

Surface Structures Involving Metal Vacancies

Thermodynamic Stability of Vanadium Oxide Surface Defects

X. Li, J. Paier, Institut für Chemie, Humboldt-Universität zu Berlin

In Short

- Atomic Level Details of Vanadium Oxide Surfaces
- Modelling Surface Reconstructions
- Surface Phase Diagrams
- Synergy between experimental and computational studies

Vanadium oxides are important active components of many solid oxidation catalysts applied in chemical industry [1]. Their precise surface structure, i.e. the atomic structures within their outermost layers will certainly affect surface reactivity, for instance towards the oxidative dehydrogenation of methanol to formaldehyde or of propane to propene. Hence, to understand reaction mechanisms unequivocally resolved surface structures represent an unquestionable prerequisite.

Our previous efforts, a collaboration between Prof. Freund (FHI Berlin) and Prof. Sauer (HU Berlin) focused on the vanadium(III) oxide $V_2O_3(0001)$ surface being stable under ultrahigh vacuum conditions (and higher temperatures) relevant for surface science studies on thin metal oxide films. For long time, the characteristic and intense infrared vibrational band, X-ray photoemission spectroscopy, as well as NEXAFS indicated a vanadyl, $V=O$, termination and thus, the surface was considered to be vanadyl terminated. However, density functional theory (DFT) predicts a number of reconstructed terminations, which are stable under more oxidative (O-rich) conditions [2]. As a consequence, these terminations thermodynamically compete with the $V=O$ termination.

Kresse and coworkers found a (under relevant conditions) stable reconstructed O_3 -termination [2]. This surface structure was obtained using the PW91-GGA exchange-correlation functional, and it involves every other subsurface V atom to move up into the surface cationic layer. Recent fast-atom diffraction results combined with DFT-GGA calculations were interpreted in strong support of the reconstructed O_3 -termination [3]. However, this is in stark contrast to the observed $V=O$ vibrational bands and the STM data (observed as well as simulated). Thus, our previous collaborative work between FHI and HU revisited this problem [4]. Since DFT within the

GGA approximation was invoked in other work to support the O_3 -termination, we checked whether results depend on the employed functional. Hybrid functional calculations, which use a certain amount of orbital-dependent Fock-exchange (FX), showed that the phase equilibrium between the $V=O$ and the reconstructed O_3 -termination is significantly shifted towards more positive values of the chemical potential of oxygen, meaning that the O_3 -termination is drastically destabilized relative to the $V=O$ termination.

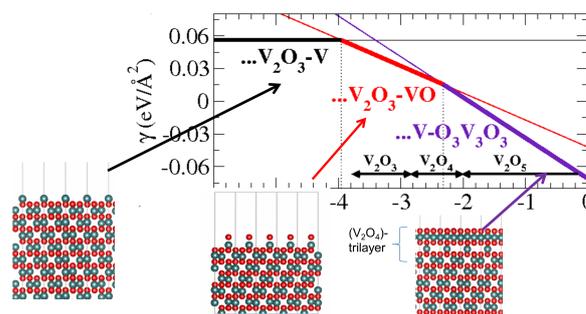


Figure 1: Structures of $V_2O_3(0001)$ terminations shown together with a phase diagram discussed in [4]. Adapted and reprinted with permission from [4]. Copyright (2015) American Physical Society.

An important question that needs to be addressed within this HLRN-project concerns stabilities of surface defects like missing vanadyl groups. Since we generated numerical evidence (consistent with observation) that hybrid functionals outperform GGA functionals, these aforementioned defect studies require the application of hybrids, which are substantially more expensive computationally compared to GGA calculations. Thus, the HLRN-III compute facilities play an important role for the success of this project. From a surface science point of view, the important point is the reconstruction, i.e. the shift of the subsurface V atom into the surface layer, because it results in a (local) V_2O_4 layer. Furthermore, the reconstruction attracts interest, because recently a similar subsurface cationic vacancy has been found for the ground state surface structure of $Fe_3O_4(001)$ by Gareth Parkinson and coworkers in Vienna [5]. Preliminary results with respect to $V_2O_3(0001)$ indicate that $V=O$ defects may trigger the O_3 -reconstruction. We firmly believe that this HLRN-project will provide the necessary insight into the problem when calculating potential defect candidate structures and comparing their stabilities by virtue of first principles thermodynamics.

The modelling of the above mentioned surfaces

will be done based on a periodic implementation of DFT and HF within the so-called projector-augmented-wave method (PAW) to describe the electron-ion interaction on a first-principles approach [6]. We will employ the Vienna *ab initio* Simulation Package (VASP) [7,8]. Shortcomings of generalized-gradient corrected exchange-correlation functionals will be addressed by the so-called HF/DFT hybrid functionals (see Ref. [9] for a recent comparative review of these methods when applied to complex solid metal oxide surfaces).

WWW

<http://www.chemie.hu-berlin.de/forschung/>

More Information

- [1] I.E. Wachs, *Dalton. Trans.* **42**, 11762 (2013). doi:10.1039/C3DT50692D
- [2] G. Kresse, S. Surnev, J. Schoiswohl, and F.P. Netzer, *Surf. Sci.* **555**, 118 (2004). doi: 10.1016/j.susc.2004.02.009
- [3] A.J. Window, A. Hentz, D.C. Sheppard, G.S. Parkinson, H. Niehus, D. Ahlbehrendt, T.C.Q. Noakes, P. Bailey, D.P. Woodruff, *Phys. Rev. Lett.* **107**, 016105 (2011). doi:10.1103/PhysRevLett.107.016105
- [4] F.E. Feiten, J. Seifert, J. Paier, H. Kühlenbeck, H. Winter, J. Sauer, H.J. Freund, *Phys. Rev. Lett.* **114**, 216101 (2015). doi:10.1103/PhysRevLett.114.216101
- [5] R. Bliem et al., *Science* **346**, 1215 (2014).
- [6] P. Blöchl, *Phys. Rev. B* **50**, 17953 (1994). doi: 10.1103/PhysRevB.50.17953
- [7] G. Kresse, J. Hafner, *Phys. Rev. B* **48**, 13115 (1993). doi:10.1103/PhysRevB.48.13115
- [8] G. Kresse, J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996). doi:10.1103/PhysRevB.54.11169
- [9] J. Paier, *Catal. Lett.* **146**, 861 (2016). doi: 10.1007/s10562-016-1735-4

Project Partners

Prof. Joachim Sauer, Prof. Hans-Joachim Freund

Funding

DFG Sonderforschungsbereich (SFB) 1109 - Understanding of Metal Oxide/Water Systems at the Molecular Scale: Structural Evolution, Interfaces, and Dissolution