Coverage-Dependent Oxidation and Reduction of Vanadium Supported on Anatase TiO₂(101)

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Abstract: Using a multi-technical approach, we studied the oxidation of anatase TiO₂(101)-supported vanadium (V) clusters at room temperature. We found by *ex situ* XPS that the highest oxidation state is +4 at sub-monolayer coverage regardless of the O₂ pressure, and STM studies revealed that the initial oxidation proceeds through oxygen-induced disintegration of V clusters into monomeric VO₂ species. By contrast, for ~2 monolayer V coverage, a partial oxidation to V⁵⁺ is achieved. By *in situ* APXPS measurements, we found that V can be maintained in the V⁵⁺ oxidation state irrespective of the coverage; however, in the sub-monolayer range, an O₂ pressure of at least ~1 × 10⁻⁵ mbar is needed. Our results suggest an enhanced reducibility of V in direct contact with the TiO₂ support compared to V in the 2nd layer, which is in line with the observed optimum V₂O₅ loading in catalytic applications just slightly below a full monolayer.

Keywords: Vanadium, oxidation, SCR catalysis, anatase TiO₂(101), X-ray photoelectron spectroscopy (XPS), ambient pressure X-ray photoelectron spectroscopy (APXPS), scanning tunneling microscopy (STM).

1. Introduction

Vanadia films supported on TiO₂ are known as excellent catalysts for various reactions such as the oxidation of SO₂ to SO₃ in sulfuric acid production, oxidation of different precursors into phthalic anhydride and selective catalytic reduction (SCR) of NO_x with NH₃ as the reducing agent [1]. To catalyze the SCR reaction ($4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 6\text{H}_2\text{O} + 4\text{N}_2$) anatase TiO₂ (a-TiO₂) is known to give higher activity than rutile (r-TiO₂), as in most catalytic applications of the vanadia / TiO₂ [2], [3]. Commonly, the catalytic cycle in vanadia / a-TiO₂ catalysis involves the oxidation/reduction between V⁵⁺ and V⁴⁺, and the V⁵⁺ oxidation state is considered to be the initial state of the catalyst [1], [4]–[7]. Optimal efficiency is achieved for sub-monolayer or monolayer coverage of vanadia, whereas vanadia multilayers are less active [4], [8]–[10]. The reason for this strong coverage dependence is presently not clear.

A fundamental understanding of the active surface in the vanadia / TiO₂ system in catalyzed reactions can be obtained by applying the surface science approach, where model catalysts are studied under ultra-high vacuum (UHV) conditions [11]. In previous studies of this kind, vanadia has been studied on a large variety of metal-oxide supports [8], [12]–[19]. In particular, vanadium-titania (V / TiO₂) and vanadia–titania (VO_x / TiO₂) systems have been studied in detail [8], [10], [20]–[37]. Preferentially single-crystalline rutile TiO₂(110) surfaces [r-TiO₂(110)] have been used as supports, because synthetic r-TiO₂ crystals are commercially available. Only few surface science studies have addressed the more relevant VO_x / a-TiO₂ system [27], [28], [34], [37], probably because of the lack of a-TiO₂ single crystals of sufficiently high quality.

Studies addressing V / r-TiO₂(110) have revealed a strong interaction between V and the support both at sub-monolayer and full-monolayer (ML) coverages [22], [24], [31], [32]. It was found that V oxidizes and TiO₂ reduces upon V deposition [21], [23], [24], [30], [33], [35]. It should be noted that the highest V oxidation state in these studies is lower than +5. Because of the importance of the V⁵⁺ oxidation state, numerous studies have aimed at a characterization of the VO_x / TiO₂ system under various oxidation

conditions [20], [22]–[25], [33], [35]. Two oxidation methods have been applied most frequently, namely post-oxidation (V deposition in UHV and subsequent oxygen exposure) and reactive evaporation (V deposition in an oxygen background). Reactive evaporation results in the growth of V_2O_3 overlayers [22]–[24], [35], whereas post-oxidation mainly results in VO_2 or mixtures of V_2O_3 and VO_2 [20], [23]–[25], [33], [35]. There is only one study wherein the growth of V_2O_5 (V^{5+}) has been achieved by post-oxidation [25].

In addition to post-oxidation and reactive evaporation, other preparations have been conducted to achieve the relevant V^{5+} oxidation state for studies in UHV. For example, Altman et al. [27]–[29] have shown that the V^{5+} oxidation state can be reached by means of oxygen-plasma-assisted molecular beam epitaxy. This preparation method has been used successfully for $r\text{-TiO}_2(110)$, $a\text{-TiO}_2(101)$ and $a\text{-TiO}_2(001)$ substrates. Finally, Wang and Madix have used the decomposition of a $VOCl_3$ precursor in water vapor to grow V_2O_5 on $r\text{-TiO}_2$ [38].

