

The effect of the supporting oxide on the activity of vanadia catalysts

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Introduction

Supported vanadium oxides (VO_x) are active in several important oxidation reactions such as the oxidative dehydrogenation of light alkanes and the oxidation of methanol to formaldehyde [1]. The strong influence of the oxide support on the reactivity is well-known, yet not understood [2-4]. Specifically, VO_x/ceria is significantly more reactive than $\text{VO}_x/\text{alumina}$. The difficulties in characterizing the surface structure of powder catalysts and in identifying the active species [5] have motivated the preparation of model catalysts such as VO_x on Al_2O_3 [6] and CeO_2 [7]. Their thorough experimental study by UHV techniques also raises questions about the assignment of spectroscopic signatures, in particular, the vibrational properties of $\text{VO}_x/\text{Al}_2\text{O}_3$ systems.

Here, we report theoretical models of $\text{VO}_x/\text{Al}_2\text{O}_3$ with a wide range of VO_x surface coverages and Al_2O_3 structures as well as of $\text{VO}_x/\text{CeO}_2(111)$ with the focus on monomeric species. Surfaces of α -, κ -, and γ - Al_2O_3 , as well as a thin alumina film on $\text{NiAl}(110)$ are considered as alumina supports. The latter corresponds to the support structure of the experimental model catalyst. We discuss the stability of the VO_x species as function of external conditions such as oxygen partial pressure, vanadia loading, and temperature. We combine this analysis with a detailed characterization of the structural, electronic and vibrational properties of these model catalysts. In doing this we are able to bridge gaps, between experimental model catalysts studied and powder catalysts used in kinetic studies at typical catalytic conditions.

To compare the catalytic activity of the different materials in oxidation reactions we calculate the energy of O defect formation (which relate to the reaction energy) and the energy of hydrogenation (which relates to the energy barrier of the rate-determining step).

Materials and Methods

The spin-polarized periodic calculations of $\text{VO}_x/\text{Al}_2\text{O}_3$ model systems are based on DFT with the PW91 functional as implemented in the VASP simulation package. Those of VO_x/CeO_2 are performed within the DFT+U framework. Statistical thermodynamics is applied in the construction of phase diagrams. The vibrational spectra are calculated using the harmonic approximation within the finite difference method.

Results and Discussion

Differently anchored VO_x species were constructed by “landing” vanadia species on the support ($\text{VO}_x/\alpha\text{-Al}_2\text{O}_3$ and $\text{VO}_x/\text{CeO}_2(111)$ in Fig. 1) or by “replacing” surface Al by V=O ($\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ in Fig. 1) [8,9]. From the $\text{VO}_x/\text{Al}_2\text{O}_3$ phase diagrams for reducing conditions (800 K, UHV), we conclude: (i) all stable species on the α -support are not reduced, and low coverage (dimeric) species possess no vanadyl oxygen atoms; (ii) all species on the thin film are also not reduced and dimeric species would rather cluster and form “taller” structures than a monolayer; (iii) polymeric species on the metastable κ - and γ -supports are partially reduced.

Furthermore, (iv) the specific alumina support structure influences the reactivity as probed using the O defect formation energy; for a given alumina phase, monovanadate species are less active than larger ones. (v) The vibrational spectra of most $\text{VO}_x/\text{alumina}$ species anchored by V–O–Al bridges show a band at $\sim 950\text{ cm}^{-1}$, which is assigned to interface modes.

For $\text{VO}_x/\text{CeO}_2(111)$ under reducing conditions we find that the most stable monomeric species on the ceria support are not reduced, but the support is. Further reduction by O defect formation (e.g., during the catalytic reaction) is particularly easy (Fig. 1) and results in an increase of the number of Ce^{3+} ions.

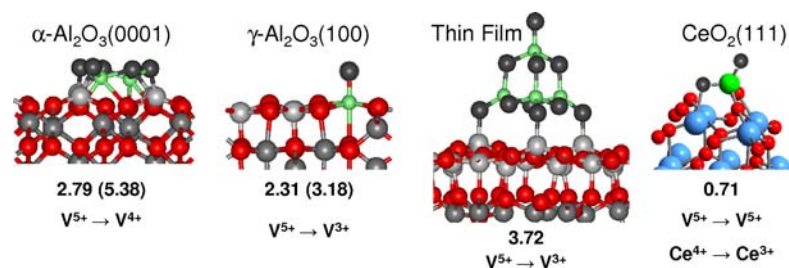


Figure 1. Examples of stable species under reducing conditions (800 K, UHV) on selected alumina supports and on ceria. Oxygen defect formation energies w.r.t. $\frac{1}{2}\text{O}_2$ in eV/atom; the numbers in parenthesis do not include lattice relaxation effects. Relevant changes in oxidation states upon reduction are indicated.

Significance

We have established computational models for $\text{VO}_x/\text{support}$ systems that are consistent with experimental knowledge for powder catalysts and thin film model catalysts and thus help to bridge the gap between them. The high catalytic activity of vanadia supported on ceria as compared to alumina has its origin in the formation of Ce^{3+} instead of V^{3+} or V^{4+} although the reaction is most likely to occur in both cases on vanadyl sites.

References

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