Adsorption of C and CH$_x$ Radicals on Anatase (001) and the Influence of Oxygen Vacancies

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**Supporting Information**

**ABSTRACT:** The adsorption of C and CH$_x$ radicals on anatase (001) was studied using DFT within the generalized gradient approximation using the Perde-Burke-Ernzerhof (PBE) functional. We have studied the influence of oxygen vacancies in and at the surface on the adsorption properties of the radicals. For the oxygen vacancies in anatase (001), the most stable vacancy is located at the surface. For this vacancy, the maximal adsorption strength of C and CH decreases compared to the adsorption on the stoichiometric surface, but it increases for CH$_2$ and CH$_3$. If an oxygen vacancy is present in the first subsurface layer, the maximal adsorption strength increases for C, CH, CH$_2$, and CH$_3$. When the vacancy is present in the next subsurface layer, we find that only the CH$_x$ adsorption is enhanced, while the maximal adsorption energies for the other radical species decrease. Not only does the precise location of the oxygen vacancy determine the maximal adsorption interaction, it also influences the adsorption strengths of the radicals at different surface configurations. This determines the probability of finding a certain adsorption configuration at the surface, which in turn influences the possible surface reactions.

We find that C preferentially adsorbs far away from the oxygen vacancy, while CH$_2$ and CH$_3$ adsorb preferentially at the oxygen vacancy site. A fraction of CH partially adsorbs at the oxygen vacancy, and another fraction adsorbs further away from the vacancy.

**A. INTRODUCTION**

One of the major concerns of the current era is global warming caused by the high concentration of greenhouse gases present in the atmosphere. The major challenge is decreasing greenhouse gas emissions, while the economy develops and global population increases. Considering all greenhouse gases, CO$_2$ and CH$_4$ contribute the most to the man-made greenhouse effect. The global warming potential of methane is even 21× higher than that of CO$_2$.

Apart from being a greenhouse gas, CH$_4$ is also the main component (70–90%) of most natural gas resources. Natural gas can be used as fuel for heating and electrical power generation. However, this requires conversion of CH$_4$ to the greenhouse gas CO$_2$. Alternatively, methane may also be utilized for the production of valuable chemicals, such as methanol, formaldehyde, higher hydrocarbons, hydrogen gas, and syngas (CO/H$_2$).

For the conversion of methane to valuable chemicals there are two different synthesis routes, the indirect and the direct route. The indirect conversion of methane is a two-step process, in which methane is first converted to syngas, to be subsequently used for methanol synthesis or Fischer–Tropsch synthesis. Syngas can be produced by steam reforming, dry reforming, or partial oxidation of methane. These processes, however, require a high energy input and typically only give low overall yields. Direct (thermal) conversion of methane does not require the energy intensive syngas synthesis. However, direct methane conversion is costly and technologically challenging and only achieves the same low overall yields. It would thus be interesting to find nonconventional synthesis routes. Plasma technology has already been used for the conversion of methane in useful chemicals. The main advantage of nonthermal plasmas is that the gas itself remains at room temperature while being activated by electron impact excitation, ionization and dissociation reactions. Plasma processes, however, are mostly nonselective. Catalytic processes, on the other hand, can be very selective but often require a certain gas composition and high temperatures. Plasma-catalysis combines the advantages of the high reactivity of plasmas and the high selectivity of catalysis by integrating the catalyst into the plasma. It is suggested that the catalyst can increase the retention time of the reacting species, thereby enhancing the conversion efficiency and selectivity, as well as the energy efficiency. Also, the lifetime of short-lived active species can be extended by adsorption at the catalyst surface.

To gain a more fundamental insight in the interaction of the plasma with the catalyst surface, we studied the adsorption of reactive CH$_x$ radicals ($x=0–3$), formed in the plasma, on an often-used catalyst, the anatase (001) titanium dioxide surface. We have chosen anatase as model system as it is the catalytically most active polymorph of titanium dioxide and is widely used in experimental plasma catalysis studies.

It is well-known that intrinsic point defects, and specifically oxygen vacancies, affect the physical and chemical properties of
titanium dioxide. Several studies already investigated the influence of defects in titanium dioxide anatase surfaces. Wang et al.\textsuperscript{15} studied the adsorption of H\textsubscript{2}O and O\textsubscript{2} on a (1 × 4) reconstructed anatase (001) surface and the influence of point defects on the adsorption using microscopic and spectroscopic techniques in combination with density functional theory (DFT). They found that on a stoichiometric surface H\textsubscript{2}O has an adsorption energy of 10.38 kcal/mol and O\textsubscript{2} does not adsorb, while near a Ti\textsuperscript{3+} defect H\textsubscript{2}O and O\textsubscript{2} molecules adsorb with a calculated adsorption energy of 22.14 and 41.51 kcal/mol, respectively. Aschauer et al.\textsuperscript{16} studied H\textsubscript{2}O adsorption on anatase (101) and the influence of subsurface defects on the adsorption using both scanning tunnelling microscopy (STM) experiments and DFT calculations. They found that H\textsubscript{2}O preferentially adsorbs in the vicinity of subsurface defects. Both the STM and DFT results suggest an enhanced binding due to the defects. The adsorption of O\textsubscript{2} was also studied on the anatase (101) surface as well as the effect of subsurface defects on this adsorption. They found no O\textsubscript{2} adsorption on the stoichiometric surface. On the reduced surface with a subsurface oxygen vacancy they found a strong adsorption in the vicinity of the defect. Also, studies of the adsorption of CO\textsubscript{2} on anatase (101) and rutile (110) surfaces have shown that surface defects significantly modify the adsorption of CO\textsubscript{2} on the reduced surface compared to the stoichiometric surface.\textsuperscript{17,18} The defect sites act as initiators for adsorption of molecules in heterogeneous catalysis. The role and properties of the defect are determined by its location on the reduced surface. It is therefore important to know the stability of the different oxygen vacancies in the anatase surface. Golberg-Oster et al.\textsuperscript{19} have shown that CH\textsubscript{3} radicals, and therefore probably also other alkyl radicals, react with the surface of TiO\textsubscript{2}. They form long-lived transients with methyl σ-bonded to the surface of TiO\textsubscript{2} nanoparticles. The authors derived that the nanoparticle–CH\textsubscript{3} bond strength should be greater than 16.7 kcal/mol,\textsuperscript{20} which is consistent with what we find in this study.

Since strong bonding is found for methyl radicals on TiO\textsubscript{2} nanoparticles\textsuperscript{20} and since defects strongly influence the adsorption of species on TiO\textsubscript{2} surfaces,\textsuperscript{15–19} it is interesting to study how methyl radicals and other methane derived radicals adsorb on the perfect and defective anatase (001) surface. In total, we performed 155 different calculations to determine the stability of different oxygen vacancies in the anatase (001) surface and the effects of these vacancies on the adsorption of CH\textsubscript{x} radicals (x = 0–3) to gain a better insight in the adsorption of CH\textsubscript{x} radicals (x = 0–3), relevant for plasma catalysis\textsuperscript{10,11,21,22} on anatase and the influence of the reduction status of the surface on the adsorption.

