Quantum study of the active sites of the $\gamma$-alumina surface: chemisorption and adsorption of water, hydrogen sulfide and carbon monoxide on aluminum and oxygen sites

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Abstract

In this work, we have performed quantum calculations, using cluster models, in order to study the reactivity of the aluminum and oxygen sites of the $\gamma$-alumina surface. Water, hydrogen sulfide and carbon monoxide molecules are employed as the test molecules for our cluster models. It is found that the tricoordinated aluminum sites of the surface are the dissociative sites for the water and the hydrogen sulfide molecules. The tetracoordinated aluminum sites are the non-dissociative adsorption sites for the water molecule, whereas they are the dissociative sites for the hydrogen sulfide molecule. The pentacoordinated aluminum sites are the non-dissociative sites for the water and the hydrogen sulfide molecules. On the aluminum sites, carbon monoxide is preferentially adsorbed via its carbon atom. In contrast to the aluminum sites, the oxygen sites of the alumina surface are not adsorption sites for water, hydrogen sulfide and carbon monoxide molecules. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The $\alpha$, $\theta$ and $\gamma$ forms are the most important crystallographic forms of alumina [1]. $\gamma$-Alumina is widely used as an acid–base catalyst and as a catalyst carrier. In particular, $\gamma$-alumina is used to support the transition metal sulfides that catalyze the hydrodesulfurization reactions in the petroleum industry [2]. $\gamma$-Alumina has a spinel-like structure [3]. Aluminum atoms occupy 10% of the tetrahedral sites and 46.7% of the octahedral sites formed by the cubic close-packed array of oxygen atoms, the other tetrahedral and octahedral sites remain unoccupied [4]. The (110) and (100) planes are supposed to be the most catalytically active [5]. Both aluminum and oxygen atoms are present on these planes; aluminum atoms are Lewis acid sites whereas the oxygen atoms are basic sites.

When the bulk of $\gamma$-alumina is cut along the (110) direction, two kinds of layers are found: on the C layer (Fig. 1(a)), the aluminum atoms are tricoordinated or tetracoordinated and the oxygen atoms are tricoordinated; on the D layer (Fig. 1(b)), the aluminum atoms are tetracoordinated and the oxygen atoms are tricoordinated. The A and the B layers are related to the...
surface that is not a catalytically active surface of $\gamma$-alumina [5].

When the bulk of $\gamma$-alumina is cut along the (100) direction (Fig. 1(c)), only one type of layer is defined where the aluminum atoms are pentacoordinated and the oxygen atoms are tricoordinated.

The molecular dynamics simulations of $\gamma$-alumina have shown that the bulk structure was well organized whereas a lot of defects were present on the surface [6,7]. In these simulations, hexacoordinated and heptacoordinated aluminum atoms are found on the surface. This result shows that the surface structures represented in Fig. 1 are the ideal cases. Since we do not know the position and the nature of the defaults that are present on the surface, we use the structural features extracted from the ideal surface plane as the starting point for our work.

Experimentally, the surface properties of $\gamma$-alumina have been studied by calorimetric and spectrometric methods. These works are related to the study of the adsorption of molecules such as water, hydrogen sulfide, hydrogen and carbon monoxide on the $\gamma$-alumina surface [8–11].

Numerous theoretical works have focused on the reactivity of the aluminum sites of the $\gamma$-alumina surface. Hirva et al. [12] performed ab initio Hartree–Fock (HF) calculations to study the adsorption of water, ammonia and pyridine molecules. Lindblad et al. [13] performed pseudopotentials HF calculations to study the adsorption of water and hydrogen chloride. Neyman et al. [14] performed density functional calculations to study the adsorption of carbon monoxide. Fleicher et al. [15] using HF semi-empirical method, and more recently Tachikawa et al. [16] using the ab initio HF method, characterized the Lewis acidity of the aluminum atoms by calculating their Mulliken atomic charges and the energy levels of the lowest unoccupied molecular orbitals of cluster models.

Hass et al. [17] focused on the dynamics of the adsorption and on the dissociation of water on the (111) surface plane of $\gamma$-alumina. Only aluminum atoms lie in this plane which are supposed to be more stable. Allowing the relaxation of the first four layers of the (111) surface plane, the authors have shown that the relaxation energy was important and that a water molecule previously adsorbed on the surface can induce and catalyze the dissociation of a second molecule on the surface. The use of quantum molecular dynamics simulations seems, for the authors, the only way to anticipate properly the surface chemistry of this material.

The effect of the surrounding of sites on the Brønsted acidity of surface hydroxyl groups of the $\gamma$-alumina surface has also been studied [18,19].