X-ray photoelectron spectroscopy (XPS) is often used to unravel the V oxidation state, because the V $2p_{3/2}$ binding energies (BE's) of the possible oxidation states (0, +2, +3, +4, +5) differ by up to 1 eV from each other [20], [23], [25], [27], [28], [32], [35], [39]–[42] (see [Table 1](#)). However, assigning oxidation states and corresponding vanadia structures (V, VO, V_2O_3 , VO_2 , V_2O_5) solely by XPS can be challenging or even misleading, because BE references usually are taken from bulk vanadia samples, and the strong interaction between V and TiO_2 needs to be taken into consideration. For example, Granozzi et al. [41] showed that several different V nanostructures share the oxidation state V^{3+} , although, formally, one would expect V^{4+} . Moreover, comparison between various XPS studies is often difficult because of problems related to the absolute BE scale [22]. Numerous reference level have been used in the literature: O 1s, Ti 2p, C 1s (adventitious), Au 4f and the Fermi edge. The given absolute BE scale can be doubtful when exclusively the V 2p core level region is presented and the nearby O 1s region not. Generally, a good comparison between XPS results of various studies can be

achieved when several BE references are given, e.g. by providing additionally the BE spacing between the O 1s and V 2p core levels [22].

Table 1: V 2p_{3/2} BE references for various V oxidation states.

Oxidation State	BE range (eV)	Ref.
0 (metallic V)	512.0–513.0	[25], [35], [39], [40], [42]
+2	512.7–513.8	[25], [35], [39]–[42]
+3	514.9–515.9	[20], [23], [25], [32], [35], [39]–[42]
+4	515.7–517.0	[23], [25], [32], [39]–[42]
+5	517.0–518.6	[25], [27], [28], [32], [39], [40], [42]

In this paper we report on a comprehensive, combined synchrotron radiation UHV-XPS, ambient pressure XPS (APXPS), and STM study addressing the oxidation of V supported on a-TiO₂(101) at room temperature (RT). Our STM studies revealed the disintegration of V particles upon O₂ exposure and made it possible to assign some of the various V 2p core level components with certainty. In the XPS studies, we investigate the effect of O₂ pressure and V coverage on the V oxidation state both *in situ* and *ex situ*. The oxidation condition ranged from $< 1 \times 10^{-5}$ mbar O₂, as used typically in UHV studies, to O₂ pressures in the mbar range. Under UHV conditions, we found that sub-monolayer V oxidizes only to the V⁴⁺ oxidation state, whereas V multilayers can be partially oxidized to the highest oxidation state, V⁵⁺. By contrast, when analyzed in 1×10^{-5} mbar O₂, the V⁵⁺ oxidation state can be reached also for sub-monolayer V coverage. This behavior shows that the V⁴⁺/V⁵⁺ redox couple is working best when the vanadia particles are in direct contact with the a-TiO₂ support.

2. Materials and methods

2.1. STM experiments

The STM experiments were performed in a commercial two-chambered UHV system with base pressures below 1×10^{-10} mbar. The main instrument in this UHV system is an STM (Aarhus-150, SPECS). Throughout this study, all STM images were acquired at RT in constant-current mode at a bias voltage of $\sim +1.2$ eV and tunneling current ~ 0.1 nA. In the preparation chamber, the samples were cleaned via cycles of sputtering and annealing. V evaporation and O₂ dosing were also accomplished in the preparation chamber.

2.2. XPS experiments

The XPS experiments were carried out at two different beamlines at ASTRID2 and MAX II, respectively. The *ex situ* XPS data were collected at the AU MatLine beamline at the ASTRID2 synchrotron at the Institute for Storage Ring Facilities (ISA) at Aarhus University [43]. This beamline is equipped with an SX-700 monochromator and a SCIENTA SES200 electron energy analyzer, which was operated at a pass energy of 75 eV and a curved analyzer slit of 0.8 mm. The beamline monochromator exit slit was set to a width of 60 μm . The base pressure in the end-station was $\sim 5 \times 10^{-10}$ mbar. The O 1s and V 2p core levels were collected with a photon energy of 610 eV, i.e. the escape depth of the photo electrons is estimated to be only ~ 5 Å [44]. Accordingly, these XPS measurements are very surface sensitive.