The results obtained in this study, apart from being valuable on their own, will be used for the parametrization of a Ti/C/O/H ReaxFF reactive force field. This force field will be used to study the dynamics and reaction mechanisms of plasma species on anatase surfaces. The ReaxFF force field is being developed by combining two existing force fields, the TiO\textsubscript{2} force field we recently developed for the study of intrinsic point defects\textsuperscript{23} and the TiO\textsubscript{2}–glycine force field of Monti et al.\textsuperscript{24} This combination of force fields will be reparameterised against a large set of first principle calculations relevant to plasma–TiO\textsubscript{2} surface interactions. The DFT results obtained in the current study are expected to greatly improve the ReaxFF description of the TiO\textsubscript{2}–CH\textsubscript{3} (x = 0–3) interactions, eventually allowing much larger spatial scales and longer time scale simulations to be performed compared to DFT.

B. COMPUTATIONAL DETAILS

All calculations were carried out at the DFT-GGA level using the Vienna ab initio simulation package (VASP).\textsuperscript{25,26} For the treatment of the exchange and correlation the Perdew–Burke–Emzerhof (PBE) functional\textsuperscript{27} was used, using plane wave basis sets and the projector-augmented wave method,\textsuperscript{28} as implemented in VASP. We have not included zero-point energy corrections as these are found to not have a significant influence on the adsorption energies of CH\textsubscript{x} species.\textsuperscript{29} We used a (2 × 2) supercell containing 48 atoms for the clean stoichiometric anatase (001) surface and four TiO\textsubscript{2} layers. The bottom layer is kept fixed at the bulk positions. A vacuum layer of ~16 Å between the surface and the adjacent layers is used to prevent the influence of neighboring slabs on the adsorption. Sampling of the Brillouin zone was performed using the Monkhorst–Pack scheme\textsuperscript{30} with 6 × 6 × 1 k-points for the periodic structures and only the gamma-point for molecules. An energy cutoff for the plane wave basis set of 500 eV was used for the investigation of the oxygen vacancy formation in anatase (001) and a cutoff of 440 eV for the study of the CH\textsubscript{3} radical (x = 0–3) adsorption on the stoichiometric and reduced anatase (001) surface. The geometry optimization was stopped when the residual forces were below 0.03 eV Å\textsuperscript{-1}. We performed spin-restricted calculations for the investigation of the oxygen vacancy formation in anatase (001) and spin-unrestricted calculations for the study of the CH\textsubscript{3} radical (x = 0–3) adsorption on the stoichiometric and reduced anatase (001) surface, respectively.

The oxygen vacancy formation energies are calculated with the following expression:

\[
E_{\text{form}} = E_{\text{surf}} - E_{\text{VO}} - \frac{1}{2}E_{\text{O}_2}
\]

In expression \(1\), \(E_{\text{surf}}\) is the total energy of the stoichiometric surface, \(E_{\text{VO}}\) is the total energy of the reduced surface, and \(E_{\text{O}_2}\) is the total energy of the optimized gas phase \(\text{O}_2\).

The adsorption energies of CH\textsubscript{x} (x = 0–3) on the stoichiometric and reduced surfaces are calculated as follows:

\[
E_{\text{ads}} = E_{\text{CH}_x} + E_{\text{surf}} - E_{(\text{CH}_x + \text{surf})}
\]

where \(E_{\text{CH}_x}\) is the energy of the optimized gas phase geometry of CH\textsubscript{x}, \(E_{\text{surf}}\) is the total energy of the respective surface, and \(E_{(\text{CH}_x + \text{surf})}\) is the total energy of the slab with CH\textsubscript{x} adsorbed. According to this definition, a more positive \(E_{\text{ads}}\) thus corresponds to a more stable configuration.

The extent of charge transfer from the CH\textsubscript{x} (x = 0–3) radical to the surface is calculated with the algorithm of Henkelman et al.\textsuperscript{31,32} using Bader charges.\textsuperscript{33}

\[\text{BO} = aR^{-2} + b \quad (a = 5.75 \text{ Å}^2; b = -1.85)\]

where R is the C–O bond length in Å.

C. OXYGEN VACANCY FORMATION ENERGIES

The calculated formation energies for different surface and subsurface oxygen vacancy defects (VO\textsubscript{x}) at the anatase (001) titanium dioxide surface are reported in Table 1. The labeling of
atom displacement when subsurface vacancies are present, which is caused by the “rigidity” and stability of the anatase (101) surface. When comparing the average and maximal atom displacement for the different oxygen vacancies in the anatase (001) (see Table 1), it is clear that the displacement of the atoms is much greater when the $V_{O1}$ vacancy is formed than when the other vacancies are formed. This is caused by the fact that at the anatase (001) surface the bridging $O_{2c}$ forms two asymmetric Ti–O bonds, having bond lengths of 1.75 and 2.23 Å. The Ti–O bonds of the neighboring $O_{2c}$ become symmetric with a bond length of 1.81 Å, once the $V_{O1}$ oxygen vacancy is formed. The better relaxation and the fact that fewer bonds have to be broken to form the vacancy, make $V_{O1}$ the most stable vacancy. The relative probabilities of the different vacancies at 300 and 1000 K are also shown in Table 1. It is found that $V_{O3}$ will not play a significant role in the adsorption of CH radicals ($x = 0–3$) later discussed in this article. Our values and trends for the formation energies of the oxygen vacancies in anatase (001) are in good agreement with previously calculated formation energies. For $V_{O1}$, $V_{O2}$, $V_{O3}$, and $V_{O4}$ formation energies in ref 36 were found to be $-92.24$, $-110.00$, $-109.77$, and $-114.38$ kcal/mol, respectively. The difference with our results can be explained by the different computational setup.

