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Adsorption, Diffusion and Desorption of Chlorine on and from Rutile $TiO_2\{110\}$: A Theoretical Investigation

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Abstract

Herein, the adsorption, diffusion and desorption of chlorine on and from stoichiometric, reduced and partially-reduced (defective) rutile $TiO_2\{110\}$ is investigated using ab-initio density functional theory (DFT) calculations. Theoretical results are compared to experimental investigations and microkinetic simulations based on DFT values are then used to verify the diffusion mechanisms assumed in those experimental investigations.

Contents

1 Introduction

Titanium dioxide (TiO_2) particles are ubiquitous in our daily lives; they are for instance used as a pigment for white paints and are the active component of sunscreen [1]. Moreover, titanium dioxide particles are utilised in industrial processes as catalyst support for heterogeneous catalysts [1, 2, 3] or as photocatalysts [4, 5]. Hence, titania particles are produced in magnitudes of millions of tons per year. The main route of titania nanoparticle production is the so-called chloride process. Raw titania is converted into titanium tetrachloride and subsequently this chloride is oxidised in a pure oxygen plasma at 1500 to 2000 K leading to titania particles. The precise mechanism of the seed formation and the growth of this seed is not known [6], even though the chloride process is a well-established industrial synthesis route. In order to elucidate the mechanism of the growth of titania nanoparticles, we investigate the surface as well as the gas phase chemistry of the formation of TiO_2 from $TiCl_4$. The thermochemistry of the titania seed formation in the gas phase was recently studied by West et alia [7]. Additionally we herein investigate the chemistry of the growth of a titania surface: Titanium dioxide is one of the best-investigated metal oxide surface, details can be found in a recent comprehensive review article by Diebold [1]. Experimental investigations on the kinetics of the surface growth of rutile titanium dioxide are however scarce. Pratsinis et al. studied the oxidation kinetics of $TiCl_4$ and determined the rate to be first order with respect to $TiCl_4$ and independent of the oxygen concentration [1, 8]. It is generally believed that after the seed is formed, $TiCl_4$ adsorbs and decomposes on the TiO_2 surface and subsequently molecular chlorine desorbs, leaving titanium atoms on the surface [8]. This titanium-covered surface is then oxidised by molecular oxygen and further $TiCl_4$ can adsorb and decompose. Bowker and co-workers investigated the kinetics of the reoxidation of reduced $TiO_2\{110\}$[9], however, the full cycle of the growth is not yet fully understood. A scheme of the presumed surface growth from layer n to layer $n+1$ is given in Figure 1. The details the elementary-step reaction mechanism of the $TiCl_4$ decomposition and chlorine formation are not fully understood. This motivated us to investigate the surface chemistry, especially the diffusion and recombination of chlorine on titanium dioxide (Figure 1, square).

Density functional theory (DFT) has proven to be a useful tool for the elucidation of reactions and diffusion processes on metals [10] -[13] and metal oxides [14] -[17]. The $\{110\}$ facet of rutile titanium dioxide was chosen because a significant quantity of experimental and theoretical studies are available for this surface [14], [18] - [24]. These publications mainly investigate the stoichiometric and partially-reduced $TiO_2\{110\}$; the reduced analogue is not studied as thoroughly [1]. The bridging oxygen atoms, which are present in the stoichiometric $TiO_2\{110\}$, are subject to much debate since they are undercoordinated and believed to be removed easily by thermal annealing. Since this mechanistic study is aimed at the high-temperature formation of titania nanoparticles, the reduced surface was included in this work. Additionally, diffusion on stoichiometric and partially-reduced $TiO_2\{110\}$ was considered, because there is experimental verification of the so-called 'hot' atom diffusion on this surface. Hot atoms are atoms, which contain a high kinetic energy originating from the energy excess that is transferred to the atom during the exothermic on-surface decomposition. It was suggested that, with this kinetic energy, these atoms can travel rather long distances on the titanium rows of stoichiometric $TiO_2\{110\}$ [25]. In order to gain more insight into this 'hot' atom diffusion process,
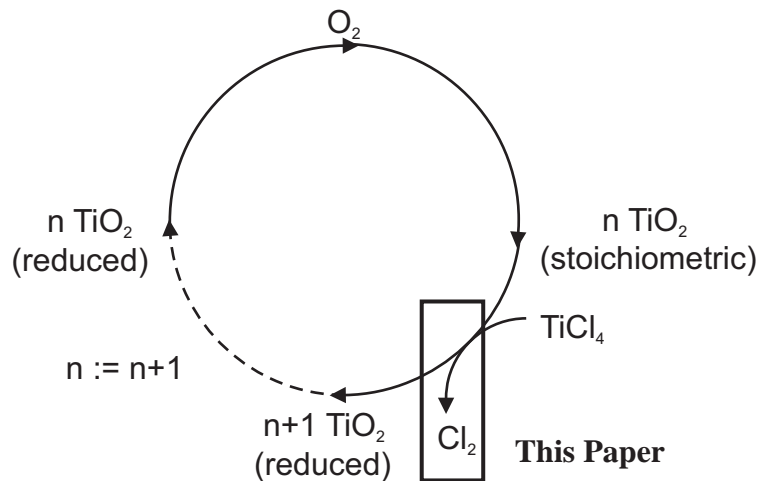
Figure 1: *Scheme of the surface growth of titanium dioxide*

the single site jump of chlorine atoms on rows of fivefold coordinated titanium atoms was investigated as well. It is moreover well-established that chlorine atoms preferentially adsorb in surface defects, such as missing bridging oxygen atoms on the (nearly) stoichiometric $TiO_2\{110\}$ surface [22] (henceforth referred to as a partially reduced surface), analogue to other adsorbates [14]. At low temperatures it was found that the chlorine adsorbs on the $Ti^{[5]}$ rows, while at higher temperature the defect sites are occupied. Vogtenhuber et al. speculated that adsorption of chlorine into defect sites is kinetically hindered [23]. In this study, we investigate the barriers of the diffusion of chlorine into these defects in order to verify this speculation. This study therefore amplifies prior studies concerned with the adsorption of chlorine [22, 23] by calculating activation barriers of surface migration of chlorine and thereby generating a microkinetic model of the surface diffusion. Ab-initio simulations of the gas phase chemistry of the combustion of $TiCl_4$ in the gas phase and the surface growth of titania nanoparticles will lay the foundation for a comprehensive population balance model [26] of seed formation and nanoparticle growth. This study aims at steering the process towards the selective formation of nano-sized particles during the flame combustion of titanium tetrachloride. This will be utilised by industrial partners to make their process more cost efficient.

