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Adsorption of O_2 on $TiO_2(110)$: A theoretical study

Chutian Shu, N. Sukumar, and C. P. Ursenbach
Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201-1881

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First-principles calculations are carried out with the objective of assigning a chemical identity to the variety of forms of molecular oxygen which are known to exist on a $TiO_2(110)$ surface. Six different geometries and spin configurations of O_2 are shown to be stable in the bridging oxygen defect site. The relationship of these results to experimental observations is discussed. © *1999 American Institute of Physics.* [S0021-9606(99)70121-2]

I. INTRODUCTION

There are practical and fundamental reasons for the ongoing interest in titanium dioxide. One practical reason is that TiO_2 has recently been harnessed for several commercial applications in the photodegradation of airborne organic waste.[1] In terms of fundamental interest, 25 years of intensive research on titanium dioxide has made it an important prototype of metal oxide catalysts, and there exists a wealth of experimental results for various adsorbates on TiO_2.[2,3] Such results motivate theoretical efforts to develop a more thorough understanding of this increasingly useful catalyst.

Molecular oxygen is believed to play a central role in photodegradation reactions. Many features of this process are already understood. Light in the near ultraviolet spectrum excites electron-hole pairs within the bulk of the catalyst. The electrons can be captured by oxygen adsorbed to the surface, and the holes can be captured by water or hydroxyl species. One view that has been expressed is that O_2 acts simply as an electron sink, with the hydroxyl initiating the chemistry. However, more recent studies point the finger at oxygen as playing a key, active role.[1] Therefore it is of some interest to understand the character of this adsorbate.

Surface science techniques are invaluable for studying chemistry on the simplest model of a heterogeneous catalyst—the single crystal surface. In this regard, detailed experimental[3] work has been conducted on the interaction of oxygen with the rutile (110) surface of TiO_2. This surface features rows of bridging oxygen atoms, and for the surface to be catalytically active, defects must be created by removal of some of these atoms. This is carried out by high temperature annealing, where the higher the temperature, the more bridging oxygens are removed. Each bridging atom removed exposes two reduced Ti^{+3} atoms and it is onto this site that an oxygen molecule can be adsorbed.[4] Two forms of adsorbed O_2 were identified a few years ago by allowing oxygen to adsorb in different temperature regimes.[5,6] The measurable distinction found between the two forms is in their photodesorption cross sections (differing by a factor of ~ 20) and in the fact that the low temperature form can photo-oxidize CO to CO_2. However, the chemical difference between the two species has not yet been resolved. It has been suggested[5] that O_2 can lie parallel or perpendicular to the surface, and can bear either a single or double negative charge (the adsorption site consists of two Ti^{+3}, either or both of which could be oxidized by O_2). Earlier ESR experiments[7] have confirmed that O_2^- is a common species on defective TiO_2 and other substrates, and that it may lie parallel to the surface. Another experimental observation is that heating the low temperature version (referred to as α-O_2) converts it irreversibly to the high temperature version (referred to as β-O_2).[5,6] Thus the high temperature β-O_2 actually has the higher binding energy, and α-O_2 is metastable.

A more recent study from the same group resolved the low temperature α-O_2 into two species.[8] Both species can photo-oxidize CO, but with different cross sections. Both are converted to β-O_2 by heating. It was speculated that these two subspecies are the result of adsorption on different kinds of defect sites, but much of the observed behavior is still unexplained.

The objective of this study is to employ electronic structure methods to model the interaction of O_2 with the $TiO_2(110)$ surface and thus provide additional information regarding the chemical identity of the various forms of adsorbed oxygen. Knowledge of the high temperature form obtained from this study would, of course, be the starting point for future investigations of the activated O_2 molecule, an understanding of which is of great importance in tracing the detailed mechanism of this catalyst.