### D. ADSORPTION OF CH$_x$ RADICALS ($x = 0–3$) ON ANATASE (001)

Now we discuss the adsorption of radical species on anatase (001) and the influence of the different oxygen vacancies on this adsorption. The different adsorption configurations are indicated as A001-x-y-z, where $x$ is the adsorbed species (C, CH, CH$_2$, and CH$_3$), $y$ indicates the surface ($S =$ stoichiometric surface, $V_n =$ reduced surface with a $V_{On}$ ($n = 1–3$) oxygen vacancy), and $z$ is an index used for identifying specific adsorption configurations. This index is consistently used for all different surfaces. $z$ consists of a number and a letter (“a”−“d”) for the reduced surfaces. The lower the number of $z$, the higher the adsorption energy on the stoichiometric surface of that species. This number thus indicates the order of stability on the stoichiometric surface. The letter indicates the location of the oxygen vacancy relative to the adsorbed species. The location will be indicated in the following paragraphs. A few examples

| adsorption configuration | $E_{ads}$ (kcal/mol) | BL$_{Ti-C}$ (Å) | BL$_{C-O}$ (Å) | BO$_{C-O}$ | $\Delta q(CH_x)/|e|$ |
|--------------------------|----------------------|----------------|----------------|------------|------------------|
| A001-C-S-1               | 153.71               | 2.09           | 1.21           | 2.08       | 1.341            |
| A001-C-S-2               | 153.40               | 2.10           | 1.21           | 2.08       | 1.345            |
| A001-C-S-3               | 118.39               | 2.22           | 1.28           | 1.66       | 0.771            |
| A001-CH-S-1              | 118.07               | 2.11           | 1.29           | 1.61       | 0.369            |
| A001-CH-S-2              | 117.27               | 2.12           | 1.29           | 1.61       | 0.388            |
| A001-CH-S-3              | 107.20               | 2.08           | 1.37/1.43      | 1.21/0.96  | 0.393            |
| A001-CH-S-4              | 83.11                | 1.33           | 1.40           |            | 1.570            |
| A001-CH-S-5              | 0.33                 | 2.10           |                |            | 0.754            |
| A001-CH2-S-1             | 84.49                | 2.18           | 1.41           | 1.04       | 0.726            |
| A001-CH2-S-2             | 84.49                | 2.18           | 1.40           | 1.08       | 0.864            |
| A001-CH2-S-3             | 56.12                | 2.43/2.19      | 1.42           | 1.00       | 0.808            |
| A001-CH2-S-4             | 54.77                | 1.45           | 0.88           |            | 1.275            |
| A001-CH3-S-1             | 29.56                | 1.43           | 0.96           |            | $-0.137$         |
| A001-CH3-S-2             | 7.80                 | 1.44           | 0.92           |            | 1.341            |
are given: A001-C-S-1 corresponds to C (x = C) adsorbed in the most stable configuration (z = 1) on the stoichiometric surface (y = S); A001-C-S-2 is the second (z = 2) most stable configuration of C (x = C) on the stoichiometric surface (y = S); A001-C-V1-1b is C (x = C) adsorbed on the reduced surface with a VO1 vacancy (y = V1) at position b (z = 1b) relative to the adsorbed C equivalent to the most stable adsorption configuration on the stoichiometric surface (z = 1b). Note, however, that this does not necessarily mean that A001-C-V1-1b is also the most stable adsorption position on the reduced anatase (001) surface.

D.1. Adsorption of CH Radicals (x = 0–3) on a Stoichiometric Anatase (001) Surface. i. Adsorption of C. For a C radical adsorbed on the stoichiometric anatase (001) surface, we find three different adsorption configurations, which in order of stability are indicated as A001-C-S-1, A001-C-S-2, and A001-C-S-3 in Table 2 and Chart 1. A001-C-S-1 and A001-C-S-2 correspond to the adsorption of C at the O2c site. This causes the spontaneous breaking of the bond between one Ti and O2c, after which a Ti–C bond is formed. The difference between A001-C-S-1 and A001-C-S-2 is the relative position of the C with respect to the asymmetric Ti–O2c bonds in the neighboring [010] row. Only a small difference is found in the strength of the adsorption, corresponding to an adsorption energy of 153.71 and 153.40 kcal/mol for A001-C-S-1 and A001-C-S-2, respectively. The charge transfer from the C to the surface and also the Ti–C and C–O2c bond lengths are found to be almost equal for A001-C-S-1 and A001-C-S-2. The third adsorption configuration, A001-C-S-3, corresponds to C adsorbed on top of the surface O in the [100] row (hereafter denoted as OVO2). This is found to be 35.32 kcal/mol less stable than the most stable adsorption configuration of C on the stoichiometric surface, A001-C-S-1. The decrease in stability relative to A001-C-S-1 coincides with an increase in the Ti–C and C–O bond lengths, from 2.09 to 2.22 Å and 1.21 to 1.28 Å, respectively. This increase in C–O bond length corresponds to a decrease in double bond character, indicated by a decrease in bond order (BO) from BO = 2.08 in A001-C-S-1 and A001-C-S-2 to BO = 1.66 in A001-C-S-3. Also, the charge transfer from C to the surface is lower than in the other two configurations.

ii. Adsorption of CH. For the CH radical, five different adsorption configurations are found. Just as is the case with C adsorbed on the surface, A001-CH-S-1 and A001-CH-S-2 correspond to the spontaneous bond breaking of a Ti–O2c bond and the formation of a Ti–C and C–O2c bond. These two configurations differ by the relative position of the CH to the asymmetric Ti–O2c bonds in the neighboring [010] row. Again, the difference between these two configurations is minimal: the adsorption energy is only 0.80 kcal/mol lower for A001-CH-S-2 relative to A001-CH-S-1. For the third configuration, A001-CH-S-3, the CH is bonded to a Ti and to both O2c and OVO2. It is found to be 10.87 kcal/mol less stable than A001-CH-S-1, showing longer C–O bond lengths of 1.37 and 1.43 Å, to be compared to a C–O bond length of 1.29 Å in the A001-CH-S-1 configuration. The charge transfer to the surface is of the same order of magnitude as for A001-CH-S-1. In the fourth CH adsorption configuration, A001-CH-S-4, CH is bonded between two O2c of neighboring [010] rows. The adsorption of the CH radical in this configuration has a significantly larger charge transfer from the adsorbed species to the surface than for the other adsorption configurations. This configuration is 34.96 kcal/mol less stable than A001-CH-S-1. For the fifth configuration, the CH radical is adsorbed on top of a OVO2. This configuration is exothermic by only 0.33 kcal/mol relative to the gas phase CH radical. This last configuration will therefore hardly contribute to the adsorption of CH on the stoichiometric anatase (001) surface, since all other adsorption configurations are much more strongly exothermic. In this configuration, no bond is present between carbon and oxygen.

iii. Adsorption of CH2. For the CH2 radical on the anatase (001) surface, four adsorption configurations are found. Again, the two most stable configurations, A001-CH2-S-1 and A001-CH2-S-2, are formed by the spontaneous bond breaking of a Ti–O2c bond and the formation of a Ti–C and C–O2c bond. The difference between the two configurations is the relative position of CH2 with respect to the asymmetrical Ti–O2c bonds in the neighboring [010] row. In this case,
However, the adsorption energy of these two configurations is found to be identical, 84.49 kcal/mol. The third most stable configuration, A001-CH2-S-3, is 28.37 kcal/mol less stable than A001-CH2-S-1 and A001-CH2-S-2. In this case, the CH2 is adsorbed on top of the Ov0 site. The two Ti–C bonds are asymmetrical, having bond lengths of 2.43 and 2.19 Å. The fourth adsorption configuration, A001-CH2-S-4, has the C of the CH2 bonded to two O2c of neighboring [010] rows. This configuration is equivalent to A001-CH3-S-4 with CH adsorbed. The C–O2c bond length in the case of CH2 is 1.45 Å, which is significantly longer than the bond length in the case of CH adsorption, which is 1.33 Å. This increase in bond length corresponds to a sharp drop in bond order from 1.40 to 0.88. The difference in adsorption energy relative to A001-CH2-S-1 is 29.72 kcal/mol. Just as in the case of A001-CH-S-4, a larger charge transfer occurs from the surface to the adsorbed CH3. As expected for both configurations, the C–O bond has a single bond character (BOC ≈ 1). We also have performed calculations on the adsorption of CH3 on a titanium atom; this led to spontaneous desorption of CH3.

