

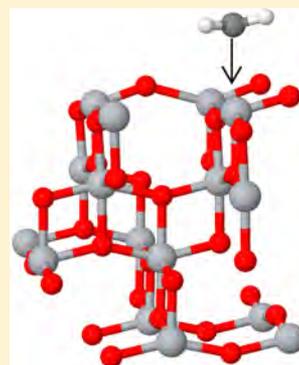
Adsorption of C and CH_x Radicals on Anatase (001) and the Influence of Oxygen Vacancies

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S 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 Perdew-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 CH₂ and CH₃. If an oxygen vacancy is present in the first subsurface layer, the maximal adsorption strength increases for C, CH, CH₂, and CH₃. When the vacancy is present in the next subsurface layer, we find that only the CH₃ 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 CH₂ and CH₃ 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, CO₂ and CH₄ contribute the most to the man-made greenhouse effect.¹ The global warming potential of methane is even 21× higher than that of CO₂.²

Apart from being a greenhouse gas, CH₄ is also the main component (70–90%) of most natural gas resources.^{3,4} Natural gas can be used as fuel for heating and electrical power generation. However, this requires conversion of CH₄ to the greenhouse gas CO₂. Alternatively, methane may also be utilized for the production of valuable chemicals, such as methanol, formaldehyde, higher hydrocarbons, hydrogen gas, and syngas (CO/H₂).

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.⁵ These processes, however, require a high energy input and typically only give low overall yields.⁶ 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.⁵ It

would thus be interesting to find nonconventional synthesis routes. Plasma technology has already been used for the conversion of methane in useful chemicals.^{7–11} 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 catalysis¹² 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,^{10,11} 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 dioxide¹³ and is widely used in experimental plasma catalysis studies.¹⁴

It is well-known that intrinsic point defects, and specifically oxygen vacancies, affect the physical and chemical properties of

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titanium dioxide. Several studies already investigated the influence of defects in titanium dioxide anatase surfaces. Wang et al.¹⁵ studied the adsorption of H₂O and O₂ 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 H₂O has an adsorption energy of 10.38 kcal/mol and O₂ does not adsorb, while near a Ti³⁺ defect H₂O and O₂ molecules adsorb with a calculated adsorption energy of 22.14 and 41.51 kcal/mol, respectively. Aschauer et al.¹⁶ studied H₂O 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 H₂O 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 O₂ was also studied on the anatase (101) surface as well as the effect of subsurface defects on this adsorption. They found no O₂ 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 CO₂ on anatase (101) and rutile (110) surfaces have shown that surface defects significantly modify the adsorption of CO₂ on the reduced surface compared to the stoichiometric surface.^{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.¹⁹ have shown that CH₃ radicals, and therefore probably also other alkyl radicals, react with the surface of TiO₂. They form long-lived transients with methyl σ -bonded to the surface of TiO₂ nanoparticles. The authors derived that the nanoparticle-CH₃ bond strength should be greater than 16.7 kcal/mol,²⁰ which is consistent with what we find in this study.

Since strong bonding is found for methyl radicals on TiO₂ nanoparticles²⁰ and since defects strongly influence the adsorption of species on TiO₂ surfaces,^{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_x radicals ($x = 0–3$) to gain a better insight in the adsorption of CH_x radicals ($x = 0–3$), relevant for plasma catalysis^{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 TiO₂ force field we recently developed for the study of intrinsic point defects²³ and the TiO₂-glycine force field of Monti et al.²⁴ This combination of force fields will be reparameterised against a large set of first principle calculations relevant to plasma-TiO₂ surface interactions. The DFT results obtained in the current study are expected to greatly improve the ReaxFF description of the TiO₂-CH_x ($x = 0–3$) 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).^{25,26} For the treatment of the exchange and correlation the Perdew–Burke–Ernzerhof (PBE) functional²⁷ was used, using plane wave basis sets and the projector-augmented wave method,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_x species.²⁹ We used a (2 × 2) supercell containing 48 atoms for the clean stoichiometric anatase (001) surface and four TiO₂ 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 scheme³⁰ 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_x 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⁻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_x 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:

$$E_{\text{form}} = E_{\text{surf}} - E_{\text{VO}} - \frac{1}{2}E_{\text{O}_2} \quad (1)$$

In expression 1, E_{surf} is the total energy of the stoichiometric surface, E_{VO} is the total energy of the reduced surface, and E_{O_2} is the total energy of the optimized gas phase O₂.

The adsorption energies of CH_x ($x = 0–3$) on the stoichiometric and reduced surfaces are calculated as follows:

$$E_{\text{ads}} = E_{\text{CH}_x} + E_{\text{surf}} - E_{(\text{CH}_x+\text{surf})} \quad (2)$$

where E_{CH_x} is the energy of the optimized gas phase geometry of CH_x, E_{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_x adsorbed. According to this definition, a more positive E_{ads} thus corresponds to a more stable configuration.

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

The bond order (BO) for the C–O bond has been calculated as follows:³⁴

$$\text{BO} = aR^{-2} + b \quad (a = 5.75 \text{ \AA}^2; b = -1.85) \quad (3)$$

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 (V_O) at the anatase (001) titanium dioxide surface are reported in Table 1. The labeling of

Table 1. Energy of Formation for Different Oxygen Vacancies in Anatase (001) (E_{form}), the Average and Maximal Atom Displacement in the Reduced Surface Relative to the Stoichiometric Surface (d_{av} and d_{max} , respectively) and the Probability of Finding Each Vacancy Relative to the Total Concentration of the Oxygen Vacancies

	E_{form} (kcal/mol)	d_{av} (Å)	d_{max} (Å)	relative probability at 300 K (%)	relative probability at 1000 K (%)
$V_{\text{O}1}$	-102.91	0.10	0.39	99.99	97.91
$V_{\text{O}2}$	-115.01	0.06	0.16	1.53×10^{-07}	0.22
$V_{\text{O}3}$	-110.78	0.06	0.15	1.87×10^{-04}	1.87
$V_{\text{O}4}$	-132.74	0.05	0.13	1.86×10^{-20}	2.96×10^{-05}

the different sites is shown in Figure 1. At the surface, $V_{\text{O}1}$ (formed by removing a 2-fold bridging oxygen in the [010]

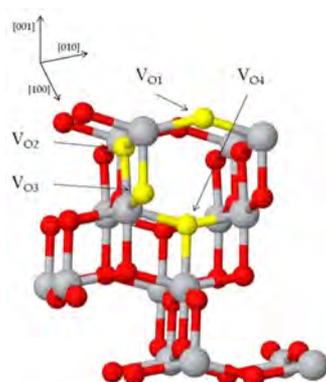


Figure 1. Different oxygen vacancies in an anatase (001) TiO_2 surface. (Ti = gray, O = red, oxygen vacancy = yellow).