II. COMPUTATIONAL DETAILS

The surface in this study is treated using a cluster model. Atoms in the vicinity of the active site are included explicitly, and layers of surrounding atoms are represented by an array of point charges. This is a commonly employed model for systems of this kind, and, although it neglects band structure effects, these would likely be small for an ionic crystal whose symmetry has been broken by creation of a defect. The minimal cluster that can be chosen for the bare surface defect is Ti_2O_9, illustrated in Fig. 1. This contains an anion vacancy and the cluster should have electronic charge of -12. In terms of formal charges it consists of 2 Ti^{+3} ions and 9 O^{-2} ions. There are two reducing electrons implied by these charges, and they can be paired or unpaired so that there are two possible spin states for the bare surface, singlet and triplet. Since the O_2 ground state is a triplet, there will be three possible spin states (singlet, triplet, quintet) for the ad-

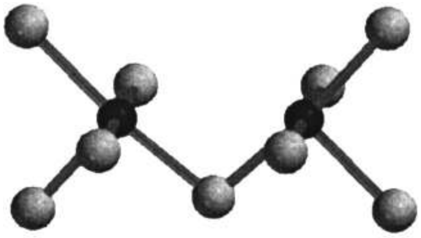


FIG. 1. Ti_2O_9 cluster used in *ab initio* portion of bare surface defect calculation. Light spheres are oxygen, dark spheres are titanium. Surrounding point charges are not shown in this figure.

sorption complex. All possible spin states must be considered in order to understand the adsorption process.

The point charges of 11 titanium and 33 oxygen atoms were used to surround the minimal *ab initio* cluster. These point charges have values of -0.9697 for oxygen and $+4$ for titanium. For this size of cluster it is unlikely that any particular choice of charges will create a highly accurate model, but this choice will at least provide a reasonable environment for the outermost oxygens of the cluster, and maintains neutrality for the whole surface.

The precise geometry of the bare surface cluster is taken from the result of plane-wave, periodic boundary condition calculations of the relaxed, nondefective (110) surface.[9] During the calculation of the adsorption complex, we fixed the geometry of the TiO_2 surface, optimizing only the O_2 molecule. For this size of cluster it is unlikely that optimizing the lattice would give more realistic results than would using the bare, nondefective surface geometry. The O_2 molecule, however, is allowed to optimize in all six degrees of freedom, without constraints of any kind.

We have used the electronic structure package Jaguar, version 3.0, from Schrödinger, Inc. We employed their LACVP** basis set[10] for cluster calculations which includes effective core potentials for titanium. The $3s$ and $3p$ electrons are treated explicitly, as including them in the effective core is well known to give poor results for first row transition metals. The 6-31G** basis set was used for calculations not involving titanium. The nondefault options used in our cluster calculation were as follows: SCF level shift of 0.8 for the bare cluster and 1.0 for the adsorption complex; ultrafine accuracy; fully analytic calculations; no Fock matrix updating; and no symmetry. The latter condition was adopted so that adsorption energies could be calculated as differences between energies of systems with the same symmetry.

The calculations are performed using density functional theory (DFT) with Becke's half-and-half method (HH)[11] as well as with his three-parameter method (B3LYP).[12] Generally speaking, the B3LYP results are considered to be more accurate, but we also found it more difficult to converge the energy in B3LYP. In calculations of O_2 on the surface we were unable to obtain properly converged B3LYP results for any spin states other than singlets.

Spin unpairing was handled at the restricted open-shell level. This has the advantage of avoiding spin contamination in the calculations, but also restricts the spin multiplicities that can be considered with a given number of unpaired electrons. Thus, two unpaired electrons can only be modeled in the triplet state, four unpaired electrons in the quintet state, etc. This will have implications for the interpretation of our results, and will be discussed below.

Vibrational O–O stretching frequencies were calculated for some cases. Zero-point energies however were neglected in computing binding energies. The highest frequency calculated (1845 cm^{-1}) corresponds to a zero-point energy of ~0.1 eV. Since only differences of frequencies would enter into the binding energy, it is very likely that their contribution would be within the error inherent in the calculation. The calculated frequencies should be useful though as guides to the identification of species.

TABLE I. Results and data for the bare surface defect calculation, for O_2, and for O_2 derivatives having bond orders of one and of three-halves.