**D.2. Adsorption on a Reduced Anatase (001) Surface.**

In section C, we investigated the formation energies of oxygen vacancies in the anatase (001) surface. Understanding the effect of these defects on the adsorption of species on the surface is essential for a more fundamental understanding of the plasma-catalytic activity of this material. We here therefore study the influence of the three most stable vacancies V01, V02, and V03 on the adsorption of CH radicals. V04 is not considered in this study as its equilibrium concentration is negligible compared to the other vacancies (see Table 1). We have studied the influence of the vacancies and their position relative to the adsorbed species on the adsorption strength of the radical species in the different configurations.

**i. Reduced Anatase (001) Surface Containing a V01 Oxygen Vacancy.** The relative position of V01 is indicated with the letters a–d, as indicated in Figure 2. Position “a” corresponds to the removal of the closest O2c oxygen (V01 oxygen) relative to the adsorbed C, position “b” to the removal of the O2c in the same [010] row as “a”. Positions “c” and “d” are equivalent to “a” and “b”, respectively, but in the neighboring [010] row. The adsorption energies of the CH2 species on the reduced anatase (001) surface containing a V01 vacancy are shown in Table 3.

**1. Adsorption of C.** For the C-radical adsorption, we find three different adsorption configurations on the nondefective (stoichiometric) surface. In Figure 3 the difference in the adsorption energy of C on the stoichiometric surface and its adsorption energy on the reduced surface with a V01 vacancy is shown. A negative ΔEads corresponds to a lower adsorption strength on the reduced surface, compared to adsorption on the stoichiometric surface. For A001-C-S-1 and A001-C-S-2, for which the adsorption interaction was almost identical on the stoichiometric surface, it is found that the influence of the presence of a V01 vacancy is nearly identical. The presence of V01 at the “a” position leads to a new adsorption configuration, in which the Ti–C–O–Ti structure becomes Ti–C–Ti since the oxygen is removed. This new configuration is identical for A001-C-V1-1 and A001-C-V1-2. For all positions of the vacancy in configurations A001-C-V1-1 and A001-C-V1-2, the adsorption energy decreases relative to A001-C-S-1 and A001-C-S-2, respectively. The largest decrease is found for the “b” position of the vacancy. The influence of the vacancy in the [010] neighboring row (position “c” and “d”) on the adsorption energy is found to be minimal (∆Eads < 5 kcal/mol). For A001-C-V1-3, a small positive ΔEads relative to A001-C-S-3 is found for all positions of the oxygen vacancy.

**2. Adsorption of CH.** For the adsorption of CH on the stoichiometric surface five different adsorption configurations were previously found (see Section D.1.i). In Figure 4 the difference between the adsorption energy of CH on the stoichiometric surface and the adsorption energy on the reduced surface with a V01 vacancy is shown. Also, in this case, the adsorption interaction was found to be almost identical for A001-CH-S-1 and A001-CH-S-2. This again leads to an influence of the oxygen vacancy that is almost identical for both configurations. Similar to C adsorption, the formation of the vacancy on position “a” leads to a new adsorption configuration. In this configuration, A001-CH-V1-1a (A001-CH-V1-2a is equivalent), the Ti–C–O–Ti structure is replaced by a Ti–C–Ti structure. This new adsorption configuration shows approximately the same adsorption energy for CH as the adsorption of CH in an A001-CH-S-1 or A001-CH-S-2 configuration on the stoichiometric surface. In the A001-CH-V1-1b and the A001-CH-V1-2b configuration the interaction of the adsorbed species is decreased significantly (∆Eads ≈ −40 kcal/mol), while for “c” and “d” the adsorption energy drops by less than 5 kcal/mol. A similar result is found for the adsorption configuration A001-CH-V1-3, that is, a limited influence (although larger than for A001-CH-V1-1 and A001-CH-V1-2) is found for the positions “a”, “c”, and “d”, and a significant decrease in adsorption strength is found for A001-CH-V1-3b. For A001-CH-V1-3a, one of the C–O bonds, found in the stoichiometric surface adsorption configuration A001-CH-S-3, is replaced by an extra Ti–C bond with a bond length of 2.48 Å. For A001-CH-V1-4, only the vacancy positions “b” and “d” exist, as “a” and “c” cannot form a configuration that is
Table 3. Adsorption Energy for the Different Adsorption Configurations ($E_{\text{ads}}$) on the Stoichiometric Surface and on the Reduced Surface with a $V_{O1}$ Oxygen Vacancy on the Different Locations “a”–“d”

<table>
<thead>
<tr>
<th>adsorbed species</th>
<th>adsorption configuration</th>
<th>stochiometric</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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<tr>
<td>C</td>
<td>A001-C-S-1</td>
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<td>31.13(N)</td>
<td>28.24(N)</td>
</tr>
</tbody>
</table>

“X” marks configurations that were found unstable or could not be created; “N” marks configurations that are no longer equivalent to the configurations on the stoichiometric surface caused by the fact that certain bonds no longer can be formed.

Recall that the A001-CH-S-5 configuration on the stoichiometric surface shows a very low adsorption energy. When a $V_{O1}$ oxygen vacancy is introduced in this configuration, this configuration spontaneously converts in A001-CH-V1-1a.