direction (O_{2c}) results in two 4-fold coordinated Ti (Ti_{4c}). This is found to be the energetically most favorable oxygen vacancy. In anatase (101) and the (1×4) reconstructed (001) anatase surface, on the other hand, it is found that subsurface vacancies are energetically more favorable than surface vacancies.³⁵ The higher stability of the subsurface vacancies relative to the surface vacancies in anatase (101) has been explained by the enhanced associated relaxation and greater

atom displacement when subsurface vacancies are present, which is caused by the “rigidness” and stability of the anatase (101) surface.³⁵ 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 $V_{\text{O}1}$ 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 $V_{\text{O}1}$ oxygen vacancy is formed. The better relaxation and the fact that fewer bonds have to be broken to form the vacancy, make $V_{\text{O}1}$ 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 $V_{\text{O}4}$ will not play a significant role in the adsorption of CH_x 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.³⁶ For $V_{\text{O}1}$, $V_{\text{O}2}$, $V_{\text{O}3}$, and $V_{\text{O}4}$ 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 $V_{\text{O}n}$ ($n = 1-3$) 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

Table 2. Adsorption Energy for the Different Adsorption Configurations (E_{ads}), the Bond Lengths of the Ti–C Bonds and C–O Bonds ($\text{BL}_{\text{Ti-C}}$ and $\text{BL}_{\text{C-O}}$), the Bond Order of the C–O Bond ($\text{BO}_{\text{C-O}}$), and the Charge Transfer from the CH_x Species to the Surface ($\Delta q(\text{CH}_x)/|e|$, where a Positive Value Corresponds to a Charge Transfer from the Adsorbate to the Surface)

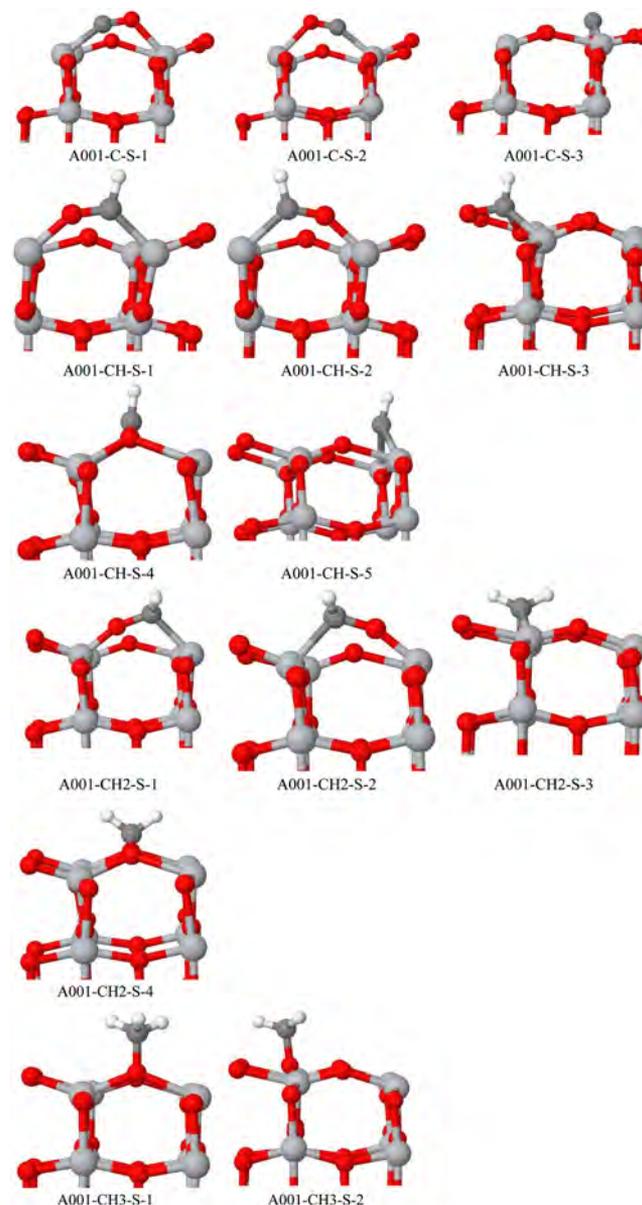
adsorption configuration	E_{ads} (kcal/mol)	$\text{BL}_{\text{Ti-C}}$ (Å)	$\text{BL}_{\text{C-O}}$ (Å)	$\text{BO}_{\text{C-O}}$	$\Delta q(\text{CH}_x)/ e $
A001-C-S-1	153.71	2.09	1.21	2.08	1.341
A001-C-S-2	153.40	2.10	1.21	2.08	1.345
A001-C-S-3	118.39	2.22	1.28	1.66	0.771
A001-CH-S-1	118.07	2.11	1.29	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 V_{O1} 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_x 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 O_{2c} site. This causes the spontaneous breaking of the bond between one Ti and O_{2c} , 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– O_{2c} 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– O_{2c} 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 $O_{V_{O2}}$). 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 first 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 breaking of a Ti– O_{2c} bond and the formation of a Ti–C and C– O_{2c} bond. These two configurations differ by the relative position of the CH to the asymmetric Ti– O_{2c} 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 O_{2c} and $O_{V_{O2}}$. 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 O_{2c} 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

Chart 1. Different Adsorption Configurations of the CH_x ($x = 0-3$) Radicals on the Stoichiometric Anatase (001) Surface^a



^aTi = light gray, O = red, C = dark gray, H = white.

configuration, the CH radical is adsorbed on top of a $O_{V_{O2}}$. 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 CH_2 . For the adsorption of the CH_2 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– O_{2c} bond and the formation of a Ti–C and C– O_{2c} bond. The difference between the two configurations is the relative position of CH_2 with respect to the asymmetrical Ti– O_{2c} 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 O_{V₀₂} 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 O_{2c} of neighboring [010] rows. This configuration is equivalent to A001-CH-S-4 with CH adsorbed. The C–O_{2c} 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 adsorbed species to the surface, relative to the other adsorption configurations of that species, due to the C being bonded to two undercoordinated O_{2c} atoms.

iv. Adsorption of CH₃. For CH₃, only two stable adsorption configurations are found. In the most stable configuration, A001-CH3-S-1, CH₃ is directly bonded to O_{2c}. In this case, the charge transfer occurs from the surface to the adsorbed CH₃. This configuration has an adsorption energy of 29.56 kcal/mol. In the second configuration, A001-CH3-S-2, CH₃ is bonded to O_{V₀₂}. In this configuration, one of the Ti–O_{V₀₂} bonds in the subsurface is broken spontaneously. A001-CH3-S-2 is found to be 21.76 kcal/mol less stable than A001-CH3-S-1 and shows a charge transfer from the adsorbate to the surface. As expected for both configurations, the C–O bond has a single bond character (BO_{C–O} ≈ 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 V_{O1}, V_{O2}, and V_{O3} on the adsorption of CH_x radicals. V_{O4} 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 V_{O1} Oxygen Vacancy. The relative position of V_{O1} is indicated with the letters a–d, as indicated in Figure 2. Position “a” corresponds to the removal of the closest O_{2c} oxygen (V_{O1} oxygen) relative to the adsorbed C, position “b” to the removal of the O_{2c} 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 V_{O1} 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 V_{O1} vacancy is shown. A negative ΔE_{ads} corresponds to a lower adsorption strength on the reduced surface, compared to adsorption on the

