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How Oxygen Vacancies Activate CO$_2$ Dissociation on TiO$_2$ Anatase (001)

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Abstract
The adsorption, dissociation and diffusion of CO$_2$ on the anatase (001) surface was studied using DFT by means of the generalized gradient approximation using the Perdew-Burcke-Ernzerhof (PBE)-functional and applying corrections for long-range dispersion interactions. Different stable adsorption configurations were identified for the fully oxidized surface. The most stable adsorption configuration is the monodentated carbonate-like structure. Small energy barriers were identified for the conversion of a physisorbed to a chemisorbed configuration. CO$_2$ dissociation is found to be unfeasible on the stoichiometric surface. The introduction of oxygen vacancy defects gives rise to new highly stable adsorption configurations with a stronger activation of the C-O bonds. This leads to the possibility of exothermic dissociation of CO$_2$ with barriers up to 22.2 kcal/mol, corresponding to chemical lifetimes of less than 4 s at 300 K. These reactions cause a CO molecule to be formed, which will easily desorb, and the reduced surface to become oxidized. It is clear that oxygen vacancy defects play a key role in the catalytic activity of an anatase (001) surface. Oxygen vacancies play an important role in the dissociation of CO$_2$ on the anatase (001) surface, and will play a significant role in complex problems, such as the catalytic conversion of CO$_2$ to value-added chemicals.
1 Introduction

One of the major concerns of the current era is the global climate changes. The intergovernmental panel on climate change reported in 2014 that each decade in the last 30 years has been successively warmer than any other since 1850. It is generally agreed upon that the main cause of global warming is the anthropogenic extension of the greenhouse effect by emission of greenhouse gasses like CO$_2$. The global CO$_2$ concentration has surpassed the 400 ppm mark in March 2015 for the first time since the measurements began.

There exist several strategies to decrease the concentration of CO$_2$ in the atmosphere, in order to mitigate the effect of greenhouse gases on the global climate. The first and most obvious strategy is the reduction of the CO$_2$ emission itself with the use of CO$_2$ neutral energetic technologies (photovoltaics, wind energy, biogas, etc.). However, it will be difficult to decrease the concentration of CO$_2$ by this strategy alone, as the global population will keep increasing and economy will further develop. To achieve a strong reduction in the global CO$_2$ concentration, this strategy could be combined with the conversion to added-value chemicals. Amongst other techniques, including e.g. plasma conversion, heterogeneous catalysis on reactive metal and metal oxide surfaces is a viable route. Indeed, this approach combines a mitigation of the greenhouse effect with the chemical conversion of CO$_2$ to useful chemicals.

In 1979 Inoue and co-workers reported that the aqueous suspension of a semiconductor (TiO$_2$, ZnO, CdS, etc.) can photoreduce CO$_2$ to form formic acid, formaldehyde, methanol and methane. Among the various catalysts reported in that paper, TiO$_2$ is often used as a model system for the catalytic properties of metal oxides.

To improve the performance of catalytic processes on TiO$_2$ it is important to get a better fundamental insight in the adsorption and activation of CO$_2$ on TiO$_2$ surfaces. In this work we study the interaction of CO$_2$ with anatase (001), and more specifically the influence of oxygen vacancies on the adsorption and activation of CO$_2$. In the study of Yu et al. it is found that the photocatalytic reduction of CO$_2$ on anatase is strongly influenced by the ratio of (101) and (001) facets in the crystal. They found that the sample with 58% (001) facet has the highest reactivity for the photocatalytic reduction of CO$_2$. Also, a higher methane production was reported for samples consisting of mostly the (001) facet than the samples consisting of mostly the (101) facet. For other small molecules it is suggested that the (001) facet has a higher reactivity compared to the most stable (101) facet. Mino et al. performed combined FTIR and DFT studies of the adsorption of CO and CO$_2$ on TiO$_2$ anatase surfaces and found that the surface Ti sites present at the (001) facet have a lower Lewis acidity than the Ti sites at the (101) facet, and the surface oxygen sites exhibit a stronger Lewis basicity on anatase (001) than on the anatase (101) surface. This strongly
influences the adsorption of \( \text{CO}_2 \) on anatase. \( \text{CO}_2 \) is mainly adsorbed in linear form on the anatase (101) surface with an adsorption energy of -11.1 kcal/mol, as the carbonate-like adsorption configuration has an adsorption energy of only -3.7 kcal/mol,\(^{21}\) while on the anatase (001) surface \( \text{CO}_2 \) adsorbs mostly in a carbonate like structure with an adsorption energy of -30.1 kcal/mol and the linear configuration only has an adsorption energy of -5.3 kcal/mol.\(^{20}\)

Apart from the inherent difference in Lewis acidity and basicity of the surfaces, it is possible to increase the Lewis basicity of the surface by introduction of oxygen vacancies.\(^{22}\) Sorescu et al. found that oxygen vacancies significantly influence the adsorption properties of \( \text{CO}_2 \) on rutile (110) and anatase (101) surfaces, and they anticipated that these defects play an important role in the complex surface chemistry of \( \text{CO}_2 \) catalysis.\(^{21,23}\) Previous studies have also shown a significant influence of the presence of oxygen vacancies on the adsorption properties of \( \text{H}_2\text{O}, \text{O}_2, \) and methane derived radicals.\(^{24-27}\) Barzan et al. have shown the unprecedented potential of TiO\(_2\) samples reduced in a H\(_2\) atmosphere in the conversion of ethylene to high density polyethylene under mild conditions and without any activator.\(^{28}\) It is shown that reduced TiO\(_2\) always has a higher catalytic activity for the reduction of \( \text{CO}_2 \) as the presence of point defects provide more active sites.\(^{29}\) The presence of Ti\(^{3+}\) generated by the presence of oxygen vacancies is suggested to facilitate \( \text{CO}_2 \) reduction.\(^{30}\) The intrinsic defects can act as initiators and activators for heterogeneous catalysis. Understanding the influence of oxygen vacancies on the adsorption and reactions of \( \text{CO}_2 \) on TiO\(_2\) is thus key for a fundamental understanding of the catalytic activity of TiO\(_2\). As the position of the defects determines the surface chemistry, we here study the adsorption and dissociation of \( \text{CO}_2 \) on anatase (001) surfaces containing one of the three most stable oxygen vacancies.\(^{27}\) For anatase (101) it has been shown experimentally\(^{31}\) and suggested by simulations\(^{32,33}\) that oxygen vacancies diffuse easily even at room temperature, therefore we expect that the same is true for anatase (001). This means that the different oxygen vacancies will all be accessible for reactions and adsorption.

