Adsorption of Methanol on Aluminum Oxide:
A Density Functional Study

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Abstract

Theoretical calculations based on density functional theory have made significant contributions to our understanding of metal oxides, their surfaces, and the binding of molecules at these surfaces. In this paper we investigate the binding of methanol at the $\alpha$-Al$_2$O$_3$(0001) surface using first-principles density functional theory. We calculate the molecular adsorption energy of methanol to be $E_{\text{ads}}^g = 1.03$ eV/molecule. Taking the methanol-methanol interaction into account, we obtain the adsorption energy $E_{\text{ads}} = 1.01$ eV/molecule. Our calculations indicate that methanol adsorbs chemically by donating electron charge from the methanol oxygen to the surface aluminum. We find that the surface atomic structure changes upon adsorption, most notably the spacing between the outermost Al and O layers changes from 0.11 Å to 0.33 Å.

Keywords: Aluminum oxide, alumina, methanol, first-principles calculations, surface, adsorption.

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1 Introduction

Today, adhesively bonded and coated aluminum structures find a range of technological applications. Understanding the factors affecting the adhesion properties of oxide covered aluminum surfaces is important for controlling the long term performance and durability of these structures. One such factor is the nature and strength of the interfacial bonds between the resins of the adhesive or coating and the substrate. Despite their technological relevance, the understanding of metal oxide surfaces in general is at a far less advanced level than most other solid surfaces. Experimental studies face complications in preparing the nearly perfect, clean surfaces needed for atomic scale surface investigations, and by the sheer complexity of the crystal and electronic structures. Theoretical studies have been impeded by the limited experimental data available for guidelines and the complexity of the oxide structures.

In this paper we present a theoretical investigation of methanol (CH$_3$OH) adsorption on clean α-Al$_2$O$_3$(0001). The choice of methanol and α-Al$_2$O$_3$(0001) is motivated by the desire to contribute to a more fundamental understanding of adhesion of organic coatings or adhesives at oxide-covered aluminum surfaces. Because of the size and chemical complexity of the binders found in coatings and adhesives, the interpretation of the adhesion mechanism can be difficult. One strategy to simplify the analysis is to study the interaction of smaller molecules (representative of the various components of the binder) with the surface. Following this approach, we will address the binding properties of the different functional groups separately.

Methanol is a good starting point for such studies as it is the smallest organic molecule with a hydroxyl group, and because it is well characterized both experimentally and theoretically. In addition to the thermodynamically stable α phase, Alumina (Al$_2$O$_3$) has a number of metastable bulk phases (γ, η, θ, κ, . . .), some being stable up to rather high temperatures. Unlike most of the metastable aluminas (the exceptions are the θ and κ phases), the atomic structure of α-Al$_2$O$_3$
and its (0001) surface is agreed upon, and therefore represents an ideal starting point for theoretical studies of adsorption on alumina surfaces. The adsorption of methanol has been studied experimentally and theoretically on a range of metal oxides, e.g., Cr₂O₃, ZrO₂, and TiO₂, but to our knowledge only one theoretical and few experimental investigations of methanol adsorption on Al₂O₃ have appeared in the literature.

Water, which also has an OH-group, has been shown to adsorb both as a molecule and dissociatively on α-Al₂O₃. It is therefore of interest to study both molecular and dissociative adsorption of methanol. In the present study our focus is on molecular adsorption on the clean and perfect (no steps or defects) (0001)-surface of α-Al₂O₃. The effect of preadsorbed hydroxyl groups and the dissociative methanol adsorption will be subject of a future study.

2 Density Functional Theory Calculations

Bulk α-Al₂O₃ has the corundum structure with alternating O and Al layers along the [0001] direction with stacking sequence ···Al–O₃–Al–Al–O₃–Al···. The (0001) surface is obtained by cleaving the crystal between any of these layers. Only the surface obtained by cleaving between two aluminum layers is non-polar. Previous studies have shown that in the absence of hydrogen and adsorbed H₂O this aluminum-terminated surface is more stable than the other (0001) surfaces. Figure shows a schematic top view of the aluminum terminated α-Al₂O₃(0001) surface.

We here use first-principles, plane-wave density-functional theory (DFT) to determine the adsorption (binding) energy and the equilibrium structure of methanol on α-Al₂O₃(0001). The merit of first-principles calculations is that no experimental input is needed for an accurate determination of structural energies. We can thus compare calculations based entirely on theory with experimental findings.
The DFT calculations were performed by employing the DACAPO code\(^{15}\) in the generalized gradient approximation, using ultra-soft pseudopotentials and periodic boundary conditions. The surface is represented by a slab of finite thickness (8.3 Å) alternating with a vacuum region (14.7 Å). The equilibrium geometries of the methanol molecule, the clean surface, and the adsorbate system are found by locally minimizing the Hellmann-Feynman forces until the sum of forces on the unrestrained atoms is less than 0.05 eV Å\(^{-1}\). By adsorbing methanol on one side of the slab only an artificial dipole is created. This artificial dipole is corrected for in a self-consistent manner.