It has been shown, both experimentally [8–11] and
theoretically [12–18], that the tricoordinated aluminum atoms of the alumina surface are stronger Lewis acids than the pentacoordinated aluminum atoms of the surface. The Lewis acidity of tetracoordinated aluminum atoms has attracted less attention in the literature [13–20]. The aim of this work is twofold:

1. to build cluster models simulating the aluminum and the oxygen surface sites of alumina; and
2. to test our cluster models and the method that we have used by studying the adsorption of some model molecules.

In our work, we focused on the adsorption of water (H$_2$O), hydrogen sulfide (H$_2$S) and carbon monoxide molecules (CO) on the aluminum and the oxygen sites of the alumina surface using quantum calculations. Finally, we shall compare our results with the theoretical and the experimental data of the literature. Our final goal in the near future will be to study the

![Fig. 2. T3 cluster model of a tricoordinated aluminum site of the C layer of the (110) perfect surface (c); (b) O4 cluster model of a tetracoordinated aluminum site of the D layer of the (110) perfect surface; and (a) O5 cluster model of a pentacoordinated aluminum site of the (100) perfect surface.](image)
adsorption of more complex systems with the alumina surface sites.

The paper is organized as follows: the construction of the aluminum site clusters, the oxygen site clusters and the computational method are presented in Sections 2 and 3; Section 4 is related to the theoretical study of the adsorption of the molecules that we have selected, on the active sites of the clusters presented in Section 2. Finally, Section 4 includes an analysis and a comparative study of the results.

2. Cluster models

The reactivity of the surfaces of solids can be studied through different approaches. Periodical approaches (Periodic Hartree–Fock [21], ab initio quantum mechanical Molecular Dynamics [22–25]) are best suited to the study of the solid state because they take into account the whole surface structure of the solid. But they entail the use of large unit cells whenever local properties such as defect sites, adsorption and chemisorption are being considered.
An alternative approach widely used is the embedded cluster method. In general, the cluster is embedded in point-charges [26] and Total Ion Potential (TIP) [27] lattice recreating the Madelung potential. In the case of γ-alumina, the spectroscopic (X-ray) methods [4] and the molecular dynamics studies [6,7] have shown that a large number of defects are found on the alumina surface, which is therefore disordered. Consequently, to be consistent with the real structure of the γ-alumina surface, one should reproduce a Madelung potential corresponding to a point-charge distribution in which the lattice positions would be a priori unknown. Moreover, as γ-alumina is not a pure ionic material, the physical concept of point-charges is less straightforward. This point will be discussed later in Section 4.1.1. Because of these points, in most of the works related to the study of the γ-alumina surface [12–16,18,19], the Madelung potential is neglected.

A limited number of atoms are used to simulate the different aluminum surface sites of the alumina surface. The geometrical parameters are derived from the structure of the perfect crystal. When the aluminum atom is in a tetrahedral site, the Al–O bond length is 1.71 Å and when the aluminum atom is in an octahedral site, the Al–O bond length is 1.95 Å. Since γ-alumina is known to be a partially covalent crystal, hydrogen atoms are used to saturate the dangling bonds. This method is often applied in the case of covalent solids [26]. The OH bond length is 0.96 Å which is the OH bond length in the water molecule. Besides, the hydrogen atoms saturate the terminal aluminum atoms in order to make them trivalent. Since the aluminum atom has three electrons on its valence shell, we reproduce here the natural valence of the aluminum atom. The Al–H bond length is 1.53 Å which is the sum of the covalent radii of the aluminum and the hydrogen atoms [28]. When built like this, these clusters have an even number of electrons and are considered as the closed shell systems. We have constructed three clusters modeling the three types of aluminum sites of the alumina surface.

The O5 cluster model represents a pentacoordinated aluminum site extracted from the D layer of the (110) surface (Fig. 2(b)). O4 reproduces the O–Al–O design of the D layer. And finally, the T3 cluster model (Fig. 2(c)) represents a tricoordinated aluminum site extracted from the C layer of the (110) surface. In its center, T3 has a part of the typical furrow of the C layer in the (110) surface.

As the aluminum site clusters, the oxygen site clusters are extracted from the surface structure. The dangling bonds are saturated in order to reproduce the atomic environment of the atoms on the surface. We have built five clusters to model the five oxygen sites of the perfect surface planes of γ-alumina. These five clusters will be named according to the classification of Knözinger et al. [5]. The IIa cluster represents a bicoordinated oxygen site from the D layer of the (110) surface plane (Fig. 3(a)). The IIIa(100) cluster represents a tricoordinated oxygen site of the (100) surface plane (Fig. 3(b)). The IIIa(110) cluster represents a tricoordinated oxygen site from the C layer of the (110) surface plane (Fig. 3(c)). The IIIb(100) cluster represents a tricoordinated oxygen site of the (100) surface plane (Fig. 3(d)) and finally, the IIIb(110) cluster represents a tricoordinated oxygen site from the D layer of the (110) surface plane (Fig. 3(e)).