### 2 Computational details

The calculations were performed using the Vienna ab initio simulation package (VASP).\(^{34,35}\) For the treatment of the exchange and correlation, the Perdew-Burke-ernzerhof (PBE) functional was applied,\(^{36}\) using plane wave basis sets and the projector-augmented wave method\(^ {37}\) as implemented in VASP. It has been shown by Sorescu et al. that long-range dispersion interactions play an important role in the interactions of \( \text{CO}_2 \) with TiO\(_2\).\(^ {21}\) Therefore, we have corrected the PBE functional with long-range dispersion interactions by applying the Tkatchenko and Scheffler method\(^ {38}\) as recently implemented in VASP.\(^ {39}\)

The stoichiometric anatase (001) surface was modelled using a (2x2) supercell containing 48 atoms corresponding to four TiO\(_2\) layers. We fixed the bottom layer of the surface at the bulk
positions and expanded the simulation box to create a vacuum layer of ~16 Å between adjacent surfaces to prevent influence of neighbouring slabs on the adsorption properties. An energy cutoff of 440 eV was used, and the sampling of the Brillouin zone was performed using 6x6x1 k-points for the surface models and only the gamma-point for the CO\textsubscript{2} and CO molecules. Geometry optimizations were performed with endpoint criterion of the residual forces to be below 0.03 eV Å\textsuperscript{-1}. Spin polarization was applied for all calculations.

The vibrational analysis was performed with the finite difference method implemented in VASP. Two sets of calculations were performed for the vibrational analysis. In the first set of calculations that were preformed, the finite difference displacements were only applied to the CO\textsubscript{2} molecule. The resulting frequencies were reported as the vibrational frequencies of the adsorbed molecule. The second set of calculations included the displacements to both the CO\textsubscript{2} molecule and the top layer of the TiO\textsubscript{2} surface. These results were used for the thermodynamical analysis as performed with the TAMKIN tool.\textsuperscript{40}

The adsorption energy of CO\textsubscript{2} on the stoichiometric and reduced surfaces is calculated as follows:

\[ E_{ads} = E_{CO2+surface} - E_{CO2} - E_{surface} \]

where \( E_{CO2} \) is the total energy of the optimized gas phase CO\textsubscript{2} molecule with zero-point energy corrections included, \( E_{surface} \) is the total energy of the respective surface with zero-point energy corrections and \( E_{CO2+surface} \) is the total energy of the respective surface with CO\textsubscript{2} adsorbed with zero-point energy corrections.

The extent of charge transfer from the surface to the adsorbed CO\textsubscript{2} molecule was calculated using Hirshfeld charges.\textsuperscript{41} To study the adsorption mechanism and the effect of the oxygen vacancies on the activation barrier of CO\textsubscript{2} reduction, we calculated the corresponding minimum energy barriers with Nudged Elastic Band (NEB)\textsuperscript{42-47} as implemented in the VASP code.

3 Results and discussion

3.1 CO\textsubscript{2} adsorption on the oxidized (non-defective) anatase (001) surface

We identified different binding configurations of CO\textsubscript{2} on the stoichiometric surface, of which a pictorial view is shown in Figure 1. The relevant bond lengths, bond angles, adsorption energies, vibrational frequencies and charge transfer are given in Table 1. The first and most stable configuration is a monodentate carbonate like structure, B(I). In this configuration, CO\textsubscript{2} binds with its oxygen atoms to two 5-fold coordinated Ti(5f) centers in the same [010] row, and with its carbon atom to the two-fold coordinated oxygen (O(2f)) center of the Ti-O(2f)-Ti bridge. The O-C-O bond angle is 129.9°. This configuration has a strong exothermic adsorption energy of -32.8 kcal/mol,
despite the energy cost of bending the CO$_2$ from its linear gas phase configuration to the bent configuration and the significant deformation of the anatase surface. The O(2f), participating in the monodentated carbonate like structure, is displaced inward by 0.8 Å, and the Ti-O(2f)-Ti angle changes from 155.2° to 179.2°. This structure has previously been reported by Mino, Indrakanti and Pipornpong, with adsorption energies ranging from -30.1 to -26.2 kcal/mol. However, they did not include zero point energy corrections nor long-range dispersion corrections.

Mino et al. reported IR frequencies for the monodentated carbonate configuration of 1587 and 1316 cm$^{-1}$ for spectra taken at room temperature of CO$_2$ adsorbed on TiO$_2$ anatase nanopowder outgassed at 823 K to remove residual co-adsorbed water and fully oxidized by exposure to O$_2$ at 723 K. These values correspond well with the values obtained in our calculation, viz. 1558 and 1313 cm$^{-1}$, respectively. The increasing C-O bond length (from 1.18 Å in gas phase to 1.28 Å in the B(I) configuration), the strong red-shift of the asymmetric stretch (from 2365 cm$^{-1}$ to 1558 cm$^{-1}$), and the significant charge transfer to CO$_2$ (-0.214 a.u.) as resulting from the adsorption, all suggest an activation of CO$_2$ for the reduction of CO$_2$. However, as shown by Pipornpong et al., dissociative adsorption of CO$_2$ on a fully oxidized anatase (001) surface has an unfavourable adsorption energy of 76.2 kcal/mol. In comparison, we find a similar dissociative adsorption energy of 67.4 kcal/mol and a dissociation energy barrier of 113.6 kcal/mol, as will be shown later. It is thus clear that CO$_2$
dissociation on the fully oxidized surface will not occur without the help of co-adsorbates that stabilize the transition state and the reaction products, i.e., CO and atomic oxygen adsorbed on the fully oxidized surface.

