Theoretical investigation of the adsorption of methanol on the (110) surface of \( \gamma \)-alumina

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Abstract

The adsorption of methanol on the (110) surface of \( \gamma \)-alumina was investigated using both ab initio and density functional theory quantum chemical methods. A \([\text{Al}_3\text{O}_9\text{H}_{10}]^+\) cluster model comprising one tetrahedral and two octahedral aluminum cations were used to describe the surface and the mechanism of adsorption of methanol. This has allowed us to rationalize the stable structures of adsorbate and the mode of bonding. The IR frequency shifts between the gas phase and the adsorbed species were also calculated and they exhibit good agreement with experiment. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Density functional theory; Cluster calculations; Ab initio calculations; Chemisorption; IR frequency shifts

1. Introduction

Catechol and its monomethylated derivatives are useful organic intermediates in pharmaceutical and agrochemical industries [1]. Among these derivatives, 3-methyl catechol is the most valuable and expensive commercial product. It is industrially produced by homogeneous catalytic methylation of catechol in the presence of mineral acid as a catalyst [1]. Previously \( \gamma \)-alumina was found to be an effective catalyst for the gas-phase methylation of catechol with methanol to selectively produce 3-methyl catechol [2–4]. This process is presented in Fig. 1.

Kinetic studies showed that at temperatures between 260\(^\circ\)-300\(^\circ\)C and at low catechol conversion, O-methylated (guaicol, A\(_2\)) and C-methylated (A\(_3\), A\(_4\)) products are formed in parallel reaction pathways. The O/C methylation ratio has been regulated by varying only acid/base properties of the catalyst, keeping all reaction operating conditions constant [4].

The mechanism of this reaction assumes adsorption of catechol and methanol on the acid–base sites of the \( \gamma \)-alumina surface. The selectivity towards O- or C-methylated products formation seems to be controlled by the amount and strength of these sites as electron-acceptors and electron-donors. The selectivity towards the C-methylated products (formation of A\(_3\) or A\(_4\)) is controlled by the orientation of adsorbed catechol on the surface. Porchet et al. [2] and Kiwi-Minsker et al. [3,4] have carried out a vibrational analysis of both adsorbed species with the aim to rationalize the type of adsorption taking place on catalyst surface. In view of the interest of the catalytic mechanism leading to the formation of 3-methyl catechol, we
decided to perform a quantum chemical modelling of the various steps of this reaction. We report here the first part of this theoretical investigation, devoted to the adsorption mechanism of methanol on the \( \gamma \)-alumina surface. This study was carried out by calculating geometries and vibrational frequencies of free methanol and of this species adsorbed as a methoxyl ion on a cluster model of the surface. In this work, we have chosen a \([\text{Al}_3\text{O}_9\text{H}_{10}]^+\) cluster comprising one tetrahedral and two octahedral aluminum cations as a model of \( \gamma \)-alumina surface. Recently it has indeed been shown that the cluster model is a suitable approach to investigate chemisorption on metallic and non-metallic solid surfaces [5–7]. The calculations have been performed using the ab initio quantum chemical method (at the Hartree–Fock and MP2 levels) as well as density functional theory (DFT).

In addition to geometries, the shifts of vibrational frequencies between free and adsorbed methanol are computed and compared with experiment [4].

**2. Computational details**

Equilibrium geometries and harmonic vibrational frequencies were calculated using both ab initio (at the Hartree–Fock and MP2 levels) and DFT methods. To this end, the GAUSSIAN 94 program package [8] was used for the ab initio calculations, with the 6-31G and 6-31G** basis sets. DFT calculations were performed using both the GAUSSIAN 94, with Becke’s three parameters hybrid method [9] using the Lee, Yang and Parr correlation functional [10] (B3LYP), and the ADF 2.1 programs [11,12], with non-local corrections of Becke [9] for exchange and Perdew [13] for correlation (BP86).

