Theoretical Investigation of H₂ Combustion on αAl₂O₃ Support

by Jennifer Synowczynski, Jan W. Andzelm, and D. G. Vlachos

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Theoretical Investigation of H$_2$ Combustion on $\alpha$Al$_2$O$_3$ Support

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Based on Density Functional Theory – Generalized Gradient Approximation (DFT-GGA) calculations, we provide a theoretical model for the effect of the catalytic support (alpha alumina oxide (αAl₂O₃)) on the dissociation of molecular hydrogen (H₂), molecular oxygen (O₂), hydroxyl (OH), water (H₂O), and the surface diffusion of oxygen and hydrogen species along the αAl₂O₃ (0001) surface. These processes are key to understanding the “inverse spillover effect” that occurs during hydrogen combustion on alumina surfaces. Our results indicate the dissociation of O₂ is not thermodynamically favored on the αAl₂O₃ surface. However, both H₂ and H₂O can dissociate, forming hydroxyls with oxygen atoms in the second atomic layer. Once dissociated, oxygen species can diffuse locally but encounter a large barrier to long-range surface diffusion in the absence of defects or other species. In contrast, the barrier to the long-range surface diffusion of hydrogen is modest under ideal conditions.

Inverse spillover effect, Al₂O₃, H₂ combustion, O, OH, H₂O adsorption
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Acknowledgments

We would like to acknowledge the High Performance Computer (HPC) Modernization program as well as the thoughtful insights of Dr. Eric Wetzel (U.S. Army Research Laboratory), Dr. Emily Carter (Princeton University), and Ioannis Bourmpakis (University of Delaware).
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1. Introduction

As the electronics behind the future warrior systems become more sophisticated, the weight of the batteries is an ever-increasing burden. One solution is to create a compact micro-burner device as shown in figure 1 (Norton et al., 2004) that combusts a higher energy density fuel such as methane (energy density = 3053 W-hr/kg compared to 125 W-hr/kg for lithium (Li)-ion batteries) and converts the released enthalpy into electrical power.

![Figure 1. Micro-burner schematic.](image)

Note: The catalytic insert consists of nanosized platinum (Pt) dispersed within porous alumina (Al₂O₃).

Although there are many computational studies that detail the complete hydrogen (H₂) combustion mechanism for reactant and product species interacting with the catalytically active Pt cluster (Mhadeshware and Vlachos, 2007), few studies consider the effect of the Al₂O₃ support. New reaction pathways can arise due to support surface termination and reactivity at the Al₂O₃/Pt interface. One example of such a pathway is the “inverse spillover effect” (ISE), which occurs when water (H₂O) chemisorbs or dissociates on the support forming mobile species that can migrate to the catalytically active particle and further promote combustion. Experimental evidence for ISE comes from the work of Wang et al. (1996) who demonstrated that carbon monoxide (CO) can liberate H₂ from an H₂O bound to Al₂O₃ support. In this report, we seek to augment the current model for H₂ micro-combustion to include reactions that are initiated on the catalytic support. Specifically, we propose a mechanism by which H₂O and H₂ dissociate on the support forming hydroxyl groups, which can further dissociate and diffuse to the catalytic particle.
2. Model Parameters and Validation

2.1 Alpha-alumina oxide (αAl_2O_3) Surface Termination

Our model (figure 2) consisted of a nine atomic layer thick, aluminum (Al)-terminated (0001) slab that is repeated under periodic boundary conditions as a 2x2 supercell with P1 symmetry and a 30Å vacuum layer to prevent any interaction between periodic images. We chose this surface based on the availability of experimental and theoretical data in the literature as well as the work of Marmier et al. (2004), who calculated surface phase diagrams as a function of temperature and the oxygen (O_2) and H_2 partial pressures for several different crystal orientations and surface terminations. The lattice parameters for the rhombohedral unit cell (a=b= 4.749 Å, c=12.991 Å) were taken directly from experimental results (Swansen, 1960) and were not optimized during the simulation. In addition, we constrained the bottom two layers of the slab to reflect the bulk Al_2O_3 geometry.

Figure 2. Cross section of fully relaxed Al-terminated αAl_2O_3 (0001) slab used for calculation. The O and Al atoms are red and magenta, respectively.