2 Computational Method

In this work the behaviour of chlorine on a $\{110\}$ facet of stoichiometric and reduced rutile titanium dioxide was studied by means of DFT calculations using the CASTEP computer code [27]. The generalised gradient approximation (GGA) as proposed by Perdew et al. was applied [28], combined with Vanderbilt ultrasoft pseudopotentials [29]. The planewave basis set was truncated at a kinetic energy of 340 eV. The Brillouin zones was sampled by a k-point mesh with a k-point spacing of $0.05\,\text{Å}^{-1}$ as generated by the Monkhorst-Pack scheme [30]. Systems that may contain net spin have been checked

using spin-polarized DFT. The surface was modelled using a four-layer TiO_2 slab with the lower three layers fixed at their positions in the bulk and the uppermost layer mobile in case of the reduced surface, if bridging-oxygen atoms were present, these were considered fully mobile as well. Previous studies have shown that this thickness is appropriate for the simulation of surface processes [14], even though it is known that the surface properties of thin TiO_2 films vary with slab thickness. Periodic boundary conditions were used to model an extended surface. A 10 Å vacuum region was placed between the periodically-repeated slabs to ensure that the adsorbate and the subsequent slab do not interact. Adsorption energies are calculated according to

$$E_{ad} = E_{surface+xCl} - (E_{surface} + \frac{x}{2}E_{Cl_2}), \qquad (1)$$

in which $E_{surface+xCl}$ stands for the total energy of chlorine adsorbed on $TiO_2\{110\}$. E_{Cl_2} stands for the total energy of molecular chlorine in elementary cell used for the surface calculations; adsorption energies are hence referenced to molecular chlorine. The transition states of the surface reactions/transformations were located on the potential energy surface (PES) by performing linear synchronous and quadratic synchronous transit calculations with conjugate gradient refinements [31]. Activation barriers are then calculated according to

$$E_a = E_{transition\,state} - E_{reactants}. \qquad (2)$$

The diffusion and desorption of chlorine on $TiO_2\{110\}$ was simulated using the DETCHEM software package by Deutschmann et al. [32], based on an elementary-step reaction mechanism derived from plane-wave DFT calculations. DETCHEM uses an Arrhenius-type equation for the determination of the surface diffusion coefficient of each migration step. The diffusion coefficient D is calculated according to

$$D = \nu_0 \exp(-\frac{E_m}{RT}) \qquad (3)$$

and ν_0 is the attempt frequency, commonly associated with the lateral vibrational mode of the adatom and E_m is the activation barrier for the surface migration, i.e. a site jump. The universal value for the attempt frequency $(1 \times 10^{-13}\,s^{-1})$ derived from transition state theory was used in our microkinetic investigation. In case of desorption the rate k_{des} is calculated according to

$$k_{des} = A \exp(-\frac{E_a^{des}}{RT}). \qquad (4)$$

The universal value for the attempt frequency is used as the pre-exponential factor A in the Arrhenius expression, as in the case of the diffusion. In the presented case, diffusion and desorption are related since a collision that leads to desorption is a diffusion process as well. The crucial difference in the case of a diatomic surface recombination is that a desorption process ends up in an already occupied site (and hence leads to formation of Cl_2), while a diffusion process ends up in an unoccupied site (and hence does not lead to a chemical reaction). The possible sites for diffusion are explained in the text; for the details of the implementation of DETCHEM see [33].

3 Results and Discussion

3.1 Reduced and Stoichiometric Rutile $TiO_2\{110\}$

Prior to investigations of the adsorption of chlorine on rutile $TiO_2\{110\}$ surfaces, the rutile TiO_2 elementary cell was optimised and subsequently two surfaces with different terminations were cleaved form this optimised elementary cell. The geometry of these surfaces, reduced and stoichiometric, was then optimised. In case of both surfaces a strong inwards relaxation of the uppermost layer is observed, which is due to the undercoordination of the surface atoms. The stoichiometric surface is characterised by bridging oxygen atoms, which are above the actual surface level (labelled with a "B" in Figure 2).
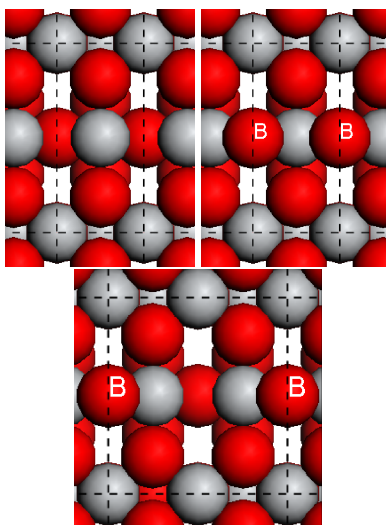
Figure 2: *top: reduced (left) and stoichiometric (right) (1×1)-$TiO_2\{110\}$ surface, titanium is depicted in light-grey, oxygen in dark-grey (red); bottom: defective, partially-reduced (1×1)-$TiO_2\{110\}$ surface, every second bridging oxygen atom is missing; the bridging oxygen atoms on the stoichiometric and partially-reduced surface are labelled with a "B"*

The reduced surface is planar before optimisation and undergoes 'roughening' during the optimisation process due to the already mentioned inwards relaxation. A partially-reduced $TiO_2\{110\}$, a surface with oxygen vacancies, was created by removing one oxygen atom from the stoichiometric (1×2) surface and optimising the geometry of this system afterwards. The surface area of a (1×1) elementary cell of the partially-reduced surface, therefore equals the surface area of the (1×2) surfaces of reduced and stoichiometric $TiO_2\{110\}$ (see Figure 2, bottom).

