Reversible Dynamic Behavior in Catalyst Systems: Oscillations of Structure and Morphology

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Exposing vanadium oxide nanoparticles on a Pd(111) surface to reducing conditions is shown to cause a spreading of the oxide over the metal until a reduced oxide phase covers the entire surface. Reoxidation reverses this process and oxide island structures and bare metal patches are reestablished.

The cycling between oxidizing and reducing gas feed conditions is a frequently used industrial practice to activate or regenerate supported metal catalysts, which typically consist of metallic nanoparticles dispersed on an inorganic oxide surface [1]. A heterogeneous supported metal catalyst is, however, a complex dynamic system which may change its catalytic properties under such reaction conditions. A common origin for reactivity changes is the modification of the surface structure and morphology of the metal and/or the oxide component of the supported catalyst. Complex physical and chemical interactions at the interface between the metal particles and the oxide support are generally invoked to be responsible for the morphology changes [2,3], which may affect the activity and selectivity of catalysts by influencing the shape of the active metal particles and their balance of surface crystallographic planes. The changes in the morphology of catalysts are often related to a wetting-dewetting behavior of the oxide over the metal phase or vice versa [4], thus emphasizing the significance of material transport processes under reaction conditions on these heterogeneous surfaces.

An important phenomenon affecting the structure and the catalytic performance of oxide supported metals concerns the encapsulation of metal particles with the support material and the decoration of their surfaces with a (partially reduced) oxide layer. Tauster et al. have created the term “strong metal-support interaction” (SMSI) to describe the state of a supported metal catalyst, containing a transition metal-oxide with a variety of possible oxidation states as the support material, which as a result of a high temperature reduction treatment showed a significantly lowered chemisorption capacity, as compared to its normal state, but an enhanced reactivity for some catalytic reactions [5,6]. The origin of the SMSI effect has been the subject of much debate in the past years [7], but there is now converging opinion in favor of the so-called encapsulation model, where the metal particles are covered with a thin layer of oxide in a reduced oxidation state [8]. A key issue of SMSI is the reversibility of this effect—the catalyst in the SMSI state can be converted back to its normal state by an oxidizing treatment. The mechanism of oxide migration and of the wetting-dewetting behavior on supported metal catalyst surfaces is a very complex but challenging materials science problem [6]. To reduce the complexity of the parameter space and to separate physical and chemical processes, thereby increasing the experimental transparency and reproducibility, it is well accepted to adopt a reductionist approach in using a catalyst model system [9,10]. Here we have employed an inverse catalyst model system to study the effects of oxidation and reduction cycles on the morphology of a heterogeneous metal-oxide surface. The inverse model catalyst consists of a metal single crystal surface, which is decorated by atomically ordered oxidic nanostructures [11]. We have fabricated a vanadium oxide-on-Pd(111) inverse catalyst surface in ultrahigh vacuum and have investigated the structural changes of the oxide phase as a result of cycled oxidation-reduction conditions using a variable-temperature scanning tunneling microscope (STM) [12]. Here we report the direct real-space observation of morphology and structure oscillations of the oxide phase as a result of alternating exposures to H2 and O2 at elevated temperature. The physical origin of the morphology and oxidation state oscillations of the oxide overlayer on the metal surface is analyzed by ab initio density functional theory (DFT) calculations in terms of the stability and interfacial structure in the Pd-vanadium oxide phase diagram as a function of the oxygen chemical potential.

Ultrathin vanadium oxide layers on Pd(111) develop a pronounced polymorphic behavior: at a given oxide coverage several different oxide phases can coexist on the Pd surface, which are distinguished by novel interface-stabilized structures which have no corresponding stable bulk counterparts [13]. The STM image of Fig. 1(a) illustrates a V-oxide/Pd(111) inverse catalyst surface containing clean Pd(111) areas, islands of a VO2 type oxide phase.