3. Computational details

The calculations were performed with the Gaussian 94 [29] computational package within the Hartree–Fock (HF) [30] approximation and the density functional theory (DFT) [31]. The B3LYP hybrid functional is used in DFT calculations [32]. The 6-31G(d) split valence basis set [33,34], augmented with polarization functions on heavy atoms, was used for every atom of the clusters and of the studied molecules. The geometrical parameters of the clusters are set to the values of the perfect crystal parameters during the adsorption of molecules. We will show in Section 4.1.1 that partial relaxation of one of our models does not significantly change the adsorption energy and the geometry of the adsorbed molecule. The adsorption energies calculated at the B3LYP/6-31G(d)//HF/6-31G(d) levels are corrected from the basis set superposition error.
using the usual counterpoise method of Boys and Bernardi [35]. The B3LYP/6-31G(d)//HF/6-31G(d) notation means that the B3LYP adsorption energy is calculated for the HF optimized geometry. Many optimized geometries other than that presented in this work were investigated during the exploratory part of this work. We selected only the structures with the largest adsorption or dissociation energy.

We have used the 6-31G(d) basis set in our B3LYP calculations because this basis has already yielded successful results for similar systems like α-alumina [36] and zeolites [37]. It is well known that the B3LYP hybrid functional yields results that are similar to MP2 results as well in the case of weak interaction [38] as for stronger interaction like chemisorption [36]. Further, the size of the calculations in DFT methods are smaller than the size of the calculations related to the usual post-HF methods like Møller–Plesset or configuration interaction methods.

The adsorption energy ($\Delta E_{\text{ads}}$), when the molecules are molecularly adsorbed, is calculated as follows:

$$\Delta E_{\text{ads}} = E(\text{molecule} + \text{cluster}) - E_{\text{BSSE}}(\text{molecule}) - E_{\text{BSSE}}(\text{cluster})$$

$E(\text{molecule} + \text{cluster})$ refers to the energy of the complex that is formed by the adsorbed molecule and the cluster. $E_{\text{BSSE}}(\text{molecule})$ and $E_{\text{BSSE}}(\text{cluster})$ are, respectively, the molecule and the cluster energy, calculated using the full basis set of the molecule and the cluster. A negative energy corresponds to a stable admolecule-cluster system.

In the case of chemisorption, when the molecule is spontaneously dissociated on the cluster, the dissociation energy ($\Delta E_{\text{diss}}$) is defined as follows:

$$\Delta E_{\text{diss}} = E(\text{dissociated molecule} + \text{cluster}) - E(\text{molecule}) - E(\text{cluster})$$

$E(\text{dissociated molecule} + \text{cluster})$ refers to the energy of the system formed by the dissociated molecule and the cluster. $E(\text{molecule})$ refers to the energy of the isolated molecule in its optimized geometry and $E(\text{cluster})$ refers to the isolated cluster energy.

4. Results and discussion

4.1. Aluminum surface sites

4.1.1. Chemisorption and adsorption of H$_2$O

Alike other oxides, if alumina is vacuum-deshydroxylated at a high temperature, then the surface adsorbs water in two forms; either the water is molecularly adsorbed or the water is dissociatively adsorbed. As water molecule is a Lewis base, it will react through its oxygen’s lone pairs of electrons with the aluminum surface sites that are Lewis acids. From the microcalorimetric measures, Hendriksen et al. [8] determined that the dissociation energy of water on γ-alumina was $\sim 190$ kJ/mol. However, it must be noticed that this value is the result of contributions from various sites and of the surface defects, whereas our value is related to a unique well-defined site of the perfect surface.

In order to check our method, we have performed some test calculations on the O5 cluster model related to the relaxation of the cluster model during the adsorption of the admolecule and related to the method used for the optimization procedure (HF or B3LYP).

Hass et al. [17] have shown in their quantum dynamics molecular study of the adsorption and the dissociation process of water on α-alumina that the relaxation of the alumina surface was important. This result was obtained by relaxing the four layers of the atoms of alumina. In our case, the size of the cluster is limited and the bonds cut to extract the cluster from the surface are terminated by hydrogen atoms to saturate the dangling bond. Thus the total relaxation of the cluster would concern those atoms that are not the atoms of the alumina surface. Then the constraints of the surface structure would not be reproduced during the relaxation procedure. Consequently, on our cluster model, it is more suitable to relax only the aluminum atom of the cluster center, which is surrounded by five oxygen atoms that has the same environment as that in the surface plane.