3. Adsorption of CH$_2$. As is the case for C and CH radical adsorption on the stoichiometric surface, the adsorption interactions of A001-CH$_2$-S-1 and A001-CH$_2$-S-2 are found to be nearly identical. In Figure 5, the difference in adsorption energy of the adsorption configurations of CH$_2$ on a reduced anatase (001) surface with a $V_{O1}$ vacancy (location = “a”–“d”) relative to the A001-CH$_2$-S-z ($z = 1$–$4$) configurations.

adsorption energy of CH$_3$ on the stoichiometric surface and the adsorption energy of CH$_2$ on the reduced surface with a $V_{O1}$ vacancy is shown. Again, the influence of $V_{O1}$ is very similar for both adsorption configurations. The A001-CH2-V1-1b and A001-CH2-V2-2b adsorption configurations show the greatest decrease in adsorption strength. The decrease in adsorption energy is found to be around 38 kcal/mol. A001-CH2-V1-1a and A001-CH2-V2-2a again correspond to a new adsorption configuration, where the Ti–C–O–Ti structure is replaced by a Ti–C–Ti structure. These new adsorption configurations are found to be the overall most stable adsorption configurations of CH$_2$ when a $V_{O1}$ oxygen vacancy is present at the surface. When the vacancy is present in the neighboring [010] row (positions “c” and “d”), the adsorption interaction in
configurations A001-CH2-V1-1 and A001-CH2-V1-2 only decreases by a small amount relative to A001-CH2-S-1 and A001-CH2-S-2, respectively. For A001-CH2-V1-3, the interaction strength increases relative to A001-CH2-S-3. The corresponding $\Delta E_{ad}$ is calculated to be around 7 kcal/mol. In these configurations on the reduced surface, one of the Ti–C bonds is broken, and CH rotates inward in the direction of the VO1 vacancy (see Supporting Information, Figure S1a). For the last configuration, A001-CH2-V1-4, only positions "b" and "d" are considered, because "a" and "c" do not lead to an adsorption configuration equivalent to A001-CH2-V1-4 on the stoichiometric surface. The adsorption energies of A001-CH2-V1-4b and A001-CH2-V1-4d decrease by ~11 kcal/mol, relative to the adsorption on the stoichiometric surface.

4. Adsorption of CH$_2$. We previously found two adsorption configurations for the CH$_3$ radical on the stoichiometric surface. In Figure 6, the difference between the adsorption energy of CH$_3$ on the stoichiometric surface and the adsorption energy on the reduced surface with a VO$_1$ vacancy (location = "a"–"d") relative to the A001-CH3-S-2 (x = 1–2) configurations.

![Image](Image 60x412 to 300x551)

**Figure 6.** Difference in adsorption energy of the adsorption configurations of CH$_3$ on a reduced anatase (001) surface with a VO$_1$ vacancy (location = "a"–"d") relative to the A001-CH3-S-2 (x = 1–2) configurations.

Energy of CH$_3$ on the stoichiometric surface and the adsorption energy on the reduced surface with a VO$_1$ vacancy is shown. A001-CH3-V1-1 remains the most stable configuration for every location of the VO$_1$ oxygen vacancy, but it is not possible to create A001-CH3-V1-1a because when VO$_1$ is formed on location "a" the oxygen of the O–CH$_3$ bond would be removed. We find that for every position of the oxygen vacancy the adsorption strength is lower than on the stoichiometric surface. This effect is largest when the VO$_1$ is located in the same [010] row as the adsorbed CH$_3$ (position "b").

For A001-CH3-S-2 the effect of the vacancy is found to be minimal, and $\Delta E_{ad}$ ranges from $-0.74$ kcal/mol for A001-CH3-V1-2a and A001-CH3-V1-2c to $+0.33$ kcal/mol for A001-CH3-V1-b and A001-CH3-V1-d.

Apart from the adsorption configurations on the reduced anatase (001) surface which have an equivalent on the stoichiometric surface, a new adsorption configuration is found to be stable on the reduced surface, A001-CH3-V1-3x (x = "a"–"d"). The adsorption of CH$_3$ on Ti was found to be stable in the proximity of a VO$_1$ oxygen vacancy. This was not the case for the stoichiometric surface, for which spontaneous desorption of CH$_3$ occurs. When CH$_3$ adsorbs on titanium in the same [010] row as VO$_1$ it folds inward, as shown in Figure 7, stabilizing the structure through two C–H···O$_{VO_2}$ interactions. This corresponds to the configurations A001-CH3-V1-3a and A001-CH3-V1-3b. The adsorption energies correspond-

5. Summary of CH$_x$ Adsorption on the Reduced Anatase (001) Surface with a VO$_1$ Oxygen Vacancy. The influence of the most stable oxygen vacancy, VO$_1$, on the adsorption of CH$_x$ radicals (x = 0–3) on an anatase (001) surface was studied in this section. The adsorption energies of the CH$_x$ species on the reduced anatase (001) surface containing a VO$_1$ vacancy are shown in Table 3. For CH$_2$ and CH$_3$ we find an increased interaction energy relative to the most stable adsorption on the stoichiometric surface. For CH$_2$, A001-CH2-V1-1a and A001-CH2-V1-2a have an adsorption energy of 99.93 kcal/mol, thus, showing an 18% increase from the 84.49 kcal/mol for the stoichiometric A001-CH2-S-1 and A001-CH2-S-2 configurations. For CH$_3$, a new stable adsorption configuration, A001-CH3-V1-3x (x = "a"–"d"), originates on the reduced anatase (001) surface. The configurations where x equals a, b, and c have an adsorption energy of 56.94, 55.71, and 31.13 kcal/mol, respectively, corresponding to a 93, 88, and 5% increase relative to the 29.56 kcal/mol for the stoichiometric A001-CH3-S-1. The influence, however, of each adsorption configuration separately on the adsorption strength can be either negative or positive. We only found an increase in adsorption strength and energy for some cases where the species are adsorbed on top of O$_{VO_2}$ and for the new adsorption configurations A001-CH2-V1-1a and A001-CH2-V1-2a. In all other cases, the adsorption energy dropped compared to the configurations on the stoichiometric surface.

6. Summary of CH$_x$ Adsorption on the Reduced Anatase (001) Surface Containing a V O$_2$ Oxygen Vacancy. The relative position of the VO$_2$ oxygen vacancy is indicated by the letters "a"–"d", as shown in Figure 2. Position "a" corresponds to the removal of the closest VO$_2$ oxygen relative to the adsorbed C$_x$ position "b" is the removal of the VO$_2$ oxygen in the same [010] row as "a". Positions "c" and "d" are equivalent to "a" and "b", respectively, but in the neighboring [010] row. The adsorption energies of the CH$_x$ species on the reduced anatase (001) surface containing a VO$_2$ vacancy are shown in Table 4.

![Figure 7](Image 357x620 to 532x749)

**Figure 7.** From left to right: A001-CH3-V1-3a and A001-CH3-V1-3c (Ti = light gray, O = red, C = dark gray, H = white).
value of increase and decrease in adsorption energy have an absolute structure the adsorption strength is decreased. Both the A001-C-V2-3a configuration and the stoichiometric surface and the adsorption energy on the reduced surface with a VO$_2$ vacancy is shown. If the vacancy is present on the side of C, the adsorption strength is enhanced. If the vacancy is present on the side of O$_{2c}$ of the Ti−C−O−Ti structure the adsorption strength is decreased. Both the increase and decrease in adsorption energy have an absolute value of ~5 kcal/mol.