The STM observations can be evaluated quantitatively as displayed in Fig. 3, and the analysis has been substantially by photoelectron spectroscopy (not shown). Figure 3 shows the percentage areas of the bare Pd patches and of the various V-oxide covered parts of the surface during a reduction-oxidation-reduction cycle, plotted versus the time of the experiment. Note that the bare Pd area (solid circles) has disappeared after the first reduction step (~2000 sec), the surface being covered entirely by s-V$_2$O$_3$, but that after the oxidation step the bare Pd is quantitatively recovered (at ~4750 sec). This indicates that the wetting-dewetting process is completely reversible. The reoxidation of the s-V$_2$O$_3$ surface follows a complex pattern as seen in Fig. 3 in the range 2200–5000 sec. After an induction period (2200–4000 sec)
s-V₂O₃ oxidizes first to the zigzag V₆O₁₄, which converts subsequently partially to the (4 × 4) V₂O₁₄ phase; at ~4500 s both oxides coexist at the surface in approximately equal amounts, a clear result of kinetic effects. At ~4500 s the gas phase O₂ has been pumped away and the (4 × 4) oxide transforms back to the zigzag phase under these mildly reducing (vacuum) conditions. At this point the bare Pd surface is recovered and the surface is partially covered by a single oxide phase (the zigzag V₆O₁₄). Subsequent reduction leads again to the completely wetted, s-V₂O₃-covered surface (5750 s). This oscillatory morphology cycle, which has been repeated many times, is illustrated schematically in the cartoon at the top of Fig. 3.

The physical origin of the reduction/oxidation behavior of V-oxides on Pd(111) is disclosed in the DFT phase diagram of Fig. 4, where the ranges of stability of the V-oxide phases are indicated by bars in the relevant parameter space of chemical potential of oxygen (μ₀) [19] and V concentration [θᵥ, in terms of monolayer (ML) coverages]. For clean Pd(111) (θᵥ = 0), chemisorbed oxygen phases [ρ(2 × 2)-O; (2 × 2)-2O] are indicated, whereas for θᵥ ≥ 2 ML, oxygen-terminated bulk-type V₂O₃ (3 layers = V₆O₁₂) represents the stable oxide phase for a wide range of oxygen potentials [13,16]. The range of interest for the “inverse model catalyst” surface concerns θᵥ ≤ 1 ML. For example, at θᵥ = 0.5 ML and μ₀ = −1.0 eV (point I), zigzag V₆O₁₄ and (4 × 4) V₂O₁₄ coexist at the surface. On lowering the oxygen potential, e.g., to μ₀ = −2.0 eV, the V₅O₁₄ oxides are predicted to become unstable and decompose into r-VO₂, s-V₂O₃ and some bare Pd patches (point II in Fig. 4). Under more drastic reduction of μ₀ (e.g., ≤ −2.25 eV, point III) the r-VO₂ phase transforms to s-V₂O₃, the s-V₂O₃ phase is thus the only stable V-oxide for low μ₀ (in the range −2.25 to −3 eV); it decomposes eventually (μ₀ ≤ −3 eV, see point IV) and the V atoms dissolve into the Pd bulk (Vsol), which is more stable than remaining adsorbed at the Pd surface [16].

The observed sequence of oxide phases upon oxidation-reduction is now readily understood, since oxidizing/reducing experimental conditions lead to an increase/decrease of the chemical potential of oxygen. The surface morphology and the wetting-dewetting behavior is the natural consequence of the spatial lattice arrangement and the packing density of the particular stable oxide phase(s). It is, however, important to recall that the oxide phases in this ultrathin layer limit are (quasi-)two-dimensional materials, which have no corresponding stable bulk structures. Kinetic effects have not been addressed here, but the surface mobility of the oxide species is clearly high, since the migration processes take place readily at 250 °C.