2.2 Model Parameters

All calculations were performed using ideal conditions (0 K, ultra high vacuum, defect free surface). The calculations were executed within the DMol^3 (Delley, 2000) module of the Materials Studio (version 4) software package using a double-numeric basis set with polarization functions (DNP) and the Perdew-Burke-Ernzerhof (PBE) (Perdue, 1996) version of the generalized gradient approximation (GGA) to represent the electron exchange and correlations. The ion cores were described by a density functional semi-core pseudopotential (DSPP) (Delley, 2002).

To validate our calculations, we compare our results for the surface reconstruction of the relaxed αAl_2O_3 (0001) slab with the results of other theoretical and experimental investigations (table 1). In agreement with other theoretical studies, our simulation predicts an 89% contraction of the
inter-atomic spacing of top surface layer and 6% expansion of the first sub-layer for the ultra-clean αAl₂O₃ (0001) surface. The predicted surface reconstruction was explained by Sousa et al. (1993) as being a result of charge redistribution due to the highly ionic nature of alumina. The experimental value for this relaxation is closer to ~50%. The discrepancy between theoretical prediction and experimental measurements may be due to the difficulty in preparing a perfectly terminated surface with no adsorbed atoms or defects.

Table 1. Comparison of theoretical and experimentally measured changes in the inter-atomic layer spacing of Al-terminated αAl₂O₃ (0001) slab with respect to their unrelaxed geometry.

<table>
<thead>
<tr>
<th>#0xygen layers</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional</td>
<td>Ours</td>
<td>Hinneman</td>
</tr>
<tr>
<td>PBE/DSPP</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>PBE/PAW</td>
<td>–89.2</td>
<td>–86.4</td>
</tr>
<tr>
<td>LDA/NCPP</td>
<td>+6</td>
<td>+4</td>
</tr>
<tr>
<td>PBE/NCPP</td>
<td>–39.9</td>
<td>–45.4</td>
</tr>
<tr>
<td>PW91/USPP</td>
<td>+18.9</td>
<td>+20.5</td>
</tr>
<tr>
<td>PW91/NCPP</td>
<td>+17.1</td>
<td>+5</td>
</tr>
<tr>
<td>PBE/PAW</td>
<td>–31.2</td>
<td>–6.8</td>
</tr>
<tr>
<td>O[2]–Al[3]</td>
<td>0</td>
<td>+1.3</td>
</tr>
<tr>
<td>O[1]–Al[4]</td>
<td>0</td>
<td>–1.3</td>
</tr>
<tr>
<td>O[5]–Al[6]</td>
<td>+4.6</td>
<td>+6.4</td>
</tr>
<tr>
<td>O[8]–Al[9]</td>
<td>–1.2</td>
<td>–0.6</td>
</tr>
</tbody>
</table>

To simulate adsorption phenomena, we added one adsorbate molecule per supercell, which is equivalent to approximately 1/12 monolayer according to Verdozzi et al. (1999), who define a monolayer as having one metal atom per surface oxygen. Binding energies were computed by subtracting the energy of the clean fully relaxed slab and the adsorbent molecule (H₂O, O₂, H₂) from the total energy of the system after adsorption. We performed barrier calculations using the linear synchronous transit (LST) method of Govind et al. (2003) to extrapolate between the reactant and product structures along the diffusion pathways illustrated in figure 3.
Figure 3. Top view of a 2x2 supercell showing allowed surface binding sites. The numbers correlate with the dissociation product and diffusion path notation referred to throughout the report. When referring to dissociation products, the endpoints of the line indicate the atoms to which the dissociated species bind.