For A001-C-S-3, which corresponds to adsorption on top of O$_{V_{O2}}$, we find a significant increase in adsorption energy for C in the A001-C-V2-3a configuration. In this configuration it is no longer possible to form a C−O bond, because the O$_{V_{O2}}$ is removed, leading to a shortening of the Ti−C bonds from 2.22 Å in A001-C-S-3 to 2.19 Å in A001-C-V2-3a. Also, an increase in adsorption strength is found for A001-C-V2-3b and A001-C-V2-3d, but a decrease is found for A001-C-V2-3c, relative to A001-C-S-3.

2. Adsorption of CH. In Figure 9, the difference between the adsorption energy of CH on the stoichiometric surface and the adsorption energy on the reduced surface with a VO$_2$ vacancy is shown. Five different adsorption configurations were found on the stoichiometric surface. A001-CH-S-1 and A001-CH-S-2, which were found to be almost identical on the stoichiometric surface, again are similarly influenced by the presence of an oxygen vacancy. As is the case for the C adsorption in the A001-C-V2-1 and A001-C-V2-2 configurations, it is found that CH adsorption is enhanced when VO$_2$ is located on the side of the C of the adsorbent (positions “a” and “c”), and the strength of adsorption is decreased when VO$_2$ is located on the side of the O$_{2c}$ of the Ti−C−O−Ti structure (positions “b” and “d”) of VO$_2$). The presence of VO$_2$ on positions “b” and “d” leads to a shortening of the Ti−C bond from 2.11 Å on the stoichiometric surface to 2.00 Å. When VO$_2$ is located in positions “a” and “c”, the CH folds inward in the direction of the VO$_2$ vacancy, with a Ti−Ti−C angle of 60.4°, where the two Ti atoms are those in the same [100] row (see Supporting Information).

1. Adsorption of C. As discussed above, A001-C-S-1 and A001-C-S-2 show almost identical adsorption energies (C on the stoichiometric surface) because of their very similar structure. For these configurations, the influence of the VO$_2$ vacancy on the adsorption energy is almost identical. In Figure 8, the difference in the adsorption energy of C on the stoichiometric surface and the adsorption energy on the reduced surface with a VO$_2$ vacancy is shown. Five different adsorption configurations were found on the stoichiometric surface. A001-CH-S-1 and A001-CH-S-2, which were found to be almost identical on the stoichiometric surface, again are similarly influenced by the presence of an oxygen vacancy. As is the case for the C adsorption in the A001-C-V2-1 and A001-C-V2-2 configurations, it is found that CH adsorption is enhanced when VO$_2$ is located on the side of the C of the adsorbent (positions “a” and “c”), and the strength of adsorption is decreased when VO$_2$ is located on the side of the O$_{2c}$ of the Ti−C−O−Ti structure (positions “b” and “d”) of VO$_2$). The presence of VO$_2$ on positions “b” and “d” leads to a shortening of the Ti−C bond from 2.11 Å on the stoichiometric surface to 2.00 Å. When VO$_2$ is located in positions “a” and “c”, the CH folds inward in the direction of the VO$_2$ vacancy, with a Ti−Ti−C angle of 60.4°, where the two Ti atoms are those in the same [100] row (see Supporting Information).

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Table 4. Adsorption Energy for the Different Adsorption Configurations ($E_{\text{ads}}$) on the Stoichiometric Surface and on the Reduced Surface with a VO$_2$ Oxygen Vacancy on the Different Locations “a”−“d”

$X$ marks configurations that were found unstable or could not be created, and N marks configurations that are no longer equivalent to the configurations on the stoichiometric surface caused by the fact that certain bonds no longer can be formed.
there is a strong stabilization with 14 kcal/mol and was not stable in the A001-CH-V1-5 configurations. The largest stabilization is found for the VO2 vacancy (location = “a” or “c”) location. In this case, the Ti−Ti−C angle is 75.1°, compared to 60.4° for A001-CH-V2-1a and 91.2° for A001-CH2-S-1 (see Supporting Information, Figure S1c). For locations “b” and “d”, for which the vacancy is located closest to the O2c-atom bonded to the C atom, a small negative influence is found on the adsorption strength (ΔEads ≈ −2.5 kcal/mol).

In the case of the A001-CH2-V2-3 configuration, it is found that A001-CH2-V2-3a shows a significant boost in adsorption strength, making it the most stable adsorption configuration of CH3 on the reduced surface. Eads is calculated to be 92.97 kcal/mol, which is an increase of 36.85 kcal/mol compared to A001-CH2-S-3 on the stoichiometric surface. In this configuration, the Ti−C bond lengths are shortened from 2.43 and 2.19 Å on the stoichiometric surface to 2.07 Å.

For A001-CH2-V2-4 the position of VO2 in locations “a”, “b”, and “c” causes two Ti−O2c bonds to break. This has a positive influence on the adsorption strength when this occurs for A001-CH2-V2-4a and A001-CH2-V2-4c and a negative influence for A001-CH2-V2-4b. For A001-CH2-V2-4d, no bond breaking occurs, and the adsorption energy decreases by ~14 kcal/mol relative to A001-CH2-S-4.

4. Adsorption of CH3. In Figure 11, the difference between the adsorption energy of CH3 on the stoichiometric surface and the adsorption energy on the reduced surface with a VO2 vacancy is shown. For all four locations of VO2 in the A001-CH3-V2-1 configuration, a negative influence on the adsorption strength is found. For A001-CH3-V3-2 it is not possible to have this configuration with the vacancy located on position “a”. The other positions of the vacancy strengthen the adsorption on the reduced surface.

Apart from the adsorption configurations on the reduced anatase (001) surface, which have an equivalent on the stoichiometric surface, a new adsorption configuration of CH3 is formed on the reduced surface with a VO2 vacancy. VO2 vacancy (location = “a”−“d”) relative to the A001-CH3-S−z (z = 1−4) configurations.

Figure 11. Difference in adsorption energy of the adsorption configurations of CH3 on a reduced anatase (001) surface with a VO2 vacancy (location = “a”−“d”) relative to the A001-CH3-S−z (z = 1−4) configurations.
Adsorption energies of the CH radical species on the reduced anatase (001) surface containing a VO2 vacancy are shown in Table 4. For VO2 we find that, in the case of CH3 and CH2, the maximal adsorption energy increases. In the case of VO2, the maximal adsorption energy increases for all CHx (x = 0–3). The configurations with the maximal adsorption energy for each adsorbed species are A001-C-V2-1a, A001-CH-V2-2a, A001-CH2-V1-3a, and A001-CH3-V2-3x (x = “a”–“b”). The influence on each adsorption configuration can be positive or negative, not only depending on the considered configuration itself, but also on the position of the oxygen vacancy relative to the adsorbent. The different influence of VO2 on the different adsorption configurations also results in a shift of the relative stabilities of the different configurations and therefore on their distribution on the surface.

iii. Reduced Anatase (001) Surface Containing a VO3 Oxygen Vacancy. The relative position of VO3 is indicated with the letters “a”–“d”, as indicated in Figure 2. Position “a” is the removal of the VO3 oxygen closest to the adsorbed C, and position “b” is the removal of the VO3 oxygen in the same [010] row as “a”. Positions “c” and “d” are equivalent to positions “a” and “b”, respectively, but in the neighboring [010] row. The adsorption energies of the CHx species on the reduced anatase (001) surface containing a VO3 vacancy are shown in Table 5.