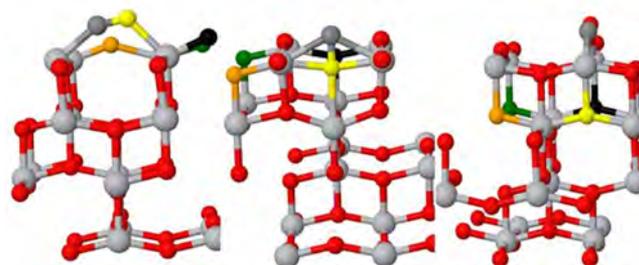


Figure 2. In this figure the locations of the oxygen vacancies are shown. From left to right: V_{O1} (A001-C-S-1), V_{O2} (A001-C-S-3), V_{O3} (A001-C-S-1). Ti = light gray, C = dark gray, O = red; Oxygen vacancy locations: “a” = yellow, “b” = black, “c” = orange, “d” = green). All oxygen vacancy locations (“a”–“d”) are relative to the adsorbed species, carbon in these examples.

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 V_{O1} vacancy is nearly identical. The presence of V_{O1} 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 (|ΔE_{ads}| < 5 kcal/mol). For A001-C-V1-3, a small positive ΔE_{ads} 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.ii). 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 V_{O1} 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 (ΔE_{ads} ≈ –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_{ads}), on the Stoichiometric Surface and on the Reduced Surface with a $V_{\text{O}1}$ Oxygen Vacancy on the Different Locations “a”–“d”^a

adsorbed species	adsorption configuration	E_{ads} (kcal/mol)				
		stoichiometric	a	b	c	d
C	A001-C-S-1	153.71	135.21(N)	120.35	148.95	150.77
	A001-C-S-2	153.40	135.21(N)	119.65	149.00	150.75
	A001-C-S-3	118.39	120.37	119.57	120.37	119.57
CH	A001-CH-S-1	118.07	117.05(N)	78.29	115.82	116.67
	A001-CH-S-2	117.27	117.05(N)	77.23	115.42	116.69
	A001-CH-S-3	107.20	105.23(N)	65.82	97.55	103.75
	A001-CH-S-4	83.11	X	69.08	X	69.08
CH_2	A001-CH2-S-1	84.49	99.93(N)	45.81	82.05	82.52
	A001-CH2-S-2	84.49	99.93(N)	46.44	80.52	82.60
	A001-CH2-S-3	56.12	63.36	63.89	63.36	63.89
	A001-CH2-S-4	54.77	X	43.86	X	43.86
CH_3	A001-CH3-S-1	29.56	X	19.35	21.72	28.79
	A001-CH3-S-2	7.80	7.06	8.13	7.06	8.13
	A001-CH3-V1-3	X	56.94(N)	55.71(N)	31.13(N)	28.24(N)

^a“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.

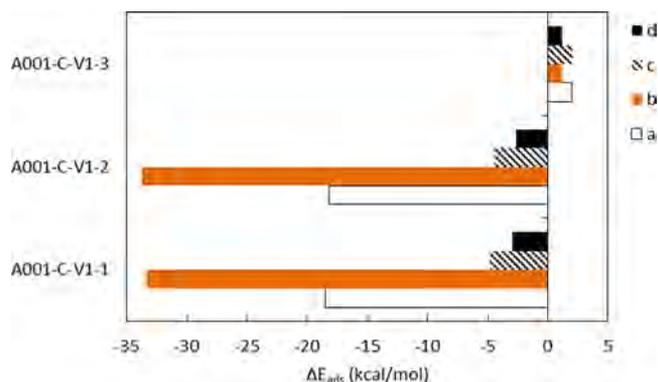


Figure 3. Difference in adsorption energy of the adsorption configurations of C on a reduced anatase (001) surface with a $V_{\text{O}1}$ vacancy (location = “a”–“d”) relative to the A001-C-S- z ($z = 1-3$) configurations.

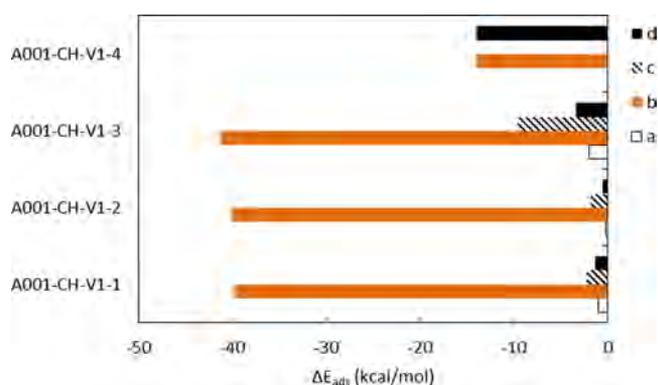


Figure 4. Difference in adsorption energy of the adsorption configurations of CH on a reduced anatase (001) surface with a $V_{\text{O}1}$ vacancy (location = “a”–“d”) relative to the A001-CH-S- z ($z = 1-4$) configurations.

equivalent to A001-CH-S-4 on the stoichiometric surface. The adsorption strength of the A001-CH-V1-4b and A001-CH-V1-4d configuration decreases significantly with respect to the A001-CH-S-4.