The *in situ* ambient pressure X-ray photoelectron spectroscopy (APXPS) experiments were carried out at the SPECIES beamline at the MAX II storage ring of the MAX IV Laboratory in Lund (Sweden), where the end-station consists of an analysis chamber and a preparation chamber [45], [46]. In both chambers the base pressure was in the low 10^{-10} mbar range. A SPECS Phoibos 150-NAP electron energy analyzer was used to collect the APXPS data. All APXP spectra were recorded with a beamline monochromator exit slit of 50 μm , an analyzer pass energy of 50 eV, and an analyzer

slit width of 0.8 mm. The O 1s and V 2p core level spectra were acquired with a photon energy of 700 eV. The BE scale was carefully calibrated using the O 1s core level obtained on clean a-TiO₂(101), which was centered at ~530.7 eV in both beamlines when referencing to the Fermi level of a gold foil that was in good electrical contact with the sample. All XPS measurements at MAX II and at ASTRID2 were acquired with the sample at RT.

2.3. Sample preparations

Natural a-TiO₂(101) single crystals (SurfaceNet) were prepared by Ar⁺ sputtering (1.5 kV, 15 min, RT) and annealing in O₂ (1×10^{-8} mbar, 20 min) at 820–950 K and subsequent sputtering followed by vacuum-annealing, likewise at 820–950 K. Several such preparation cycles (with and without O₂) were conducted until the surfaces were found clean (judged by STM and XPS) and characterized by large terraces. In total, five a-TiO₂(101) single crystals were used for the STM and XPS studies.

V was evaporated onto the a-TiO₂(101) surfaces at RT by means of an e-beam evaporator (SPECS). A rod of V metal with $d = 2$ mm from Goodfellow was used (99.8% V). The V coverage is given in ML, with 1 ML defined as one V atom per Ti surface atom in the a-TiO₂(101) surface, i.e. two V atoms per surface unit cell or, equivalently, 9.7×10^{-14} V atoms / cm². Using STM measurements, the flux was calibrated by varying the deposition time and found to be ~ 0.2 ML min⁻¹. During XPS measurements at the beamlines, the V coverage was estimated using the ratio between the attenuating O 1s and growing V 2p peak areas [47]–[49].

3. Results

3.1. Scanning Tunneling Microscopy

First we studied the growth of V on a-TiO₂(101) by STM. For an overview, Fig. 1 shows a series of STM images of V / a-TiO₂(101) for V coverages of 0.1 ML, 0.2 ML, 0.4 ML, and 0.8 ML, respectively. It can be seen in Fig. 1a–c that embedded single V atoms (“V_{sub}”, dashed white circles), single-layered and bi-layered V clusters (marked by squares and pentagons, respectively) co-exist, as previously reported [34]. Interestingly, we observed the V_{sub} species within a wide coverage range. At the highest V coverage (Fig. 1d) single- and bi-layered V clusters are predominant. For high V coverages (Fig. 1c, d) it was difficult to resolve the surface lattice and to unambiguously assign features associated with V_{sub}.

Regarding the homogeneously-sized V clusters seen in Fig. 1, note that they appeared at all coverages and that their density scales with the coverage. This indicates that the morphology of the V clusters did not change significantly with increasing V coverage (if at all). The formation of two-layer thick V clusters even at low V coverage is indication for a competing growth mechanism determined by the high oxygen affinity of V and strong V–V bonds [26].

In order to obtain structural information on oxidized V species we also studied the oxidation of V / a-TiO₂(101) with O₂, see Fig. 2. To do so, we scanned continuously the same surface area at RT while dosing O₂ at pressures between 5×10^{-9} and 1×10^{-7} mbar. When exposing the V / a-TiO₂(101) surface to O₂ at RT, it can be excluded that bulk impurities diffuse out of a-TiO₂ toward the surface. As shown in Fig. S1 in the supplementary information, such phenomena only occur upon O₂ exposure at elevated temperatures.

Fig. 2a shows the selected surface area before we let in O₂ into the chamber. This STM image was obtained following the deposition of 0.2 ML V onto a-TiO₂(101). Large bright features (black arrows) and numerous small bright features (dashed white circles) appeared. The large bright features originate from V clusters, and the small bright

features from V_{sub} species (embedded V) [34]. The V_{sub} species are better resolved in the zoom-in STM image depicted in Fig. 2c.

Fig. 2b shows the surface morphology after oxidation for approximately 30 min. The most distinct change is an increase in the V cluster density *on* the surface, which increased three-fold. Specifically, numerous small particles appeared, with an apparent diameter of 4 to 6 Å and an apparent height of ~ 1.3 Å. At the same time, most of the larger V clusters observed before O_2 exposure disappeared. Accordingly, we ascribe the appearance of the small particles to V oxidation induced re-dispersion, transforming V / a-TiO₂(101) into VO_x / a-TiO₂(101). To guide the eye, a few particles that have re-dispersed upon oxidation are marked in Figs. 2a and 2b by black arrows. It should also be noted that the point-like features associated with V_{sub} disappeared after the oxidation.