On reduced $TiO_2\{110\}$ there are two different titanium sites, one in which the Ti is fourfold coordinated, one in which the Ti atom is fivefold coordinate. Hereafter, we refer to the fivefold sites as $Ti^{[5]}$ and the fourfold sites as $Ti^{[4]}$. Both sites form rows along the (001) direction on the surface, these rows are separated by rows of oxygen (see Figure 2). On the stoichiometic surface, the $Ti^{[5]}$ rows are vacant, while the $Ti^{[4]}$ sites are covered with bridging oxygen atoms, and hence sixfold coordinated.

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3.2 Chlorine Adsorption on $TiO_2\{110\}$

3.2.1 Reduced Surface

Firstly, the adsorption of one and two chlorine atoms on reduced (1×1)-$TiO_2\{110\}$ was studied, corresponding to a surface coverage of 0.5 and 1 monolayer (ML). It has not escaped our attention that this coverage is above the maximum coverage observed by experiments. However, as this study is aimed at a high temperature process and surface science studies are usually carried out at much lower temperature, we cannot exclude the high coverage regime, at least not for very short time spans on small areas. The chlorine atom is most stable on fourfold-coordinated Ti atoms ($Ti^{[4]}$), a stable species could be identified in bridged and atop coordination. In atop position on $Ti^{[4]}$ atoms (along the (001) direction) the chlorine atom is located 2.38 Å above the Ti and its adsorption energy is -2.89 eV. In the bridged position, the chlorine is located 1.9 Å above the surface plane with Ti-Cl bond length of 2.41 Å. The adsorption energy is -2.89 eV equal to that in the atop position and hence it can be concluded that both adsorption sites have to be considered. On fivefold coordinated $Ti^{[5]}$ atoms, chlorine is bound significantly less strongly to the surface. The atop position is more stable with an adsorption energy of -0.85 eV, as opposed to -0.13 eV for the bridged position. In the bridged position the Ti-Cl bond length is 2.61 Å and the chlorine is located 2.16 Å above the surface plane, while in the atop position, the chlorine atom is located 2.38 Å above the surface. For coverage of 1 ML, the most stable adsorption geometry contains one chlorine atom in the atop position on fivefold Ti and one chlorine atom in the bridged position on fourfold Ti. This configuration is 0.6 eV more stable than both chlorine atoms adsorbed in an atop position; a stable structure in which both chlorines are adsorbed in bridged positions could not be found. Hence, two chlorines on (1×1)-$TiO_2\{110\}$ will adsorb as depicted in Figure 3.
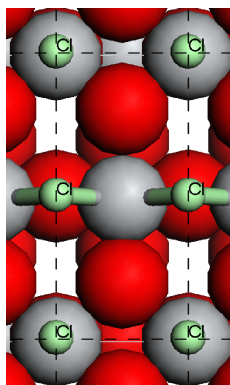
Figure 3: *Most stable adsorption geometry for 1 ML chlorine on reduced $TiO_2\{110\}$, on $Ti^{[5]}$ sites chlorine accommodates in atop position, on $Ti^{[4]}$ sites adsorption in bridged position is preferred; red (dark-grey) balls represent oxygen atoms, light-grey balls represent titanium atoms*

The average adsorption energy for this configurations is 1.56 eV Cl^{-1}. If both chlorine atoms are adsorbed in atop fashion, the average adsorption energy is 1.26 eV Cl^{-1} and thus considerably lower than the atop-bridged average adsorption energy (1.56 eV Cl^{-1}). For the subsequent studies on the reduced TiO$_2${110} we therefore first occupied Ti$^{[4]}$ sites with bridged chlorine atoms and Ti$^{[5]}$ sites with atop chlorine. Also in the case of a (1×2) elementary cell of reduced TiO$_2${110}, Cl adsorbs preferentially in atop configuration on Ti$^{[5]}$ while, according to our calculations, the bridged adsorption site is favoured in the case of the Ti$^{[4]}$ atoms. The adsorption energy in the atop position on Ti$^{[5]}$ is -1.03 eV, the adsorption on a bridged site on Ti$^{[4]}$ is significantly higher, with an adsorption energy of -3.00 eV. According to this adsorption scheme, the evolution of the adsorption energy per Cl with increasing coverage is depicted in Figure 4.
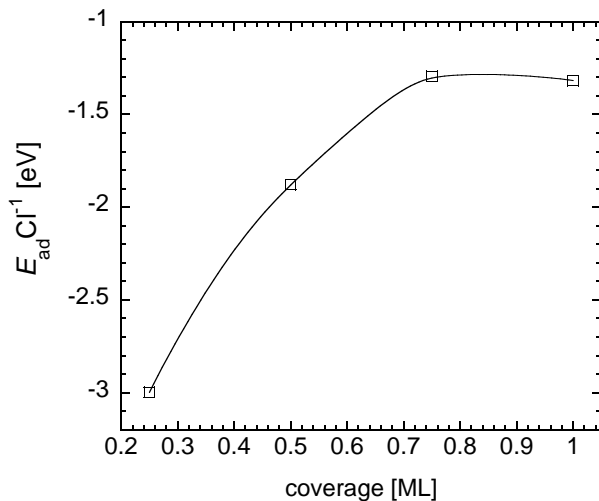
Figure 4: *Evolution of the average adsorption energy of chlorine on reduced (1×2)-TiO$_2${110}, first Ti$^{[4]}$ sites were occupied in bridged position and afterwards Ti$^{[5]}$ sites were occupied in atop fashion*

The drastic decrease in the adsorption energy between the coverage 0.25 ML and 0.5 ML is owing to both bonding competition [11] (the two chlorine atoms share bonds with the same surface Ti atom and hence compete for electron density offered by the surface atom) and lateral adsorbate-adsorbate repulsion.