The partial relaxation of the O5 cluster during adsorption leads to the molecular adsorption of the water molecule. We have tried several starting positions of the water molecule (with hydrogen atoms down towards the cluster, with the symmetry plane of the molecule flat to the cluster atoms, etc.) and
we report here the final geometry related to the deeper minimums. The B3LYP adsorption energy related to this structure is equal to \(-110\) kJ/mol (Table 1). This value is smaller than the experimental value determined by Hendriksen et al. [8] related to the dissociation of water on \(\gamma\)-alumina. The pentacoordinated aluminum site must be considered as the non-dissociative site of the surface.

Fig. 4(a) shows the geometry of the water molecule adsorbed on the O5 cluster obtained at the HF level. The water molecule is perpendicular to the symmetry plane of the cluster. The O1–Al distance between the oxygen atom of the water molecule and the pentacoordinated aluminum atom of the cluster is equal to 2.05 Å. The O–H bonds of the water molecule are eclipsed with the Al–O bonds of the cluster. The Al–O2 bond length of the partially relaxed O5 cluster is equal to 1.84 Å whereas the Al–O2 bond length in the non-relaxed O5 cluster is equal to 1.95 Å. Then, after the relaxation of the O5 cluster during the adsorption of the water molecule, the aluminum atom underpenetrates the plane of the four oxygen

\[
\begin{align*}
\Delta E_{\text{ads}} (\text{kJ/mol}) & \quad \text{With cluster relaxation} \quad \text{Without cluster relaxation} \\
& \quad \text{HF optimization} \quad \text{B3LYP optimization} \quad \text{HF optimization} \quad \text{B3LYP optimization} \\
R_{\text{Al–O2}} (\text{Å}) & \quad 1.84 \quad 1.86 \quad 1.95 \quad 1.95 \\
R_{\text{O1–Al}} (\text{Å}) & \quad 2.05 \quad 2.04 \quad 1.96 \quad 1.98 \\
R_{\text{O1–H}} (\text{Å}) & \quad 0.96 \quad 0.96 \quad 0.96 \quad 0.98 \\
\text{HO1H (°)} & \quad 108 \quad 108 \quad 109 \quad 109 \\
\end{align*}
\]

Table 1
Adsorption energy (kJ/mol) of the water molecule on the pentacoordinated aluminum atom of the O5 cluster with and without the partial relaxation of the cluster. \(R_{\text{Al–O2}} (\text{Å})\) is the distance between the pentacoordinated aluminum atom and the oxygen atom in the cluster, \(R_{\text{O1–Al}} (\text{Å})\) is the distance between the oxygen atom of the water molecule and the pentacoordinated aluminum atom of the cluster. \(R_{\text{O1–H}} (\text{Å})\) and \(\text{HO1H (°)}\) are, respectively, the OH bond length and the HOH valence angle of the adsorbed water molecule.

Fig. 4. Adsorbed water molecule on the O5 cluster: (a) HF optimization with partial cluster relaxation; (b) B3LYP optimization with partial cluster relaxation; (c) HF optimization without partial relaxation of the cluster; and (d) B3LYP optimization without partial optimization of the cluster.
of the cluster. The O–H bond length and the H–O–H angle of the adsorbed water molecule on the O5 cluster are, respectively, equal to 0.96 Å and 108°. The O–H bond length and the H–O–H angle of the isolated water molecule in gas phase are, respectively, equal to 0.95 Å and 105°. The adsorption of water on the O5 cluster does not perturb the chemical bonding inside the water molecule.

The charge transfer between the water molecule and the cluster is calculated as the difference of the Mulliken atomic charges of the water molecule before and after the adsorption on the cluster. The charge transfer from the water molecule to the O5 cluster is equal to 0.27 electron. This result shows that the aluminum atom acts as a Lewis acid in alumina.

Also, we have performed the adsorption of the water molecule with the partial relaxation of the O5 cluster done within the B3LYP hybrid functional. The adsorption energy is equal to −127 kJ/mol whereas when the relaxation is done at the HF level the adsorption energy is equal to −110 kJ/mol. Then, in the case of the partial relaxation of the cluster during the water adsorption, the HF and the B3LYP calculations lead to the same results.