To gather further details on the oxidation of V / a-TiO₂(101) we carefully analyzed time-lapsed zoom-in STM images (Fig. 2c–f). The first zoom-in STM image is representative of the V / a-TiO₂(101) surface imaged in UHV (no O_2 exposure). In this case, we did not observe disintegration, agglomeration or diffusion of the clusters. In contrast, in the presence of 1×10^{-8} mbar O_2 (Fig. 2d–e) we observed the disintegration of particles.

Upon O_2 exposure, the V_{sub} species were either covered by diffusive VO_x particles (dashed squares) or underwent an oxygen-induced migration to the surface. In the last zoom-in STM image (Fig. 2f) that was recorded at 1×10^{-7} mbar O_2 , we observed only a few remaining embedded V features. Comparing Fig. 2e and 2f, it can be recognized that VO_x particles reside at the same sites that were (originally) occupied by V_{sub} species.

3.2. Ex situ X-ray photoelectron spectroscopy (XPS)

To gather information on the electronic structure, we examined V / a-TiO₂(101) surfaces by synchrotron-based XPS at ASTRID 2. Before studying their oxidation with

O₂, we first studied the V oxidation state directly after V deposition onto a-TiO₂(101) for various coverages (see Fig. 3). The XP V 2p_{3/2} spectra recorded following five separate preparations are presented in Fig. 3a. The spectra and their deconvolutions are offset from each other, with the spectrum corresponding to the smallest V coverage at the bottom (0.17 ML). At this low V coverage the dominant V 2p_{3/2} core level appeared as a broad feature, consisting of at least two components that are located at ~516.0 eV and ~513.5 eV BE's, respectively. These V 2p_{3/2} BE values correspond to V oxidation states +4 (515.7-517.0 eV) and +2 (512.7–513.8 eV), respectively (see Table 1). It can be seen that the V⁴⁺ component at ~516.0 eV is dominant exclusively at the lowest V coverage, and that the V²⁺ component at ~513.5 eV increases steadily for increasing V coverage. For the V / a-TiO₂(101) surface with the highest V coverage (~1.95 ML) shown at the top we additionally found V⁰, that is metallic V. In Fig. 3b, the compositions of the V 2p_{3/2} core level as function of the V coverage (found by fitting) are shown as bar graphs. From Fig. 3 it is clear that the higher the V coverage, the lower the V oxidation state.

We now turn to our *ex situ* post-oxidation XPS experiments performed at ASTRID 2. Fig. 4a shows O 1s and V 2p core level spectra recorded after three preparations. The spectrum of the clean a-TiO₂(101) surface is shown at the bottom. Following V deposition at RT (0.3 ML) we obtained the spectrum in the middle, and the uppermost spectrum was acquired after subsequent O₂ exposure at 1.0 × 10⁻⁷ mbar (20 L O₂). Regarding the O 1s core level, we found that two components are needed for a satisfying fit, in agreement with previous work [50] [51]. The main component of the O 1s core at ~530.7 eV originates from threefold-coordinated lattice O, and the second, much smaller component at higher BE (~532.7 eV) from surface O species [50]. Following V deposition, we found the two spin-orbit-split V 2p core levels at BE's ~20 eV lower than that of the O 1s core level. Similarly as in Fig. 3, the V 2p_{3/2} core level appeared at this V coverage as a broad feature, consisting of V⁴⁺ and V²⁺ components located at ~516.0 eV (V⁴⁺) and ~513.5 eV (V²⁺) BE's, respectively. Following oxidation of

V / a-TiO₂(101) at RT (1.0×10^{-7} mbar O₂, 20 L), the shape of the V 2p_{3/2} core level changed such that the V⁴⁺ component at high BE, which is the minor component directly after deposition, became dominant (see inset of Fig. 4a). That is, overall the V 2p_{3/2} core level shifted to higher BE, as expected when an oxidation reaction occurs. For V / a-TiO₂(101) with V = 0.3 ML, the ratio between the integrated areas of the two components is found to be V²⁺/ V⁴⁺ $\sim 3 / 2$. In contrast, for VO_x / a-TiO₂(101) we found V²⁺/ V⁴⁺ $\sim 1 / 4$. This is a clear indication that the expected oxidation reaction indeed occurred, even though the V⁴⁺ oxidation state is not reached completely. Note that the integrated area of the V 2p_{3/2} core level is identical to that obtained for V / a-TiO₂(101). This indicates that there is no loss of V upon oxidation. Concomitant with the changes in the V 2p_{3/2} region, we observed a small increase of the O 1s peak area, which further underlines that oxygen was added to the system.

