# Experimental details:

STM experiments were performed with a home-build variable-temperature STM equipped with a mechanically cut Pt/Ir Tip, in a UHV chamber with a base pressure < 1×10-10 mbar.(ref or supporting)

# Results:

The Clean surface:

The anatase TiO2 (101) surface exhibits a saw tooth like structure with ridges of 2-fold coordinated surface oxygen’s (2f-O, OBr) running along the [010]-direction with five fold coordinated titanium sites (5f-Ti) between these OBr rows. (Ref)

Vanadia covered surface (fig. 1a / 1d):

Upon vanadia deposition (details found in supporting information) bright features are present on the a-TiO2 surface, these are assigned to clusters of V2O5 (seen in figure 1A). Majority of the bright features are oval-shaped (assigned type A) and extending across an OBr rows, along the [010]-direction (indicate on figure). A second feature bright feature was found (assigned type B), which consist of an elongated feature along the [010]-direction and an additional feature across the neighboring OBr rows, other irregular features are ascribed to reduced vanadia species (V4+).

The corresponding XP-spectrum is shown in figure 1D, here showing the O1s- and V2p-regions, the insert shows the V2p3/2 region with a two component fit being the V5+- and V4+- state in orange and grey respectively. The fitted XP-spectrum reveals the 70% of the deposited vanadia exists in the V5+- state.

In-situ STM (fig 1a-c)

Figure 1 A-C, shows the vanadia covered surface before (fig.1A), after (fig.1B) and during (fig.1C) water exposure. Before water exposure type A (described previously) is the most commonly feature, after water exposure the most common feature is type B. *In situ* experiments, scanning while exposing to water (5×10-7 mbar), figure 1C, revels a third feature (assigned type C). The type C structure consists of two larger features running along the [010] – direction and two smaller features also running along the [010] – direction, however positioned across the neighboring OBr rows.

In-situ XPS (fig. 1 e-f)

Corresponding XP-spectra, of the O1s region, to the STM-images shown in fig. A-C, is seen in figure 1E. Here O1s XP-spectra of before (grey), after (green) and during (blue) water exposure is shown. The insert in figure 1E supplies a zoom-in of the high binding energy shoulder, in this region traces of –OH groups (532 eV) and molecular water (534 eV) are found. After exposure of water (exposure in langmuir) an increase in the –OH signal is seen (green) and during water exposure we see an increase in both the –OH and molecular water signal. No change was observed on a sample without vanadia (see supporting information). In order to highlight the difference figure 1F shows the difference spectra between the before water exposure spectrum and the after/during water exposure.

In-situ movies (suppl. Movie 1 og 2)

Supplementary Movie 1 and 2 is *in situ* STM measurements where water is exposure at maximum 3×10-7 mbarand 5×10-7 mbarrespectively. Suppl. Movie 1 were recorded after vanadia deposition, here conversion from type A to type C and from type B to type C are seen. After 30 min of pump down supplementary movie 2 was started, here vanadia – clusters was most commonly found as type B. During supple. movie 2 water is re-exposed and all type B and left over unreacted type A converts into type C. In the last part of suppl. Movie 2 we measure during the pump down, (e.g. the water valve is closed) and here the back conversion from type C to type B is seen.

In-situ distributions (fig. 2)

We are able quantify the phenomena observed in suppl. movie 1 and 2, this I seen in figure 2. Here figure 2A shows the pressure during supplementary movie 1 and figure 2C the distribution between type A, B and C.

Suppl.movie 1

As time progresses in supplementary movie 1, the water pressure is stepwise increased (see fig.2A) the distributions between the vanadia types is shown in figure 2C. Here type A is shown in grey, type B in green and type C in blue, in the starting frame 69% of the vanadia species is found as type A and 30% as type B. When Water pressure is increased type C starts to appear, along with the disappearance of type A and B.

Conversion rate in suppl. movie

Through suppl. Movie 1 we observe that the number of vanadia species found as type B is declining rapidly with increasing water pressure. The rate for converting type A to C is not as rapid as the conversion from type B to C, however this conversion is seen throughout the movie. At the end of supplementary movie 1, type C is the most common vanadia species (60%), however some type A is still not converted (30%).

Suppl. movie 2

Succeeding supplementary movie 1 we pumped out water (for ~30 min.) and measured a different spot of the sample. As for movie 1 the pressure and distribution among vanadia species were measured in movie 2, this is seen in figure 2B and 2D, respectively. The starting frame in movie 2, 20% of the vanadia species were found as type A and 75% as type B. Upon water exposure (5×10-7) all type B vanadia species converts into type C and in the next few frames, all type A follows. In supplementary movie 2 we see full conversion from type A and B to type C, and after this we close the valve introducing water and start pumping out water. In the pumping tail (15min. – end) we were able to measure that back conversion from type C to type B, we observe no conversion back to type A (even after ~12 hours of pump down).

Partial experimental conclusion

Based the STM and XPS measurements, we conclude that type A consist of two vanadium in the V5+ - state, as this single feature splits up in to two features when converted into type C. Type B contain hydroxyls groups (se fig 1E and F) likely by adding a molecule onto the V2O5, type A cluster, making it 2 × VO3H. Type C contains both hydroxyls groups and molecular water (see fig. 1E and F) likely by adding a water molecule to type B, thus the molecular form: H2O + 2 × VO3H.