Apart from the strong chemisorbed monodentate carbonate configuration, there exist several physisorbed configurations, which form shallow metastable intermediates upon adsorption of CO$_2$ from the gas phase (see configurations L(I), L(II) and L(III) in Figure 1). In particular, when CO$_2$ undergoes physisorption it will subsequently convert to the B(I) configurations over low energy barrier pathways. These barriers range from 0.2 kcal/mol to 0.8 kcal/mol, and hence the conversion from any of the physisorbed configurations to the B(I) chemisorbed configuration will easily occur, even at room temperature. However, diffusion from one chemisorbed configuration to a neighbouring adsorption site requires crossing an energy barrier of 30.4 kcal/mol, which is not easily accessible at low temperatures. As this barrier is comparable to the desorption energy of 32.8 kcal/mol, desorption and diffusion will be competitive at elevated temperatures.

Table 1. Adsorption properties of CO$_2$ on a stoichiometric TiO$_2$ anatase (001), for the gas phase, chemisorbed (B(I)) and several physisorbed (L(I), L(II), L(III)) configurations; The bond lengths between Ti and O of CO$_2$, r(Ti-O$_{CO2}$), between the surface O and C, r(O$_{surf}$-C), and between C and O of CO$_2$, r(C-O$_{CO2}$), the bond angle of CO$_2$, $\alpha$(OCO), the adsorption energy, vibrational frequencies $\nu$(CO$_2$), the charge transfer from the surface to CO$_2$, $\Delta$q(CO$_2$) and the activation energy for diffusion to a B(I) adsorption configuration $E_a$.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>r(Ti-O$_{CO2}$) (Å)</th>
<th>r(O$_{surf}$-C) (Å)</th>
<th>r(C-O$_{CO2}$) (Å)</th>
<th>$\alpha$(OCO) (deg.)</th>
<th>$E_{ads}$ (kcal/mol)</th>
<th>$\nu$(CO$_2$) (cm$^{-1}$)</th>
<th>$\Delta$q(CO$_2$) (a.u.)</th>
<th>$E_a$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(I)</td>
<td>2.073, 2.088</td>
<td>1.323</td>
<td>1.177, 1.177</td>
<td>180.0</td>
<td>-32.82</td>
<td>1558</td>
<td>1315</td>
<td>844</td>
</tr>
<tr>
<td>L(I)</td>
<td>2.956, 2.924</td>
<td>1.177, 1.177</td>
<td>177.7</td>
<td>-7.31</td>
<td>2356</td>
<td>1315</td>
<td>615</td>
<td>615</td>
</tr>
<tr>
<td>L(II)</td>
<td>2.460</td>
<td>2.514</td>
<td>1.187, 1.170</td>
<td>173.5</td>
<td>-6.19</td>
<td>2344</td>
<td>1304</td>
<td>622</td>
</tr>
<tr>
<td>L(III)</td>
<td>3.089, 3.249</td>
<td>1.177, 1.176</td>
<td>179.7</td>
<td>-4.34</td>
<td>2358</td>
<td>1317</td>
<td>634</td>
<td>620</td>
</tr>
</tbody>
</table>

3.2 CO$_2$ adsorption on a reduced (defective) anatase (001) surface

As mentioned in the introduction, the behaviour of reactive species under the influence of oxygen vacancies present in TiO$_2$ is a key factor in its catalytic activity. In our previous work we determined the formation energy of different oxygen vacancies in anatase (001). The position of the different oxygen vacancies is shown in Figure 2. The formation energies for V$_{O1}$, V$_{O2}$, V$_{O3}$, and V$_{O4}$ are 102.9, 115.0, 110.8, and 132.7 kcal/mol, respectively. We will only investigate the influence of V$_{O1}$, V$_{O2}$ and V$_{O3}$, as V$_{O4}$ is too unstable to have a significant influence on the adsorption of CO$_2$.27
3.2.1 CO$_2$ adsorption near an oxygen vacancy

In this section, we investigate the influence of the presence of different oxygen vacancies on the adsorption properties of the stable adsorption configurations found on the fully oxidized surface. The adsorption energies of CO$_2$ on the oxygen vacancy containing surface as well as the original adsorption strengths (i.e., on the fully oxidized surface) are shown in Figure 3. In panel a, site 0 corresponds to the stoichiometric configuration (i.e., without an oxygen vacancy present in the surface). Sites 1 and 2 correspond to an oxygen vacancy present closest to the adsorbed CO$_2$, and the vacancy present on the position of the neighbouring O(2f) in the same [010] row (see Figure 2) of the stoichiometric surface, respectively. Sites 3 and 4 are equivalent to sites 1 and 2, respectively, but in the neighbouring [010] row. In panel b, site 0 corresponds to the configuration on the stoichiometric surface and site 1 corresponds to the oxygen vacancy present closest to the adsorbed CO$_2$ molecule. For B(I), site 2 is equivalent to site 1 as the removal of any of the V$_{O2}$ oxygen atoms will result in the same adsorption configuration due to symmetry. For L(I), the oxygen vacancy is located in the parallel [010] row, and for L(II) and L(III) the oxygen vacancy is located in the parallel [100] row. In panel c, site 0 corresponds to the configuration on the stoichiometric surface. Sites 1 and 2 correspond to the V$_{O3}$ oxygen vacancy present closest to the adsorbed CO$_2$ and the vacancy present in the same [010] row of the neighbouring [100] row, respectively. Sites 3 and 4 are equivalent to sites 1 and 2, respectively, but in the neighbouring [010] row.