Fig. 4b shows Ti 2p core level spectra corresponding to the spectra presented in Fig. 4a. For V / a-TiO₂(101), a shoulder at low BE is seen that is not present in the Ti 2p core level spectrum of clean a-TiO₂(101). The appearance of this shoulder reveals the formation of Ti³⁺ species. We propose that Ti³⁺ formation is caused by charge transfer from V to TiO₂, which is consistent with the oxidation of V that is in contact with a-TiO₂(101). From additional experiments (see Fig. S2) we learnt that the Ti³⁺ component continues to increase as more V is deposited, whereas the overall Ti 2p integrated area attenuates. Following the oxidation of the V / a-TiO₂(101) surface (third spectrum in Fig. 4b), the Ti 2p core level reverted to reflect almost completely Ti⁴⁺, consistent with VO_x / a-TiO₂(101) formation.

In an attempt to prepare VO_x / a-TiO₂(101) surfaces with V in a higher oxidation state, we exposed a similarly prepared V / a-TiO₂(101) sample to O₂ in the mbar range (Fig. 5). This was achieved by transferring the sample to a small load-lock chamber, followed by O₂ exposure at 8 mbar for 10 min. After the exposure, the load-lock chamber was pumped out and the sample transferred back to the analysis chamber. In Fig. 5a, O 1s and V 2p core level spectra are compared for a V / a-TiO₂(101) surface (~ 0.3 ML V) and

the VO_x / $\alpha\text{-TiO}_2(101)$ surface obtained after oxidation. For the V / $\alpha\text{-TiO}_2(101)$ surface we found a 50-to-50 mixed oxide between V^{2+} and V^{4+} , as described above. After the oxidation in the load-lock, the V oxidation state turned completely into V^{4+} . However, V was not detected in the highest oxidation state, V^{5+} , even after this large exposure.

In addition to the experiments with V coverages below one ML we conducted post-oxidation experiments for ~ 2 ML V coverage (Fig. 5b). The bottom spectrum shows the O 1s and V 2p core levels acquired directly after V deposition. Inspection of the V $2p_{3/2}$ core level reveals that V is predominantly metallic (BE ~ 512.7 eV), but our deconvolution analysis additionally reveals the presence of a mixed oxide states, namely V^{2+} (37%) and V^{4+} (16%), respectively (see inset of Fig. 5b). Following oxidation steps at 4×10^{-6} mbar (middle curve) and 1×10^{-5} mbar O_2 (top curve), respectively, the V $2p_{3/2}$ core level clearly shifted to higher BE. Now curve fitting shows the absence of a metallic component and that a new component in the range of V^{5+} (see Table 1) has emerged at ~ 517.4 eV. In both spectra acquired after the oxidation, the three components (oxidation states 2+, 4+, and 5+, respectively) account for $\sim 24\%$, $\sim 56\%$, and $\sim 20\%$ of the total integrated area. Thus, we achieved the wanted V^{5+} oxidation state by O_2 exposure at 4×10^{-6} mbar when the V coverage was ~ 2 ML. However, a complete oxidation to the V^{5+} oxidation state was not achieved in these *ex situ* experiments.

3.3. *In situ* ambient pressure X-ray photoelectron spectroscopy (APXPS)

To further elaborate on the oxidation of V / $\alpha\text{-TiO}_2(101)$ at higher O_2 pressures and, eventually, to reach more complete oxidation to V^{5+} , we conducted *in situ* post-oxidation experiments at the SPECIES APXPS-setup at Max II. Fig. 6 shows a series of APXP spectra collected at different O_2 pressures. Again, we started with a V / $\alpha\text{-TiO}_2(101)$ sample with ~ 0.33 ML V, and we observed a mix of V^{2+} (25%) and V^{4+} (75%) oxidation states. At 1×10^{-5} mbar O_2 pressure, the V^{2+} component disappeared and the V $2p_{3/2}$ core level shifted towards higher BE with the main component at ~ 517.5 eV BE

(75%), corresponding to V^{5+} . A shoulder at ~ 516.4 eV BE (25%) was still present at this O_2 pressure that originates from V^{4+} . Upon further increase of the O_2 pressure to 1×10^{-1} mbar, the main component (V^{5+}) was found slightly shifted to ~ 517.7 eV, and the V^{5+} integrated area increased at the expense of the V^{4+} component ($V^{5+} / V^{4+} = 86\% / 14\%$). Interestingly, after evacuation of the chamber, until a residual gas pressure of $\sim 1 \times 10^{-7}$ mbar was reached, we observed a slight V reduction. Specifically, the V^{4+} component increased from 14 % to 20% and the V^{5+} component decreased from 86 % to 80%. A control experiment wherein V / a-TiO₂(101) was fully oxidized by means of an oxygen cracker (see Fig. S3) confirmed that BE's of 517.5 to 517.7 eV of the V 2p_{3/2} core level indeed correspond to the V^{5+} oxidation state. The results of all oxidation experiments are summarized In Table S1.