Recall that the A001-CH-S-5 configuration on the stoichiometric surface shows a very low adsorption energy. When a $V_{\text{O}1}$ 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-CH2-S-1 and A001-CH2-S-2 are found to be nearly identical. In Figure 5, the difference between the

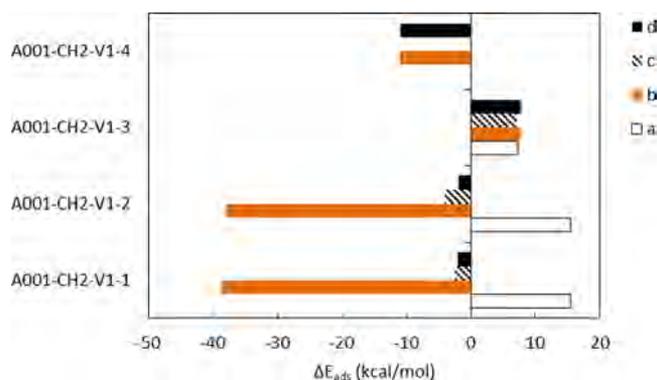


Figure 5. Difference in adsorption energy of the adsorption configurations of CH_2 on a reduced anatase (001) surface with a $V_{\text{O}1}$ vacancy (location = “a”–“d”) relative to the A001-CH2-S- z ($z = 1-4$) configurations.

adsorption energy of CH_2 on the stoichiometric surface and the adsorption energy of CH_2 on the reduced surface with a $V_{\text{O}1}$ vacancy is shown. Again, the influence of $V_{\text{O}1}$ 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-V1-2a 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 $V_{\text{O}1}$ 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 ΔE_{ads} 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 V_{O_1} 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_3 . We previously found two adsorption configurations for the CH_3 radical on the stoichiometric surface. In Figure 6, the difference between the adsorption

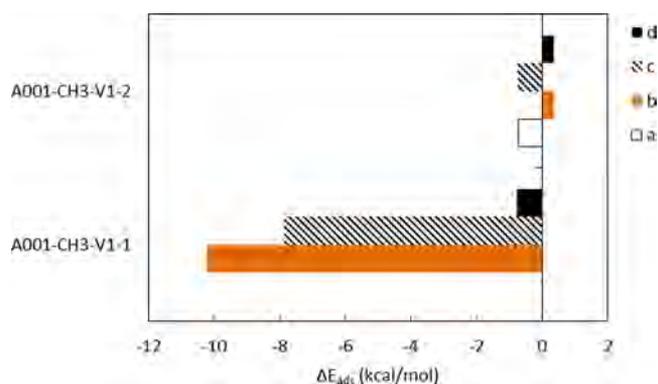


Figure 6. Difference in adsorption energy of the adsorption configurations of CH_3 on a reduced anatase (001) surface with a V_{O_1} vacancy (location = “a”–“d”) relative to the A001-CH3-S- z ($z = 1$ – 2) configurations.

energy of CH_3 on the stoichiometric surface and the adsorption energy on the reduced surface with a V_{O_1} vacancy is shown. A001-CH3-V1-1 remains the most stable configuration for every location of the V_{O_1} oxygen vacancy, but it is not possible to create A001-CH3-V1-1a because when V_{O_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 V_{O_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 ΔE_{ads} 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-V1-3 x ($x = \text{“a”–“d”}$). The adsorption of CH_3 on Ti was found to be stable in the proximity of a V_{O_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 V_{O_1} , it folds inward, as shown in Figure 7, stabilizing the structure through two C–H \cdots O $_{\text{V}_{\text{O}_2}}$ interactions. This corresponds to the configurations A001-CH3-V1-3a and A001-CH3-V1-3b. The adsorption energies correspond-

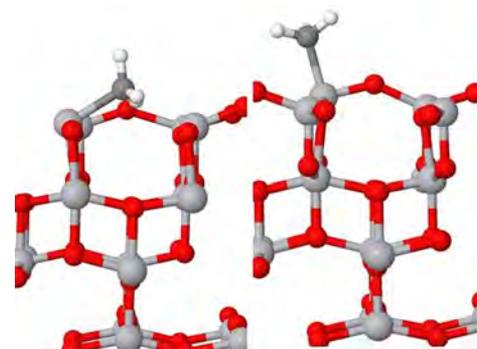


Figure 7. From left to right: A001-CH3-V1-3a and A001-CH3-V1-3c (Ti = light gray, O = red, C = dark gray, H = white).

ing to these adsorption configurations are 56.94 and 55.71 kcal/mol, respectively, which is significantly greater than 28.79 kcal/mol for the most stable adsorption configuration corresponding to one of the configurations on the stoichiometric surface, A001-CH3-V1-1d. For adsorption occurring in the neighboring [010] row it is not possible for CH_3 to fold inward. This corresponds to configurations A001-CH3-V1-3c and A001-CH3-V1-3d, for which we calculate the adsorption energies to be 31.13 and 28.24 kcal/mol, respectively. The presence of a V_{O_1} vacancy thus stabilizes the adsorption of CH_3 on a titanium atom in the proximity of this vacancy.

5. Summary of CH_x Adsorption on the Reduced Anatase (001) Surface with a V_{O_1} Oxygen Vacancy. The influence of the most stable oxygen vacancy, V_{O_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 V_{O_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-V1-3 x ($x = \text{“a”–“d”}$), 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 $\text{O}_{\text{V}_{\text{O}_2}}$ 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.

ii. Reduced Anatase (001) Surface Containing a V_{O_2} Oxygen Vacancy. The relative position of the V_{O_2} oxygen vacancy is indicated by the letters “a”–“d”, as shown in Figure 2. Position “a” corresponds to the removal of the closest V_{O_2} oxygen relative to the adsorbed C, position “b” is the removal of the V_{O_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 V_{O_2} vacancy are shown in Table 4.

Table 4. Adsorption Energy for the Different Adsorption Configurations (E_{ads}) on the Stoichiometric Surface and on the Reduced Surface with a V_{O_2} Oxygen Vacancy on the Different Locations “a”–“d”^a

adsorbed species	adsorption configuration	E_{ads} (kcal/mol)				
		stoichiometric	a	b	c	d
C	A001-C-S-1	153.71	158.71	148.64	158.71	148.64
	A001-C-S-2	153.40	158.39	148.20	158.39	148.20
	A001-C-S-3	118.39	137.56(N)	120.61	111.20	124.37
CH	A001-CH-S-1	118.07	125.31	117.10	125.31	117.10
	A001-CH-S-2	117.27	126.12	116.68	126.12	116.68
	A001-CH-S-3	107.20	X	111.23	88.57	103.02
	A001-CH-S-4	83.11	115.23	115.30	72.92	68.61
	A001-CH-S-5	0.33	106.89	64.65	100.93	52.49
CH_2	A001-CH2-S-1	84.49	86.46	81.96	86.46	81.96
	A001-CH2-S-2	84.49	86.77	81.79	86.77	81.79
	A001-CH2-S-3	56.12	92.97	56.72	47.91	62.88
	A001-CH2-S-4	54.77	61.42	43.60	61.43	40.86
CH_3	A001-CH3-S-1	29.56	26.35	25.37	26.35	25.37
	A001-CH3-S-2	7.80	X	8.81	15.35	11.03
	A001-CH3-V2-3	X	33.99(N)	33.99(N)	X	X

^aX 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.

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 V_{O_2} vacancy on the adsorption energy is almost identical. In Figure 8, the difference in the adsorption energy of C on the

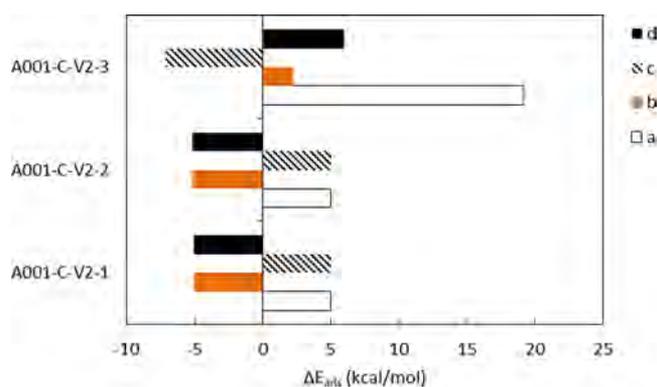


Figure 8. Difference in adsorption energy for the adsorption configurations of C on a reduced anatase (001) surface with a V_{O_2} vacancy (location = “a”–“d”) relative to the A001-C-S- z ($z = 1-3$) configurations.

stoichiometric surface and the adsorption energy on the reduced surface with a V_{O_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 $\text{O}_{V_{\text{O}_2}}$, 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 $\text{O}_{V_{\text{O}_2}}$ 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

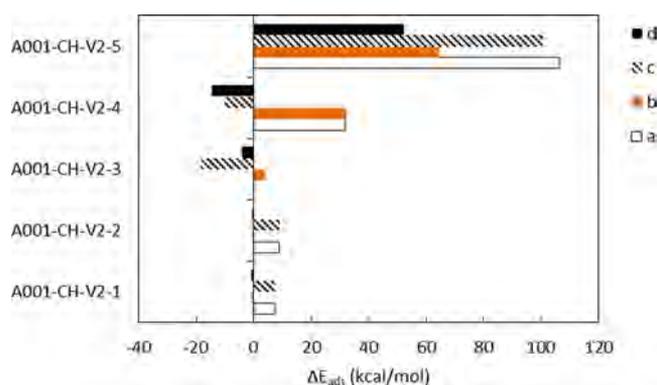


Figure 9. Difference in adsorption energy of the adsorption configurations of CH on a reduced anatase (001) surface with a V_{O_2} vacancy (location = “a”–“d”) relative to the A001-CH-S- z ($z = 1-5$) configurations.

adsorption energy on the reduced surface with a V_{O_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 V_{O_2} is located on the side of the C of the adsorbent (positions “a” and “c”), and the strength of adsorption is decreased when V_{O_2} is located on the side of the O_{2c} of the Ti–C–O–Ti structure (positions “b” and “d” of V_{O_2}). The presence of V_{O_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 V_{O_2} is located in positions “a” and “c”, the CH folds inward in the direction of the V_{O_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, Figure S1b). For A001-CH-V2-3, the position of V_{O_2} on position “a” leads to configuration A001-CH-V2-1a and so is not calculated separately. The adsorption energy of A001-CH-V2-3b increases by ~ 4 kcal/mol relative to A001-CH-S-3. The adsorption energy for A001-CH-V2-3c drops significantly by 18.62 kcal/mol and the adsorption energy of A001-CH-V2-3d drops by ~ 4 kcal/mol.

While CH is bonded to two O_{2c} in the A001-CH-S-4 configuration, it is bonded to two O_{2c} and the two Ti, between the removed oxygen, in the A001-CH-V2-4a and A001-CH-V2-4b configurations. The O_{2c} -C bond lengths are increased from 1.33 Å (BO = 1.40) to 1.42 Å (BO = 1) in A001-CH-S-4. The adsorption energy increases significantly ($\Delta E_{\text{ads}} \approx 32$ kcal/mol). A001-CH-V2-4c on the other hand leads to the breaking of a Ti- O_{2c} bond on each side of the adsorbed CH, which causes the O_{2c} -C bonds to shorten to 1.28 Å. This leads to a decrease in adsorption strength ($\Delta E_{\text{ads}} \approx 18$ kcal/mol). For A001-CH-V2-4d the adsorption strength drops significantly ($\Delta E_{\text{ads}} \approx -14$ kcal/mol).

On the stoichiometric surface, A001-CH-S-5 was found to be only slightly exothermic relative to the gas phase CH (0.33 kcal/mol) and was not stable in the A001-CH-V1-5 configurations. However, in the A001-CH-V2-5 configurations, there is a strong stabilization with ΔE_{ads} ranging from 52.2 to 106.6 kcal/mol. The largest stabilization is found for the V_{O_2} locations “a” and “c”, corresponding to V_{O_2} located in the same [100] row as the adsorbed CH. In the configuration A001-CH-V2-5a, the O_{2c} -Ti-C-H dihedral angle changes from 100° in A001-CH-S-5 to 37° in the A001-CH-V2-5a configuration. In A001-CH-V2-5c, $O_{V_{O_3}}$ migrates spontaneously to the location between where $O_{V_{O_2}}$ and $O_{V_{O_3}}$ were.

3. Adsorption of CH_2 . In Figure 10, the difference between the adsorption energy of CH_2 on the stoichiometric surface and

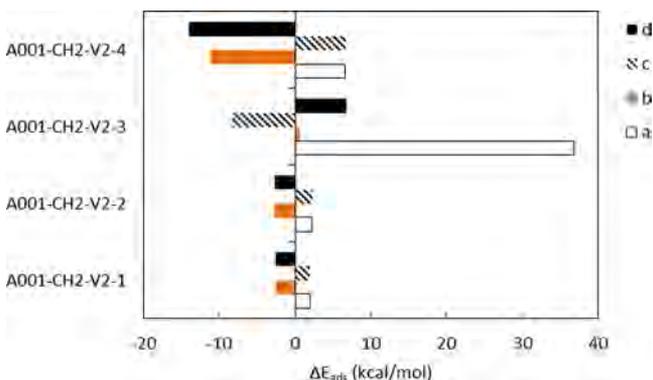


Figure 10. Difference in adsorption energy of the CH_2 adsorption configurations on a reduced anatase (001) surface with a V_{O_2} vacancy (location = “a”–“d”) relative to the A001-CH2-S- z ($z = 1$ –4) configurations.

the adsorption energy on the reduced surface with a V_{O_2} vacancy is shown. Similar to our previous observations, it is found that for A001-CH2-S-1 and A001-CH2-S-2 the influence of the V_{O_2} vacancy is almost identical. For positions “a” and “c”, for which the vacancy is located closest to the C atom, a positive influence on the adsorption strength is found. However, the increase in adsorption energy is only ~ 2 kcal/mol, while for the CH adsorption in the A001-CH-V2-1a configuration an increase of ~ 7 kcal/mol was found. Again the C atom is tilted inward in the A001-CH2-V2-1 and A001-CH2-

V2-2 configurations, if the vacancy is located on the “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 O_{2c} -atom bonded to the C atom, a small negative influence is found on the adsorption strength ($\Delta E_{\text{ads}} \approx -2.5$ 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 CH_2 on the reduced surface. E_{ads} 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 V_{O_2} in locations “a”, “b”, and “c” causes two Ti- O_{2c} 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 CH_3 . In Figure 11, the difference between the adsorption energy of CH_3 on the stoichiometric surface and

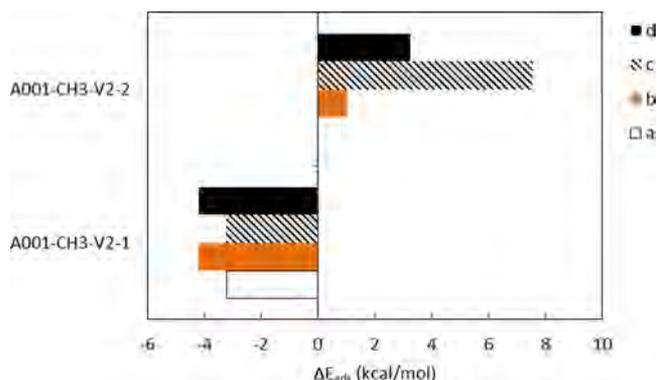


Figure 11. Difference in adsorption energy of the adsorption configurations of CH_3 on a reduced anatase (001) surface with a V_{O_2} vacancy (location = “a”–“d”) relative to the A001-CH3-S- z ($z = 1$ –2) configurations.

the adsorption energy on the reduced surface with a V_{O_2} vacancy is shown. For all four locations of V_{O_2} in the A001-CH3-V2-1 configuration, a negative influence on the adsorption strength is found. For A001-CH3-V2-2 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 is found to be stable on the reduced surface, A001-CH3-V2-3 x ($x =$ “a”–“b”). The adsorption of CH_3 on Ti was found to be stable in the close proximity of a V_{O_2} oxygen vacancy. This was not the case for the stoichiometric surface, for which spontaneous desorption of CH_3 occurs. Only A001-CH3-V2-3a and A001-CH3-V2-3b were found to be stable. These configurations correspond to CH_3 being adsorbed on top of one of titanium atoms which are located in the same [100] row as the V_{O_2} vacancy. They have an adsorption energy of 33.99 kcal/mol, which is greater than 26.35 kcal/mol for A001-CH3-

Table 5. Adsorption Energy for the Different Adsorption Configurations (E_{ads}) on the Stoichiometric Surface and on the Reduced Surface with a V_{O_3} Oxygen Vacancy on the Different Locations “a”–“d”

adsorbed species	adsorption configuration	E_{ads} (kcal/mol)				
		stoichiometric	a	b	c	d
C	A001-C-S-1	153.71	149.51	151.94	152.97	150.38
	A001-C-S-2	153.40	149.55	151.54	152.76	149.64
	A001-C-S-3	118.39	117.47	111.38	117.47	111.38
CH	A001-CH-S-1	118.07	115.89	115.84	116.42	117.11
	A001-CH-S-2	117.27	115.43	115.55	116.70	115.67
	A001-CH-S-3	107.20	96.95	106.67	98.34	104.51
	A001-CH-S-4	83.11	89.81	89.60	89.81	89.60
	A001-CH-S-5	0.33	56.40	96.56	56.40	96.56
CH_2	A001-CH2-S-1	84.49	84.27	83.23	82.00	83.32
	A001-CH2-S-2	84.49	84.24	82.91	81.86	83.05
	A001-CH2-S-3	56.12	51.46	55.73	51.46	55.73
	A001-CH2-S-4	54.77	54.56	55.80	54.56	55.80
CH_3	A001-CH3-S-1	29.56	30.07	30.78	28.81	28.68
	A001-CH3-S-2	7.80	-4.18	6.53	-4.18	6.53
	A001-CH3-V3-3	X	37.04	21.57	24.77	27.10

V2-1a. Adsorption of CH_3 in the [100] row neighboring the one containing the V_{O_2} oxygen vacancy results in spontaneous migration of the V_{O_2} oxygen vacancy to a V_{O_1} vacancy. The presence of a V_{O_2} vacancy stabilizes the adsorption of CH_3 on a titanium atom in close proximity of the vacancy.

5. Summary of CH_x Adsorption on the Reduced Anatase (001) Surface with a V_{O_2} Oxygen Vacancy. The influence of the presence of a V_{O_2} vacancy on the adsorption of CH_x radicals ($x = 0-3$) on the anatase (001) surface has been studied in this section. The adsorption energies of the CH_x species on the reduced anatase (001) surface containing a V_{O_2} vacancy are shown in Table 4. For V_{O_1} we find that, in the case of CH_2 and CH_3 , the maximal adsorption energy increases. In the case of V_{O_2} , the maximal adsorption energy increases for all CH_x ($x = 0-3$). 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 ($x = \text{“a”} - \text{“b”}$). 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 V_{O_2} 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 V_{O_3} Oxygen Vacancy. The relative position of V_{O_3} is indicated with the letters “a”–“d”, as indicated in Figure 2. Position “a” is the removal of the V_{O_3} oxygen closest to the adsorbed C, and position “b” is the removal of the V_{O_3} 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 CH_x species on the reduced anatase (001) surface containing a V_{O_3} 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 V_{O_3} vacancy is shown. The influence of V_{O_3} on A001-C-S-1 and A001-C-S-2 is found to be almost identical. The adsorption is influenced the most for positions “a” and “d” of V_{O_3} , with $\Delta E_{\text{ads}} \approx -3.8$ kcal/mol. It is found that for A001-C-V3-3a and A001-C-V3-3c the adsorption strength is not influenced significantly ($\Delta E_{\text{ads}} \approx -0.9$ kcal/mol). For A001-C-

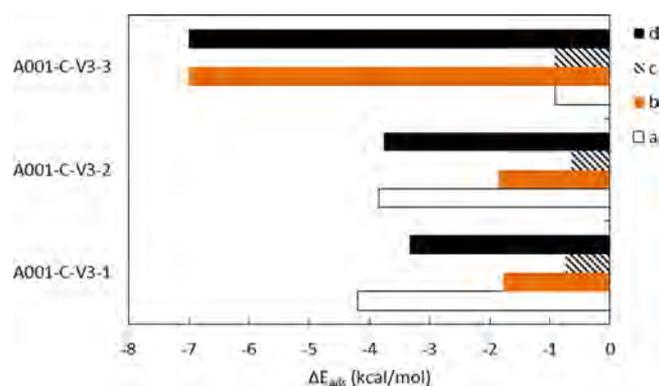


Figure 12. Difference in adsorption energy of the adsorption configurations of C on a reduced anatase (001) surface with a V_{O_3} vacancy (location = “a”–“d”) relative to the A001-C-S-z ($z = 1-3$) configurations.