	HH	B3LYP	Expt.
Energy of triplet bare surface ($E_h = 27.212$ eV)	−824.070 68	−832.539 40	
Energy of singlet bare surface (E_h)	−823.969 73	−832.456 26	
Mulliken charges of triplet Ti	0.63, 0.50	0.34, 0.33	
Mulliken charges of singlet Ti	0.71, 0.71	0.51, 0.51	
Spin density of triplet Ti	0.91, 0.96	0.90, 0.91	
Energy of $^3O_2$ (E_h)	−148.868 42	−150.316 11	
Energy of $^1O_2$ (E_h)	−148.799 91	−150.257 44	
Length of $^3O_2$ double bond (Å)	1.191	1.214	
Length of $^1O_2$ double bond (Å)	1.193	1.216	
Length of O–O bond in HO_2 (Å)	1.313	1.332	
Length of O–O bond in H_2O_2 (Å)	1.422	1.455	
Frequency of O–O stretch in $^3O_2$ (cm^{-1})	1845	1693	1580[a]
Frequency of O–O stretch in HO_2 (cm^{-1})	1253	1174	1098[b]
Frequency of O–O stretch in H_2O_2 (cm^{-1})	1051	1002	866[c]
Length of Ti–$O_{bridging}$ bond (fixed) (Å)	1.805	1.805	

[a] References 13 and 14.
[b] Reference 15.
[c] Reference 16.

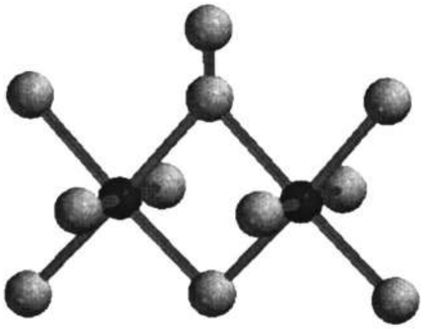


FIG. 2. O_2 adsorbed at anion defect site in perpendicular orientation.

III. RESULTS

A. Reference systems

We calculated the energy for the bare surface and O_2 molecule separately and took the sum of these for the triplets as the reference energy for later calculation of binding energies. We used two methods for the energy calculation, HH and B3LYP. We also performed calculations on isolated O_2 and, as a reference, on HO_2 and H_2O_2 which have bond orders of 3/2 and 1, respectively. These results, along with vibrational data from Refs. 13–16, are displayed in Table I.

B. O_2 perpendicular to surface

Next we performed calculations for O_2 approaching the bare surface in a perpendicular orientation, as illustrated in Fig. 2. We attempted calculations on all possible spin states, singlet, triplet, and quintet. Our initial guess geometry consisted of a doubly bonded oxygen molecule whose lower atom (O_{prox}) was 1.698 Å above the plane containing the Ti^{+3} ions. This structure was then optimized to an energy minimum, and results for the triplet and quintet minima are shown in Table II.

The singlet state is not stable in this geometry.

C. O_2 parallel to surface

When O_2 is parallel to the surface, there is an additional orientational degree of freedom in the plane of the surface, and we found that there are two stable orientations in this class, both singlets. These are illustrated in Figs. 3 and 4, and the results of calculations are shown in Table III.

Triplet and quintet states are not stable in this geometry.

TABLE II. Results from calculations of O_2 adsorbed at anion defect site in perpendicular orientation.

	HH	
	triplet	quintet
Binding energy (eV)	1.249	3.060
Length of O–O bond (Å)	1.197	1.229
Length of Ti–O bond (Å)	2.183	2.134
Mulliken charges for Ti	0.52, 0.52	0.53, 0.53
Mulliken charge of O_{prox}	−0.26	−0.41
Mulliken charge of O_{dist}	0.46	0.60
Spin density for Ti	0.92, 0.92	0.94, 0.94
Spin density for O_{prox}	0.01	0.40
Spin density for O_{dist}	0.01	1.50
Frequency of O–O stretch (cm^{-1})	···	1779

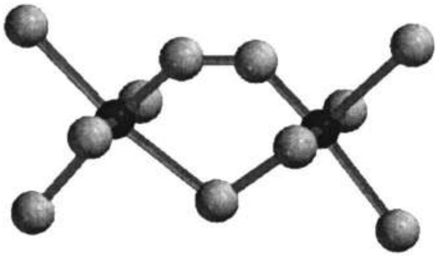


FIG. 3. O_2 adsorbed at anion defect site parallel to both the surface and to the Ti–Ti line.

D. O_2 tilted toward surface

In the context of experimental studies it has been speculated that there are two stable geometries for O_2 on the surface of $TiO_2(110)$, namely, parallel and perpendicular. One of the strengths of theoretical studies is to aid experimental procedures by predicting other possible configurations of microscopic system. For example, while our studies began by consideration of the geometries just mentioned, it soon became clear that a tilted geometry (illustrated in Fig. 5) was the favored geometry in some circumstances.