2.3 Electron Spin State

The reaction chemistry of oxygen involved reactions on Al$_2$O$_3$ surfaces cannot be adequately described without careful consideration of the triplet-to-singlet spin conversion that occurs when the 2$pIg^*$ orbitals hybridize with the surface states. We find the energy difference between the triplet and the singlet ground state of free O$_2$ to be 19.3 kcal/mol, which is in good agreement with the experimentally measured value of 22.6 kcal/mol (Herzberg, 1950). Figure 4 shows adsorption structures and dissociation products for O, H, O$_2$, H$_2$, and H$_2$O on the Al-terminated αAl$_2$O$_3$ (0001) surface. For all adsorption/dissociation products except figure 4A, 4E, and 4J, the lowest energy spin state was singlet. In table 2, we detail the key molecular features for these structures as well as their binding energies. From table 2, it is clear that triplet states result in tighter O=O bonds and a local elongation of the Al$^{[1]}$-O bonding scheme. The spin state has no apparent effect on the length of hydroxyl or Al$^{[1]}$-H$^{[ads]}$ bonds. Based on the binding distances, it would appear that the triplet to singlet spin conversion occurs between 2 and 1.9Å above the surface for molecular O$_2$ and between 1.8 and 1.5 Å for atomic oxygen. However, this can only be verified by carefully sampling both the singlet and triplet potential energy surfaces as the adsorbing species approaches the surface.
Figure 4. Adsorption and dissociated structures for (A) oxygen tetrahedron, (B) oxygen bridge, (C) hydrogen tetrahedron, (D) hydrogen, (E) 1-1 molecularly adsorbed O\textsubscript{2}, (F) 1-2 dissociated O\textsubscript{2}, (G) 2-2 dissociated O\textsubscript{2}, (H) 1-2 dissociated H\textsubscript{2}, (I) 1-4 dissociated H\textsubscript{2}, (J) 2-2 dissociated H\textsubscript{2}, (K) 1-1 molecularly adsorbed H\textsubscript{2}O, (L) 1-2 dissociated H\textsubscript{2}O, (M) 1-4 dissociated H\textsubscript{2}O, and (N) the key indicating atomic layer to which atom originally belonged.
Table 2. Effect of spin state on $O_2$ adsorption binding energies and bond lengths. The ID notation refers to the structures in figure 4.

<table>
<thead>
<tr>
<th>Atomic Oxygen Adsorption</th>
<th>$E_{binding}$ (kcal/mol)</th>
<th>$O_{ads}$-$O^{[2]}$ (Å)</th>
<th>$O_{ads}$-$Al^{[1]}$ (Å)</th>
<th>$\angle_{bond}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet A</td>
<td>-42</td>
<td>1.782</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>Singlet A</td>
<td>-30 [-35]</td>
<td>1.767</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>Triplet B</td>
<td>-18</td>
<td>1.508</td>
<td>1.797</td>
<td>49</td>
</tr>
<tr>
<td>Singlet B</td>
<td>-49 [-53]</td>
<td>1.546</td>
<td>1.803</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomic Hydrogen Adsorption</th>
<th>$E_{binding}$</th>
<th>$H_{ads}$-$O^{[2]}$ (Å)</th>
<th>$H_{ads}$-$Al^{[1]}$ (Å)</th>
<th>$\angle_{bond}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet C</td>
<td>-20</td>
<td>1.626</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>Singlet C</td>
<td>-36</td>
<td>1.625</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>Triplet D</td>
<td>-98</td>
<td>0.971</td>
<td>1.594</td>
<td>124</td>
</tr>
<tr>
<td>Singlet D</td>
<td>-116</td>
<td>0.972</td>
<td>1.593</td>
<td>124</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecular Oxygen Adsorption / Dissociation</th>
<th>$E_{binding}$</th>
<th>$O=O$ (Å)</th>
<th>$O_{ads}$-$Al^{[1]}$ (Å)</th>
<th>$\angle_{bond}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet E</td>
<td>-7</td>
<td>1.255</td>
<td>1.997</td>
<td>107</td>
</tr>
<tr>
<td>Singlet E</td>
<td>-13</td>
<td>1.276</td>
<td>1.959</td>
<td>110</td>
</tr>
<tr>
<td>Triplet F</td>
<td>21</td>
<td>1.364</td>
<td>1.895</td>
<td>74</td>
</tr>
<tr>
<td>Singlet F</td>
<td>-3</td>
<td>1.393</td>
<td>1.851</td>
<td>76</td>
</tr>
<tr>
<td>Triplet G</td>
<td>51</td>
<td>1.499</td>
<td>1.837</td>
<td>48</td>
</tr>
<tr>
<td>Singlet G</td>
<td>25</td>
<td>1.522</td>
<td>1.823</td>
<td>49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecular Hydrogen Dissociation</th>
<th>$E_{binding}$</th>
<th>$H_{ads}$-$O^{[2]}$ (Å)</th>
<th>$H_{ads}$-$Al^{[1]}$ (Å)</th>
<th>$\angle_{bond}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet H</td>
<td>-15</td>
<td>0.982</td>
<td>1.594</td>
<td>110, 120</td>
</tr>
<tr>
<td>Singlet H</td>
<td>-14</td>
<td>0.981</td>
<td>1.593</td>
<td>110, 120</td>
</tr>
<tr>
<td>Triplet I</td>
<td>-14</td>
<td>0.971</td>
<td>1.621</td>
<td>120, 113</td>
</tr>
<tr>
<td>Singlet I</td>
<td>-10</td>
<td>0.972</td>
<td>1.615</td>
<td>121, 112</td>
</tr>
<tr>
<td>Triplet J</td>
<td>-85</td>
<td>0.973</td>
<td>1.593</td>
<td>127, ----</td>
</tr>
<tr>
<td>Singlet J</td>
<td>-67</td>
<td>0.973</td>
<td>1.593</td>
<td>127, ----</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$H_2O$ Adsorption / Dissociation</th>
<th>$E_{binding}$</th>
<th>$H_{ads}$-$O^{[2]}$ (Å)</th>
<th>$O_{ads}$-$Al^{[1]}$ (Å)</th>
<th>$\angle_{OAIO}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triplet K</td>
<td>-27 [-23]</td>
<td>0.982</td>
<td>1.982</td>
<td>----, 87</td>
</tr>
<tr>
<td>Singlet K</td>
<td>-26 [-23]</td>
<td>0.983</td>
<td>1.987</td>
<td>----, 86</td>
</tr>
<tr>
<td>Triplet L</td>
<td>-40 [-33]</td>
<td>0.982</td>
<td>1.740</td>
<td>110, 112</td>
</tr>
<tr>
<td>Singlet L</td>
<td>-38 [-33]</td>
<td>0.981</td>
<td>1.740</td>
<td>109, 114</td>
</tr>
<tr>
<td>Triplet M</td>
<td>-38 [-33]</td>
<td>0.972</td>
<td>1.759</td>
<td>121, 97</td>
</tr>
<tr>
<td>Singlet M</td>
<td>-34 [-33]</td>
<td>0.973</td>
<td>1.758</td>
<td>122, 97</td>
</tr>
</tbody>
</table>