The optimized geometry of the isolated (gas phase) methanol molecule is in excellent agreement with experiments, with bond lengths and bond angles deviating from the experimental values\(^{4}\) by \(\sim 1\%\). The most important bond angle and lengths for the present study are given in Table 1. Upon optimization of the clean \(\alpha\)-Al\(_2\)O\(_3\) (0001) atomic structure, the inter-plane spacing is relaxed from the bulk spacing. The distance between the adjacent outermost aluminum and oxygen layer is reduced by 87.2 \%, in good agreement with previous theoretical work\(^{8,9,13}\).

### 3 Results and Discussion

In our calculations we allow for molecular adsorption of one methanol molecule per surface unit cell (Fig. 1), or one molecule per exposed Al atom. Methanol adsorbs by the transfer of electronic charge from the O atom of methanol to create a bond to the exposed Al atom. Upon the adsorption of methanol, the layer spacing of \(\alpha\)-Al\(_2\)O\(_3\) (0001) changes markedly. We find that the spacing between the top Al and O layers changes from 0.11 Å to 0.33 Å, whereas the lateral change of bond length between the surface O atoms and the surface Al atoms is small (1–5\%). The changes in bond lengths within the adsorbed methanol molecule are modest (1–4 \%). The bond lengths of methanol in the gas phase and as adsorbed on the alumina surface are listed in Table 1.
The adsorption energy per methanol molecule is calculated from

\[
E_{\text{ads}}^{(g)} = - (E_{\text{tot}} - E_s - E_{\text{m}}^{(g)}),
\]

where \(E_{\text{tot}}\) is the total energy of the system per unit cell, \(E_s\) is the energy for the clean aluminum oxide surface per unit cell, and \(E_{\text{m}}^{(g)}\) is the energy of a methanol molecule away from the surface. We calculate two adsorption energies for methanol, one for moving the methanol molecules from the surface all the way into the gas phase \((E_{\text{m}}^{(g)})\), and one for moving a complete layer of methanol structurally unchanged off the surface \((E_{\text{m}})\). The latter is dominated by the strength of the Al-O\(_m\) bond (‘m’ labels atoms in the molecule), and can very accurately be calculated by present-day DFT approximations. The \(E_{\text{m}}^{(g)}\) adsorption energy includes energetic contributions from the structural changes within the molecule, as well as interactions between the methanol molecules ( adsorbate-adsorbate interactions).

We can compare our calculated adsorption energies with those of experimental measurements. However, for all results of the experiments it should be kept in mind that the chemisorption of methanol on Al\(_2\)O\(_3\) is very sensitive to surface defects and the presence of adsorbed water or hydrogen on the surface. In contrast, in our calculations we investigate a perfect (no defects or steps) clean \(\alpha\)-Al\(_2\)O\(_3\)(0001) surface. From our DFT calculations we find that the energy of the Al-O\(_m\) bond is \(E_{\text{ads}} = 1.01\) eV/molecule (23.3 kcal/mol) and that \(E_{\text{ads}}^{(g)} = 1.03\) eV/molecule (23.8 kcal/mol), the small difference of 0.02 eV/molecule indicating the calculated effect of the molecule-molecule interactions and the structural changes in the methanol molecule. Given the difficulty in carrying out experimental measurements on methanol adsorption on clean alumina surfaces, these theoretically obtained adsorption energies agree reasonably well with the value 0.77 eV/molecule (17.7 kcal/mol) obtained from temperature programmed desorption experiments at low coverages. In an UHV-chemisorption experiment on thin \(\alpha\)- and \(\gamma\)-Al\(_2\)O\(_3\) films at low coverage an adsorption energy \(\sim 0.3\) eV/molecule (7 kcal/mol) was found.

Figure 3 shows a contour plot of a cross section of the electron density difference \(\Delta n(r)\) in a slice approximately through the outermost Al and O atoms of the
surface and the O and (hydroxyl-group) H atoms of the adsorbed methanol. $\Delta n(r)$ measures how electron charge is moved in space due to the adsorbate-surface interaction. The electron density difference is defined as $\Delta n(r) = n_{m+s}(r) - n_s(r) - n_m(r)$, where $n_{m+s}(r)$ is the electron density of the full adsorbate system, $n_s(r)$ is the electron density of the surface without methanol, and $n_m(r)$ is that of methanol without the surface. The atomic positions are in all cases kept fixed as for the full adsorbate system, thus $\Delta n(r)$ shows the change in electron density exclusively due to the presence of the adsorbate.