The ADF program, developed by Baerends et al. [11], is based on the use of Slater-type orbitals (STO). For the atomic orbitals of aluminum (3s, 3p), carbon, oxygen (2s, 2p) and hydrogen (1s), an uncontracted triple-\( \zeta \) STO basis set [14] was employed. This basis set was augmented by a p-polarization function in the case of hydrogen, whereas for the aluminum, carbon and oxygen atoms an extra d polarization function was added. The inner cores of aluminum (1s\(^2\)2s\(^2\)2p\(^6\)) as well as carbon (1s\(^2\)) and oxygen (1s\(^2\)) were treated by the frozen core approximation [12]. A set of auxiliary s-, p-, d- and f- STO functions, centered on all nuclei, was used to fit the molecular electron density. They represent the Coulomb and exchange potentials accurately in each SCF cycle [15]. The numerical integration was developed by te Velde et al. [16]. In all ADF calculations, the accuracy of total energies was \(10^{-5}\) hartrees, and the SCF convergence criterion used for the gradient was \(10^{-3}\) hartrees.

It is well known that the ab initio method at the SCF level tends to overestimate vibrational frequencies (10%–12% in general) because both electron correlation and anharmonicity corrections are neglected. A correction factor is therefore generally introduced, typically, 0.89 at the Hartree–Fock and 0.94 at the MP2 levels, respectively, because only anharmonicity effects are present in the latter case, and these values are used here. Finally, the factor we applied for the DFT vibrational frequencies is 0.97 as the electron
correlation is taken into account by DFT. It can be reduced to 0.95 in some cases and a different factor can be even used for each vibrational mode, but in our case, the same value was used for all the normal modes, comprising the C–H ones, which are generally not very well described without anharmonicity corrections [17]. However, their introduction is an intricate task which goes beyond the scope of the present study. The choice of this scaling factor was made according to recent publications of Pople et al. [18] and Wong et al. [19]. In order to facilitate the choice of a model cluster, the (110) surface of γ-alumina was modelled with the Surface Builder module of the CERIUS2 package [20], using X-ray crystallographic data [21]. For the geometry optimization of adsorbed methanol, the atoms of γ-alumina were frozen in their cristallographical positions and the coordinates of the methoxyl ion only were optimized.

3. Results and discussion

3.1. Determination of the cluster model of the γ-alumina

The present study is limited to the non-polar (110) surface of γ-alumina exhibiting both aluminum and oxygen ions. At temperatures higher than 100°C this surface is formed by unsaturated aluminum cations, oxygen anions and hydroxyl groups, according to Peri’s model [22]. Its properties towards reactions such as alcoylation can be described by considering this surface as made of acidic and basic sites [23], or more generally as electron-acceptor and electron-donor sites. Recently, some ideal models of the active surface of γ-alumina have been suggested by Peri [22] and Knözinger [24,25]. These authors have concluded that the (110) surface is the most favorable for catalytic activity. This surface was shown to exhibit hollow sites, because of the non-equivalent tetrahedral and octahedral aluminum ions, and which are most probably responsible for methanol adsorption. From experimental studies of the H2O and CO interaction with different modifications of alumina, it was shown that the tetrahedral aluminum sites have a more pronounced Lewis acid character than the octahedral ones [26,27].

Previous calculations performed for dye molecules adsorbed on γ-alumina have shown that the (110) surface may be adequately modelled by small clusters containing 1–3 Al atoms [28–30]. The following requirements regarding the minimum cluster size for a specific adsorption site is that all the nearest neighbors of aluminum ions should be included in the
cluster, with dangling bonds saturated by OH or HOH groups [30]. The cluster of minimum size used to model the (110) surface of \( \gamma \)-alumina should contain aluminum atoms presenting the two types of coordination. We selected a \([\text{Al}_3 \text{O}_9 \text{H}_{10}^+]\) cluster (Fig. 2) because the presence of the second octahedral site is necessary to describe properly the coordination site. The choice of a positively charged \([\text{Al}_3 \text{O}_9 \text{H}_{10}^+]\) cluster is justified by the fact that the first step of the adsorption is the loss of H\(_1\) by methanol and OH\(_2\) by alumina, leading to water formation. The charge of our cluster is therefore such that its interaction with CH\(_3\)O\(_) will lead to a neutral system (see Section 3.3).