Fig. 4(b) shows the geometry of the adsorbed water molecule on the O5 cluster. One can notice that the geometries obtained at the HF level (Fig. 4(a)) and with the B3LYP hybrid functional (Fig. 4(b)) are similar. The O1–Al bond length between the oxygen atom of the water molecule and the pentacoordinated aluminum atom of the cluster is equal to 2.04 Å and the Al–O2 bond length of the partially relaxed O5 cluster is equal to 1.86 Å. Then, the adsorption of the water molecules performed with the optimization procedure at the HF and B3LYP level lead to the same results. The Al–O2 distance in the cluster is 5% smaller than in the perfect cluster structure.

We have also studied the adsorption of the water molecule fixing the geometrical parameters of the cluster during the adsorption of the water molecule. The B3LYP adsorption energy is equal to −127 kJ/mol when the optimization is done at the HF level and −126 kJ/mol when the optimization is done within the B3LYP functional (Table 1). The optimized structure of the water molecule on the O5 cluster obtained at the HF level and obtained at the B3LYP level are, respectively, shown in Fig. 4(c) and (d). The water molecule is molecularly adsorbed in a plane perpendicular to the symmetry plane of the cluster. The main difference in comparison with the geometry optimized with the partial relaxation of the cluster is the O1–Al distance between the oxygen atom of the water molecule and the pentacoordinated aluminum atom of the cluster (1.96 Å for the HF optimization and 1.98 Å for the B3LYP optimization). The aluminum atom in a non-relaxed cluster is more accessible for the oxygen atom of the water molecule than in the partially relaxed cluster because this atom is in the same plane as the four oxygen atoms, whereas when the cluster is partially relaxed during the adsorption, it goes down under the plane of the four oxygen atoms. Consequently, the values of the adsorption energy related to the non-relaxed cluster are smaller than the values of the energies related to the relaxed cluster. However, the difference between the adsorption energy calculated with and without the partial relaxation of the cluster is in the order of magnitude of the error induced by our approximations.

Consequently, as the B3LYP optimization needs more computational time than the HF optimization, and as the partial relaxation of the cluster does not change significantly the results of the adsorption, in the following structures will be optimized at the HF level and the adsorption

<table>
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<th>H2O</th>
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<th>CO</th>
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<tr>
<td>O5</td>
<td>−127 (adsorption)</td>
<td>−62 (adsorption)</td>
<td>−35</td>
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<tr>
<td>O4</td>
<td>−154 (adsorption)</td>
<td>−147 (dissociation)</td>
<td>−58</td>
</tr>
<tr>
<td>T3</td>
<td>−190 (dissociation)</td>
<td>−110 (dissociation)</td>
<td>−43</td>
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Table 2
Dissociation and adsorption energies (kJ/mol) of the water, hydrogen sulfide and carbon monoxide molecule on the pentacoordinated aluminum site of the O5 cluster (Fig. 2(a)), on the tetracoordinated aluminum site of the O4 cluster (Fig. 2(b)) and on the tricoordinated aluminum site of the T3 cluster (Fig. 2(c)).
energies will be computed within the B3LYP functional.

As on the pentacoordinated aluminum atom of the O5 cluster model, on the tetracoordinated aluminum atom of the O4 cluster the water molecule is molecularly adsorbed. The adsorption energy is equal to $-154$ kJ/mol (Table 2). This value is smaller than the experimental value of Hendriksen et al. [8]. The tetracoordinated aluminum site of the surface must be considered as the non-dissociative adsorption site. The optimized structure of the water molecule adsorbed on the tetracoordinated aluminum atom is shown in Fig. 5(b). The water molecule is situated in the symmetry plane of the cluster with its oxygen atom above the aluminum atom. The Al–O distance between the tetracoordinated aluminum atom and the water oxygen atom is 1.87 Å. This distance, smaller than the Al–O distance between the pentacoordinated aluminum atom of the O5 cluster and the oxygen atom of the water molecule, corresponds to a higher interaction energy.

In comparison with the geometrical parameters of the isolated molecule, the geometrical parameters of the adsorbed molecule on the O4 cluster change only very slightly. The OH bond lengths of the adsorbed molecule is equal to 0.96 Å and the H–O–H angle is equal to 114°. However, the H–O–H bond angle of the adsorbed molecule is 9° greater than the isolated molecule. This difference results from the electrostatic interactions between the hydrogen atoms of the water molecule and the oxygen atoms of the cluster.

The charge transfer is found to be 0.32 electron. This positive result indicates that the charge transfer develops from the water molecule towards the cluster. This result agrees with the Lewis acidic nature of the aluminum atom.