It is useful to add a comment on the traditional framework of describing the wetting-dewetting of an overlayer on a substrate in terms of interfacial energies. For an overlayer to spread out on a substrate (wetting), the interfacial free energies γ must satisfy the relation

$$\gamma_{\text{overlayer}} + \gamma_{\text{interface}} < \gamma_{\text{substrate}}$$

where γoverlayer and γsubstrate are the surface free energies of the metal and the oxide overlayer, respectively, and γinterface is the interfacial free energy between substrate and overlayer. The oxides under consideration are the
$r$-VO$_2$ and V$_{5,6}$O$_{14}$ phases under oxidizing conditions, and the s-V$_2$O$_3$ and a possible three-dimensional bulk-type V$_2$O$_3$ phase under reducing conditions. Since all oxide layers are oxygen-terminated at the outer (vacuum) surface (see Fig. 2 and Ref. [13]), their surface energies may be assumed to be similar to the first approximation. The interfacial free energy $\gamma_{\text{interface}}$ of s-V$_2$O$_3$ and bulk-V$_2$O$_3$ is then the decisive factor determining the wetting behavior under reducing conditions, and it is essentially determined by the bonding interaction at the oxide-metal interface. The s-V$_2$O$_3$ layer is vanadium terminated, but the bulk-V$_2$O$_3$ is oxygen terminated at the interface to the Pd [13,16]. The V-Pd bonding is fairly strong and has been calculated by DFT to be $\sim$2.5 eV per V atom, whereas the binding energy between the oxygen-terminated bulk-V$_2$O$_3$ and the Pd substrate is much less ($\sim$ 400 meV per O atom). Therefore, $\gamma_{\text{interface}}$ of s-V$_2$O$_3$ is much smaller than that of the bulk-type V$_2$O$_3$ phase, thus driving the reduced system into a wetting condition.

The inverse catalyst model system employed in this study has allowed the specification at the atomic level of the structures and the energetics of the different oxide phases involved in the observed morphology changes during oxidation-reduction cycles on a heterogeneous metal-oxide surface. It is expected that the observations reported here reflect a more general behavior of wetting-dewetting on heterogeneous transition metal-oxide–metal surfaces, and that quasi-two-dimensional oxide phases specific to the metal-oxide interface play a decisive role in the materials transport processes on supported metal catalysts.

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[12] The experiments were carried out in an ultrahigh vacuum variable-temperature STM (Oxford Instruments) at $\sim$250 °C in the presence of O$_2$ or H$_2$ ambients, using a tracking software algorithm to compensate for the small thermal drift of the instrument. The same area of the surface could therefore be imaged during the time of the whole experiment (1–2 h).


[14] The V-oxide decorated Pd(111) surface has been prepared by evaporating 0.5 ML vanadium metal (1 ML is related to the atomic density of the Pd(111) surface, i.e., corresponds to $1.52 \times 10^{15}$ V atoms/cm$^2$) in $2 \times 10^{-7}$ mbar O$_2$ onto the clean Pd(111) surface at 250 °C, followed by gentle annealing at 300 °C.


[17] Note that the stoichiometry of the V$_5$O$_{14}$ model is only formally higher than V$_2$O$_5$, since the oxygen termination at the oxide-metal interface is shared with the Pd surface atoms. Both zigzag and (4 x 4) oxide models are experimentally supported by STM and phonon spectra in high-resolution electron energy loss spectroscopy. The (4 x 4) and zigzag V-oxides transform into VO$_2$ and s-V$_2$O$_3$ upon annealing in vacuum to $\approx$ 300 °C.

[18] The induction period is presumably due to the necessity of generating sufficient free Pd sites (starting at defects) for the activation (dissociation) of O$_2$.

[19] The chemical potential $\mu_O$ is related to the oxygen pressure $p$ and the temperature through $\mu_O(T, p) = \mu_O(T, p^0) + 1/2kT\ln(p/p^0)$. $\mu_O = 0$ corresponds to a pressure at which oxygen condenses at the surface; $\mu_O = -1$ eV corresponds to $p \approx 10^{-7}$ mbar at 520 K.