The number in brackets is from Gamallo, 2007.
The number in brackets is from Haas, 2000.

Since an objective of this research is to establish whether dissociated oxygen from the alumina support can diffuse to the catalytic particle and all possible surface diffusion pathways include a bridging conformation, we chose to perform our barrier calculations using a singlet spin state for both the reactant and products. This is the most accurate method to explore the effects of crystal symmetry and surface reconstructions on the dissociation and diffusion barriers for reaction.
pathways that do not involve a spin change. In future studies, we will perform a detailed sampling of both the triplet and singlet potential energy surfaces using the constrained geometry method to assess the reaction barriers for pathways that involve spin-to-triplet transformations.

3. Results and Discussion

3.1 Effects of Adsorption on Surface Reconstruction

In table 3, we demonstrate the effect of the adsorption of different species on both the local and long-range reconstruction of the \( \alpha Al_2O_3 \) (0001) surface. Both H and O can directly bind with similar binding energies (~ -30 kcal/mol) to the surface Al\(^{[1]}\) forming a tetrahedron with neighboring O\(^{[2]}\) atoms. By saturating the surface Al\(^{[1]}\), the O\(^{ads}\) reduces the driving force for the contraction of the first inter-atomic layer. Although H binds closer to the surface Al\(^{[1]}\) than O, both H and O produce the same elongation of the local Al\(^{[1]}\)-O\(^{[2]}\) bonding scheme. H and O can also directly bind to the O\(^{[2]}\) atoms. However, in this configuration, there are significant differences in both the adsorption structures and binding energies (\( E_{\text{bind}}^{O} \sim -50 \), \( E_{\text{bind}}^{H} \sim -116 \) kcal/mol). Whereas O pulls the Al\(^{[1]}\) ~ 8% away from the surface, H drives Al\(^{[1]}\) deeper into the lattice. The closer the binding site is to an Al\(^{[1]}\) site, the deeper it is driven into the lattice and the greater the asymmetrical lengthening of the local Al\(^{[1]}\)-O\(^{[2]}\) bonding scheme. This has a profound effect on the relaxation of the top two inter-atomic layers. As the surface Al\(^{[1]}\) is driven into the lattice, it reduces the ability of the oxygen layer to charge compensate for excess charge on the remaining unsaturated surface aluminum atoms, resulting in a smaller contraction of the first inter-atomic layer.
Table 3. Effect of adsorption on surface reconstruction.