4. Discussion

Firstly, we discuss the growth mode of V on a-TiO₂(101). From our STM work we know that facile embedding of V atoms occurs at the initial deposition, whereas single- and bi-layered V clusters nucleate on the surface at little higher coverages, likewise in the sub-monolayer range (Fig. 1). The bi-layered V clusters are energetically quite favorable, because they seem not to result from the agglomeration of single-layered particles. The observed growth of two-layer thick V clusters at low V coverage rather than the formation of a V wetting layer is in good agreement with previous studies addressing V / r-TiO₂(110) [35], [52]. Regarding XPS results on this matter, we reported recently that the V^{2+} oxidation state arises upon initial V deposition onto a-TiO₂(101) from clusters and atoms on the surface, whereas embedded V atoms corresponds to the V^{4+} state [16]. This assignment is supported by the STM and XPS series of increasing V coverage presented here (Figs. 1 and 3), because V clusters become predominant at higher coverage, whereas embedded V atoms are predominant at very low coverage. Furthermore, with increasing V coverage, the V^{4+} component diminished relatively to

the V^{2+} component (Fig. 3). Note, however, that the integrated area of the V^{4+} component initially continues to increase with increasing V coverage. Thus, V still has access to the a-TiO₂(101) surface even at relatively high V coverage. These XPS results are consistent with the formation of 3D clusters and, thus, point against a complete wetting of the a-TiO₂(101) surface.

We now discuss the STM results summarized in Fig. 2, where the disintegration of V particles is seen upon O₂ exposure onto V / a-TiO₂(101). This observation can be explained by the adsorption and dissociation of O₂ molecules on V clusters, because this leads to the formation of V–O bonds and weakening of the V–V bonds. This interpretation is consistent with the fact that the V–O bond is significantly stronger than the V–V bond, ~400 kJ / mol vs. ~269 kJ / mol [26]. Accordingly, it can be envisaged that VO_x species are formed upon O₂ exposure that subsequently separate from the (original) V cluster. The geometric structure of the formed VO_x species cannot be gathered from the STM images depicted in Fig. 2. However, we deduce from the STM images that the newly created VO_x species are, most likely, monomeric.

Turning to our *ex situ* XPS results addressing post-oxidation of V / a-TiO₂(101) (see Figs. 4 and 5), we distinguish between sub-monolayer and multilayer range. In Fig. 7, we present a summary of the identified V oxidation states obtained within numerous single XPS measurements (note that the single data points are not necessarily measured in consecutive experiments, even though they are connected by dotted lines). We plot the relative contributions to the V 2p_{3/2} core level ($V^0 + V^{2+} + V^{4+} + V^{5+} = 1$) as function of the O₂ pressure. The latter is justified because the O₂ pressure influences the V oxidation state more than the O₂ exposure. This can be seen from Fig. 5b where the second O₂ exposure at nearly identical pressure did not lead to clear changes in the V 2p_{3/2} core level.

Directly after V deposition (no O₂ exposure), we found mixed oxidation states, with the V^{4+} contributions as the highest oxidation state (see left side of Fig. 7). For ~0.3 ML V

coverage, the V^{4+} contribution is dominating, whereas metallic V is predominant for V coverages in the multilayer range. In this latter case, V is oxidized to a much smaller extent, simply because a lower number of V atoms are in direct contact with the a-TiO₂(101) surface. Following post-oxidation of V / a-TiO₂(101) at RT we found a large V^{4+} component regardless of the V coverage.

In the sub-monolayer range (in Fig. 7, see the symbols filled with grey color), we can compare the *ex situ* XPS data with our STM data (see Fig. 2). On this basis, we can rule out that the increase in the V^{4+} component formed upon oxidation is caused by an increase in embedded V atoms, because they are absent in the STM images (Figs. 2b, f). Thus, the V^{4+} component found for VO_x / a-TiO₂(101) has a different origin than the V^{4+} component observed directly after V deposition. Accordingly, we conclude that the strong V^{4+} component obtained after post-oxidation arises from the newly formed, monomeric VO_x species that are seen in the STM images depicted in Figs. 2b,f. Because only VO and VO₂ are monomeric among the vanadium oxides (V₂O₃ and V₂O₅ are dimeric), VO₂ configurations are most probable. VO₂ configurations as predominant species on VO_x / a-TiO₂(101) in the sub-monolayer case are also consistent with the absence of a V^{5+} component in the V 2p_{3/2} core level spectra.