On the tricoordinated aluminum atom of the T3 cluster, the water molecule is spontaneously dissociated (Fig. 5(c)). The dissociation energy is equal to $-190$ kJ/mol (Table 2). The value that we have calculated ($-190$ kJ/mol) is in very good agreement with the experimental value determined by Hendriksen et al. [8] ($-190$ kJ/mol), even if the exact coincidence between the two numerical values has no intrinsic significance.

Our calculated value is much smaller than those of Sanz et al. [20] who performed an HF ab initio embedded cluster (Al$_{12}$O$_5$) calculation. This dissociation energy on the same type of aluminum site is found to be $-564$ kJ/mol. However, these authors have used a smaller basis set than ours (the (9s5p)/(4s3p) basis set for oxygen atoms [39,40] and the (7s4p/4s2p) basis set for the aluminum atoms [41]), but this cannot account for the difference. The discrepancy is more probably due to the model they used. Their embedded cluster represents a purely ionic solid whereas ours is a mixed ionic-covalent model more adapted to the physical properties of γ-alumina. Consequently, in the case of γ-alumina, it is more appropriate to use a non-embedding method.

The dissociation of the water molecule produces the bonding of an OH group on the tricoordinated...
aluminum atom and the protonation of an oxygen atom not directly bound to the Al center (Fig. 5(c)). The Al–O distance between the tricoordinated aluminum atom and the oxygen atom of the OH group is 1.74 Å. This distance, close to the Al–O distance in γ-alumina, shows that a covalent bond is created. Then, the aluminum atom is in a tetrahedral surrounding.

The B3LYP dissociation energy of the water molecule on the tricoordinated aluminum site of the T3 cluster (−190 kJ/mol) is in good agreement with the experimental value. The tricoordinated aluminum site must be considered as a chemisorption site of the alumina surface.

The B3LYP adsorption energy related to the adsorption of the water molecule on the tetracoordinated aluminum (−154 kJ/mol) and the adsorption energy related to the adsorption of the water molecule on the pentacoordinated aluminum site (−126 kJ/mol) are lower than the experimental values. Therefore, the tetracoordinated aluminum sites and the pentacoordinated aluminum sites must be considered as non-dissociative adsorption sites.

4.1.2. Chemisorption and adsorption of H₂S

Water molecules and hydrogen sulfide molecules are simultaneously present during the hydrodesulfurization reaction of hydrocarbons in petroleum industry. Both the water molecule and the hydrogen sulfide molecule are polar molecules, but the dipole moment of the water molecule is larger than the dipole moment of the hydrogen sulfide molecule. Similar to the water molecule, the hydrogen sulfide molecule reacts with the aluminum atoms of the alumina surface through its sulfur lone pairs of electrons. The hydrogen sulfide molecule is also a Lewis base. Meyer et al. [9] have determined during a microcalorimetric study that the dissociation energy of H₂S on alumina was equal to −120 kJ/mol. As for the water molecule, this value is the result of the contribution of the different surface sites of γ-alumina.

On the pentacoordinated aluminum site of the O5 cluster, H₂S is molecularly adsorbed (Fig. 6(a)). The adsorption energy is equal to −62 kJ/mol (Table 2). The adsorption energy of the hydrogen sulfide molecule on the pentacoordinated aluminum atom of the O5 cluster (−62 kJ/mol) is lower than the experimental value (−120 kJ/mol) which is related to the dissociative surface sites. The pentacoordinated aluminum sites must be considered as a non-dissociative adsorption site.

The plane of the adsorbed H₂S molecule is perpendicular to the symmetry plane of the O5 cluster. The S–H bonds of the hydrogen sulfide molecule are eclipsed with the Al–O bond of the cluster. The Al–S distance is equal to 2.55 Å.

As for the adsorption of the water molecule on the O5 cluster, the geometrical parameters of the isolated hydrogen sulfide molecule are similar to the geometrical parameters of the adsorbed hydrogen sulfide.

![Fig. 6. (a) Adsorbed hydrogen sulfide molecule on the pentacoordinated aluminum atom of the O5 cluster; (b) dissociated hydrogen sulfide molecule on the tetracoordinated aluminum atom of the O4 cluster; and (c) dissociated hydrogen sulfide molecule on the tricoordinated aluminum atom of the T3 cluster.](image-url)
molecule. The S–H bond length and the H–S–H angle of the adsorbed hydrogen sulfide molecules are, respectively, equal to 1.33 Å and 96° and the S–H bond length and the H–S–H angle of the isolated hydrogen sulfide molecule in gas phase are, respectively, equal to 1.33 Å and 94°. The adsorption does not significantly impact the geometry of the H₂S molecule.