<table>
<thead>
<tr>
<th>Layer 1</th>
<th>Layer 2</th>
<th>ΔAl(^{[1]})</th>
<th>Al(^{[1] \cdot O^{[2]}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>Å</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>-89</td>
<td>+6</td>
<td>1.704 1.704 1.704</td>
</tr>
<tr>
<td>O (A)</td>
<td>-83</td>
<td>+6</td>
<td>+11</td>
</tr>
<tr>
<td>O (B)</td>
<td>-98</td>
<td>+9</td>
<td>+8</td>
</tr>
<tr>
<td>H (C)</td>
<td>-87</td>
<td>+6</td>
<td>+11</td>
</tr>
<tr>
<td>H (D)</td>
<td>Non uniform</td>
<td>-14</td>
<td>1.841 1.747 1.746</td>
</tr>
<tr>
<td>O (E)</td>
<td>-90</td>
<td>+7</td>
<td>+7</td>
</tr>
<tr>
<td>O (F)</td>
<td>-84</td>
<td>+4</td>
<td>+9</td>
</tr>
<tr>
<td>O (G)</td>
<td>-86</td>
<td>+13</td>
<td>+13</td>
</tr>
<tr>
<td>H (H)</td>
<td>-83</td>
<td>+10</td>
<td>+13</td>
</tr>
<tr>
<td>H (I)</td>
<td>-84</td>
<td>+9</td>
<td>+11</td>
</tr>
<tr>
<td>H (J)</td>
<td>Non uniform</td>
<td>-16</td>
<td>1.844 1.837 1.745</td>
</tr>
<tr>
<td>H(_2)O (K)</td>
<td>-104</td>
<td>+6</td>
<td>+6</td>
</tr>
<tr>
<td>H(_2)O (L)</td>
<td>-83</td>
<td>+9</td>
<td>+13</td>
</tr>
<tr>
<td>H(_2)O (M)</td>
<td>-85</td>
<td>+7</td>
<td>+11</td>
</tr>
</tbody>
</table>

Note: Layer 1 and Layer 2 are the percent change in the 1st and 2nd inter-atomic layers with respect to their bulk coordinates. A negative sign for Layer 1 or 2 represents a contraction of the layer. ΔX\(^{\text{bind}}\) calculates how much the adsorbate pulls the surface Al\(^{[1]}\) site from its original relaxed position. Al\(^{[1]} \cdot O^{[2]}\) are the surface bonds neighboring the adsorption site.

O\(_2\) and H\(_2\)O can molecularly adsorb to surface Al\(^{[1]}\) with binding energies of ~20kcal/mol; whereas, H\(_2\) cannot. O\(_2\) adsorbs closer to the surface than H\(_2\)O and does not change the contraction of the first inter-atomic layer. In contrast, molecularly adsorbed H\(_2\)O causes the surface Al\(^{[1]}\) to contract below the O\(^{[2]}\) atoms, changing the surface termination from Al-terminated to O-terminated although the Al and O atoms are nearly co-planar.

As shown in figure 4, there are three unique configurations for the dissociated products, henceforth referred to as 1-2, 1-4, and 2-2 dissociation. H\(_2\) can form all three dissociation products; however, H\(_2\)O cannot form 2-2 dissociation products and O\(_2\) cannot form 1-4 dissociation products. In comparing the dissociation products, the following trends are clear: (1) dissociation reduces the contraction of the first inter-atomic layer regardless of which species is dissociating and (2) E\(^{\text{bind}}\) O\(_2\) > E\(^{\text{bind}}\) H\(_2\) > E\(^{\text{bind}}\) H\(_2\)O. In regards to which type of dissociation product has the lowest energy, it depends on which species are present. For both H\(_2\)O and O\(_2\), the lowest energy dissociation products are 1-2; however, for H\(_2\), the lowest energy dissociation product is 2-2.