Seven protons (H\(_s\)) were incorporated in the cluster which saturate the O–Al dangling bonds. Three other protons (H\(_n\)) were added to terminal hydroxyl groups to satisfy the condition of a formal +1 charge on the cluster. This ensures that the final system comprising this cluster and the methoxyl ion fulfills the electroneutrality requirement. The choice of the positions of all these protons was dictated by symmetry arguments.

### 3.2. Geometrical and vibrational study of free methanol

We have studied only the most stable conformer of methanol (the *anti* one) [31–33]. The results are shown in Table 1, which compares our theoretical values with experimental data obtained by Blom et al. [31] using electron diffraction and microwave spectroscopy.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HF 6-31G**</th>
<th>MP2 6-31G**</th>
<th>B3LYP 6-31G**</th>
<th>BP86(^a)</th>
<th>Experiment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(C1–O2)</td>
<td>1.399</td>
<td>1.421</td>
<td>1.418</td>
<td>1.410</td>
<td>1.425</td>
</tr>
<tr>
<td>d(O2–H4)</td>
<td>0.942</td>
<td>0.963</td>
<td>0.965</td>
<td>0.974</td>
<td>0.945</td>
</tr>
<tr>
<td>d(C1–H1)</td>
<td>1.088</td>
<td>1.093</td>
<td>1.101</td>
<td>1.104</td>
<td>1.094</td>
</tr>
<tr>
<td>d(C1–H2)</td>
<td>1.088</td>
<td>1.093</td>
<td>1.101</td>
<td>1.104</td>
<td>1.094</td>
</tr>
<tr>
<td>d(C1–H3)</td>
<td>1.081</td>
<td>1.086</td>
<td>1.093</td>
<td>1.097</td>
<td>1.094</td>
</tr>
<tr>
<td>( \angle ) (O2–C1–H2)</td>
<td>112.14</td>
<td>112.45</td>
<td>112.84</td>
<td>112.79</td>
<td>112.0</td>
</tr>
<tr>
<td>( \angle ) (O2–C1–H3)</td>
<td>107.33</td>
<td>106.53</td>
<td>106.93</td>
<td>106.60</td>
<td>107.0</td>
</tr>
<tr>
<td>( \angle ) (O2–C1–H4)</td>
<td>109.65</td>
<td>107.29</td>
<td>107.72</td>
<td>108.23</td>
<td>108.5</td>
</tr>
</tbody>
</table>

\(^a\) See computational details for a description of the basis set used.

\(^b\) Refs. [31–33].

Table 2

Comparison of vibrational frequencies (cm\(^{-1}\)) calculated for the free gaseous methanol in C\(_3\) symmetry using different methods and basis sets. These values have been corrected applying the adequate scaling factor (see text)

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>HF 6-31G**</th>
<th>MP2 6-31G**</th>
<th>B3LYP 6-31G**</th>
<th>BP86(^a)</th>
<th>Experiment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_\alpha ) C–O</td>
<td>1029</td>
<td>1016</td>
<td>1031</td>
<td>1019</td>
<td>1033</td>
</tr>
<tr>
<td>( \delta ) H–C–O</td>
<td>1058</td>
<td>1048</td>
<td>1063</td>
<td>1081</td>
<td>1076</td>
</tr>
<tr>
<td>( \delta ) H–C–H</td>
<td>1143</td>
<td>1134</td>
<td>1114</td>
<td>1115</td>
<td>1145</td>
</tr>
<tr>
<td>( \delta ) H–C–O</td>
<td>1326</td>
<td>1323</td>
<td>1344</td>
<td>1314</td>
<td>1334</td>
</tr>
<tr>
<td>( \delta ) CH(_3)</td>
<td>1445</td>
<td>1444</td>
<td>1455</td>
<td>1399</td>
<td>1451</td>
</tr>
<tr>
<td>( \delta ) H–C–H</td>
<td>1453</td>
<td>1467</td>
<td>1463</td>
<td>1416</td>
<td>1466</td>
</tr>
<tr>
<td>( \delta ) H–C–H</td>
<td>1464</td>
<td>1482</td>
<td>1481</td>
<td>1433</td>
<td>1473</td>
</tr>
<tr>
<td>( \nu_\gamma ) C–H</td>
<td>2810</td>
<td>2908</td>
<td>2896</td>
<td>2932</td>
<td>2848</td>
</tr>
<tr>
<td>( \nu_\gamma ) C–H</td>
<td>2853</td>
<td>2975</td>
<td>2940</td>
<td>2986</td>
<td>2961</td>
</tr>
<tr>
<td>( \nu ) C–H</td>
<td>2917</td>
<td>3047</td>
<td>3026</td>
<td>3066</td>
<td>3006</td>
</tr>
<tr>
<td>( \nu ) O–H</td>
<td>3732</td>
<td>3675</td>
<td>3706</td>
<td>3710</td>
<td>3667</td>
</tr>
</tbody>
</table>

\(^a\) See computational details for a description of the basis set used.

\(^b\) Refs. [31–33].
Examination of Table 1 shows that HF results obtained using the 6-31G** basis set lead to an underestimation of C–O and C–H bond lengths. As usual, going beyond the HF method by introducing dynamical electron correlation (MP2 values) increases these bond lengths, and they are in good agreement with experiment. It is noteworthy that B3LYP results are very close to MP2, both being obtained using the 6-31G** basis set. Finally, BP86 results are slightly less satisfactory. As usual again, C–H bond lengths are best predicted by MP2 calculations, DFT results leading to overestimated values. Finally, Table 1 shows that all the methods lead to close agreement with experiment as far as bond angles are concerned.

In Table 2 we present a comparison between the computed frequencies of methanol and the gas phase experimental values reported by Blom et al. [31]. The experimental O–H stretching frequency is affected in the liquid phase by hydrogen bonding, which leads to some discrepancy between calculations and experiment [33]. The C–H stretching frequencies in methanol are split by Fermi resonance, which induces shifts in frequencies of 1%–2%. Finally, anharmonicity effects are also responsible for a 3%–5% correction in the C–H frequencies. On account of all these factors, it is not easy to compare the theoretical results with experiment.

Our results are nevertheless close to those obtained by Hameka et al. in their experimental and theoretical study of some saturated alcohols [33]. Table 2 shows that the largest discrepancy between the methods used is found for C–H stretching frequencies. Moreover, the most interesting vibrational mode in the present study is the C–O stretch as it is directly affected by adsorption. Table 2 shows that this frequency is underestimated by all the methods used. The B3LYP calculations lead to the best agreement ($\Delta \nu = 2 \text{ cm}^{-1}$) with the experiment, but HF/6-31G** results are equally good ($\Delta \nu = 4 \text{ cm}^{-1}$). The bending modes are well described by all the methods ($\Delta \nu = 7–20 \text{ cm}^{-1}$), the best results being the MP2/6-31G** and B3LYP/6-31G** ones with an average error less than 1%.

3.3. Adsorption of methanol on the alumina cluster

Several mechanisms have been reported for the adsorption of alcohols on $\gamma$-alumina. Comparing the IR spectrum of the adsorbed methanol with aluminum methoxide, Greenler has concluded [34] that the surface species formed by the adsorption is probably a methoxide surface compound. In contrast, Kagel has shown [35] that the adsorption of methanol on $\gamma$-alumina surface is temperature dependent: near room temperature both physisorbed alcohol and chemisorbed alkoxide species are formed. According to Busca et al [36], several chemisorbed species may be found, depending on temperature, one of them corresponding to a bidented species with the OH group of methanol bound to aluminum and oxygen surface atoms. Finally, in the experimental conditions reported by Porchet et al. [2–4], methanol mainly adsorbs as a bidented species on $\gamma$-alumina, i.e. corresponding to this species of Busca et al. Methanol deprotonation by a basic hydroxyle of the surface involves water formation and Porchet et al. have shown that this occurs during the adsorption.

