



Oxygen activation on oxide surfaces: A perspective at the atomic level



Hans-Joachim Freund*

Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

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ABSTRACT

Thin oxide films have been used as model supports to unravel the influence of the oxide–metal and oxide–gas interface. We discuss the influence of defects in the oxide lattice and the oxide surface on properties of adsorbed species, in particular the formation of oxide particles from a deposited transition metal onto ceria and of adsorbed oxygen from the gas phase. Here we correlate the structure of the particles, as revealed by a combination of STM and spectroscopic as well as theoretical calculations, with their reactive properties. The nature of the involved defects is characterized by adsorption of Au as a way to correlate the influence of various defects of different structure on the Au charge state. In a second case study, we demonstrate the influence of dopants within the supporting oxide on the adsorption of oxygen on a defect free surface. This is shown to be potentially relevant for the activation of methane in oxidative methane coupling reactions, as recently demonstrated.

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1. Introduction

Adsorption on defect-free oxides is generally weak given the high degree of bond saturation at their surface and the large gap, in particular, that governs their electronic structure [14,15,24,26,31,38,44,45,52–54,58]. Metal atoms deposited onto pristine oxides have essentially two means to interact with the surface [58]. The first one, being accessible to all atoms, arises from van der Waals or dispersive forces, i.e., the adatom gets polarized in the Madelung field of the oxide and experiences dipolar coupling to the surface. Depending on the atom polarizability, the resulting adsorption energies are of the order of 0.5 eV or below for a single atom. The second interaction channel that is relevant for open-shell d- and f-elements is direct hybridization between orbitals of the ad-species and the oxide surface. Especially the overlap between the d-states of transition metal atoms and the 2p orbitals of the surface oxygen plays an important role and enables an increase in the metal-oxide bond strength to more than 1.0 eV [27,28,57]. Naturally, this channel is dominant for metals with partly filled d-shells (Cr, Mn, Fe, V) and loses influence for semi-noble and noble metals, e.g., Pt, Cu, Ag, and Au. Oxide materials are never perfect and therefore surface defects need to be considered as potential binding sites for any adsorbate (ref. J. Haber in [10]). In particular, with respect to oxidation of hydrocarbons, the interaction of oxygen from the gas phase with surface defects has been considered essential for oxygen

binding to the surface, forming the so called “electro-phyllic” oxygen, while the lattice oxygen was considered to be “nucleo-phyllic”. According to a proposal by Callahan and Grasselli [5], the concentration of “Nucleo-phyllic” lattice oxygen in direct contact with the active center, controls the selectivity of the catalytic reaction with respect to total oxidation. They called this scenario “site isolation principle”. The active centers may be associated with oxide defects.

Oxide defects often give rise to considerable variations in the electrostatic potential, which originate from unbalanced charges and cannot be screened due to the low density of free carries in the insulating material. In covalently bound oxides, dangling bond states may emerge at the defect site, reflecting the rigid lattice structure of the system that does not support bond reorganization. Whereas dangling bond states are highly susceptible to form covalent bonds to metal adatoms, electrostatic forces and charge transfer processes become relevant in the presence of charged defects in ionic oxides. Oxygen vacancies in MgO, for example, are able to exchange electrons with metallic adsorbates, which enable strong Coulomb attraction between both partners. Defect-mediated interaction schemes exceed the binding potential of the regular surface by up to a factor of three, underlining the significance of such lattice irregularities for the nucleation and growth of metals on oxide materials and adsorption in general. A particularly interesting approach to modify the adsorption strength without generating surface defects is the insertion of charge sources directly into the oxide lattice (Fig. 1).

In such a scenario, doping with aliovalent impurity ions may be exploited to introduce charges into the interior of thick films and even bulk oxides. Also in this case, charge transfer into the

* Tel.: +49 30 8413 4100; fax: +49 30 8413 4101.

E-mail address: freund@fhi-berlin.mpg.de

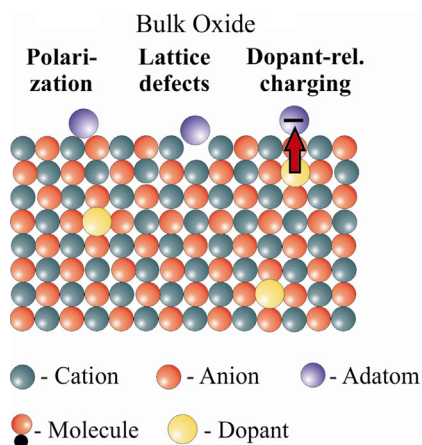


Fig. 1. Different binding mechanisms of adsorbates on bulk oxides.

ad-species has been revealed, the direction of which is given by the nature of the dopant in conjunction with the electronegativity of the adsorbate. Again, charge exchange is connected with a considerable increase of the adsorption strength [32]. In the following, we will substantiate those general considerations on the basis of two case studies carried out in the authors laboratory.

2. VO_x oxide clusters supported on $\text{CeO}_2(111)$ for methanol oxidation [3]

In the spirit of what was argued in the introduction, we have studied the deposition of vanadium onto a thin $\text{CeO}_2(111)$ film grown on $\text{Ru}(0001)$. The film has been chosen such (5–8 O–Ce–O tri-layers), that the metal substrate does not influence the chemistry on the films surface in any noticeable way.

Recently, comprehensive studies of the structure of vanadia clusters on $\text{CeO}_2(111)$ thin films as a function of vanadia coverage have been performed [3].