3.2.2 Stoichiometric surface

On the stoichiometric surface, there are considerably fewer possibilities for adsorption since only Ti$^{[5]}$ sites are vacant. Cl adsorbs preferentially in the atop fashion, 2.51 Å above the titanium atoms in case of the (1×1) elementary cell. The adsorption energy is positive with 0.43 eV on the stoichiometric, as opposed to the exothermic adsorption in case of the reduced counterpart. Spin polarised calculations confirmed the endothermicity of the adsorption. A stable adsorption geometry in which the chlorine is accommodated in the bridged fashion could not be identified. Also on the (1×2) elementary cell, the adsorption is energetically unfavourable with respect to molecular gas phase chlorine in the atop

fashion (E_{ad} = 0.59 eV), while a stable bridged species could not be found. In the stable atop adsorption site, Cl resides 2.20 Å above the titanium ion. The "inversion" of the heat of adsorption of Cl on $Ti^{[5]}$ upon addition of oxygen on the $Ti^{[4]}$ rows (i.e. stoichiometric versus reduced surface) already indicates that chlorine desorption and oxidation of the surface are likely to be coupled in the surface growth of $TiO_2\{110\}$. Chlorine is strongly bound to the surface and oxidation of adjacent titanium sites significantly weakens the bonding to the surface. In this case it makes adsorbed chlorine unfavourable compared to molecular chlorine in the gas phase. This in turn means that if chlorine atoms collide in the vicinity of stoichiometric parts of the surface they are highly likely to desorb.

### 3.2.3 Partially-Reduced Surface

Cl can reside on three different adsorption sites on a partially-reduced $TiO_2\{110\}$ (see Figure 2, bottom): a. on $Ti^{[5]}$ vis-à-vis the defect site or b. on $Ti^{[5]}$ vis-à-vis the remaining bridging oxygen and c. in a bridged fashion in the vacancy resembling the missing oxygen atom. Our calculations determine that adsorption in the defect site is, by far, the most energetically favoured option (E_{ad} = −1.88 eV) 1.47 eV lower in energy than the atop position vis-à-vis the defect site (E_{ad} = −0.41 eV) and 1.36 eV more stable than the atop position vis-à-vis the remaining bridging oxygen (E_{ad} = −0.53 eV). This is in accordance with calculation by Vogtenhuber et alia [22, 23]. In the defect site the Cl is located 1.81 Å above the surface plane, which is considerably lower than the 2 Å distance determined experimentally by Hebenstreit et al. [20]. Since, in case of defect sites, spin effects could indeed play a crucial role, the geometry was recalculated assuming it was spin-polarised. In this case the chlorine is still located 1.81 Å above the surface plane with a Ti-Cl distance of 2.43 Å confirming the results of the spin-paired calculations. The adsorption geometry on the $Ti^{[5]}$ row is similar to the adsorption on stoichiometric $TiO_2\{110\}$, however, the Ti-Cl bond is considerably longer on the stoichiometric surface (stoichio: 2.51 Å, part.-red.: 1.81 Å). When comparing the adsorption energies for Cl in the atop position on reduced, partially-reduced and stoichiometric rutile titanium dioxide, it becomes apparent that the oxidation of the surface significantly weakens the Ti-Cl bond (red: −0.85eV > part.-red.: −0.53 eV / -0.41 eV > stoichio.: + 0.43 eV).

3.3 Diffusion on $TiO_2\{110\}$

3.3.1 Reduced Surface

The transition states for single-site jumps of chlorine on $TiO_2\{110\}$ were located on the PES and the activation energy of the surface transformation was calculated based on this transition state. Four scenarios are possible: Cl can diffuse on $Ti^{[5]}$ or $Ti^{[4]}$ rows (scenario 1 and 2) and additionally chlorine atoms can traverse between rows, i.e. from $Ti^{[4]}$ to $Ti^{[5]}$ and vice versa (scenarios 3 and 4). In the case of Cl adsorbed on-top on $Ti^{[5]}$ on (1 x 1)-$TiO_2\{110\}$, the activation energy of a single-site jump to an adjacent atop-$Ti^{[5]}$ site was calculated to be 0.76 eV. The transition state is located at 0.5 of the reaction coordinate (in which 0 denotes the initial state and 1 the final state), as expected for a surface transformation between two equivalent sites. The single site jump form one bridged-$Ti^{[4]}$

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position to an adjacent bridged- $Ti^{[4]}$ position is, according to our calculations, much less likely. The transition state is located at 0.5 of the reaction coordinate in the atop position and the activation energy was calculated to be 2.54 eV and therefore, according to our ab-initio calculations, this process will only be relevant at elevated temperatures. Diffusion between bridged-$Ti^{[4]}$ and atop-$Ti^{[5]}$ sites is activated by 0.21 eV, while the back transformation is activated by 2.24 eV. The transition state of the site jump from atop-$Ti^{[5]}$ to bridged-$Ti^{[4]}$ is located rather early on the reaction coordinate at 0.35, in accordance with Hammond's postulate [34]. The transitions state of the back reaction is consequently located rather late on the reaction coordinate at 0.65. A single-site jump of chlorine from an atop- $Ti^{[5]}$ site to an adjacent one on a (1×2) cell is activated by 0.65 eV. The transition state is, as expected, located at 0.5 on the reaction coordinate (Figure 5).
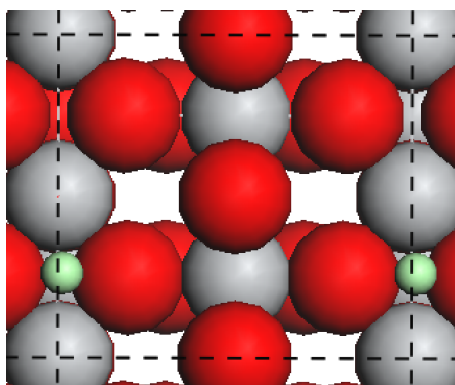
Figure 5: *Transition state of site jump on a $Ti^{[5]}$ row on stoichiometric $TiO_2\{110\}$*
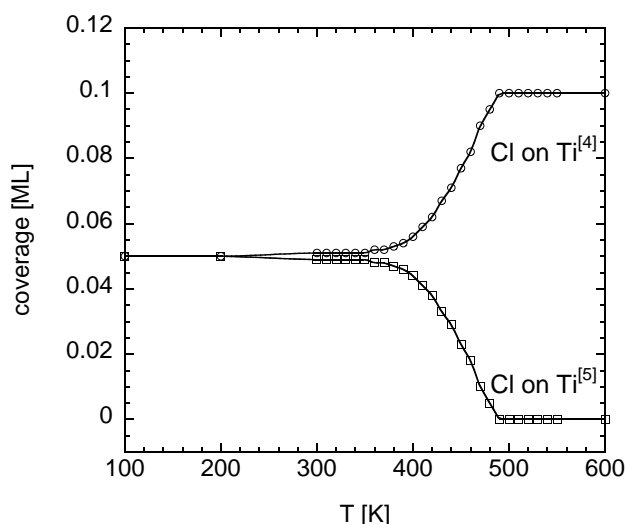
Figure 6: *Distribution of chlorine on the two different Ti sites on reduced $TiO_2\{110\}$ as a function of temperature; after reaching the temperature sufficient to activate the single site jump from the less stable $Ti^{[5]}$ site to the more stable $Ti^{[4]}$ site, all chlorine is located in bridged position on $Ti^{[4]}$*

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At lower coverage the process is therefore more likely, because the activation barrier is 14.5 % lower. A single-site jump of chlorine from an atop-Ti[5] site to an adjacent bridged-Ti[4] site on a (1×2) cell seems to be even more likely. The activation energy for this process is 0.24 eV, while the back-transformation, the diffusion from a bridged- Ti[4] site to an atop-Ti[5] site is activated by 2.22 eV. At low temperature it can therefore be expected that chlorine atoms will preferably be present on rows of fourfold Ti atoms. On these rows, Cl is located in the bridged position. The site jump from one to the subsequent bridged site is activated by 0.51 eV according to our results. For the single-site jump from an atop-Ti[5] site to an adjacent atop-Ti[5],with a chlorine atom in a neighbouring bridged-Ti[4] position, the diffusion barrier decreases to 0.58 eV. This is compared to a barrier of 0.65 eV without the neighbouring chlorine. These results lead to the conclusion that, in the lower temperature range, chlorine can diffuse along the rows of either four- or fivefold Ti atoms and can diffuse from a fivefold row to a fourfold row (E_a = 0.24 eV). The reverse process, the diffusion from a fourfold to a fivefold row, is blocked in the lower temperature regime (E_a = 2.22 eV), but possible at elevated temperature. In order to support these assumptions, a microkinetic simulation of the diffusion of Cl on a reduced surface was carried out. A reduced $TiO_2\{110\}$ surface covered with a tenth monolayer chlorine was considered. Chlorine is assumed to be distributed homogeneously on the surface, i.e. 0.05 ML on Ti[5] sites and 0.05 ML on Ti[4] sites. Desorption is neglected in this model, but considered later. From Figure 6 it can be seen that, from a temperature of 360 K, chlorine diffuses from the Ti[5] sites to the more stable Ti[4] sites. Above 480 K, all chlorines are located in the bridged position on Ti[4] sites. Diffusion back to the Ti[5] row is, according to our calculations, only important above 1000 K. Later in this paper it will be discussed how desorption of molecular chlorine influences this diffusion process.

3.3.2 Stoichiometric Surface

Since there are fewer possibilities for adsorption on stoichiometric $TiO_2\{110\}$, vide supra, there are consequently less possibilities for diffusions, i.e. there is only one possibility for diffusion namely the single-site jump from an atop to an adjacent atop position on Ti[5]. On the (1×1), this transformation is activated by 0.55 eV considerably less than on the reduced counterpart (0.76 eV). In contrast, on the (1×2) we calculate a slightly higher activation barrier for this single site jump on the stoichiometric surface (0.68 eV) than on the reduced counterpart (0.65 eV). Diebold et al. assumed that the large Cl-Cl separations observed in experiments are due to a confinement of the energy gained upon adsorption along the (001) direction. This, however, cannot explain why chlorine atoms are often found on different Ti[5] rows. They assumed that, in principle, the chlorine could 'push' its way through the oxygen bridges but would loose most of its kinetic energy in the process. Chlorine atoms separated by two oxygen bridges (i.e. two Ti[5] rows apart) could therefore not be explained by such a diffusion mechanism. This motivated us to investigate the energy landscape for the movement of chlorine on Ti[5] confined by two rows of bridging oxygens. The energy landscape was created by optimising different fixed positions (x and y constrained), while the height of the Cl above the surface (z coordinate) was allowed to relax. This landscape shows that the bridging oxygen atoms on the stoichiometric surface confine any movement of the chlorine atom in direction of the (001) orientation.

3.3.3 Partially-Reduced Surface

In order to verify the speculation that diffusion into oxygen vacancies might be kinetically blocked at room temperature published by Vogtenhuber et al. [23], we studied the diffusion of Cl on partially reduced (1×2) $TiO_2\{110\}$. Locating the transition state of the diffusion of chlorine from the $Ti^{[5]}$ row into the surface defect, the activation barrier was determined to be 0.27 eV. Spin polarised calculations confirm the low activation barrier of this surface diffusion process. Therefore, our results suggest that the diffusion from the $Ti^{[5]}$ site into the defect cannot be kinetically hindered, since this transformation is possible already in the lower regime, vide infra. However, STM experiments by Diebold et al. conducted at room temperature determined that the chlorine reside on $Ti^{[5]}$ rows instead of in oxygen vacancies. Our results are therefore contradictory [25]. An energy scheme of the diffusion along a $Ti^{[5]}$ row next to bridging oxygen atoms and into a oxygen vacancy in given in Figure 7, the corresponding structures are depicted beneath the energy scheme.

Since it is known from STM experiments that Cl can diffuse along the $Ti^{[5]}$ rows (i.e. along the (001) direction) and our results determine the activation barrier for these single-site jumps to be 0.55 eV, while the barrier is 0.25 eV for the diffusion into a vacancy, our results are contradictory to the proposed kinetic blocking. Nevertheless, our results support the assumption published by Diebold et al. in which hopping through the vacancies in the bridging oxygen rows is discounted as a major route for traversal of chlorine to an adjacent $Ti^{[5]}$ row on defective stoichiometric $TiO_2\{110\}$. The potential energy surface of chlorine in an oxygen vacancy has two minimum pathways leading out of this site back onto $Ti^{[5]}$ rows. Via either pathway, an energy barrier of 1.72 eV has to be overcome indicating that this diffusion process is indeed negligible at room temperature[25]. In order to support our assumption, a kinetic model of the Cl diffusion based on our ab-initio results was carried out. A stoichiometric $TiO_2\{110\}$ surface in which every 6th bridging oxygen site is vacant was modelled assuming periodic boundary conditions (see Figure 8).

Furthermore, a low chlorine coverage was assumed so that collision and desorption of chlorine atoms can be neglected. The activation energy for diffusion of Cl vicinal to bridging oxygen atoms was taken from the calculations on the stoichiometric surface, while the activation barriers for the diffusion in front of and into a vacancy were taken from the calculation on the partially reduced surface. Calculating the surface overlayer as a function of temperature shows that, from 600 K on, defect sites are occupied while, from 900 K on almost all the chlorines are diffused into the oxygen vacancy Figure 9).

Nevertheless, this cannot explain why chlorine atoms travel long distances on rows at room temperature, while they do not occupy the vacancies at this temperature. A possible explanation for this is the confinement of the kinetic energy of the chlorine atom along the (001) direction the bridging oxygen atoms direct all the kinetic energy along this trajectory and hence the chlorine shoots past the defect without diffusing into it. Only if the chlorine atoms come to a stop (due to the loss of kinetic energy) at the entrance to a defect site will it diffuse into the defect site. Diebold et al. suggested a cannon ball like adsorption of chlorine to explain why chlorine atoms are located on different $Ti^{[5]}$ rows posterior to adsorption and they neglect diffusion through defect sites. To verify this assumption, a further kinetic simulation of the evolution of the surface overlayer was per-
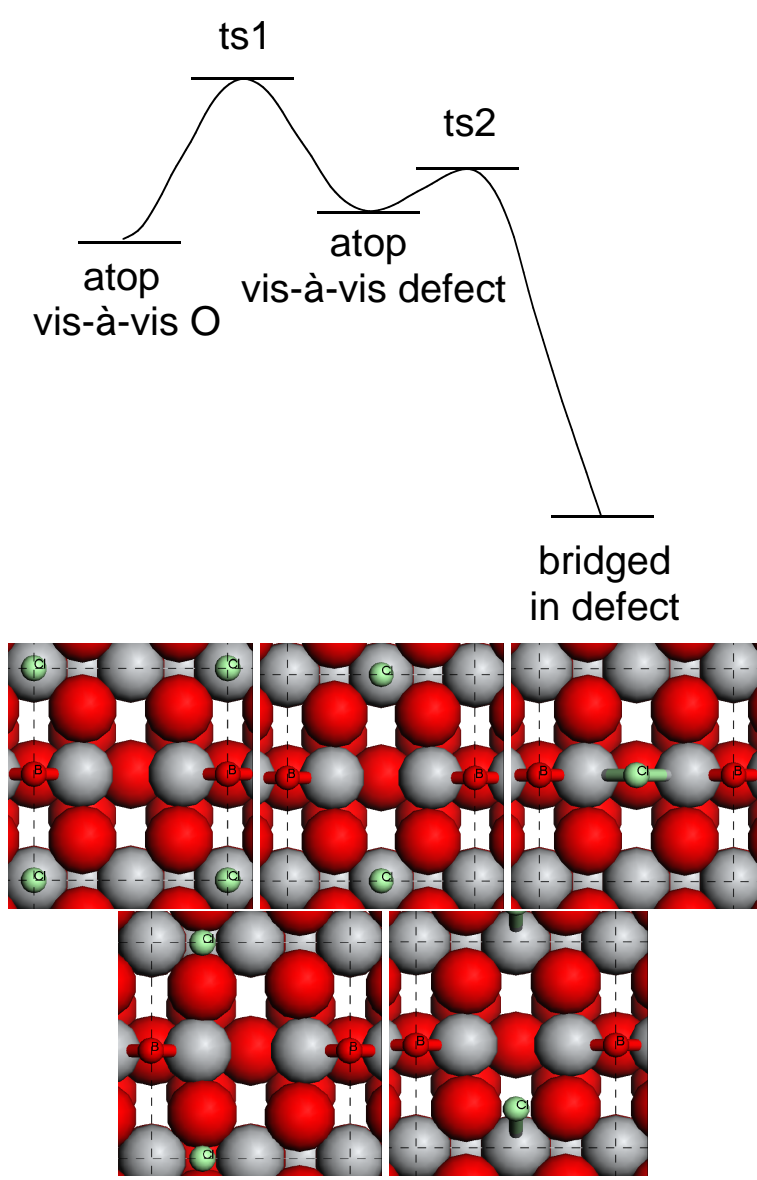
Figure 7: *Energy scheme and structures of the diffusion of chlorine from a $Ti^{[5]}$ row into a oxygen vacancy on partially-reduced $TiO_2\{110\}$, stable structures are depicted in the upper row, transition state in the lower row*
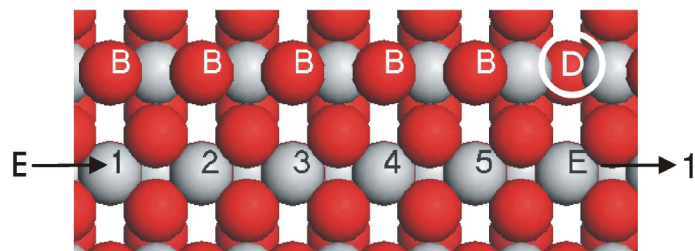
Figure 8: *Elementary cell of the surface used for the kinetic simulation, also in this case periodic boundary conditions are assumed. Every 6th bridging oxygen atom is missing, $Ti^{[5]}$ adsorption sites next to bridging oxygen atoms are numbered from 1 to 5, $Ti^{[5]}$ adsorption site vis--vis a defect site is labelled with an E (for entrance), the defect itself is labelled with a D.*
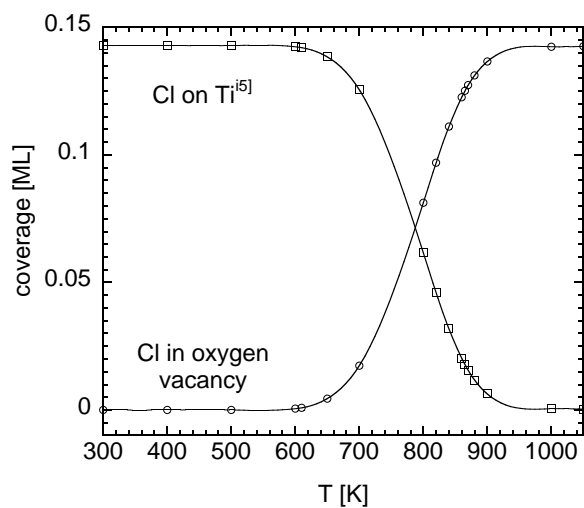
Figure 9: *Evolution of the chlorine overlayer on $TiO_2\{110\}$ starting from a situation in which all chlorines are located as remotely as possible from the defect site*

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formed. The starting point of this temperature evolution study was a surface in which the chlorine atoms are located exclusively in oxygen vacancies. In order to elucidate at which temperature chlorine atoms can escape the stable defect adsorption site, the temperature evolution of the surface overlayer was simulated based on the mechanism developed by DFT. According to this simulation, chlorine can only leave the defect site at temperatures above 800 K and diffusion out of the defect is absolutely negligible at temperatures used in surface science studies. Consequently our results support the suggestions that an alternative pathway for the traversal of chlorine atoms between $Ti^{[5]}$ rows, such as the cannon-ball mechanism [25], must indeed be considered.

3.4 Cl_2 formation from $TiO_2\{110\}$

3.4.1 Reduced $TiO_2\{110\}$

For many adsorption processes, it is assumed that they are energetically strictly uphill. In order to determine if this is also the case for the processes studied herein, or if there is a maximum on the desorption coordinate, i.e. a transition state, the formation of molecular chlorine in the gas phase was investigated from the most stable adsorption structure, namely the atop-$Ti^{[5]}$-bridged-$Ti^{[4]}$ on (1×1) and (1×2) $TiO_2\{110\}$. Prior to calculating the desorption process, an end-point namely molecular chlorine above $TiO_2\{110\}$ had to be determined. A stable structure in which molecular chlorine is located 3.12 Å above the surface plane of $TiO_2\{110\}$ parallel to the surface plane was determined for both elementary cells by our optimisations. The Cl-Cl bond length of 1.95 Å is in agreement with the experimental value (1.99 Å). Subsequently, the transition state of the reaction between two chlorines adsorbed in atop-$Ti^{[5]}$ and bridged-$Ti^{[4]}$ positions on both (1×1) and (1×2) $TiO_2\{110\}$ and Cl_2 above those surfaces was located on the PES. As expected, the process is energetically strictly uphill. Also in case of the formation of molecular chlorine from the less stable atop-atop configuration it appears that the process is energetically strictly uphill on both elementary cells and hence the inverted adsorption energy can be considered the activation barrier of the reaction. Since at low temperatures diffusion to atop-$Ti^{[5]}$ sites is kinetically blocked, it is suggested that chlorines on $Ti^{[4]}$ rows are stable because the activation energy for desorption is too high (3.12 eV). At higher temperatures chlorine atoms can diffuse from bridged-$Ti^{[4]}$ to atop-$Ti^{[5]}$; from atop-$Ti^{[5]}$ chlorine desorption is much more probable, since the activation energy is considerably lower, i.e. 1.10 eV.

Recalculating the microkinetic model of the surface diffusion on the reduced surface including desorption, shows that this assumption is indeed correct. We compare the mechanism for diffusion-desorption with the pure diffusion mechanism (Figure 10).