In general, the influence of the oxygen vacancy stays limited compared to the influence found on different TiO$_2$-surfaces. The adsorption energy does not change more than 5 kcal/mol for the bent configuration, and changes by about 2 kcal/mol for the physisorbed configurations. Also, the presence of the vacancy does not lead to additional charge transfer, and the bond length and red shift
also stay very similar. In contrast, on the anatase (101) surface, it was found in literature that for the bent configuration the adsorption energy changes by up to 13 kcal/mol and for the physisorbed configuration up to 4.5 kcal/mol.\textsuperscript{21}

Only for the V\textsubscript{O1} vacancy, a strong influence is found for the B(I) configuration, and this only occurs when the oxygen vacancy is present in the same [010] row and neighbouring the Ti-O(2f)-Ti bridge at which CO\textsubscript{2} is adsorbed. In this case a strong destabilisation of the binding configuration is found. The adsorption energy increases from -32.8 kcal/mol on the fully oxidized surface to 1.1 kcal/mol on the reduced anatase (001) facet. The destabilization originates from both electronic and structural causes. The electronic destabilisation occurs due to the binding of the Lewis base centers of CO\textsubscript{2}, i.e., the oxygen atoms, directly to the Lewis base centers of the surface (i.e., Ti\textsuperscript{3+}), which are generated upon the introduction of an oxygen vacancy. Moreover, the carbon, the Lewis acid center, is not directly bonded to the Ti\textsuperscript{3+} centers, thus not leading to any stabilisation of the adsorbed configurations.

Apart from this first electronic contribution, we expect the largest part of the destabilization to originate from the relaxation of the surface, which occurs after the formation of the V\textsubscript{O1} oxygen vacancy, and which is counteracted by the adsorbed CO\textsubscript{2} molecule. The Ti-O(2f)-Ti angle is 145.6° for the stoichiometric surface and becomes 102.8° upon reduction for the Ti-O(2f)-Ti moiety located in the same [010] row as the oxygen vacancy. Once CO\textsubscript{2} adsorbs, this angle increases to 167.1° for B(I) located above the Ti-O(2f)-Ti bridge neighbouring the oxygen vacancy, thus introducing stress on the surface and thereby destabilizing the adsorption configuration.

The generally small influence of the reduction of the surface on the adsorption configurations of the stoichiometric surface compared to the generally larger influence as found on the anatase (101) surface by Sorescu et al.\textsuperscript{21} can be explained by the inherent difference in Lewis acidity and basicity of both surfaces. As mentioned above, Mino et al.\textsuperscript{19,20} performed combined FTIR and DFT studies on the adsorption of CO and CO\textsubscript{2} on anatase (001) and (101) facets. They concluded that on the (001) facet the Lewis acidity of the Ti-centers is lower compared to the (101) facet, as indicated by the strong bonding of the Ti-cations with the O(2f) anions, resulting in a more screened electrostatic potential. The Lewis basicity of the surface oxygen sites, on the other hand, is higher on the (001) facet, as indicated by the up-shift of the valence band characterized by the O 2sp states with the main contribution coming from the O(2f) sites.

In the study of Sorescu, it is found that on the stoichiometric anatase (101) surface CO\textsubscript{2} preferentially adsorbs in a nearly gas phase structure, Sorescu-L(I) ($E_{\text{ads}} = -11.1$ kcal/mol), while the bent configurations, Sorescu-B(I) ($E_{\text{ads}} = -3.7$ kcal/mol) and Sorescu-B(II) ($E_{\text{ads}} = -0.3$ kcal/mol), are unfavourable, as a result of the lower Lewis basicity of the surface oxygens compared to anatase
If then an oxygen vacancy is introduced in the surface, new Lewis base centers are introduced causing a significant stabilization of the Sorescu-B(II) configuration ($E_{\text{ads}} = -16$ kcal/mol), which has a comparable structure as the B(I) configuration on the anatase (001) surface. However, on the anatase (001) surface the monodentated carbonate like structure B(I) is very stable ($E_{\text{ads}} = -32.8$ kcal/mol). This stronger interaction is due to the stronger Lewis basicity of the O(2f) surface oxygens, as also indicated by the greater charge transfer of -0.214 a.u. from the surface to CO$_2$ for B(I) compared to a charge transfer of -0.146 a.u. for Sorescu-B(II). In reality, this difference in charge transfer is likely to be larger, since the charge transfer for Sorescu-B(II) was calculated with the Bader method, while in this paper we employ the Hirshfeld method, and the Bader method tends to give larger charges compared to the Hirshfeld method. The smaller influence of the presence of oxygen vacancies in anatase (001) is thus due to the already large inherent Lewis basicity of anatase (001), and further increasing the Lewis basicity does not lead to significant change in interaction.

![Figure 3](image1.png)

**Figure 3.** The adsorption energy of the adsorption configurations of CO$_2$ on a reduced anatase (001) surface with a a) V$_{O1}$ vacancy b) V$_{O2}$ vacancy c) V$_{O3}$ vacancy.

Apart from the possible influence of the reduction of the TiO$_2$ surface on the original adsorption configurations, new adsorption possibilities also arise on the reduced surfaces. A pictorial view of the newly formed adsorption configurations is shown in Figure 4, and the relevant bond lengths, bond angles, adsorption energies, vibrational frequencies and charge transfer is given in Table 2.

### 3.2.2 CO$_2$ adsorption at an oxygen vacancy

#### 3.2.2.1 At the surface bridging oxygen vacancy, V$_{O1}$

Three new adsorption configurations, D$_{\text{VO1(I)}}$ to D$_{\text{VO1(III)}}$, are found on the reduced surface containing a V$_{O1}$ vacancy (see Figure 4). D$_{\text{VO1(I)}}$ and D$_{\text{VO1(II)}}$ are configurations which
arise when an oxygen atom is removed from the surface. D_VO1(I) has an adsorption energy of -48.65 kcal/mol (see Table 2) and has a structure similar to the monodentated carbonate configuration B(I), which had an adsorption energy of -32.8 kcal/mol. However, opposed to the latter configuration, the carbon is no longer bonded to the surface Lewis base center, O(2f), as this is no longer available, but now binds to the newly formed Lewis base centers, the Ti$^{3+}$ atoms. The strong stabilization is thus caused by the strong interaction of carbon with the metallic centers, and not due to interactions of the CO$_2$ oxygen atoms with the titanium atoms. A larger charge transfer from the surface to the CO$_2$ molecule is found for D_VO1(I) than for B(I), i.e., -0.338 a.u. vs. -0.214 a.u., respectively. Almost all this charge is transferred to the carbon atom: we calculate a charge of -0.247 a.u. to be transferred to the carbon compared to the charge located on the carbon atom in the gas phase geometry, while the charge on the oxygen atoms only changes by -0.039 a.u. and -0.052 a.u. The greater charge transfer to CO$_2$ and the stronger red-shift of the CO$_2$ vibrations in D_VO1(I) compared to B(I) indicates a better activation of the CO$_2$ molecule for CO$_2$ splitting. However, the C-O bond lengths do not change significantly (cf. Table 1 and Table 2). Pipornpong et al. reported a similar structure on the reduced anatase (001) surface, denoted as CO$_2$/[TiO2+Vo]-C’ in their publication. They found an adsorption energy of -93.74 kcal/mol for their adsorption configuration, which is much larger than the -48.65 kcal/mol reported in this work. We suspect that this significant difference might be caused by their use of frozen clusters. These frozen clusters do not allow relaxation of the surface when the oxygen vacancy is created, which causes a structure that is significantly less stable and therefore increases the adsorption energy as the adsorption of CO$_2$ will release a significant part of the stress in the structure.

The D_VO1(II) configuration (see Figure 4) is an adsorption configuration in which CO$_2$ is bent and one oxygen is located on the position where a surface oxygen atom was removed to create the vacancy. The adsorption energy is -25.25 kcal/mol (see Table 2). A strong charge transfer is noticeable to the carbon atom, caused by the weakened interaction with the oxygen located at the oxygen vacancy site, as this oxygen now fills the oxygen vacancy. The C-O bond length is increased from 1.177 Å in the gas phase to 1.346 Å for the oxygen located at the oxygen vacancy site and to 1.289 Å for the oxygen located above the Ti$^{3+}$ site. The total charge transfer to CO$_2$ is -0.422 a.u., which is larger than for any previously discussed adsorption configuration. Most of this transferred charge is located on the carbon atom with a change of -0.286 a.u. compared to the gas phase structure. In this configuration, a strong red shift is again found, from 2365 cm$^{-1}$ to 1207 cm$^{-1}$. The longer C-O bonds, strong red shift and the significant charge transfer indicate the strongest activation of CO$_2$ reduction to CO thus far.
The last configuration that was found to be stable on the anatase (001) surface containing a surface oxygen vacancy is D_VO1(III) (see Figure 4). We have also tried obtaining this configuration on the stoichiometric surface. However, we find it spontaneously converts to B(I). Only when located near the surface oxygen vacancy, this configuration is found to be stable. The adsorption configuration is -1.64 kcal/mol (see Table 2). As this configuration is only slightly stable, we expect it to either convert to B(I) or D_VO1(I), or else desorption will occur and not contribute significantly to the reactivity of anatase (001) with respect to reduction of CO$_2$. The C-O bonds are less activated than in the other obtained configurations. In particular, we find a smaller red shift of the asymmetric stretch, shorter C-O bonds, and a smaller charge transfer compared to the other chemisorbed configurations.

We have tried to reproduce the structure CO$_2$/[TiO$_2$+Vo]-C of Pipornpong et al. In this non-dissociative adsorption configuration the oxygen vacancy is filled with one of the oxygen atoms of CO$_2$, and CO$_2$ is oriented in a similar manner as D_VO1(III). However, we found that this configuration is not stable and spontaneously converts to D_VO1(I). Possibly, Pipornpong et al. found this structure to be stable as the result of their frozen cluster approach, which can erroneously create an energy barrier between these two configurations.

3.2.2.2 At the first subsurface oxygen vacancy, V$_{O2}$

One new adsorption configuration, D_VO2(I), is found on the reduced surface containing a V$_{O2}$ oxygen vacancy. In this configuration, CO$_2$ takes on a bent configuration and is very comparable to the D_VO1(I) configuration (see Figure 4). However, the CO$_2$ in this case is bonded to two Ti$^{3+}$ atoms located in the same [100] row as opposed to the same [010] row. The adsorption energy for the D_VO2(I) configuration is -25.50 kcal/mol (see Table 2), which is significantly lower than the -32.96 kcal/mol found for the monodentated carbonate-like structure B(I) if a V$_{O2}$ vacancy is present in the vicinity of the adsorbed CO$_2$ molecule. However, just as is the case for the D_VO1(I) configuration, a larger charge transfer to CO$_2$ is found compared to the B(I) configurations. In view of this larger charge transfer and the comparable red-shift of the CO$_2$ vibrations (see Table 3), we expect a greater activation of CO$_2$ in this bonding configuration.

3.2.2.3 At the second subsurface oxygen vacancy, V$_{O3}$

When a V$_{O3}$ oxygen vacancy is present, we find two new monodentated carbonate configurations on the anatase (001) surface. The only difference between the two configurations is their orientation relative to the oxygen vacancy. In the D_VO3(I) configuration, the oxygen atom of CO$_2$ that is bonded to the surface, is located above the titanium atom located at the oxygen vacancy site, while in the D_VO3(II) configuration this oxygen is located above the titanium atom in the same [010] row and neighbouring [100] row. As mentioned before we have tried to create similar
configurations on the stoichiometric surface but found these to spontaneously convert to the B(I) configuration, also when \(\text{V}_\text{O}_3\) is located in the neighbouring [010] row. The lower stability of \(\text{D}_\text{VO}_3\text{(I)}\) and \(\text{D}_\text{VO}_3\text{(II)}\) compared to the B(I) configuration and the similarity between the three configurations, indicates that the \(\text{D}_\text{VO}_3\text{(I)}\) and \(\text{D}_\text{VO}_3\text{(II)}\) will easily convert to B(I). Thus we do not expect a strong activation of the \(\text{CO}_2\) molecule for \(\text{CO}_2\) dissociation in these configurations. We rather expect that first a conversion of \(\text{D}_\text{VO}_3\text{(I)}\) and \(\text{D}_\text{VO}_3\text{(II)}\) to a B(I) configuration or diffusion of the oxygen vacancy creating a \(\text{V}_{\text{O}_1}\) or \(\text{V}_{\text{O}_2}\) oxygen vacancy takes place, after which further reactions can occur.

Figure 4. The new adsorption configurations of \(\text{CO}_2\) on a reduced anatase (001) surface with different oxygen vacancies, in side view and top view (upper and lower panels, respectively). See text for explanation. (Ti = blue, \(\text{O}_{\text{TiO}_2}\) = red, \(\text{O}_{\text{CO}_2}\) = red and yellow plus sign, C = brown)

Table 2. Adsorption properties of \(\text{CO}_2\) on the reduced TiO\(_2\) anatase (001) surfaces with different oxygen vacancies: The bond lengths between Ti and O of \(\text{CO}_2\), \(r(\text{Ti-O}_{\text{CO}_2})\), between the surface O and C, \(r(\text{Os-C})\), and between C and O of carbon, \(r(\text{C-O})\), the bond angle of \(\text{CO}_2\), \(\alpha(\text{OCO})\), the adsorption energy, vibrational frequencies \(\nu(\text{CO}_2)\), and the charge transfer from the surface to \(\text{CO}_2\), \(\Delta q(\text{CO}_2)/|e|\).

| Configuration | \(r(\text{Ti-O})\) (Å) | \(r(\text{Os-C})\) (Å) | \(\nu(\text{OCO})\) (deg.) | \(E_{\text{ads}}\) (kcal/mol) | \(\nu(\text{CO}_2)\) (cm\(^{-1}\)) | \(\Delta q(\text{CO}_2)/|e|\) |
|---------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Gas phase     | 1.177, 1.177           | 180.0                  | 2365                   | 1316                   | 632                    | 631                    |
| \(\text{D}_\text{VO}_1\text{(I)}\) | 2.075, 1.973           | 1.272, 1.286           | 125.1                  | -48.65                 | 1503                   | 767                    | 455 | -0.338 |
| \(\text{D}_\text{VO}_1\text{(II)}\) | 1.971, 2.642           | 1.289, 1.346           | 108.9                  | -25.25                 | 1207                   | 728                    | 363 | -0.422 |
| \(\text{D}_\text{VO}_1\text{(III)}\) | 2.016, 1.472           | 1.200, 1.300           | 134.7                  | -1.64                  | 1852                   | 740                    | 714 | -0.228 |
| \(\text{D}_\text{VO}_2\text{(I)}\) | 2.008, 1.994           | 1.265, 1.270           | 126.1                  | -25.50                 | 1577                   | 757                    | 469 | -0.314 |
| \(\text{D}_\text{VO}_3\text{(I)}\) | 1.932, 1.365           | 1.218, 1.335           | 128.6                  | -24.12                 | 1734                   | 739                    | 824 | -0.256 |
| \(\text{D}_\text{VO}_3\text{(II)}\) | 1.905, 1.366           | 1.213, 1.347           | 126.9                  | -23.56                 | 1754                   | 729                    | 825 | -0.252 |

3.3 CO\(_2\) adsorption at 300K on anatase (001)

At non-zero temperature we find that the CO\(_2\) adsorption is destabilized, reducing the adsorption strength of the chemisorbed configuration from -32.8 kcal/mol at 0 K to -22.9 kcal/mol at
300 K on the fully oxidized surface. The physisorbed configurations become metastable and the adsorption is endothermic with an adsorption energy ranging from 1.4 to 4.2 kcal/mol, maintaining the same order in stability as at absolute zero. The diffusion barriers from the physisorbed configurations to the bent carbonate configuration decrease for the L(I) configuration from 0.8 kcal/mol at 0 K to 0.7 kcal/mol at 300 K, and increase for L(II) and L(III) with a maximal barrier of 1.8 kcal/mol at 400 K for L(III). The rate constants for the conversion of the physisorbed configuration to the chemisorbed configuration are in the order of $10^{11}$ – $10^{12}$ s$^{-1}$. However, diffusion barriers between adsorption sites for B(I) is unlikely to occur at these temperatures as the reaction rate equals $8.1 \times 10^{11}$ s$^{-1}$ at 300 K. The influence of oxygen vacancies on the adsorption stays similar at elevated temperatures compared to their influence at absolute zero. All adsorption energies at absolute zero, 300 K and 400 K are given in Table 3.

Table 3. The adsorption energies on the stoichiometric and reduced surfaces at absolute zero, 300 K and 400 K in kcal/mol. The endothermic and endergonic adsorption configurations are given in red.

<table>
<thead>
<tr>
<th></th>
<th>Absolute zero</th>
<th>300 K</th>
<th>400 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>site 1</td>
<td>site 2</td>
</tr>
<tr>
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<td>-32.96</td>
<td>32.96</td>
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<tr>
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<tr>
<td>L(III)</td>
<td>-4.34</td>
<td>5.00</td>
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</tr>
</tbody>
</table>

3.4 CO₂ dissociation on anatase (001)

3.4.1 Stoichiometric anatase (001) surface
As previously mentioned, the dissociation of CO$_2$ on the fully oxidized anatase (001) surface is unlikely to occur without the help of co-adsorbates to stabilize the transition state and the reaction products. We find a dissociative adsorption energy of 67.4 kcal/mol. In the dissociation mechanism, as determined using NEB and shown in Figure 5, we start from the B(I) configuration, as this configuration showed to be the most promising for CO$_2$ activation as inferred from the calculated charge transfer to CO$_2$, the significant elongation of the C-O bonds and the red shift in the vibrations. However, we find that B(I) first converts to L(II), which is not activated compared to the gas phase CO$_2$. The reaction proceeds further through the rotation of the CO$_2$ molecule, resulting in a transition state with the carbon atom being bonded to Ti and one of the oxygen atoms bonded to O(2f), while maintaining a bent configuration. Subsequently, the C-O bond of the corresponding atoms breaks and CO and O remain adsorbed on the TiO$_2$ surface. The corresponding energy barrier corrected for the ZPE is 113.6 kcal/mol, and the reaction enthalpy of the dissociation is equal to 98.9 kcal/mol. The corresponding dissociation rate at 300 K is $4.4 \times 10^{-11}$ s$^{-1}$. Therefore, this reaction is highly unlikely to occur on the fully oxidized surface, even at elevated temperatures. However, in the previous sections we found that the presence of oxygen vacancies yields newly available adsorption configurations with an apparent higher activation than B(I) and the possibility to stabilize the reaction products by the healing of the vacancy. We shall now discuss the CO$_2$ dissociation for these new adsorption configurations on the reduced surface.