The methanol molecule will probably adsorb on the defects and edges of the (110) surface of $\gamma$-alumina and not on perfectly flat regions. Preferred adsorption sites are likely to be located on tetrahedral aluminum atoms, which lie in a relatively exposed surface position. These atoms appear after partial removal of surface OH groups. The adsorption of alcohols on oxides involves an acid–base reaction and proceeds in a way analogous to water adsorption. The isolated hydroxyl groups on the surface are involved in the reaction and the most basic group can deprotonate the alcohol. The resulting bidented methoxyl-ions bind to two Lewis acid sites (the Al$^{3+}$ of the catalyst surface). Isotopic studies have confirmed that the O–H bond was broken during adsorption of methanol on the alumina surface [1,36]. Consequently, methanol makes a covalent bond with the surface of $\gamma$-alumina with the release of one water molecule, as shown by IR measurements [1,2,36]. Consequently, we assumed, in our calculation, that a previous deprotonation of methanol happens, leading to the formation of a water molecule, and this step is not considered here. As Porchet et al. have observed the release of water probably as a result of the deprotonation of methanol during its adsorption, this gives undoubtedly credibility to the reaction scheme suggested by Moravek [37]. Therefore we assumed in the present work that this mechanism prevails and chose to calculate this model of adsorption.
Fig. 3 displays the structure of the methoxyl-ion adsorbed on the cluster model and the corresponding geometrical parameters are presented in Table 3. Unfortunately, it was not possible to compare these results with experiment, as structural data are not available in the literature [2].

The results obtained by the various methods are close to each other. The DFT method leads to bond lengths generally longer than those obtained at the HF level. Comparing the results of Tables 1 and 3, one notices that the C–O bond becomes slightly shorter when methanol is adsorbed (1.412 Å versus 1.421 Å for B3LYP). This is in agreement with the suggestion of Berteau et al. [38] concluding that C–O takes a

Table 3
Geometry of the absorbed species. Distances in Å and angles in degrees

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HF 6-31G**</th>
<th>B3LYP 6-31G**</th>
<th>BP86*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d (\text{Al–O}) )</td>
<td>1.783</td>
<td>1.795</td>
<td>1.796</td>
</tr>
<tr>
<td>( d (\text{C–O}) )</td>
<td>1.394</td>
<td>1.412</td>
<td>1.427</td>
</tr>
<tr>
<td>( \angle (\text{O–C–O}) )</td>
<td>116.70</td>
<td>116.00</td>
<td>110.38</td>
</tr>
<tr>
<td>( \angle (\text{O–C–H1}) )</td>
<td>111.03</td>
<td>111.63</td>
<td>110.05</td>
</tr>
<tr>
<td>( \angle (\text{O–C–H2}) )</td>
<td>110.39</td>
<td>110.60</td>
<td>110.77</td>
</tr>
<tr>
<td>( \angle (\text{O–C–H3}) )</td>
<td>111.53</td>
<td>110.18</td>
<td>109.26</td>
</tr>
<tr>
<td>( \angle (\text{Al–O–C–H3}) )</td>
<td>180.00</td>
<td>180.00</td>
<td>180.00</td>
</tr>
</tbody>
</table>

* See computational details for a description of the basis set used.

Table 4
Vibrational frequencies (\( \text{cm}^{-1} \)) for the absorbate. These values have been corrected applying the adequate scaling factor (see text)

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>HF 6-31G**</th>
<th>B3LYP 6-31G**</th>
<th>BP86*</th>
<th>Experiment*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu \text{ C–O} )</td>
<td>1096</td>
<td>1078</td>
<td>1079</td>
<td>1090</td>
</tr>
<tr>
<td>( \delta \text{ H–C–O} )</td>
<td>1174</td>
<td>1148</td>
<td>1122</td>
<td>—</td>
</tr>
<tr>
<td>( \delta \text{ H–C–O} )</td>
<td>1131</td>
<td>1183</td>
<td>1159</td>
<td>1186</td>
</tr>
<tr>
<td>( \delta \text{ CH}_3 )</td>
<td>1412</td>
<td>1457</td>
<td>1368</td>
<td>—</td>
</tr>
<tr>
<td>( \delta \text{ H–C–H} )</td>
<td>1459</td>
<td>1463</td>
<td>1421</td>
<td>—</td>
</tr>
<tr>
<td>( \delta \text{ H–C–H} )</td>
<td>1453</td>
<td>1506</td>
<td>1426</td>
<td>—</td>
</tr>
<tr>
<td>( \nu \text{ C–H} )</td>
<td>2840</td>
<td>2872</td>
<td>2912</td>
<td>2824</td>
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<tr>
<td>( \nu \text{ C–H} )</td>
<td>2890</td>
<td>2962</td>
<td>2976</td>
<td>2844</td>
</tr>
<tr>
<td>( \nu \text{ C–H} )</td>
<td>2868</td>
<td>3000</td>
<td>3042</td>
<td>2949</td>
</tr>
</tbody>
</table>