Initially, chlorine leaves the surface (the coverage decreases by 0.005 ML, 5 %) due to collisions of chlorine atoms on $Ti^{[5]}$. Subsequently, the partial chlorine coverage on $Ti^{[5]}$ decreases owing to desorption of molecular chlorine and diffusion to the more stable bridged site on $Ti^{[4]}$, which makes further collisions on $Ti^{[5]}$ improbable. Hence, the overall surface coverage stays constant and, above 480 K, all chlorines reside on $Ti^{[4]}$. Since the activation barrier for the single-site jump to the $Ti^{[5]}$ rows is lower than the activation barrier for desorption from $Ti^{[4]}$ sites, it can furthermore be concluded that Cl
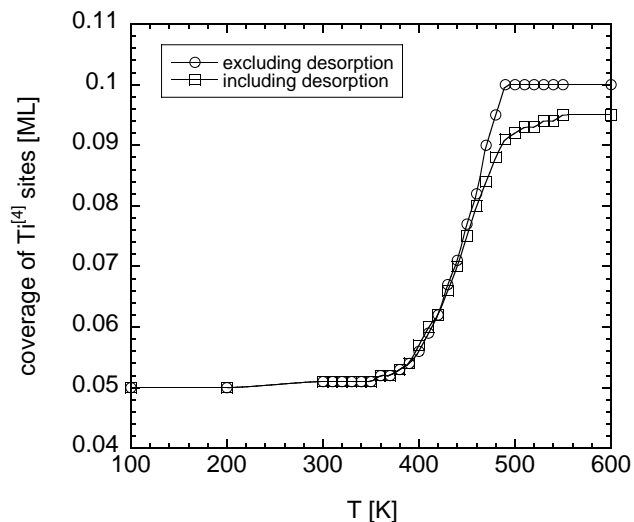
Figure 10: *Difference in the coverage of the* $Ti^{[4]}$ *sites as function of the temperature with and without accounting for desorption*

diffuses to the less stable site first and subsequently desorbs from those. According to our kinetic simulations, a full desorption of the chlorine from $TiO_2\{110\}$ will not occur below 1000 K. Also, in the case of a hypothetical fully chlorine covered $TiO_2\{110\}$ surface ($\theta = 1$ ML), chlorine adsorbed on $Ti^{[4]}$ stays stable, while it desorbs from $Ti^{[5]}$. A simulated temperature programmed desorption (TPD) procedure shows that the desorption temperature from $Ti^{[5]}$ sites is 595 K, while chlorine is stable in the bridged position on $Ti^{[4]}$. It has, however, to be mentioned that PW91 calculations tend to overestimate adsorption energies. This suggests that desorption temperatures determined by our simulations might be overestimated as well. Preliminary results of the oxygen adsorption on reduced $TiO_2\{110\}$ and previous results on defected titania [14] show that oxygen has a preference for $Ti^{[4]}$ sites as well and additionally binds stronger to those sites. This immediately suggests that, upon adsorption of oxygen, chlorine could be forced onto the $Ti^{[5]}$ sites and would subsequently desorb from there. A more detailed study of the adsorption of oxygen and its co-adsorption with chlorine on the same surfaces is underway. These results will form the basis of a comprehensive kinetic Monte-Carlo simulation of the competition of diffusion and desorption of chlorine on titania surfaces.

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4 Conclusions

A comprehensive study of the adsorption, diffusion and desorption of chlorine on stoichiometric and different reduced $TiO_2\{110\}$ surfaces is presented. The most stable adsorption sites and geometries for atomic chlorine were determined. The diffusion of chlorine to different sites and geometries was investigated on those different surfaces by determining the transition state of the surface transformation process. This study therefore amplifies prior studies, which focus on the adsorption of chlorine [22, 23]. Our DFT results suggest that diffusion of a chlorine atom from a $Ti^{[5]}$ row to a $Ti^{[4]}$ row on reduced $TiO_2\{110\}$ is likely, since the activation barrier is rather low. The back-transformation, however, is significantly higher. This leads to the assumption that at low temperatures, the $Ti^{[4]}$ rows on $TiO_2\{110\}$ are occupied with chlorine in the bridged position. At high temperatures, the atop-$Ti^{[5]}$ positions will be occupied for short time spans, because chlorine atoms can diffuse there as well. The temperature necessary for the diffusion to atop-$Ti^{[5]}$ positions, however, is higher than the desorption energy from those sites, indicating that any collision on those rows will lead to desorption of molecular chlorine. Consequently, the coverage of $Ti^{[5]}$ sites with chlorine will remain low at elevated temperatures. Our investigation of chlorine single-site jumps on $Ti^{[5]}$ rows on stoichiometric $TiO_2\{110\}$ surfaces show that the diffusion barrier is with 0.55 - 0.65 eV rather low and the 'hot' atom diffusion observed by STM is therefore to be expected. Not least because the kinetic energy will be confined within two potential 'walls' caused by the rows of bridging oxygen atoms. In the case of defective, partially reduced $TiO_2\{110\}$, our DFT calculations and microkinetic simulations could not elucidate why chlorine atoms are found on $Ti^{[5]}$ adsorption sites when oxygen vacancies are present. If diffusion along the (001) direction on $Ti^{[5]}$ rows is possible, diffusion into the oxygen vacancy should not be blocked since the activation barrier for the jump into a vacancy is considerably lower than the jump to a vicinal $Ti^{[5]}$ site. A possible explanation for this is that the chlorine atoms shoot by the defect sites since all their kinetic energy is confined along the (001) direction. Preliminary results of the oxygen adsorption on reduced $TiO_2\{110\}$ show that oxygen has a preference for $Ti^{[4]}$ sites as well and additionally binds stronger to those sites. This immediately suggest that upon adsorption of oxygen, chlorine could be forced onto the $Ti^{[5]}$ sites. Since oxygen coverage decreases the bond strength of Cl on $Ti^{[5]}$ drastically, desorption of molecular chlorine from these sites becomes very likely. These findings immediately suggest that a dynamic interplay between oxygen adsorption (oxidation) and chlorine desorption exists. A more detailed study of the adsorption of oxygen and its co-adsorption with chlorine on the same surfaces is underway.

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