A singlet calculation was attempted in the perpendicular geometry, but the oxygen molecule's geometry was optimized in a tilted position, one oxygen approximately in the position of the missing bridging oxygen, the other higher above the surface but bonded to one of the titanium atoms. Also, when a triplet calculation was performed starting from the geometry of Fig. 4, a similar tilted geometry was obtained. The tilted geometry could thus potentially play a role in oxygen adsorption on the surface. Its results are summarized in Table IV.

IV. DISCUSSION

We begin this discussion by analyzing in more detail the nature of electronic structure and bonding in the various stable species discovered.

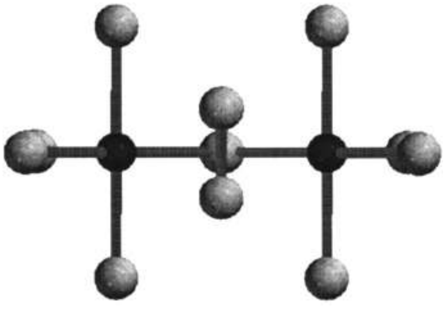


FIG. 4. Top-down view of O_2 adsorbed at anion defect site parallel to the surface and perpendicular to the Ti–Ti line.

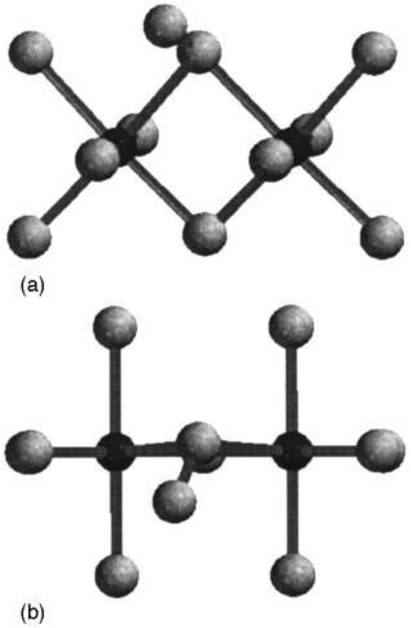
TABLE III. Results from calculations of O_2 adsorbed parallel to the surface.

	HH		B3LYP
Orientation w.r.t. Ti–Ti bond	singlet perpendicular	singlet parallel	singlet perpendicular
Binding energy (eV)	3.654	0.826	4.081
Length of O_2 bond (Å)	1.387	1.347	1.413
Length of Ti–O bond (Å)	1.937	1.756	1.962
Mulliken charges of Ti	0.91	0.86	0.64
Mulliken charges of O_2	−0.31	−0.17	−0.23

A. Analysis of the various observed configurations

1. Perpendicular geometries

In the quintet perpendicular state the O–O bond length changes only 3% from that of the O_2 molecule, which means that the O_2 of the adsorption complex is likely still of a double bond nature. The distance between the Ti atoms and the proximal atom of the oxygen molecule (2.13 Å) is fairly large compared to the Ti–O_{bridging} bond length (1.80 Å) which suggests that the interaction is weak. The total Mulliken charge for O_2 is very small (0.2). This of course has no strict physical meaning, but suggests that there is not much electron transfer between O_2 and the defect site. The individual Mulliken charges on O_2 however indicate a significant dipole. All of this suggests that O_2 is only physically adsorbed on the surface, and the nature of the interaction between the oxygen molecule and the defect is largely that of charge/induced dipole. This is supported by consideration of the Kohn–Sham orbitals, which generally are a good approximation to the Hartree–Fock orbitals. Nearly all of the molecular orbitals of ground state triplet oxygen and the ground state triplet surface retained their integrity in the complex. Only the σ orbital formed from axial p orbitals of the O_2 atoms underwent significant mixing with orbitals of the surface. The Mulliken charges and spin densities of the titanium atoms further attest to a primarily nonchemical interaction between adsorbate and surface.


(a)

(b)

FIG. 5. O_2 adsorbed at anion defect site in tilted geometry in (a) side view and (b) top view.