The charge transfer from the H₂S molecule towards the cluster is equal to 0.22 electron, which is consistent with the Lewis acid nature of the pentacoordinated aluminum atom of the cluster.

On the tetracoordinated aluminum atom of the O4 cluster, the H₂S molecule is spontaneously dissociated (Fig. 6(b)). The dissociation energy is equal to −147 kJ/mol (Table 2). The dissociation energies that we have calculated with respect to the dissociation of H₂S on the O4 cluster (−147 kJ/mol) is in the same order of magnitude of the experimental results of Meyer et al. [9]. In contrast to the water molecule, the tetracoordinated aluminum sites of the O4 cluster must be considered as the dissociative sites of the alumina surface for the hydrogen sulfide molecule.

When the H₂S molecule is dissociated in the S–Al–O2 plane (Fig. 5(b)), an oxygen atom directly bound to the Al center is protonated. The Al–S bond length is equal to 2.22 Å. This value is consistent with 2.29 Å, which is the sum of the covalent radii of the aluminum atom and the sulfur atom [28], and indicates that a covalent bond is created between the aluminum atom and the sulfur atom.

As for the O4 cluster, the H₂S molecule is spontaneously dissociated on the tricoordinated aluminum atom of the T3 cluster (Fig. 6(c)). The dissociation energy is equal to −110 kJ/mol (Table 2). The dissociation energies that we have calculated with respect to the dissociation of H₂S on the T3 cluster (−110 kJ/mol) are in good agreement with the experimental result of Meyer et al. [9]. The tricoordinated aluminum sites of the γ-alumina surface must be considered as the dissociative sites for the hydrogen sulfide molecule. The dissociation of the H₂S molecule produces the bonding of an SH group on the tricoordinated aluminum atom of the T3 cluster and the protonation of an oxygen atom of the cluster not directly bound to the Al center. The Al–S bond length is found to be 2.25 Å. As for the O4 cluster, a covalent bond is created between the sulfur atom of the SH group and the tricoordinated aluminum atom of the cluster.

For the hydrogen sulfide molecule, the pentacoordinated aluminum sites are the adsorption sites, whereas the tetracoordinated and the tricoordinated aluminum sites are the dissociative sites of the γ-alumina surface.

4.1.3. Adsorption of CO

The CO molecule is usually considered experimentally and theoretically as a probe molecule for the surface study of many materials [42,43]. In quantum calculations, the CO molecule is interesting because its interactions with the substrates are very subtle mainly because its dipole moment is weak [44]. We
study the adsorption of the CO molecule with the aluminum atom sites considering the Al–CO orientation and the Al–OC orientation in order to compare the effect of the CO orientation on the adsorption energy and to evaluate the limits of our model. The experimental adsorption energies of CO on alumina vary from $-53$ to $-20$ kJ/mol [11]. Because of the weak interaction between carbon monoxide and alumina, and the number of different surface sites, including the defaults, it is not experimentally possible to assign the adsorption energy to the different surface sites.

For all of our cluster models, the C-down orientation was always preferred in opposition to the O-down orientation in agreement with the experimental observations of Zecchina et al. [45]. In the same manner, the interaction of carbon monoxide through its $\pi$-system does not yield to stable structures.

On the pentacoordinated aluminum atom of the O5 cluster, CO is vertically adsorbed in the symmetry plane of the cluster (Fig. 7(a)). The distance between the carbon atom of the carbon monoxide molecule and the pentacoordinated aluminum atom of the O5 cluster is equal to 2.27 Å. This distance is longer than 2.02 Å which is the sum of the covalent radii of the aluminum atom and the carbon atom. The C–O bond length of the adsorbed carbon monoxide molecule and the C–O bond length of the isolated carbon monoxide molecule in gas phase are, respectively, equal to 1.10 Å and 1.11 Å. The adsorption does not perturb the chemical bonding of the carbon monoxide molecule. This result shows that the interaction between carbon monoxide and alumina is weak. This is consistent with the adsorption energy which is equal to $-43$ kJ/mol (Table 2).

On the O4 cluster, the adsorbed CO molecule is situated in the symmetry plane of the cluster (Fig. 7(b)). The distance between the carbon atom of the carbon monoxide molecule and the tetracoordinated aluminum atom of the O5 cluster is equal to 2.15 Å. The C–O bond length is equal to 1.11 Å. The adsorption energy of the carbon monoxide on the O4 cluster is equal to $-58$ kJ/mol (Table 2). As for the adsorption on the pentacoordinated aluminum atom of the O5 cluster, the CO molecule is unperturbed by the adsorption on the tetracoordinated aluminum atom of the O4 cluster.