### 3.1 O\(_2\) Molecular and Dissociative Adsorption

The molecular and 1-2 dissociative adsorption of O\(_2\) from free O\(_2\) appears to be spontaneous. However, the actual barrier for direct and indirect (i.e., from 1-2 molecularly adsorbed) dissociation cannot be determined using the LST transition state method because the reaction involves a triplet-singlet spin conversion, which can only be accurately described by sampling both the triplet and singlet potential energy surfaces. Nevertheless, we can accurately calculate
the barriers to the further dissociation of 1-2 into 2-2 products since the minimum energy structure for both of these structures is a singlet spin state. We find that the further dissociation of 1-2 adsorption products is highly endothermic and not kinetically favorable ($E_{\text{rxn}} = 28$ kcal/mol, $E_{\text{barrier}} = 53$ kcal/mol). Given these results, the indirect dissociation of O$_2$ is not considered a viable source for isolated substrate bound atomic oxygen.

### 3.2 H$_2$O Adsorption and Dissociation

The question arises as to whether dissociated H$_2$O can serve as a source of substrate bound oxygen. To answer this question, we investigated the following five pathways for the adsorption and dissociation of H$_2$O:

1. Free H$_2$O molecularly (figure 4K) adsorbs to Al$^{[1]}$.

2. Free H$_2$O dissociates into a 1-2 conformation (figure 4L) by forming hydroxyls with Al$^{[1]}$ and its first nearest neighboring O$^{[2]}$.

3. Free H$_2$O dissociates into a 1-4 conformation (figure 4M) by forming hydroxyls with Al$^{[1]}$ and its second nearest neighboring O$^{[2]}$.

4. Adsorbed H$_2$O (figure 4K) dissociates into a 1-2 conformation.

5. Adsorbed H$_2$O (figure 4K) dissociates into a 1-4 conformation.

Our results indicate that H$_2$O spontaneously dissociates into both 1-2 and 1-4 conformations. Both dissociated products have equivalent adsorption energies. H$_2$O can also adsorb molecularly to surface Al with a slightly higher energy than its dissociated product ($\sim+10$ kcal/mol). The barrier for the molecular adsorption of H$_2$O is 0.083 kcal/mol, which is within the limits of the accuracy of the model. Once molecularly adsorbed, the barrier to further dissociation into 1-2 and 1-4 products are 23 and 9.6 kcal/mol, respectively. Experimentally (Elam, 1998), there has been no evidence found for the existence of molecularly adsorbed H$_2$O. Since the energy released due to spontaneous dissociation from free H$_2$O is well in excess of the barriers for dissociation from molecular H$_2$O, our results suggest that if molecular H$_2$O exists on the surface, it is unlikely to have a long lifetime.

The next series of questions that arise is (1) Can hydrogen diffuse away from dissociated H$_2$O? and (2) Can the remaining Al$^{[1]}$OH hydroxyl group further dissociate into a H and O pair? We find that the easiest paths for the H to diffuse away from dissociated H$_2$O are paths 10, 13, 15 ($E_{\text{barrier}} \sim 17–24$ kcal/mol). These paths avoid the influence of Al$^{[1]}$ and Al$^{[3]}$ atoms. For all other paths considered, the barrier to the diffusion of H from dissociated H$_2$O was $>40$ kcal/mol. The barrier to the further dissociation of the remaining Al$^{[1]}$OH hydroxyl into 2-2 and 2-4 O••H dissociation pairs is 45 and 34 kcal/mol, respectively.
3.3 O Surface Diffusion

The final question to be answered is whether the isolated substrate bound O that is produced from the dissociation of H2O can diffuse across the Al2O3 surface to the catalytic particle to promote combustion. In table 4, we provide barrier calculations for diffusion of O and H between all allowed surface sites. We find that O can easily diffuse from Al[1] tetrahedron (figure 4A) to a bridging (figure 4B) conformation (E_{\text{barrier}} = 4 \text{ kcal/mol}). Once in a bridging conformation, O can diffuse between bridging sites that neighbor the same surface Al[1] (E_{\text{barrier}} = 27 \text{ kcal/mol}). However, jumping to bridging sites on a different surface Al[1] atom requires a minimum of 47 kcal/mol. We also calculated the diffusion barrier for a concerted diffusion path in which O_{\text{ads}} displaces an O_{2}, which then moves into a bridging site on the neighboring Al[1]. The barrier to concerted O diffusion is 61 kcal/mol. These results suggest that in the absence of any other species, O becomes localized near the surface Al[1] sites. However, several of the diffusion paths involve singlet to triplet conversion and need to be further studied before this conclusion can be confirmed.

