Structure of the $V_2O_3(0001)$ Surface with and without Adsorbed Oxygen: DFT Cluster Model Studies

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Abstract

Vanadium oxide (III), which can be formed as a product of a deep reduction of V_2O_5, is characterrized by a rhombohedral crystal structure exposing preferentially the (0001) surface. This surface can be terminated by either O or V atoms leading to intrinsic OVV', VV'O and V'OV bulk terminations, see Fig. 1. As a result of oxygen adsorption the $V_2O_3(0001)$ surface may become enriched in its oxygen content forming surface vanadyl (VO_t) as well as bridging (VO_bV) groups and leading to $O_tV'O$ (O adsorption at V'OV) and $O_b^{(2)}VV'$ (O adsorption at VV'O) terminations, see Fig. 1. In order to study the effect of surface oxygen on structural and catalytic properties of the $V_2O_3(0001)$ surface cluster model calculations using the density-functional-theory approach are performed [1-3]. Here the different intrinsic (OVV', VV'O, V'OV) and oxygen induced ($O_tV'O$, $VO_b^{(2)}V$) terminations are described by embedded surface clusters as large as $V_{14}O_{37}H_{26}$. Layer relaxation of the surfaces is obtained from constrained geometry optimizations where the layers are considered as rigid sub-units. Further, surface binding energies based on cluster total energy differences are used to identify energetically preferred terminations.

The $V_2O_3(0001)$ surface is found to undergo strong relaxation where the topmost layers of the metal terminated surfaces relax inwards by as much as 30%. This inwards relaxation is partially relieved as a result of oxygen adsorption which influences also the electronic structure. Oxygen adsorbing above metal centers can form surface vanadyl groups VO_t as well as bridging VO_bV species where the adsorbate binds very strongly (7-8 eV per oxygen in both cases). The bridging surface species results also in lateral relaxation of the $V_2O_3(0001)$ surface forming a distorted honeycomb structure for an oxygen coverage $\Theta = 1/3$ (O_bVV' termination) and a zig-zag chain structure for $\Theta = 2/3$ (O_b^2VV' termination). The latter is consistent with recent results from STM experiments on thin $V_2O_3(0001)$ films grown on Cu_3Au [4]

References

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Figure

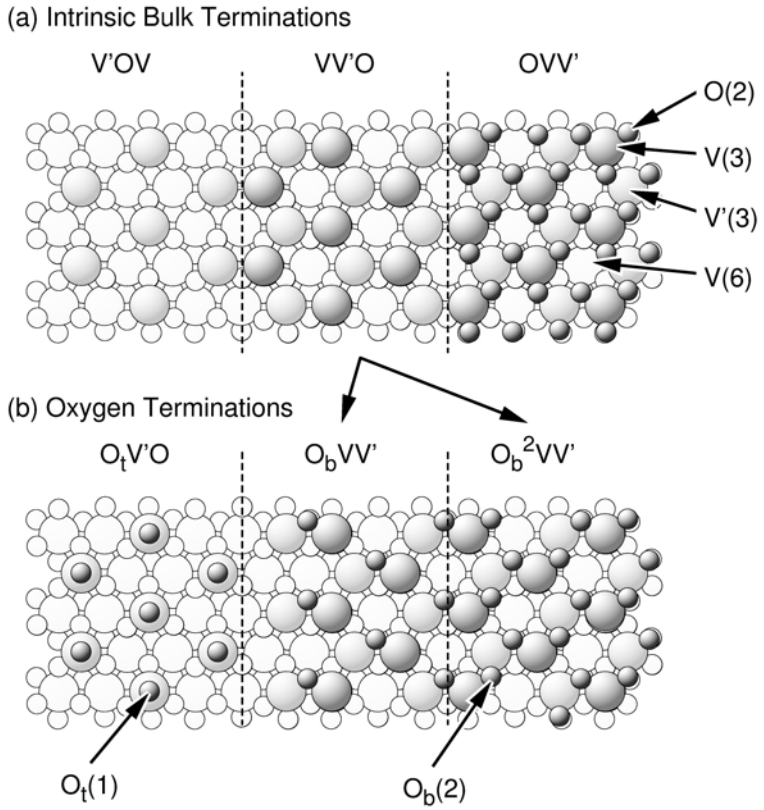

Fig. 1. Top view of the $V_2O_3(0001)$ surface for different terminations. The atom centers are shown by large (vanadium) and small (oxygen) balls and labeled accordingly where the numbers in parenthesis denote the coordination. (a) Intrinsic bulk terminations OVV', VV'O, V'OV. (b) Oxygen induced terminations, $O_tV'O$ derived from V'OV with additional vanadyl oxygen O_t, O_bVV' and O_b^2VV' derived from VV'O with additional bridging oxygen O_b.