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 V_{O_3} vacancy is shown. We find that

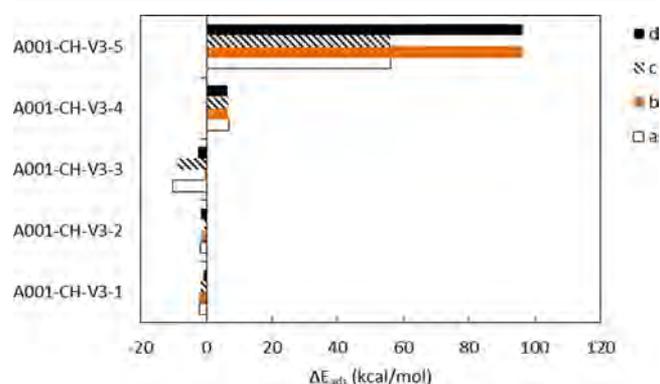


Figure 13. Difference in adsorption energy of the adsorption configurations of CH on a reduced anatase (001) surface with a V_{O_3} vacancy (location = “a”–“d”) relative to the A001-CH-S-z ($z = 1-5$) configurations.

V_{O_3} influences the adsorption in the A001-CH-V3-1 and A001-CH-V3-2 configurations in a similar way. The adsorption energy decreases by ~ 2.2 kcal/mol for A001-CH-V3-1a and A001-CH-V3-1b and with ~ 1.8 kcal/mol for A001-CH-V3-2a and A001-CH-V3-2b. The influence of V_{O_3} 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. ($\Delta E_{\text{ads}} \approx -10$ kcal/mol for A001-CH-V3-3a and $\Delta E_{\text{ads}} \approx -9$ kcal/mol for A001-CH-V3-3b). For all positions of V_{O_3} 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_{V₀₂} in A001-CH-V3-5a and A001-CH-V3-5c closest to V_{O_3} undergoes spontaneous migration to the middle of the location of O_{V₀₂} and O_{V₀₃} in the stoichiometric surface. The adsorption energy increases by ~ 56 kcal/mol. If V_{O_3} 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 ~ 96 kcal/mol.

3. Adsorption of CH₂. In Figure 14 the difference in adsorption energy of CH₂ on the stoichiometric surface and on

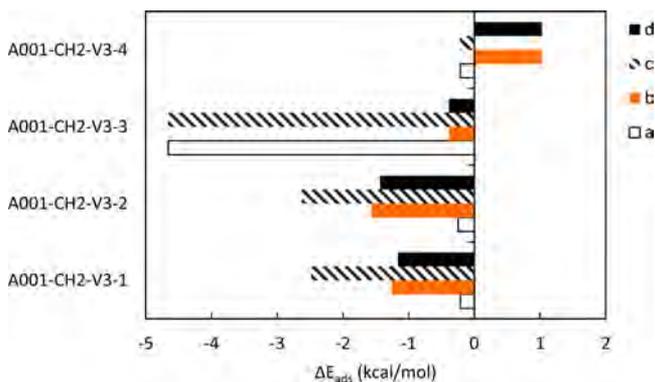


Figure 14. Difference in adsorption energy for the adsorption configurations of CH₂ on a reduced anatase (001) surface containing a V_{O_3} vacancy (location = “a”–“d”) relative to the A001-CH2-S-z (z = 1–4) configurations.

the reduced surface with a V_{O_3} vacancy is shown. For A001-CH2-V3-1 and A001-CH2-V3-2, the influence of V_{O_3} is found to be almost identical. The drop in adsorption energy ranges from ~ -0.21 kcal/mol for A001-CH2-V3-1a to ~ -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} bonds breaks on each side of the adsorbed CH₂. 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 ($\Delta E_{\text{ads}} = 0.22$ kcal/mol). In this configuration, none of the Ti–O_{2c} bonds are broken.

4. Adsorption of CH₃. In Figure 15 the difference in adsorption energy of CH₃ on the stoichiometric surface and on the reduced surface with a V_{O_3} vacancy is shown. The adsorption of CH₃ in configuration A001-CH3-V3-1 is not

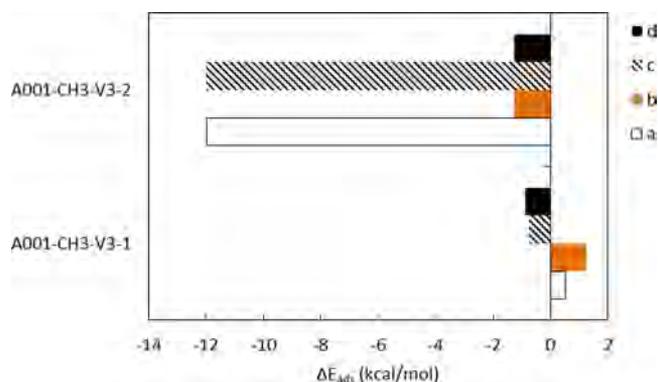


Figure 15. Difference in adsorption energy for the adsorption configurations of CH₃ on a reduced anatase (001) surface with a V_{O_3} vacancy (location = “a”–“d”) relative to the A001-CH3-S-z (z = 1–2) configurations.

influenced significantly: The change in adsorption energy ranges from -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 CH₃ 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 CH₃ 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 CH₃ being adsorbed on top of titanium in the same [010] row as the V_{O_3} 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 CH₃ 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_{O_3} Oxygen Vacancy. The influence on the adsorption of CH_x radicals (x = 0–3) of V_{O_3} in an anatase (001) surface has been studied in this section. The V_{O_3} vacancy increases the maximal adsorption strength only for the CH₃ radical. The adsorption configuration of CH₃ 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

Table 6. Relative Probability of Finding an Adsorbed C Particle in a Certain Region of the Surface

% oxygen vacancies surface region	0%	2.50%	5%	10%	11.11%	16.67%	25%
	relative probability (%)						
stoichiometric	100.00	99.60	98.89	89.03	0.00	0.00	0.00
V _{O1}	0.00	0.39	1.10	10.93	99.64	99.42	99.11
V _{O2}	0.00	0.00	0.00	0.04	0.32	0.52	0.81
V _{O3}	0.00	0.00	0.00	0.00	0.04	0.06	0.08
V _O (total)	0.00	0.40	1.11	10.97	100.00	100.00	100.00

Table 7. Relative Probability of Finding an Adsorbed CH Particle in a Certain Region of the Surface

% oxygen vacancies surface region	0%	2.50%	5%	10%	11.11%	16.67%	25%
	relative probability (%)						
stoichiometric	100.00	95.74	88.86	42.03	0.00	0.00	0.00
V _{O1}	0.00	4.20	10.99	57.20	98.67	98.16	97.73
V _{O2}	0.00	0.06	0.15	0.77	1.33	1.83	2.26
V _{O3}	0.00	0.00	0.00	0.00	0.01	0.01	0.01
V _O (total)	0.00	4.26	11.14	57.97	100.00	100.00	100.00