1. Adsorption of C. In Figure 12 the difference in adsorption energy of C on the stoichiometric surface and on the reduced surface with a VO3 vacancy (location = “a”–“d”) relative to the A001-C-S-z (z = 1–3) configurations.

5. Summary of CHx Adsorption on the Reduced Anatase (001) Surface Containing a VO3 Oxygen Vacancy. The influence of the presence of a VO2 vacancy on the adsorption of CHx radicals (x = 0–3) on the anatase (001) surface has been studied in this section. The adsorption energies of the CHx species on the reduced anatase (001) surface containing a VO2 vacancy are shown in Table 4. For VO1 we find that, in the case of CH2 and CH3, the maximal adsorption energy increases. In the case of VO2, the maximal adsorption energy increases for all CHx (x = 0–3). The configurations with the maximal adsorption energy for each adsorbed species are A001-C-V2-1a, A001-CH-V2-2a, A001-CH2-V1-3a, and A001-CH3-V2-3x (x = “a”–“b”). The influence on each adsorption configuration can be positive or negative, not only depending on the considered configuration itself, but also on the position of the oxygen vacancy relative to the adsorbent. The different influence of VO2 on the different adsorption configurations also results in a shift of the relative stabilities of the different configurations and therefore on their distribution on the surface.

V2-1a. Adsorption of CH3 in the [100] row neighboring the one containing the VO2 oxygen vacancy results in spontaneous migration of the VO2 oxygen vacancy to a VO1 vacancy. The presence of a VO2 vacancy stabilizes the adsorption of CH3 on a titanium atom in close proximity of the vacancy.

V3-3b, on the other hand, the adsorption strength drops by ~7 kcal/mol.

2. Adsorption of CH. In Figure 13 the difference in adsorption energy of CH on the stoichiometric surface and on the reduced surface with a VO3 vacancy is shown. We find that...
V$_{O3}$ influences the adsorption in the A001-CH-V3-1 and A001-CH-V3-2 configurations in a similar way. The adsorption energy decreases by $\sim$2.2 kcal/mol for A001-CH-V3-1a and A001-CH-V3-1b and with $\sim$1.8 kcal/mol for A001-CH-V3-2a and A001-CH-V3-2b. The influence of V$_{O3}$ on positions “c” and “d” is weaker. For A001-CH-V3-3, the influence of the vacancy is found to be the greatest if it is located in the same [100] row as the adsorbed CH. ($\Delta E_{ad} \approx -10$ kcal/mol for A001-CH-V3-3a and $\Delta E_{ad} \approx -9$ kcal/mol for A001-CH-V3-3b). For all positions of V$_{O3}$ we find a positive influence on the adsorption energy in the A001-CH-V3-4 configuration. For these configurations, one of the Ti--O$_{2c}$ bonds is broken on each side of the adsorbed CH. The C--O$_{2c}$ bond lengths decrease from 1.33 Å in the A001-CH-S-4 configuration to 1.28 Å in the A001-CH-V3-4 configuration.

The O$_{V_{O3}}$ in A001-CH-V3-5a and A001-CH-V3-5c closest to V$_{O3}$ undergoes spontaneous migration to the middle of the location of O$_{V_{O3}}$ and O$_{V_{O3}}$ in the stoichiometric surface. The adsorption energy increases by $\sim$56 kcal/mol. If V$_{O3}$ is located at positions “b” or “d”, then one Ti--C bond breaks spontaneously, and the CH points upward on top of Ti. The adsorption energy increases with $\sim$96 kcal/mol.

3. Adsorption of CH$_2$. In Figure 14 the difference in adsorption energy of CH$_2$ on the stoichiometric surface and on the reduced surface with a V$_{O3}$ vacancy is shown. For A001-CH2-V3-1 and A001-CH2-V3-2, the influence of V$_{O3}$ is found to be almost identical. The drop in adsorption energy ranges from $\sim$0.21 kcal/mol for A001-CH2-V3-1a to $\sim$2.48 kcal/mol for A001-CH2-V3-1c relative to the adsorption on the stoichiometric surface. For A001-CH2-V3-3a and A001-CH2-V3-3c, the adsorption energy goes down by 4.66 kcal/mol, while a decrease of only 0.39 kcal/mol is found if the oxygen vacancy is present in the neighboring [100] row. For A001-CH2-V3-4b and A001-CH2-V3-4d, one Ti--O$_{2c}$ bond breaks on each side of the adsorbed CH$_2$. The adsorption strength increases in this configuration relative to the A001-CH2-S-4 configuration. A001-CH2-V3-4a and A001-CH2-V3-4c show a small drop in adsorption strength ($\Delta E_{ad} = 0.22$ kcal/mol). In this configuration, none of the Ti--O$_{2c}$ bonds are broken.

4. Adsorption of CH$_3$. In Figure 15 the difference in adsorption energy of CH$_3$ on the stoichiometric surface and on the reduced surface with a V$_{O3}$ vacancy is shown. The adsorption of CH$_3$ in configuration A001-CH3-V3-1 is not influenced significantly: The change in adsorption energy ranges from $\sim$0.88 kcal/mol for A001-CH3-V3-1d to 1.22 kcal/mol for A001-CH3-V3-1b.

For A001-CH3-V3-2 it is found that the presence of the oxygen vacancy decreases the CH$_3$ adsorption energy for all vacancy positions. For A001-CH3-V3-2a and A001-CH3-V3-2c the adsorption becomes unstable with respect to the gas phase CH$_3$ radical. A001-CH3-V3-2b and A001-CH3-V3-2d, on the other hand, remain stable.

Apart from the adsorption configurations on the reduced anatase (001) surface, which have an equivalent on the stoichiometric surface, a new adsorption configuration is found to be stable on the reduced surface, A001-CH3-V3-3x ($x = "a"-"d")$. A001-CH3-V3-3a and A001-CH3-V3-3b correspond to CH$_3$ being adsorbed on top of titanium in the same [010] row as the V$_{O3}$ vacancy. They have an adsorption energy of 37.04 and 21.57 kcal/mol, respectively. This means that A001-CH3-V3-3a is more stable than A001-CH3-V3-1b, which has an adsorption energy of 30.78 kcal/mol. In the neighboring [010] row the adsorption of CH$_3$ on top of a titanium atom results in the adsorption configurations A001-CH3-V3-3c and A001-CH3-V3-3d, with an adsorption energy 24.77 and 27.10 kcal/mol, respectively.