The perpendicular triplet state appears to have a very similar interaction between oxygen and the surface as the quintet. The bond lengths are similar, and consideration of the orbitals suggests that it is singlet oxygen physisorbed on the triplet surface by the same mechanism as in the quintet state. Note that the splitting (in HH theory) between triplet and quintet adsorption energies ($0.067E_h$) is very similar to the singlet–triplet splitting ($0.069E_h$) of O_2. The difference between the quintet and triplet is essentially just the spin state of the oxygen molecule.

2. Parallel geometries

Configurations parallel to the surface occur only in the singlet state and only in high symmetry, perpendicular or

TABLE IV. Results from calculations of O_2 adsorbed in a tilted configuration.

	HH		B3LYP
	triplet	singlet	singlet
Binding energy (eV)	2.735	2.424	3.096
Length of O_2 bond (Å)	1.307	1.345	1.349
Length of Ti_{sing}–O_{prox} bond (Å)	2.033	1.723	1.749
Length of Ti_{doub}–O_{prox} bond (Å)	1.890	1.966	1.988
Length of Ti_{doub}–O_{dist} bond (Å)	2.022	1.856	1.907
Mulliken charges of Ti_{sing}	0.67	0.90	0.65
Mulliken charges of Ti_{doub}	0.88	0.78	0.47
Mulliken charges of O_{prox}	−0.38	−0.45	−0.37
Mulliken charges of O_{dist}	0.20	0.02	0.08
Spin density of Ti_{sing}	0.97	⋯	⋯
Spin density of Ti_{doub}	0.03	⋯	⋯
Spin density of O_{prox}	0.19	⋯	⋯
Spin density of O_{dist}	0.78	⋯	⋯
Coordinates of O_{prox}	−0.433, 0.095, 1.304	0.069, −0.151, 1.188	0.084, −0.151, 1.227
Coordinates of O_{dist}	0.538, 0.739, 1.895	0.466, 0.970, 1.815	0.550, 0.956, 1.841
Frequency of O–O stretch (cm^{-1})	1342	1557	1332

parallel to the Ti–Ti line. Optimization from a 45° orientation for instance leads to the former of these. In the parallel states, the O_2 bond length (1.35–1.41 Å) is intermediate between the double bond of free O_2 (1.19–1.21 Å) and the single bond of H_2O_2 (1.44–1.47 Å). The Ti–O distances all indicate formation of bonds. The Mulliken charges, although lacking in rigorous meaning, suggest that there has been transfer of electron density to O_2 from the Ti atoms, consistent with reduction of bond order by one half, and suggests a charge–charge interaction between adsorbate and adsorption site. There is substantial mixing between the surface orbitals and $2p$ orbitals of O_2. The high symmetry allows ready identification of orbitals with significant π^* character, and these are both fully occupied in both configurations.

There are also significant differences between the two surface-parallel configurations. When perpendicular to the Ti–Ti line, O_2 has a much longer Ti–O bond length and a much lower energy. Its length (1.94 Å) is about the length of an equatorial Ti-O bond in the bulk crystal (1.95 Å). When parallel to the Ti–Ti line the Ti–O bond length (1.76 Å) is even shorter than the Ti-O_{bridging} bond length (1.80 Å). There is apparently steric crowding which also serves to decrease the binding energy. This is also manifest in the O_2 bond lengths, where we note that the geometry of Fig. 4 has the largest value of this parameter for any of the stable states observed, it being actually midway between the O–O bond lengths of HO_2 and H_2O_2.

3. Tilted geometries

As with the parallel geometries, the O_2 bond length for both of these structures is intermediate between that of a single and a double bond. The Mulliken charges indicate some degree of electron transfer to the oxygen molecule. The Ti–O bond lengths indicate that the proximal O_2 oxygen is bound to both Ti atoms, while the distal oxygen is bound only to one. There is significant mixing between surface orbitals and all O_2 orbitals arising from atomic *p*-orbitals. Thus a state of chemisorption clearly exists.

Naturally the two spin states differ somewhat in their electronic structure. In the singlet state both π^* orbitals are significantly mixed with surface orbitals and doubly occupied. In the triplet state, only one π^* orbital is mixed extensively with the surface in doubly occupied orbitals. The two unpaired electrons occupy (1) a π^*-like orbital, weighted towards the distal oxygen and (2) the *d*-shell of Ti_{sing} (i.e., the titanium atom bonded to a single atom of O_2). We also note that, in the triplet state, Ti_{sing}–O_{prox} is the longest of the optimized Ti–O bonds, while in the singlet state it is the shortest. One could perhaps say that in the singlet state O_2 is bound to the whole defect site, while in the triplet state it is better described as being bound to a single titanium atom.