Table 4. Surface diffusion of bound O and H.

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Note: O diffusion along paths 1, 2, 12, 3, 7, and 11 involves a triplet-singlet spin change and must be studied in more detail before the diffusion barriers can be verified.

We also studied whether the presence of pre-adsorbed H can promote O diffusion. We find that pre-adsorbed H nearly eliminated the barriers to O diffusion around Al[1] sites and reduced the barriers along paths 10, 13, and 15 by 17 kcal/mol. However, this improvement was not adequate to allow O to completely transverse a unit cell. Alternatively, when O and H are allowed to diffuse as a pair, the maximum barrier encountered while traversing the unit cell is 24 kcal/mol. These results suggest that the presence of both mobile O and H species are required for O surface diffusion.
3.4 \( \text{H}_2 \) Dissociation

\( \text{H}_2 \) cannot molecularly adsorb to the Al terminated \( \alpha \text{Al}_2\text{O}_3 \) surface; however, it is both thermodynamically and kinetically favorable for \( \text{H}_2 \) to dissociate into 1-4 (\( E_{\text{barrier}} = 20 \) kcal/mol, \( E_{\text{rxn}} = -9 \) kcal/mol) and 2-2 (\( E_{\text{barrier}} = 2 \) kcal/mol, \( E_{\text{rxn}} = -60 \) kcal/mol) dissociation products. These results support the experimental measurements of Wang (1996), who postulated that \( \text{H}_2 \) adsorbed to the \( \text{Al}_2\text{O}_3 \) support resulted in a dramatic increase in the \( \text{H}_2 \) response during temporal analysis of products (TAP).

3.5 \( \text{H} \) Surface Diffusion

From the results in table 4, we find that \( \text{H} \) can diffuse from a \( \text{Al}^{[1]} \) tetrahedron site (figure 4C) to either the first (\( E_{\text{barrier}} = 18 \) kcal/mol) or second nearest neighboring O atom (\( E_{\text{barrier}} = 26 \) kcal/mol). Once in these conformations, diffusion between \( \text{O}^{[2]} \) sites neighboring the same surface \( \text{Al}^{[1]} \) site is unlikely (\( E_{\text{barrier}} = 42 \) kcal/mol). However, \( \text{H} \) can diffuse between \( \text{O}^{[2]} \) sites neighboring different \( \text{Al}^{[1]} \) sites with barriers of 18 and 34 kcal/mol, depending on how close the sub-surface \( \text{Al} \) atoms are to the diffusion path.

4. Conclusions

In summary, we provide a theoretical model for reaction processes that occur on the \( \text{Al}_2\text{O}_3 \) substrate and influence combustion at the catalytic particle. Our model suggests that \( \text{H}_2\text{O} \) is a primary source of mobile O and H species. Once dissociated, H can diffuse away from dissociated \( \text{H}_2\text{O} \) leaving behind an \( \text{Al}^{[1]}-\text{OH} \) hydroxyl, which can also further dissociate creating a 2-2 \( \text{O}^\bullet\bullet\text{H} \) pair. Although isolated O atoms encounter large barriers to surface diffusion, the 2-2 dissociated \( \text{O}^\bullet\bullet\text{H} \) pair can diffuse with a barrier ~24 kcal/mol. We also find that \( \text{H}_2 \) dissociation is an active source of mobile H species. Although \( \text{O}_2 \) can adsorb molecularly, it cannot further dissociate to create mobile O. However, given that the presence of pre-adsorbed H had a profound influence on the surface diffusion of O, it may be likely that H can also influence the dissociation of molecularly adsorbed \( \text{O}_2 \).
5. References


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