Considering the post-oxidation of V / a-TiO₂(101) with V coverages in the multilayer range, Figs. 5b and 7 show that the V^{4+} component is largest likewise in this case (in Fig. 7, see the symbols filled with blue color). However, now there are also V^{5+} and V^{2+} contributions. Given that there is absolutely no V^{5+} contribution in V 2p_{3/2} core level spectra for V coverages in the sub-monolayer range, we conclude that the V^{5+} component in the multilayer case arises from oxidized V species in the (original) “2nd” V layer that are further away from the a-TiO₂(101) substrate. The fact that a V^{2+} component persisted in the post-oxidation experiments with O₂ pressures up to 1×10^{-5} mbar might be related to the larger size of the V particles in case of V coverages in the multilayer range. Even though V particles disintegrate upon oxidation, it is possible that not all V atoms are accessible to O₂. Additionally, it can be envisaged that VO_x species

formed upon oxidation are again reduced in UHV when the O₂ gas was pumped away. In any case, the *ex situ* XPS data summarized in Figs. 4, 5 and 7 underline that V species at the interface are more difficult to oxidize to V⁵⁺ than V species that are further away from the a-TiO₂(101) substrate.

In Fig. 8, we have summarized the results of the *in situ* APXPS experiments conducted at MAX II. In addition to the data presented in Fig. 6 (V coverage ~0.33 ML, see the series of bar graphs at the bottom), Fig. 8 includes the results of a similar *in situ* oxidation experiment (data not shown) where the initial V coverage was ~0.11 ML (upper series of bar graphs). The overall trends are similar for the two V / a-TiO₂(101) surfaces studied in the APXPS experiments. A mix of V⁴⁺ and V⁵⁺ contributions resulted in both experimental series, with V⁵⁺ being clearly dominant. Note that no V²⁺ component persisted in an O₂ background. At the end of each experimental series the V⁴⁺ component increased again after the evacuation of the chamber (right column). Thus, the VO_x / a-TiO₂(101) system reduces alone due to reestablishing of the vacuum, indicating that the created vanadia species in the sub-monolayer regime are highly reducible.

A closer look reveals interesting differences in the two experimental series compared in Fig. 8. Specifically, it is striking that the V⁴⁺ component is larger throughout the series of experiments corresponding to ~0.11 ML V than in the series belonging to ~0.33 ML V. We attribute this difference to the presence of the a-TiO₂(101) surface. Specifically, isolated VO₂ species are predominant at low V coverage because we started with numerous isolated, monomeric V centers. Thus, when starting from V / a-TiO₂(101) with a low V coverage it is difficult to create dimeric V₂O₅ species, corresponding to V⁵⁺ oxidation state. Furthermore, comparing the two experimental series also reveals that the a-TiO₂(101) support facilitates the reduction of VO_x / a-TiO₂(101) upon evacuation of the chamber. This is evident from the clearly larger V⁴⁺ component found for ~0.11 ML V.

On the basis of the APXPS results (Figs. 6 and 8), we propose that the V^{5+} oxidation state was also reached during the O_2 exposure in the *ex situ* experiments, but, upon re-establishing the vacuum, such vanadia species reduced back to species corresponding to V^{4+} . Thus, for obtaining and maintaining the V^{5+} oxidation state, that is crucial for high catalytic activity in SCR catalysis [4], [5], [8], [9], we believe that ambient pressure conditions are essential.

The presented XPS, APXPS and STM data offer a simple explanation for the observed optimum V_2O_5 loading in SCR catalysis just slightly below a full ML [4], [8]–[10]. Very low coverages are detrimental for SCR catalysis, because the TiO_2 support hampers reaching the essential V^{5+} oxidation state. When the coverage is close to a full ML, dimeric V_2O_5 structure in the catalytically active V^{5+} oxidation state can be formed, and high catalytic activity is possible. These species in V^{5+} oxidation state are easily reducible due to their direct contact with the α - TiO_2 support and associated charge transfer. When, however, the V loading is higher than one ML, the enhanced reducibility of the V_2O_5 structures due to the TiO_2 support is not given any longer. Because the reduction of V^{5+} to V^{4+} is very crucial – it is believed to be the rate determining step in the SCR reaction at high temperature [6] – the SCR catalytic activity is reduced for V loadings that are higher than one ML. Even though the reduction reaction in SCR catalysis is associated with H transfers from NH_3 molecules, the important role of the oxide support, particularly its electronic properties, that make this reduction possible, is very clear from our combined experimental study.

5. Conclusions

In summary, we have shown by *ex situ* XPS measurements that oxidation of V / α - $TiO_2(101)$ by O_2 at RT leads to the gradual formation of vanadium species in oxidation state +4 at the expense of initially formed V^{2+} species. This conversion from V^{2+} to V^{4+} depends essentially on the O_2 pressure. For coverages in the sub-monolayer range, a

