two lattice vectors **a** and **c** and by the fractional coordinate *u*. The anatase (001) surface has been cut from the bulk whose parameters have been previously optimized [38] and it is depicted in Fig. 1a: it consists of twofold and threefold coordinated oxygen atoms (indicated as O(2f) and O(3f)) and fivefold and sixfold coordinated titanium atoms (indicated as Ti(5f) and Ti(6f)); the titanium ions exposed to the contact with the adsorbates are only the Ti(5f) ones. The O(2f) and Ti(5f) atoms represent the Lewis basic and acid sites, respectively.

A stoichiometric and non-polar termination is obtained by terminating the adopted slab on a O(2f) atom and considering only slabs consisting of multiples of 6 atomic layers according to the following sequence of planes: O-Ti-O-O-Ti-O. The effect of the slab thickness on the surface formation energy (E_s) and the surface structure has been checked by taking into account the full optimization of slabs having a number of atomic layers included in the range from 6 to 30. The surface formation energy easily converges to a value of 1.47 J/m² for the unrelaxed slabs and to 1.35 J/m² for the relaxed ones starting from a surface constituted by 12 atomic layers. Moreover, this thickness is enough also to reach the convergence on the atomic relaxations which are summarized in Table 1: the largest displacements concern the first four most exposed ions. The results obtained both for E_s and for the surface structure are comparable with those found at DFT/LDA level by Lazzeri et al. [39]. According to this study, the 12-atomic layer slab has been adopted for the simulation of the adsorption.

The dissociation of the H₂O molecules involves the Ti(5f) and O(2f) atoms: the hydroxyl group corresponding to the adsorption of an OH group on the Ti(5f) is indicated as terminal OH group while

that resulting from the adsorption of a H atom on the O(2f) is defined as bridging one. The calculations concerning the hydroxylated surface have been performed by using a periodicity equal to (3×3) in order to avoid the interaction between the two hydroxyl groups: in fact, the aim of this study consists in evaluating separately the effects arising from the interaction between one of the two considered OH groups and the nearest surface Lewis acid site involved in the interaction with the molecule. Since the considered surface has a surface area large enough to make negligible the reciprocal influence between the two hydroxyl groups, it represents a good model for reaching the isolation of the investigated OH groups. The hydroxylated surface has been obtained from the full optimization of the system which is depicted in Fig. 1b. The optimised O-H bond lengths are 0.961 Å for the terminal OH group and 0.988 Å for the bridging one.

Adsorption on the clean surface

The adsorption on the clean surface has been simulated by placing the CO molecule in an initial geometry perpendicular to the surface with the carbon atom above the Ti(5f) of the relaxed surface. The final geometry has been obtained by relaxing all the atoms constituting the system. The effects due to the lateral interactions between adsorbed molecules have been studied by considering the adsorption at different periodicities ($n \times m$), i.e. at different surface area. In general, the magnitude of the lateral effects depends on the kind of molecule considered and plays a key role in the adsorption process: in fact, the presence of a molecule can influence the interaction between a neighbouring molecule and the surface in a strong manner. Of course, the lateral effects depend also on the considered surface coverage: it usually occurs that the higher is the coverage, the stronger is the influence on the adsorption.

Before performing the geometry optimization of the adsorbate-substrate system, the molecule arranged in a free monolayer, having the same periodicity used to simulate the surface, has been optimized. The calculated CO bond length in the isolated optimized molecule is equal to 1.127 Å which is in good agreement with the experimental value of 1.128 Å [40]. No variations with respect to the case of the isolated molecule have been observed during the optimization of the free monolayer.

