

# Atomic-scale view of hydration and redox of VO<sub>x</sub> supported on $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001)

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## Introduction

Hydration, activation (reduction) and oxidation of supported catalysts are common processes encountered during the life cycle of a catalyst. Numerous UHV model system studies with catalysts supported on single crystal substrates have provided rich information of the atomic-scale structure of catalysts in the hydrated, dehydrated and activated phases [1]. However, it is often questionable to extend experimental conclusions deduced from UHV measurements to ambient pressure reaction conditions. This so-called “pressure gap” can be narrowed if systematic comparison can be made between atomic-scale structures resulted from the UHV processes and corresponding ambient processes.

The X-ray standing wave (XSW) method has been developed to study the bonding geometry of impurities in bulk, adsorbed atoms on surfaces and at the liquid-solid interface [2]. Recently, a model-independent, element-specific direct-space imaging technique has been developed that is based on Fourier synthesis of the atom density distribution from the XSW coherent fractions and positions [3]. We used the X-ray photoemission spectroscopy (XPS) and the X-ray standing wave (XSW) imaging method to study redox induced adsorption geometry change of the vanadium cations supported on a single crystal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) surface both in the UHV and ambient conditions.

## Materials and Methods

One-half monolayer (ML) of vanadium was deposited on clean  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) at RT by molecular beam epitaxy (MBE). The oxidation and subsequent reduction of supported VO<sub>x</sub> was achieved by exposure to atomic oxygen and atomic hydrogen, respectively, while the sample was kept at room temperature. *In situ* XSW and XPS measurements were performed under UHV.

For the ambient study, a hydrated phase was produced by brief exposure of the MBE prepared samples to air. For the XSW measurements the sample was installed inside a Be-dome mini-chamber and was kept in a high vacuum during the measurements. Inside the Be-dome, the sample was mounted on a heater with a graphite filament embedded in pyrolytic boron nitride and the reduction process was carried out by annealing the sample at 450 °C under a continuous flow of 2% hydrogen balanced with 98 % He gas. Prior to the reduction treatments the hydrated samples were heated at 180 °C under flowing oxygen gas environment.

## Results and Discussion

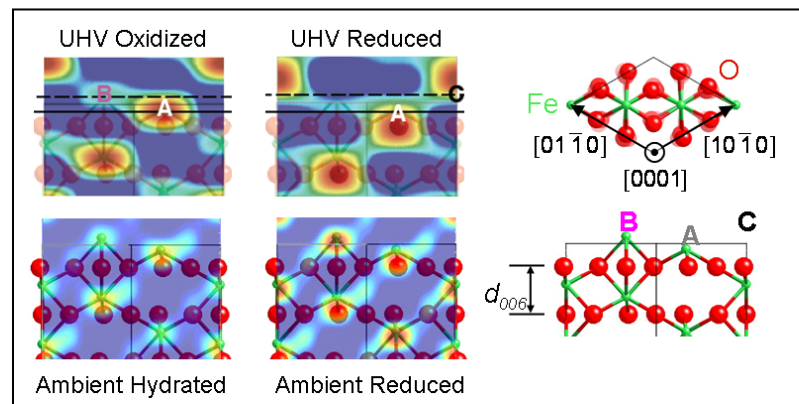
In the UHV study the as-deposited VO<sub>x</sub> phase has been characterized by V<sup>3+</sup> adsorbed in A- and C-sites (See Fig. 1). After exposure of the as-deposited phase to the atomic

oxygen the V atoms change to 5+ oxidation state and occupy A- and B-sites. Subsequent exposure of the oxidized phase to the atomic hydrogen moved the V back to A- and C-sites and changed oxidation state to 3+ [4].

The hydration of MBE prepared as-deposited sample changed oxidation state of V from 3+ to 5+. The XSW analysis indicates that in the hydrated phase V occupies A- and B-sites similar to the UHV prepared oxidized phase. The 2% hydrogen annealing reduced the vanadium cations to 3+ and V occupies A- and B-sites instead of A- and C-sites, which are observed from the UHV prepared reduced phase. These different adsorption geometries and overall height of V cation after ambient reduction process can be related to 1) the existence of hydroxyl groups on the surface and 2) the reduction method involving molecular hydrogen annealing in the current study [5].

## Significance

Comparison of atomic-scale structures of UHV processed and ambient processed phases could narrow “pressure gap” between model study and practical application.



**Figure 1.** The 2D cuts through the XSW measured 3D vanadium atomic density maps for the V/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) surface after UHV and ambient processes. As a reference projections of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ball and stick model is overlapped with the 2D cuts. The high-symmetry sites A, B, and C are indicated.

## References

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