complete conversion to V^{4+} was achieved at 1×10^{-5} mbar O_2 . Accompanying *in situ* STM studies showed that the oxidation proceeds through oxygen-induced disintegration of metallic V clusters into monomeric VO_2 species. In the *ex situ* XPS experiments, complete oxidation to the highest oxidation state (V^{5+}) was not achieved at sub-monolayer V coverage. We ascribe this finding to a high reducibility of VO_x species that are directly attached to the a- $TiO_2(101)$ surface, indicating a change of the redox properties caused by the a- TiO_2 surface. However, the wanted V^{5+} oxidation state could be reached for V coverage higher than one monolayer at $\sim 4 \times 10^{-6}$ mbar O_2 . Only a partial oxidation to V^{5+} could be achieved, probably because only V atoms that are screened from the a- TiO_2 surface can be fully oxidize to V^{5+} in vacuum. Our APXPS studies revealed that V in the sub-monolayer range can only maintain the V^{5+} oxidation state if the O_2 pressure is 1×10^{-5} mbar or higher. This result cannot be achieved by *ex situ* XPS measurements. We thus can conclude that *in situ* APXPS studies are essential to further our understanding of SCR catalysis over V_2O_5 / a- TiO_2 .

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://.....>

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Fig. 1. Series of STM images ($24 \times 24 \text{ nm}^2$) for increasing V coverage on anatase $\text{TiO}_2(101)$. Examples of embedded V (dashed white circle), single-layered and bi-layered V clusters (squares and pentagons, respectively) are marked. V coverages: a) 0.1 ML, b) 0.2 ML, c) 0.4 ML, d) 0.8 ML.

Fig. 2. Oxidation of V / a-TiO₂(101) at RT studied by *in situ* STM. a) Metallic V (0.2 ML) deposited in UHV ($24 \times 24 \text{ nm}^2$). b) Same area as a) following ~ 30 min in O₂ background (up to 1×10^{-7} mbar). Black arrows indicate examples of V particles that undergo disintegration. c–f) *Time-lapsed* STM images ($12 \times 12 \text{ nm}^2$) recorded *in situ* during oxidation in up to 1×10^{-7} mbar O₂. Time interval between STM images ~ 60 s.

Fig. 3. a) $V 2p_{3/2}$ core levels ($h\nu = 610$ eV) recorded on five different $V / a\text{-TiO}_2(101)$ samples with different V coverage. b) XPS peak fit analysis, showing the relative distributions of V oxidation states on $V / a\text{-TiO}_2(101)$, corresponding to the spectra shown in a).

Fig. 4. a) O 1s and V 2p core level spectra ($h\nu = 610$ eV) and peak fit analysis for clean α -TiO₂(101), V / α -TiO₂(101) (0.3 ML V in UHV at RT) and VO_x / α -TiO₂(101) prepared by O₂ exposure at 1×10^{-7} mbar at RT (~ 20 L O₂). b) Corresponding Ti 2p spectra ($h\nu = 530$ eV).

Fig. 5. O 1s and V 2p core level spectra ($h\nu = 610$ eV). a) V deposition (0.28 ML) on a-TiO₂ (101) in UHV at RT and subsequent O₂ exposure at 8 mbar O₂. b) V deposition (2 ML) on a-TiO₂(101) and subsequent O₂ exposures at 4×10^{-6} mbar O₂ and 1×10^{-5} mbar O₂, respectively, again at RT.

Fig. 6. Ambient-pressure *in situ* XPS measurements at RT: O 1s and V 2p core level spectra ($h\nu = 700$ eV) plus their deconvolution. The spectra were recorded within one experimental series starting from the bottom curve (0.33 ML V deposition), followed by O_2 backgrounds at 10^{-5} mbar, 10^{-1} mbar, and 10^{-7} mbar (evacuation of the chamber), respectively.

Fig. 7. Summary of all XPS peak fit analyses of the *ex situ* oxidation experiments (MatLine). The relative distributions of V oxidation states are given for V / a-TiO₂(101) and VO_x / a-TiO₂(101) as function of the O₂ pressure. We distinguish between sub-monolayer (grey) and multilayer range (blue).

Fig. 8. APXPS peak fit analysis of two oxidation series corresponding to 0.11 V ML (upper panel) and 0.33 ML (lower panel), respectively. Relative distributions of V oxidation states following V deposition for two V coverages (left column), and how these distributions change upon *in situ* oxidation (the two columns in the middle), as well as after evacuation of the chamber (right column). O₂ pressures are given beneath of each bar graph.

Highlights

- The oxidation of anatase $\text{TiO}_2(101)$ -supported vanadium (V) by O_2 is studied in a pressure range between UHV and 8 mbar at room temperature.
- Multilayer V coverages can be partly oxidized to V^{5+} in UHV but sub-monolayer V not.
- For V in the sub-monolayer range the V^{5+} oxidation state can be maintained if the O_2 pressure is 1×10^{-5} mbar or higher.
- The oxidation of metallic V clusters proceeds through oxygen-induced disintegration into monomeric VO_2 species.
- There is an enhanced reducibility of vanadia species that are in direct contact with the anatase TiO_2 support, which is in line with the observed optimum V_2O_5 loading in catalysis.

Graphical Abstract