The most important structural parameters of the CO-anatase (001) system as function of the periodicity are reported in Table 2: the optimized adsorbate-substrate systems referring to the (2×2) and (3×3) are shown in Figs. 2a and 2b, respectively. As it can be seen from Table 2, for the (1×1) , (1×2) and (2×1) periodicities, the C-O bond length remains approximately the same, while it slightly decreases for the (2×2) and largely increases for the (3×3) ones. Considering the $(1 \times m)$ and $(n \times 1)$ periodicities, the increasing of m and n values gives rise to a decrease of the C-Ti distance and to an increase of the O-C-Ti angle. The C-Ti distance value for the (2×1) periodicity is slightly bigger than that in the (2×2) one, while it is largely smaller than that in the (1×2) one. Considering also to the behaviour of the O-C-Ti angle, it can be deduced that the lateral effects along the x- and y-directions are not the same and then the increase of m results in a different adsorbate-substrate interaction with respect to the increase of n . Concerning the largest considered periodicity, i.e. the (3×3) one, it can be seen that it is associated to the smallest value for the C-Ti distance and the O-C-Ti angle and to the highest value for the C-O length. In particular, the magnitude of this parameter can be related to that of a typical double C-O bond and can be explained by the presence of an interaction between the CO molecule and the O(2f) bound to the Ti(5f) involved in the adsorption. The formation of this additional bond between the O(2f) ion and the C atom leads to a large increase of the distance between the O(2f) and the Ti(5f) involved in the interaction with the molecule: in fact, this distance is about 2.2 Å for the (2×2) and 3.1 Å for the (3×3) periodicities.

Concerning the adsorption energetics, the attention has been focused only on the interaction energy (E_{int}) because the main aim is to study the behaviour of the strength of the bond between the molecule and the surface with respect to the variations due to the lateral effects and to the presence of the OH groups. In fact, the adsorption energy (E_{ads}) is a compromise between E_{int} and the distortion energy which represents the energy associated with the variation of the geometry of both the adsorbate and the substrate. In our calculations, a negative (positive) value of E_{int} means that there is attraction (repulsion) between the adsorbate and the substrate. Since the calculations are periodic, also the lateral interaction energy (E_{int}^L) has been considered: by analogy to E_{int} , a negative (positive) value of E_{int}^L means that there

is attraction (repulsion) between the adsorbed molecules. Lastly, the net interaction energy (E_{int}^N) given by the sum of the two previous energies has been estimated. All the three energies, which have been corrected for the basis set superposition error (BSSE) employing the Counterpoise (CP) method [41], are reported in Table 3. As it is expected, the lateral interaction energy decreases as the periodicity increases: in particular it assumes the largest value for the (1×1) case while is null for the (3×3) one. Focusing on E_{int}^N , it can be seen that the smallest value is related to the (1×1) periodicity: this is in agreement with the weak interaction found by Mguig et al. [13]. As it has been observed for the C-Ti distance and the O-C-Ti angle, the (2×2) periodicity is associated to a value similar to that of the (2×1) one and bigger than that of the (1×2) one. Finally, the adsorption on the (3×3) surface results in a very large interaction energy. This can be due to the formation of the additional bond between the C atom and the O(2f) ion.

The adsorbed CO stretching frequency (ν_{CO}), whose blue-shift is correlated to the electrophilicity of the adsorption site [4], has been calculated for both the (2×2) and (3×3) periodicities; the value referring to the isolated optimized molecule is 2135 cm^{-1} and this is comparable with the experimental one (2143 cm^{-1} [23]). The adsorption on the (2×2) and the (3×3) surfaces is associated to a value of ν_{CO} equal to 2168 and 1708 cm^{-1} , respectively. This indicates that the adsorption on the smallest surface slightly increases the strength of the CO bond while the interaction with the biggest one leads to a large decrease of this strength which assumes a value typical of a double CO bond. In general, it can be concluded that the adsorption on the biggest surface is associated with the strongest adsorbate-substrate interaction and the largest variation of the CO stretching frequency. This can be due to the near absence of the lateral effects which lead to a decrease of the adsorption strength in the other cases.

Adsorption on the hydroxylated surface

The adsorption on the hydroxylated surface has been carried out by placing the CO molecule in an initial geometry having the carbon atom above the Ti(5f) nearest to one of the two hydroxyl groups. For

the terminal OH group, two cases have been considered: in fact, the molecule can be placed above the nearest titanium ion along the x- or the y- direction. The former case is indicated as Structure (I) while the latter as Structure (II). The case referring to the adsorption near to the bridging OH group is indicated as Structure (III). As for the adsorption on the clean surface, the final adsorbate-substrate system has been obtained by relaxing all the atoms of both the molecule and the surface and the resulting optimized structures are shown in Fig. 2(c-e). It is important to notice that in all the cases, there is not formation of an additional bond between the O(2f) and the C atom as it has been observed for the adsorption on the clean (3 × 3) surface.