5. Summary of CH$_x$ Adsorption on the Reduced Anatase (001) Surface with a V$_{O3}$ Oxygen Vacancy. The influence on the adsorption of CH$_x$ radicals ($x = 0$−3) of V$_{O3}$ in an anatase (001) surface has been studied in this section. The V$_{O3}$ vacancy increases the maximal adsorption strength only for the CH$_3$ radical. The adsorption configuration of CH$_3$ with the new maximal adsorption energy is A001-CH3-V3-3a. The adsorption energy corresponding with this configuration is 37.04 kcal/mol, which is an increase of 25% relative to A001-CH3-S-1. As is the case for the other vacancies, the influence on each adsorption configuration can be positive or negative, thereby changing the relative distribution of the adsorbent on the surface.

D.3. Effect of Oxygen Vacancy Defects on the Distribution of Adsorbed CH$_x$ ($x = 0$−3) Radicals on the Anatase (001) Surface. We have shown in section D.2 that the presence of oxygen vacancy defects in an anatase (001) surface influences the adsorption of C and CH$_x$ ($x = 1$−3) radicals at the surface. In this section we will determine the relative probability of finding an adsorbed particle in a certain adsorption configuration either on a stoichiometric part of the surface or at or near an oxygen vacancy at equilibrium.
conditions. We determine the relative probability by using the Frenkel equation:

$$\tau_{\text{config}} = \frac{1}{\nu_0} \times \exp \left( \frac{E_{\text{ads}}}{k_B \times T} \right)$$

(4)

where $\tau_{\text{config}}$ is the mean lifetime of the particle in a certain adsorption configuration and $\nu_0$ is the vibrational frequency of the adsorbed particle. We calculated $\nu_0$ for a number of different adsorption configurations and found that $\nu_0$ varies with a factor between 0.66 and 3.61. However, we found for adsorption configurations, for which $\nu_0$ varies strongly from the $\nu_0$ of the most stable configuration, that the exponential part of eq 4 varies with at least 11 orders of magnitude. These findings allow us to assume $\nu_0$ to be constant, since the influence of $\nu_0$ on the mean lifetime will be insignificant compared to the influence of the exponential part of eq 4. This allows us to calculate the relative probability (see eq 5) of a configuration $i$ by multiplying the average lifetime, $\tau_{\text{config},i}$, by the percentage, $n_i$, of adsorption sites for which this configuration exists divided by the sum of the product of the average lifetime and percentage of adsorption sites for each configuration $j$, assuming $\nu_0$ to be a constant:

$$p_i = \frac{n_i \times \tau_{\text{config},i}}{\sum n_j \times \tau_{\text{config},j}} = \frac{n_i \times \exp(E_{\text{ads}}/k_B \times T)}{\sum n_j \times \exp(E_{\text{ads}}/k_B \times T)}$$

(5)

We divided the surface into four regions, namely, a stoichiometric region, where no oxygen vacancies are present near the adsorbed particle, and one region for each vacancy, to determine the influence of the oxygen vacancies on the adsorption. We also give a weight to each oxygen vacancy based on their equilibrium distribution in the surface at 400 K. As can be seen in Tables 6−9, $V_{O1}$ will have by far the greatest influence on the adsorption distribution, caused by the much greater abundance of $V_{O1}$ in the surface with respect to $V_{O2}$ and $V_{O3}$. The oxygen vacancy regions we defined consist of nine adsorption sites per oxygen vacancy, one for the oxygen vacancy and eight for the direct surroundings of this vacancy. We have studied the adsorption at different concentrations of oxygen vacancies showing the importance of reduced states in the surface.

In Table 6 the relative probability of finding the adsorbed carbon in a certain region of the anatase (001) surface at equilibrium conditions is shown. At low defect concentrations almost all carbon will be present in the stoichiometric region of
the surface. At an oxygen vacancy concentration of 11.11% the concentration of C on the stoichiometric region drops to 0.00%, since at this concentration no more stoichiometric region is left for C to adsorb. However, the probability of finding carbon adsorbed in the adsorption configurations A001-C-V1-1d or A001-C-V1-2d is 94.6% for an 11.11% oxygen vacancy concentration, indicating that C preferentially will stay in the adsorption configuration A001-C-V1-1d or A001-C-V1-2d.

For the oxygen vacancies in anatase (001) we found that a surface oxygen vacancy is the most stable vacancy, in contrast to oxygen vacancies in anatase (101) and (110). The maximal adsorption energy on the stoichiometric anatase (001) surface is 153.71 kcal/mol, while on the (001) surface in the presence of oxygen vacancies the maximal adsorption energy increases to 158.71 kcal/mol (+3.3%) for VO2. Also, for the CH radical adsorption, the maximal adsorption energy drops from 18.07 kcal/mol on the stoichiometric surface to 17.05 kcal/mol (−0.9%) and 115.89 kcal/mol (−1.8%) for VO1 and VO3, respectively, and increased to 126.12 kcal/mol (+6.8%) for VO2.

Apart from influencing the maximal adsorption strength, oxygen vacancies are also found to influence the stability of the various adsorption configurations differently, which results in a different probability of each adsorption configuration. We have studied the distribution of the adsorbed particles on the anatase (001) surface at different oxygen vacancy concentrations. We find that C preferentially adsorbs far away from the oxygen vacancy, while CH2 and CH3 adsorb preferentially at the oxygen vacancy site. CH3 partially adsorbs preferentially further away from the vacancy and partially at the oxygen vacancy. The oxygen vacancies significantly influence the distribution of adsorbed CH4 particles, which will in turn influence the accessible (new) reaction pathways for the adsorbed species. Based on these results, future computational quantum mechanical and classical studies targeting the reaction pathways themselves may be envisaged, taking into account the influence of oxygen vacancies on the pathways and the dynamics of adsorption and desorption, in order to gain a more fundamental insight in plasma-catalytic conversion of greenhouse gases.

**ASSOCIATED CONTENT**

**Supporting Information**

A graphical representation of the adsorption configurations A001-CH2-V1-3a, A001-CH2-V2-1a, and A001-CH2-V2-1a is provided. These representations provide an insight into the magnitude of the out-of-plane tilting from the carbon when compared to the graphical representations of A001-CH2-S-3, A001-CH-S-1, and A001-CH2-S-1, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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REFERENCES

(3) Khiliyuk, L. F.; Chilingar, G. V.; Robertson, J. O.; Endres, B. Typical Composition of Natural Gases. Gas Migration 2000, 238–247.