* See computational details for a description of the basis set used.

Table 5
Vibrational frequency shifts (\( \text{cm}^{-1} \)) between the free and asorbed methanol calculated using different methods and basis sets (\( \Delta \nu = \nu_{\text{adsorbed}} - \nu_{\text{free}} \))

<table>
<thead>
<tr>
<th>Frequency shifts</th>
<th>HF 6-31G**</th>
<th>B3LYP 6-31G**</th>
<th>BP86*</th>
<th>Experiment*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \nu (\text{C–O}) )</td>
<td>67</td>
<td>47</td>
<td>60</td>
<td>57</td>
</tr>
<tr>
<td>( \Delta \nu (\text{H–C–O}) )</td>
<td>195</td>
<td>161</td>
<td>155</td>
<td>148</td>
</tr>
</tbody>
</table>

* See computational details for a description of the basis set used.

b Ref. [2].
partial double bond character upon adsorption. The Al–O–C angle is larger than the C–O–H angle in free methanol. Several effects can be at the origin of this feature, such as the formation of a hydrogen bond with the nearest OH group and steric effects caused by the surface of catalyst (see Fig. 3).

Comparing the vibrational frequencies of the adsorbate species (Table 4) with experimental data [2,4], one observes that HF/6-31G** results are very close to experiment, as the discrepancies are 2 cm
\[^{-1}\] for the C–O stretching mode and 26 cm
\[^{-1}\] for the first H–C–H bending. The C–O bond stretch is characterized by a frequency near 1090 cm
\[^{-1}\] (1096 cm
\[^{-1}\] for HF/6-31G**). The experimental vibration at 1186 cm
\[^{-1}\] is connected with the in-plane deformation of the CH\(_3\) group. Examination of Table 4 shows that there are no experimental bands characteristic of a physisorbed methanol species (absence of the 1480, 1440 and 1420 cm
\[^{-1}\] bending bands). Moreover, a physisorbed methanol should be characterized by a stretching C–O frequency at roughly 1034 cm
\[^{-1}\] as in the free molecule, but no such vibrational frequencies were observed for adsorbed species. On the contrary, the C–O bond stretch is characterized by a frequency near 1090 cm
\[^{-1}\] which shows that during the dissociative adsorption of alcohols on alumina a shift of the stretching frequencies towards higher wave numbers occurs. Thus, the C–O bond becomes stronger and exhibits a double bond character as deduced from the analysis of the bond distances (Tables 1 and 3). These results are in good agreement with the dissociative adsorption mechanism of methanol on \(\gamma\)-alumina suggested by Moravek [37] (see Fig. 4).

Table 4 shows that the frequencies calculated using the HF/6-31G** method are in best agreement with experiment, but one should rather consider the frequency shifts between free and adsorbed methanol [39] (Table 5).

Whereas HF/6-31G** calculations lead to \(\Delta\nu(\text{C–O})\) and particularly \(\Delta\nu(\text{H–C–O})\) shifts in rather poor agreement with experiment [4], the corresponding values obtained using DFT/BP86 are very satisfactory. However, the shifts calculated using DFT/B3LYP/6-31G** are very close to the latter ones, which confirms that DFT methods are adequate to reproduce such properties.

As a conclusion, the present study supports the dissociative mechanism proposed by Moravek [37] for the adsorption of alcohols on \(\gamma\)-alumina. Methanol adsorbs on a tetrahedral aluminum ion forming a covalent bond. This is confirmed by the calculated vibrational frequencies.

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References