![Figure 5](image.png)

**Figure 5.** The CO$_2$ dissociation minimal energy pathway starting from B(I) on the stoichiometric anatase (001) surface. No zero-point energy corrections are included in the minimal energy pathway shown.

### 3.4.2 Reduced anatase (001) surface

We here discuss the reaction possibilities and rates for CO$_2$ dissociation in the presence of the different oxygen vacancies. We exclude the V$_{O3}$ vacancy as we found that the dissociation reaction would be endothermic by around 50 kcal/mol, and would hence not yield a feasible dissociation
possibility. We rather expect that the $\text{V}_\text{O}_{3}$ vacancy will be healed by the diffusion of a surface or subsurface oxygen to the $\text{V}_\text{O}_{3}$ site, thereby creating a $\text{V}_\text{O}_{1}$ or $\text{V}_\text{O}_{2}$ vacancy, respectively.

As starting points for the activation of the dissociation reaction on the reduced anatase (001) surface with a $\text{V}_\text{O}_{1}$ oxygen vacancy, we used three different adsorption configurations, i.e., D\_VO1(I), D\_VO1(II), and D\_VO1(III), for which the minimal energy pathways are shown in Figure 6, Figure 7 and Figure 8, respectively. The reactions all resulted in the oxygen vacancy being healed, similar to the reaction mechanism for $\text{CO}_2$ dissociation on the reduced rutile (110)\textsuperscript{51}, and the reduced anatase (101)\textsuperscript{21}. $\text{CO}$ is adsorbed on the now fully oxidized surface, with an adsorption energy of -8.3 kcal/mol at absolute zero and -0.06 kcal/mol at 300 K, relative to the gas phase $\text{CO}$ and the fully oxidized surface.

For D\_VO1(I) (see Figure 6) the minimal energy pathway first crosses a small energy barrier of 1.3 kcal/mol, to yield a minimum which is 0.05 kcal/mol less stable than D\_VO1(I). In this minimum, the $\text{CO}_2$ molecule is bonded with its carbon atom to one Ti$^{3+}$ atom and with one of its oxygen atoms to the other Ti$^{3+}$. The reaction subsequently continues over an energy barrier of 18.1 kcal/mol. At the transition state, we find that $\text{CO}_2$ is already dissociated. The overall reaction is endothermic with a corresponding reaction enthalpy (corrected for the ZPE) of 14.9 kcal/mol. As the barrier for the backward reaction in which $\text{CO}_2$ and the oxygen vacancy are recreated is 3.2 kcal/mol and the desorption energy of $\text{CO}_2$ is 0.06 kcal/mol at 300 K, these reactions will be competitive. The reaction rate for dissociation at 300 K is 1.08 s$^{-1}$.

For D\_VO1(II) we find a barrier of 7.3 kcal/mol (see Figure 7). At the transition state, the C-O bond length has increased from 1.35 Å to 1.83 Å, after which it will convert to an adsorbed CO on the fully oxidized surface. The reaction is exothermic with a reaction enthalpy of -6.4 kcal/mol. The equilibrium constant at 300 K is equal to 1.0x10$^5$, with a dissociation rate of 5.44x10$^6$ s$^{-1}$.

**Figure 6. The $\text{CO}_2$ dissociation minimal energy pathway starting from D\_VO1(I) on the reduced anatase (001) surface. No zero-point energy corrections are included in the minimal energy pathway shown.**

For D\_VO1(II) we find a barrier of 7.3 kcal/mol (see Figure 7). At the transition state, the C-O bond length has increased from 1.35 Å to 1.83 Å, after which it will convert to an adsorbed CO on the fully oxidized surface. The reaction is exothermic with a reaction enthalpy of -6.4 kcal/mol. The equilibrium constant at 300 K is equal to 1.0x10$^5$, with a dissociation rate of 5.44x10$^6$ s$^{-1}$.
We also performed a nudged elastic band calculation for the dissociation pathway of the D_VO1(III) configuration. This configuration had an adsorption energy of only -1.6 kcal/mol at absolute zero and 8.5 kcal/mol at 300 K, so it will not significantly contribute to the overall dissociation of CO₂. This configuration first converts to the L(II) configuration with no barrier, after which the CO₂ in the L(II) configuration crosses a barrier of 6.5 kcal/mol. The overall reaction enthalpy is equal to -32.0 kcal/mol, so if a reaction occurs it is unlikely that the reformation of D_VO1(III) will occur, as the equilibrium constant for dissociation is 6.54x10⁻¹⁸. This pathway also shows that once CO₂ is adsorbed in the L(II) configuration, it only has to cross a barrier of 6.5 kcal/mol to dissociate, resulting in a dissociation reaction rate of 9.2x10⁵ s⁻¹ at 300 K. This reaction is competitive to the conversion of L(II) to B(I), which had a barrier of 0.2 kcal/mol.

As starting points for the activation of the dissociation reaction on the reduced anatase (001) surface with a V_O₂ oxygen vacancy, we used two different adsorption configurations, i.e., D_VO2(I) and B(I) adsorbed with one of the oxygen atoms of CO₂ bonded to one of the Ti³⁺ centers. The
corresponding reaction mechanisms are shown in Figure 9 and Figure 10, respectively. Both reactions result in the oxygen vacancy being healed, and CO being adsorbed on the now fully oxidized surface with an adsorption energy of -8.3 kcal/mol at absolute zero and -0.06 kcal/mol at 300 K, relative to the gas phase CO and the fully oxidized surface.