Whereas an Al atom in the bulk of $\alpha$-Al$_2$O$_3$ is sixfold coordinated, the surface Al atom ($\text{Al}_s$) on the Al-terminated (0001) surface is only three-fold coordinated, making this site a strong electron acceptor. When methanol adsorbs, the O atom of methanol ($\text{O}_m$) binds to $\text{Al}_s$ by donating electron density to creation of the $\text{Al}_s$-$\text{O}_m$ bond, forming a dative (covalent) bond. This is seen in Figure 3 as an increase in electron density on the axis directed along the $\text{Al}_s$-$\text{O}_m$ bond and a depletion of electron density at $\text{O}_m$. Calculating the electron transfer from the electron density difference $\Delta n(r)$ we find that roughly 0.05 electrons are transferred to the $\text{Al}_s$-$\text{O}_m$ bond from the lone-pair electrons on $\text{O}_m$.

It is worth noting that the adsorption energy found here for methanol is very similar to the adsorption energy for water on $\alpha$-Al$_2$O$_3$(0001). Hass et al. obtained a molecular adsorption energy of 1.01 eV/molecule (23.3 kcal/mol) in the low-coverage regime by DFT calculations, as well as the bond lengths reproduced in Table 1. The similarity between water and methanol molecular adsorption is not too surprising. The parts of methanol taking an active part in the binding to the surface are the $\text{O}_m$ and $\text{H}_m$ atoms of the hydroxyl group, similar to the OH group of adsorbed water.
4 Summary

We have performed first-principles density-functional theory calculations on the molecular adsorption of methanol at the $\alpha$-Al$_2$O$_3$(0001) surface. With one methanol molecule adsorbed per surface aluminum atom the adsorption energy is calculated to be $E_{\text{ads}}^g = 1.03$ eV/molecule. With molecule-molecule interactions taken into account, the adsorption energy is slightly less, $E_{\text{ads}} = 1.01$ eV/molecule. An electron density difference plot shows that methanol adsorbs by donating electron charge from the methanol oxygen to create a bond to the surface aluminum. Upon adsorption of methanol, the surface atomic structure changes. Most notably, the spacing between the top Al and O layers change from 0.11 Å to 0.33 Å.

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Table 1: Calculated adsorption energies and selected bond lengths and bonding angle for methanol adsorbed on $\alpha$-Al$_2$O$_3$(0001). Subscript ‘m’ labels atoms in the molecule, and ‘s’ atoms at the surface. H$_m$ is the hydrogen of the hydroxyl group, and H$_{Me}$ the methyl-group hydrogen nearest to the surface. The bond lengths are compared to the low-coverage bond lengths of molecularly adsorbed water as found by DFT calculations in Ref. [13].

|                  | Gas phase methanol | Adsorbed methanol | Adsorbed H$_2$O (Ref. [13]) |
|------------------|--------------------|-------------------|-----------------------------|
| $E_{ads}^g$ (eV/molecule) | -                  | 1.01              | -                           |
| $E_{ads}$ (eV/molecule)   | -                  | 1.03              | 1.01                        |
| $d$(O$_m$–Al$_s$) (Å)    | -                  | 1.995             | 1.953                       |
| $d$(H$_m$–O$_s$) (Å)     | -                  | 1.735             | -                           |
| $d$(O$_m$–H$_m$) (Å)     | 0.979              | 1.022             | 0.978                       |
| $d$(C$_m$–O$_m$) (Å)     | 1.426              | 1.441             | -                           |
| $d$(H$_{Me}$–O$_s$) (Å)  | -                  | 2.699             | -                           |
| $\angle$C$_m$O$_m$H$_m$ (deg) | 108.7             | 111.3             | -                           |
Figure 1: Schematic top view of the \( \alpha-\text{Al}_2\text{O}_3(0001) \) surface terminated by half a layer of aluminum. The open circles represent oxygen atoms, the full circles aluminum atoms. The \( 1 \times 1 \) hexagonal surface unit cell is shown.

Figure 2: Ball-and-stick model of methanol adsorbed at the \( \text{Al}_2\text{O}_3 \) surface. Only the outermost O and Al surface layers are shown. The bond between the methanol oxygen \( (O_m) \) and the surface aluminum \( (\text{Al}_s) \) is shown as a dashed line. The atoms are named according to Table II.
Figure 3: Contour plot of the electron density difference $\Delta n(r)$ in a cut perpendicular to the surface and passing through the surface Al ($Al_s$) and the methanol O ($O_m$). The atoms $O_s$ and $H_m$ are slightly out of plane. The four atoms approximately in the plane are indicated by circles and named according to Table I. The bond between the methanol oxygen and the surface aluminum is indicated by the long-dashed line. The contour spacing is 0.02 electrons/$\AA^3$ with solid (dashed) lines for gain (loss) of negative charge.