In all cases, the CO bond length of the adsorbed molecule and the CO bond length of the isolated molecule are very similar. These results show that the CO molecule is rather unperturbed by the adsorption and that the interaction between the carbon monoxide molecule and alumina is weak.

In our work, the adsorption energies calculated are in the same order of magnitude of the experimental results and are closed to each other (Table 1).

### 4.2. Oxygen surface sites

#### 4.2.1. Deprotonation of oxygen surface sites

Numerous theoretical works are related to the study of the Brønsted acidity of oxide surfaces [18,19,46]. It was, therefore, quite natural that we should test our clusters by calculating the deprotonation energy of the oxygen surface sites. The deprotonation energy (ΔDPE) is the amount of energy required to segregate a proton from an oxygen atom.

The ΔDPEs that we have calculated are large and
positive (Table 3). The deprotonation reaction is an endothermic process; the protons are strongly bound to the oxygen sites. The lowest ΔDPEs are related to the deprotonation of the tricoordinated oxygen atoms (Type III). As a consequence, the protons bound to the tricoordinated oxygen atoms are the most acidic ones. In fact, the aluminum atoms bound to the oxygen atom polarize the OH bond and consequently, the more the oxygen atom is bound to aluminum atoms the more the OH bond will be polarized and accordingly the acidity will increase [46]. In the case of δ-alumina, Nortier et al. [46] found deprotonation energies ranging from 1423 to 1541 kJ/mol. As in γ-alumina, the aluminum atoms in δ-alumina are located in the tetrahedral and octahedral sites formed by the oxygen lattice. The ΔDPEs that we have calculated are in the same order of magnitude (Table 3). The Brønsted acidity of the γ- and δ-alumina are similar.

4.2.2. H₂O, H₂S and CO adsorption on oxygen surface sites

Several attempts to adsorb the water molecule and the hydrogen sulfide molecule through their hydrogen atoms and the carbon monoxide molecule on the different oxygen site clusters did not materialize in stable structures.

In the case of the adsorption of the water molecule and the hydrogen sulfide molecule, the interactions of the hydrogen atoms of the molecules and the oxygen atom sites are not strong enough to lead to stable structures in comparison with the interactions between the oxygen atoms or the sulfur atom of the molecules with the aluminum sites. The aluminum atoms of the alumina surface are the active center of the surface.

The CO molecule is a nucleophilic molecule as the oxygen atoms of the clusters. The interaction of the CO molecule with the oxygen atoms is repulsive. Consequently, no stable structure is observed.

5. Conclusion

The relaxation of the cluster during the adsorption does not significantly affect the adsorption scheme of the water molecule on the O5 cluster. In this work, we show that the use of non-ionic cluster models satisfactorily reproduce the chemistry of γ-alumina surface sites. The B3LYP/6-31G(d)//HF/6-31G(d) method leads to structures and energies almost identical to the direct optimization at the B3LYP level, whereas the computational effort is noticeably reduced. The aluminum surface sites of γ-alumina dissociate H₂S more easily than the H₂O molecule. This result agrees with the experimental dissociation energy of the SH bond (344 kJ/mol) and of the OH bond (427 kJ/mol) [28]. Water interacts more potently than hydrogen sulfide with the Lewis acid sites of alumina. Our results are in good agreement with those of Fhami et al. [47] and Casarin et al. [48] who have found that water was adsorbed twice more strongly on titanium atoms than was hydrogen sulfide on titanium dioxide.

In contrast to Pacchioni et al. [49] who have found that on MgO both the Mg–CO and the Mg–OC orientations were energetically similar, we have found that on the aluminum surface sites of γ-alumina, the Al–CO orientation is always preferred. This result can be related to the more Lewis acidic nature of the aluminum atom than the magnesium atom. The same results are found by Fahmi et al. [43] concerning CO adsorption on titanium dioxide.

The oxygen sites of the γ-alumina surface are not the adsorption sites for the water, hydrogen sulfide and CO molecules. This result agrees with the works of Ferro et al. [50], who have found that the magnesium atoms are the reactive sites of MgO.

The aluminum surface sites can be split into two classes. The first class consists of the aluminum dissociation sites: the tricoordinated and the tetracoordinated aluminum sites that are present on the (110) surface. The second class consists of the adsorption aluminum sites, the pentacoordinated aluminum sites that are present on the (100) surface. It seems that the (110) surface planes are the most active planes of the γ-alumina surface. These results will be useful in the near future, as we intend to study the reactive adsorption of more complex molecules on the same substrate.

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