For D_VO2(I) an exothermic dissociation is found. The dissociation of CO$_2$ follows a rotation of CO$_2$ crossing a barrier of 22.2 kcal/mol. In the dissociation process, one of the oxygen atoms heals the vacancy and CO stays adsorbed on the resulting stoichiometric surface. The total reaction enthalpy equals -26.3 kcal/mol. For this reaction to occur at a sufficient rate, elevated temperatures are needed. We find the reaction rate to increase from $1.1 \times 10^{-3}$ s$^{-1}$ to 17 s$^{-1}$ upon increasing the temperature from 300 K to 400 K. When this reaction takes place, the backward reaction is not likely to occur as the reaction barrier is 49.5 kcal/mol at 300 K.

![Figure 9. The CO$_2$ dissociation minimal energy pathway starting from D_VO2(I) on the reduced anatase (001) surface. No zero-point energy corrections are included in the minimal energy pathway shown.](image)

The CO$_2$ in the B(I) configuration on the reduced anatase surface containing a V$_{O2}$ vacancy will first undergo a rotation out of the [010] plane, into the direction of the oxygen vacancy. The first barrier, corresponding to this rotation, is 3.4 kcal/mol, resulting in the formation of an intermediate structure. In this structure, one of the oxygen atoms of CO$_2$ heals the vacancy, and the resulting Ti-O$_{CO2}$ bond lengths are 2.07 Å and 2.18 Å. The carbon atom stays bonded to all of the three original oxygen atoms of the B(I) configuration. The reaction pathway continues by the elongation of the C-O bond from the oxygen that is filling the V$_{O2}$ oxygen vacancy. The bond elongates from 1.38 Å in the intermediate structure to 1.74 Å in the transition state. In this process, a barrier of 18.2 kcal/mol needs to be overcome. After healing the oxygen vacancy, the D_VO1(I) configuration is formed, and the dissociation of CO$_2$ will then occur through the pathway of D_VO1(I). The overall reaction is exothermic and the reaction enthalpy is equal to -18.9 kcal/mol. The rate limiting step in this reaction mechanism is the elongation of the C-O bond from the oxygen that is filling the V$_{O2}$ oxygen.
vacancy, causing the reaction rate to drop to 0.28 s\(^{-1}\) at 300 K, which increases to 7.7 \times 10^2 s^{-1} at 400 K.

All energy barriers at absolute zero, 300 K and 400 K and all rate constants for diffusion and dissociation at 300 K and 400 K are given in Table 4.

Figure 10. The CO\(_2\) dissociation minimal energy pathway starting from B(I) on the reduced anatase (001) surface containing a V\(_{O2}\) oxygen vacancy. No zero-point energy corrections are included in the minimal energy pathway shown.

Table 4. The energy barriers at absolute zero, 300 K and 400 K and rate constants for diffusion and dissociation at 300 K and 400 K. The cells for conversion of the physisorbed states to the chemisorbed B(I) configuration are shown in grey, and the backward reaction in orange. For the dissociation, the cells corresponding to the reaction from the dissociated state to the adsorbed CO\(_2\) configurations are given in grey, and the dissociation is given in orange. The rates below 1 s\(^{-1}\) are given in red. In this table Int. is the contraction of intermediate.
4 Conclusion

We have studied the adsorption of CO$_2$ and the activation for CO$_2$ dissociation on the fully oxidized and reduced anatase (001) surfaces using density functional theory calculations with long range dispersion energy corrections. On the fully oxidized surface we identified four different adsorption configurations for CO$_2$: One strongly chemisorbed bent configuration, B(I), and three linear physisorbed configurations, L(I)-L(III), which almost retain their gas phase properties. We also studied the influence of the introduction of different oxygen vacancies on the aforementioned adsorption configurations. The influence of the different vacancies on the adsorption configurations found on the stoichiometric surface stays limited, except when the CO$_2$ is adsorbed in the B(I) configuration on top of the Ti-O(2f)-Ti moiety neighbouring a V$_{O1}$ oxygen vacancy in the same [010] row. This configuration is strongly destabilized through the counteraction of the relaxation of the surface after formation of the vacancy, and the interaction of Lewis base centers. New adsorption configurations originate from the presence of oxygen vacancies in the anatase (001) surface. For the different oxygen vacancies we found a total of six new bent adsorption configurations. Just as with the B(I) configuration, significant charge transfer to CO$_2$, large vibrational red shifts, and sizeable elongations of the C-O bonds indicate a substantial bond weakening for these newly formed adsorption configurations. For D$_{VO1}$(III), D$_{VO3}$(I), and D$_{VO3}$(II) we found a smaller red shift than for B(I). CO$_2$ dissociation on a fully oxidized anatase (001) surface starting from the B(I) adsorption configuration is unlikely to occur, as the corresponding barrier equals 113.6 kcal/mol. In the presence of the V$_{O3}$ vacancy, we found that the reaction is endothermic with at least 45 kcal/mol, and hence also unlikely to happen. However, we found significantly lower reaction barriers in the
presence of the other oxygen vacancies, as these vacancies provide a means of stabilizing the end products, by using one of the oxygen atoms of the CO$_2$ molecule to heal the oxygen vacancy. As D_VO1(III) converts to L(II) without a barrier and the barrier for dissociation starting from the physisorbed configuration is 6.54 kcal/mol, direct dissociation after physisorption is competitive with the conversion of the physisorbed configuration to the bent monodentated carbonate-like structure B(I). All dissociations starting from different adsorption configurations, except for the D_VO1(I) configuration, on the reduced surfaces are exothermic. The end product for all these reaction pathways is a CO molecule being adsorbed on the fully oxidized surface with an adsorption energy of -8.3 kcal/mol with respect to the gas phase CO and the fully oxidized surface. The results of this study show that oxygen vacancies play a significant role in the dissociation of CO$_2$ on the anatase (001) surface, and thus we anticipate they will play an important role in complex problems, such as the conversion of CO$_2$ to value-added chemicals.

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6 References


Oxygen vacancies play a key role in the catalytic activity of TiO₂ Anatase (001).