Fig. 2 shows STM images of $\text{VO}_x/\text{CeO}_2(111)$ surface at increasing vanadia coverage, that is, from 0.1 to 4.3 atom/nm². Random distribution of vanadia species together with the absence of preferential nucleation sites suggests a strong interaction between vanadia species and the underlying ceria support. In the atomically resolved image (Fig. 2a), the protruding spots (ca. 3 Å in diameter and 1.2 Å in height) appear to be monomers positioned atop protrusions in the ceria substrate. Increasing vanadia coverage first resulted in a higher density of monomeric species and the simultaneous formation of dimers, trimers, and ill-defined large aggregates with a relatively broad size distribution, which are indicative for kinetically limited growth of the vanadia particles deposited at room temperature. The monomeric species are thermally the least stable. Annealing to 700 K caused monomers to sinter, ultimately producing vanadia trimers and heptamers, particularly at higher coverage. The distance between the protrusions within the trimers and heptamers (~3.9 Å) is basically the same as measured on the pristine ceria films. The apparent height of these islands, ca. 1.3 Å, is about the same as for monomers. The respective IRA spectra revealed only bands at 1000–1040 cm⁻¹, which, combined with the XPS results showing vanadium only in a +5 oxidation state, strongly suggest these species to be vanadyls (V=O) in nature. The IRAS band shifts from 1006 cm⁻¹ for monomers to 1033 cm⁻¹ for trimers and further to 1040 cm⁻¹ for heptamers and larger oligomers (see Fig. 2c), ultimately approaching the frequencies (~1045 cm⁻¹) observed for vanadia three-dimensional nanoparticles supported on alumina and silica thin films [19,22]. This shift is characteristic for the onset of dipole coupling between neighboring V=O groups in the oligomers and is fully supported by DFT calculations [48,56].

Therefore, the present model systems allow one to establish a direct structure–spectroscopy correlation for oxide supported vanadia clusters.

These well-defined systems were further studied with respect to oxidative dehydrogenation of methanol with the aim to understand the support effects observed on this reaction on the real catalysts [12]. Methanol oxidation on vanadia supported on both $\text{CeO}_2(111)$ single crystal and polycrystalline ceria has previously been studied by the group of Vohs [13,48,55,56].

We have reported TPD spectra of methanol on ceria supported vanadia have been reported as a function of vanadia coverage [2]. The pristine $\text{CeO}_2(111)$ surface of a film grown on $\text{Ru}(0001)$ shows a formaldehyde desorption signal at ~565 K. In the presence of vanadia, the desorption peak shifts to ~590 K. Note that in those experiments methanol was exposed to the sample at 300 K. As the coverage of vanadia increases, the integral intensity of the peak decreases and finally becomes negligible for the highest VO_x coverage. Two peaks related to the interaction of methanol with the vanadia/ceria surfaces appear at lower temperatures, (~370 K) and (~475 K).

It is clear that the formation of formaldehyde at 370 K is only observed at low and intermediate vanadia coverages, where monomeric vanadia-species were identified by IRAS. An STM study [3] showed that these species exhibit low thermal stability and that they sinter on heating. The peak at 475 K may partially be due to polymeric vanadia species, formed during the temperature ramp. For the highest coverage of vanadia, where large polymeric species dominate the surface structure prior to the temperature ramp, the peak at 475 K is shifted to about 500 K, and the overall reactivity diminishes. Therefore, low temperature reactivity observed for vanadia/ceria relates both to high dispersion of vanadia and to the degree of reduction of the ceria support close to V=O species, as indicated by photoelectron spectroscopy (not shown here).

Among several possible schemes for methanol adsorption, the one shown in Fig. 3a agrees best with the key experimental findings observed, that is, depletion of the V=O band in IRAS, V reduction in XPS, and available, reduced Ce sites in close proximity to V=O serving as binding sites for methoxy.

It appears that the support effects reported in the literature for real vanadia catalysts [4,39,49] are related to the stabilization of small and isolated vanadia species by reducible oxide supports. Another important factor that controls the reactivity is that ceria stabilizes vanadium in the form of vanadyls. To illustrate this, Fig. 3b shows the IRA spectra for the vanadium deposited at 100 K and then stepwise annealed to 300, and 700 K in UHV. The formation of V=O is clearly observed upon annealing to 300 K, which can only be explained by vanadyl oxygen incorporated from ceria support.

Further, annealing causes sintering, which is accompanied by the band shift toward higher frequencies, which agrees well with the data shown in Fig. 2.

The results of DFT calculations nicely prove this scenario [3]. When a V atom is deposited on the perfect $\text{CeO}_2(111)$ surface, four electrons are transferred from V 3d states into Ce 4f states, thus creating four Ce^{3+} ions and leaving vanadium in the +4 oxidation state (see Fig. 3). There is, however, an isomeric structure of the V/ $\text{CeO}_2(111)$ system with 1.48 eV less energy, in which oxygen atoms have rearranged such that a vanadyl bond is formed and a subsurface oxygen defect is created in the third oxygen layer of ceria. Further DFT calculation by the Sauer group [33] reveal migration barriers for monomer species as high as 1.95 eV, which indicates that such species are kinetically “locked in”.

In order to characterize point defects (oxygen vacancies) on and below the surface of $\text{CeO}_2(111)$, we have used titration with Au atoms, which also reveal charge states, characteristic for specific defects [36,37]. The density of defects in the film was controlled by the final annealing step in the preparation. While annealing

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