The most important structural parameters of the investigated systems are reported in Table 4. As it can be seen, the C-O bond length decreases as a consequence of the adsorption and its value is smaller than that obtained by the adsorption on the clean surface. The C-Ti distance and the O-C-Ti angle values are similar to those resulting from the interaction of the molecule with the clean (2 × m) surface.

Table 5 reports the interaction energy: as consequence of the big periodicity used for this study, the lateral interaction energy is null and then, E_{int} is equal to E_{int}^N . As it can be observed, the energy associated to the Structure (I) is similar to that of the Structure (III) and is smaller than that of the Structure (II): the behaviour of the three energies follows the trend of the C-Ti distance: in fact, the shorter is the distance, the bigger is the energy. In general, all the three energies are much smaller than that associated to the adsorption on the clean (3 × 3) surface. This arises from the fact that the adsorption on the hydroxylated surface does not lead to the formation of an additional bond between the O(2f) ion and the C atom.

The adsorbed CO stretching frequency is also reported in Table 5 along with the blue-shift calculated with respect to the isolated optimized molecule. The value of ν_{CO} related to the Structure (I) is almost equal to that of the Structure (II) and smaller than that associated to the Structure (III). It is interesting to notice that the trend of the frequencies does not follow exactly that of the interaction energies: this can be explained by considering that the value of the frequency does not depend only by the adsorbate-substrate interaction but also on the presence of the nearby OH group. It is important to note that the ν_{CO}

associated to the CO adsorbed on the hydroxylated surface is slightly bigger than that resulting from the interaction with the clean (2×2) surface but is much bigger than that related to the adsorption on the clean (3×3) surface. As in the case of the interaction energy, this is a consequence of the absence of the additional bond between the undercoordinated oxygen of the surface and the carbon atom of the molecule.

Considering the comparison with the blue-shifts observed at the experimental level which are equal to about 45 and 65 cm^{-1} [42-44], it has to be noticed that the smallest one is comparable with the values obtained for the adsorption on the hydroxylated surface and is very different with respect to those arising from the interaction with the clean surface.

Conclusions

This work reports a quantum-mechanical investigation of the adsorption of CO on the clean and hydroxylated anatase (001) surface; the study related to the hydroxylated surface has been carried out for the first time. The simulation of CO adsorbed on the clean surface has been performed by considering different periodicities in order to take into account the possible lateral effects. The results show that the molecule adsorbs by interacting only with the titanium ion and then the C-O bond strength slightly increases when small periodicities are used. Interestingly, when a very small surface coverage is adopted, a double adsorbate-substrate interaction occurs, i.e. the carbon atom of the molecule interacts both with the penta-coordinated titanium ion and the di-coordinated oxygen ion. The additional interaction with the surface oxygen leads to a very large decrease of the C-O bond strength which assumes the character typical of a double bond.

The hydroxylated surface has been modeled by considering two different kinds of OH groups, i.e. a terminal and a bridging one. In order to limit the lateral effects and to isolate the two hydroxyl groups, the largest periodicity adopted for the adsorption on the clean surface has been chosen. The results show that the adsorption near one of the two OH groups gives rise to an increase of the C-O bond strength and that no additional bond between the di-coordinated oxygen ion and the carbon atom is formed. This

means that in a regime of low coverage, the molecule behaves in a strongly different way in the case of clean or hydroxylated surface.

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Table 1. Displacement of the anatase (001) surface ions as function of the number of atomic layers.^a

	Number of atomic layers				
	6	12	18	24	30
O ₁ (x)	-0.10	-0.10	-0.10	-0.10	-0.09
O ₁ (z)	0.02	0.00	0.00	0.01	0.02
Ti ₂ (x)	0.07	0.05	0.05	0.05	0.05
Ti ₂ (z)	-0.05	-0.06	-0.05	-0.05	-0.04
O ₃ (x)	-0.10	-0.07	-0.07	-0.07	-0.07
O ₃ (z)	-0.01	-0.02	-0.02	-0.01	0.00
O ₄ (x)		0.04	0.04	0.05	0.05
O ₄ (z)		0.00	0.00	0.01	0.01
Ti ₅ (x)		-0.01	-0.01	0.00	0.00
Ti ₅ (z)		0.00	0.00	0.01	0.01
O ₅ (x)		0.00	0.00	-0.01	-0.01
O ₅ (z)		0.00	0.00	0.01	0.01

^a displacements are given in angstroms. Labels refer to Fig. 1a.