Table 8. Relative Probability of Finding an Adsorbed CH₂ Particle in a Certain Region of the Surface

% oxygen vacancies surface region	0%	2.50%	5%	10%	11.11%	16.67%	25%
	relative probability (%)						
stoichiometric	100.00	0.00	0.00	0.00	0.00	0.00	0.00
V _{O1}	0.00	100.00	100.00	100.00	100.00	100.00	100.00
V _{O2}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V _{O3}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V _O (total)	0.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 9. Relative Probability of Finding an Adsorbed CH₃ Particle in a Certain Region of the Surface

% oxygen vacancies surface region	0%	2.50%	5%	10%	11.11%	16.67%	25%
	relative probability (%)						
stoichiometric	100.00	0.00	0.00	0.00	0.00	0.00	0.00
V _{O1}	0.00	100.00	100.00	100.00	100.00	100.00	100.00
V _{O2}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V _{O3}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V _O (total)	0.00	100.00	100.00	100.00	100.00	100.00	100.00

conditions. We determine the relative probability by using the Frenkel equation:³⁷

$$\tau_{\text{config}} = \frac{1}{\nu_0} \times \exp\left(\frac{E_{\text{ads}}}{k_B \times T}\right) \quad (4)$$

where τ_{config} is the mean lifetime of the particle in a certain adsorption configuration and ν_0 is the vibrational frequency of the adsorbed particle. We calculated ν_0 for a number of different adsorption configurations and found that ν_0 varies with a factor between 0.66 and 3.61. However, we found for adsorption configurations, for which ν_0 varies strongly from the ν_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 ν_0 to be constant, since the influence of ν_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 ν_0 to be a constant:

$$P_i = \frac{n_i \times \tau_{\text{config},i}}{\sum_j n_j \times \tau_{\text{config},j}} = \frac{n_i \times \exp(E_{\text{ads},i}/k_B \times T)}{\sum_j n_j \times \exp(E_{\text{ads},j}/k_B \times T)} \quad (5)$$

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 as far away as possible from the oxygen vacancy. At an oxygen vacancy concentration of 25% we find that the probability of finding C adsorbed in the adsorption configurations A001-C-V1-1d or A001-C-V1-2d decreases with about 5%. A large part of this decrease is caused by an increase in probability of finding C in the adsorption configurations A001-C-V1-1c or A001-C-V1-2c.

In Table 7 the relative probability of finding the adsorbed CH radical in a certain region of the anatase (001) surface at equilibrium conditions is shown. The influence of oxygen vacancies on the adsorption of CH is larger than for C. For a vacancy concentration between 5 and 10% we find that the probability of finding the CH near an oxygen vacancy becomes larger than 50%. At 10% defect concentration we find 8.5% of the adsorbed CH at the V_{O1} oxygen vacancy in the A001-CH-V1-1a configuration. This means that a fraction of CH would be adsorbed close to the vacancy, where the influence of the vacancy on possible reactions will be the greatest. However, 48.7% is found in a [010] row neighboring the V_{O1} oxygen vacancy. The probability of finding CH in the A001-CH-V1-1a configuration increases to 14.7, 24.4, and 37.6% for an oxygen vacancy concentration of 11.11, 16.67, and 25%, respectively.

In Table 8 the relative probability of finding the adsorbed CH_2 radical in a certain region of the anatase (001) surface at equilibrium conditions is shown. The probability of finding CH_2 in the A001-CH2-V1-1a at equilibrium conditions is almost 100% at all oxygen vacancy concentrations, while on the stoichiometric surface CH_2 is distributed equally between the A001-CH2-S-1 and A001-CH2-S-2 configurations.

In Table 9 the relative probability of finding the adsorbed CH_3 radical in a certain region of the anatase (001) surface at equilibrium conditions is shown. For CH_3 , we find that almost all adsorbed CH_3 can be found in either the A001-CH3-V1-3a or the A001-CH3-V1-3b adsorption configuration at all oxygen vacancy concentrations.

From the results in this section it becomes clear that oxygen vacancies significantly influence the distribution of the adsorbed particles at the surface and create new possible adsorption configurations. This in turn will have an effect on which reaction pathways will be accessible for the adsorbed particles, apart from the possible changes to reaction barriers, which can be either a positive or a negative effect. It can therefore be concluded that oxygen vacancies are expected to have a profound effect on the possible reaction products that can be formed during plasma-catalytic conversion of methane to useful chemicals.

E. CONCLUSIONS

Detailed density-functional theory calculations at the PBE level were carried out to elucidate the adsorption configurations and energies of CH_x radicals ($x = 0-3$) on stoichiometric and reduced anatase (001) surfaces in the presence of oxygen vacancies. 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 (1×4) -

reconstructed anatase (001) surfaces, which are found to be the most stable in the subsurface.³⁵

On the stoichiometric anatase (001) surface we find that the maximal adsorption energies for C, CH, CH_2 , and CH_3 are 153.71, 118.07, 84.49, and 29.56 kcal/mol, respectively. The presence of oxygen vacancies in and at the surface influences the maximal adsorption energy. For the adsorption of the C-radical the adsorption energy dropped from 153.71 kcal/mol on the stoichiometric surface to 150.77 kcal/mol (−1.9%) and 152.97 kcal/mol (−0.5%) for V_{O1} and V_{O3} , respectively, and increases to 158.71 kcal/mol (+3.3%) for V_{O2} . Also, for the CH radical adsorption, the maximal adsorption energy drops from 118.07 kcal/mol on the stoichiometric surface to 117.05 kcal/mol (−0.9%) and 115.89 kcal/mol (−1.8%) for V_{O1} and V_{O3} , respectively, and increased to 126.12 kcal/mol (+6.8%) for V_{O2} . For CH_2 , we found an increase in maximal adsorption energy from 84.49 kcal/mol on the stoichiometric surface to 99.93 (+18.3%) and 92.97 kcal/mol (+10.0%) for V_{O1} and V_{O2} , respectively, and a drop to 84.27 kcal/mol (−0.3%) for V_{O3} . For CH_3 , however, we find an increase in the maximal adsorption energy from 29.56 kcal/mol on the stoichiometric surface to 56.94 kcal/mol (+92.6%) in the presence of V_{O1} , to 33.99 kcal/mol (+15.0%) for V_{O2} and 37.04 kcal/mol (+25.3%).

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 CH_2 and CH_3 adsorb preferentially at the oxygen vacancy site. CH partially adsorbs preferentially further away from the vacancy and partially at the oxygen vacancy. The oxygen vacancies significantly influence the distribution of adsorbed CH_x 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 coadsorption, 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-CH-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

The authors declare no competing financial interest.

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