B. Determination of α and β states

It is the principal purpose of this study to characterize the α_1, α_2, and β forms of oxygen on $TiO_2(110)$, and to gain insight into the chemistry of these adsorption states.

Since the β state is more thermodynamically favored it should have the lowest energy. From the results shown above, this suggests that the β state is the singlet complex of O_2 adsorbed parallel to the surface and perpendicular to the Ti–Ti line of the defect site. It has the lowest energy among all states obtained. Moreover this geometry was obtained by minimization from more than one starting geometry, which is further evidence of its stability. However it is also clear that this *cannot* be the geometry of the α states as well. Since this geometry can be obtained from only one electronic configuration, i.e., no unpaired electrons, the α states cannot be simply another spin state of the same geometry, but must have a distinct geometry.

From experiment we can assume that formation of the α state from the gas phase is more dynamically favored than that of the β state. This consideration would likely eliminate the singlet complex in which the oxygen molecule is parallel to both the surface and to the Ti–Ti line. The approach to this configuration would be more sterically hindered by adjacent bridging oxygens than would an approach into the β state geometry. The perpendicular geometry, and possibly the tilted geometry, could be considered as less sterically hindered. Another factor is polarization of the approaching molecule by the cationic active site to create an induced dipole. This would yield an additional potential energy term in the molecule–surface interaction that would give a kinetic advantage over species adsorbing in an orientation parallel to the surface. Such a dipole is evident in the physisorbed perpendicular geometry as well as the chemisorbed tilted geometry, thus strengthening the case for neglecting the Fig. 3 geometry.

The other species which is of relatively high energy is the perpendicular triplet. Again, the required kinetic favorability of the α species would make the occurrence of this state very unlikely. There is no reason to think that $^3O_2$ and the triplet surface would combine to form what is essentially $^1O_2$ physisorbed to the triplet surface.

On the other hand, formation of the perpendicular quintet would seem very natural. Among other things, it is spin allowed. However, we stop short of assigning it as an α species. To judge adequately between it and the two tilted states one would need to consider the size of barriers to adsorption and interconversion of the three species, and this would in turn require consideration of curve-crossing between spin states. This is beyond the scope of the present study. Nevertheless, we at least predict that the α state is a geometry in which the oxygen atoms of the adsorbed molecule are inequivalent, which would allow them to possess an infrared O–O stretching signal. Calculated frequencies are given in Tables II and IV, and their reliability can be estimated from results in Table I. Wong[17] and Bytheway and Wong[18] have performed systematic studies of vibrational frequency prediction by DFT methods and estimate that, using scaling factors of ~0.97, the B3LYP frequencies have a root-mean-square error of 30–40 cm^{-1} for 6-31G* and 6-311G* basis sets. This seems consistent with our calculations of O_2 and HO_2, but H_2O_2 is less accurate. The HH frequencies have not been studied systematically, but in this work they strongly overestimate the O–O stretch. Calculation of frequencies in the adsorbed state is made more approximate yet by the fact that the surface is not relaxed. This would presumably be less of a problem the more weakly oxygen is bound to the surface. All things considered, it seems reasonable to predict that the perpendicular geometry would have a frequency in the region of 1500–1600 cm^{-1}, while the singlet bent state would be in the 1230–1300 cm^{-1} range, with the triplet state of a similar magnitude but at a lower frequency.

We can also comment on the α_1 and α_2 species. One speculation is that these arise from adsorption onto different sites.[8] However, identification of three different candidates for the α state provide the alternative possibility that differences in geometry or spin are responsible for the differing behaviors.

V. CONCLUSIONS

Using theoretical methods of density functional theory we have found six different stable configurations of O_2 within a defect of the $TiO_2(110)$ surface. One of these, a singlet state parallel to the surface has been identified as the β state described by Yates *et al.*[5,6] Two other states have been discounted as playing a significant role in surface chemistry. The three remaining states each have one oxygen atom closer to the surface than the other, and are suggested to be possible candidates for the α_1 and α_2 states.[8]

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