Table 2. Optimized parameters for the CO - anatase (001) system as function of the periodicity ($n \times m$).^a

	(1 × 1)	(1 × 2)	(2 × 1)	(2 × 2)	(3 × 3)
C–O	1.128	1.126	1.126	1.125	1.199
$\Delta(\text{C–O})^b$	0.001	-0.001	-0.001	-0.002	0.072
C–Ti	2.428	2.401	2.329	2.326	2.148
O–C–Ti	166.9	169.0	173.4	174.0	120.7

^a lengths and angles are reported in angstroms and degrees, respectively.

^b variation of the CO bond length with respect to the isolated optimized molecule (1.127 Å).

Table 3. Interaction energies of the CO - anatase (001) system as function of the periodicity ($n \times m$).^a

	(1 × 1)	(1 × 2)	(2 × 1)	(2 × 2)	(3 × 3)
E_{int}	-5.26	-8.76	-20.03	-20.08	-193.67
E_{int}^L	2.97	1.31	1.70	0.04	0.00
E_{int}^N	-2.29	-7.45	-18.33	-20.04	-193.67

^a energies are given in $\text{kJ}\cdot\text{mol}^{-1}$.

Table 4. Optimized parameters for the CO - hydroxylated anatase (001) system.^a

	Structure (I) ^b	Structure (II) ^b	Structure (III) ^b
C–O	1.123	1.123	1.122
$\Delta(\text{C-O})^c$	-0.004	-0.004	-0.005
C–Ti	2.338	2.315	2.358
O–C–Ti	176.1	174.9	176.1

^a lengths and angles are reported in angstroms and degrees, respectively.

^b Structures (I) and (II) refer to the adsorption near a terminal OH group along the x- and y- direction, respectively; Structure (III) is related to the adsorption near a bridging OH group (see text).

^c variation of the CO bond length with respect to the isolated optimized molecule (1.127 Å).

Table 5. Interaction energy and CO stretching frequency of the CO - hydroxylated anatase (001) system.^a

	Structure (I) ^b	Structure (II) ^b	Structure (III) ^b
E_{int}^N	-21.33	-32.44	-24.05
ν_{CO}	2181	2184	2192
$\Delta\nu_{\text{CO}}^c$	46	49	57

^a E_{int}^N and ν_{CO} are given in $\text{kJ}\cdot\text{mol}^{-1}$ and cm^{-1} , respectively.
^b Structures (I) and (II) refer to the adsorption near a terminal OH group along the x- and y- direction, respectively; Structure (III) is related to the adsorption near a bridging OH group (see text).
^c variation of the CO stretching frequency with respect to the isolated optimized molecule (2135 cm^{-1}).

FIGURE CAPTIONS

Figure 1. (a) Model of the anatase (001) surface: Ti(5f) and Ti(6f) indicate penta- and esa-coordinated titanium cations while O(2f) and O(3f) correspond to di- and three-coordinated oxygen anions. (b) Model of the hydroxylated anatase (001) surface: OH (I) represents the terminal OH group while OH (II) corresponds to bridging one. (a) and (b) have been obtained by using the XCRYSDEN program [45].

Figure 2. (a) Model of the CO - anatase (001) (2×2) system; (b) Model of the CO-anatase (001) (3×3) system; (c) Model of the CO – hydroxylated anatase (001) system resulting from the adsorption of CO on the Ti(5f) near the terminal OH group along the x-direction; (d) Model of the CO – hydroxylated anatase (001) system obtained from the adsorption of CO on the Ti(5f) near the terminal OH group along the y-direction ; (e) Model of the CO – hydroxylated anatase (001) system corresponding to the adsorption of CO on the Ti(5f) near the bridging OH group. In (a) – (e) only the outermost surface ions are depicted; the dashed lines represent the bonds between CO and TiO₂. (a) – (e) have been obtained by using the XCRYSDEN program [45].

Figure 1

Figure 2