Zoom-ins. Figure 3

Following a single vanadia cluster through a water exposure is shown in figure 3. The three found states (before = type A, after = type B and during = type C water exposure), are shown enlarged in figure 3, here the 5f-Ti sites are indicated by grey circles and white lines guides the eye to rows they form on the surface, between the white 5f-Ti lines the OBr rows are found. Figure 3A shows type A, that consist of a single oval-shaped feature, extends across a OBr row and have an apparent height of 5.2 Å (supplementary figure 1). It is centered between three 5f-Ti sites, which form a “left pointing” triangle.

Type B

Figure 3B, shown the enlarged type B cluster, this cluster consist of a two main features: one smaller and bright feature (with an apparent height of 4 Å) that a centered between three 5f-Ti sits that form a “right” pointing triangle. The second feature is position to the right of the first, across the 5f-Ti row. This feature is extended between two “right” pointing triangle sites with a width of 2 × Ti-Ti distances and has an apparent height of 3.2Å.

Type C

Figure 3C, shows an enlarged type C cluster, is consists of a double feature (dumbbell – shaped) positioned slightly of center of a 5f-Ti site, it resembles previous reported molecular water features (Ref) and has an apparent height of 1.8 Å. Two larger features are found the right of the first feature; these features are again found between three 5f-ti sites, which form a “right pointing triangle. The two larger features found in figure 3C are separated by a “right” pointing triangle site making its total length 3 × Ti-Ti distances with an apparent height of 2 Å.

Partly concluding 2 vanadium atoms

Since we track them same vanadia cluster trough a single water exposure we conclude that water is the only addition to the starting cluster. Starting with a type A cluster is converted into type C during water exposure (also seen in supplementary movie 1) we observe a split of the single oval features into 2 separate features (the larger features of type C). On this basis we conclude, type A, B and C consists two vanadium atoms.

DFT bridge

In order to reveal the structure of the experimental found structure we have preform a number of DFT based calculations.

DFT. Figure 4

All DFT structures presented has been found through an automated global minimum search (see supporting information). A 6×2×1 cell has been used for final calculation and the slab includes two oxygen vacancies to describe the experimentally reduced TiO2 – crystal. (see supporting information for further details)

We have considered several combinations of water, vanadium and oxygen (see supporting information), but here is presented three compositions consistent with the experimental findings.

Description of structures:

The three compositions are: V2O5, V2O5 + H2O, V2O5 + 2 × H2O, the lowest energy structures are shown in figure 4 A,B and C. Figure 4A shows the lowest energy structure for a V2O5 – cluster (side- and top view, it forms a dimer – like structure, which extends across a OBr row. The left part of the V2O5 – cluster is protruding far in to the vacuum, also being the most protruding of all found structures (compared to side view in figure 4 B and C).

The addition of a water molecule to the V2O5 – cluster (V2O5 + H2O) leads to the structure seen in Figure 4B. This cluster consists of two VO3H particles, which are sitting on different 5f-Ti rows. The addition of a water molecule thus cause both the splitting of the V2O5 - dimer and dissociation of the water molecule. Maybe more

The addition of a second water molecule does leads to a restructuring of the cluster and adsorption of a molecular water. Figure 4C shows the lowest energy configuration, which includes two VO3H particles, similar to the one water molecule structure, however the two VO3H particles are positioned on the same 5f-Ti row and the additional water molecule is adsorbed on the neighboring row to the left. The addition of the second water molecule then drives one VO3H-particle to the neighboring row upon adsorption.

# figure 4D, will write this later, NEB calculation, barrier estimated to 1.5 eV

Assignment of DFT structures:

We propose the correlation between the structures found through DFT (figure4 A,B and C) and the features observed by STM (figure3 A,B and C), such that: figure 3A corresponds to the structure presented in figure 4A and following same logic for 3B corresponds to 4B and 3C corresponds to 4C.

Stating with figure 3A and 4A, the DFT resembles the oval-shape of type A and as it includes vanadium in the V5+ -state it is in agreement with the measured XPS-results.

Type B (figure 3B) does not directly resemble the structure in figure 4B, however allowing one VO3H-paritcle to diffuse between two adsorption sites it does (se figure 4D). This structure includes hydroxyls groups as well, which fit to the XPS – results presented in figure 1E and F.

Type C (figure 3C) resembles the structure presented in figure 4C as the two VO3H – particles resembles the two larger features of type C and the two smaller features resemble an adsorbed water molecule (ref). The finding that the proposed structure both includes hydroxyls groups and molecular water fits with presented XPS – results (figure 1E and F).

Energy landscape figure 4E

We have now presented three states of vanadia before, after and during water exposure together with corresponding proposed structures based on DFT. As the structures presented does not include the same number of water molecules, we compare the different structures by the energy gain. This quantity is the cluster-adsorption energy subtracted by the number of water molecules times the adsorption energy of a water molecule adsorbed far away from the cluster (see supplementary information). This value describes which structure is energetically favorable: before, after and during water exposure. The energy gain is displayed in figure 4E, where we introduce three structural motifs: dimer, cis and trans.

Structural configurations descriptions

The dimer configuration is presented in figure 4A, the cis configuration is presented in figure 4C, this configurations refers to a structure where two VO3H particles are positioned the *same* row (therefore cis). The trans configuration is presented in figure 4B, then refers to VO3H particles positioned on opposite rows (therefore trans).

Figure 4E

In the absent of water only the dimer configuration exists, this is taken as reference (an energy gain of 0 eV, see figure 4E). The addition of one molecule the cis drops significantly in energy compared to the dimer and the cluster gain even more energy by transforming into the trans configuration. Adding the second water molecule the dimer gain energy however insignificantly compared to the cis and trans configurations. Here the cis and trans configurations now swap and the cis configuration becomes the most stable configuration. Going from one to two water molecules also lowers the energy ever so slightly of the trans configuration.

Discussion and outro: