Probing the metal sites of a vanadium oxide–Pd(111) ‘inverse catalyst’: adsorption of CO

F.P. Leisenberger, S. Surnev, G. Koller, M.G. Ramsey, F.P. Netzer *
Institut für Experimentalphysik, Karl-Franzens-Universität Graz, A-8010 Graz, Austria
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Abstract

The adsorption of CO on V-oxide covered Pd(111) multicomponent surfaces, so-called ‘inverse catalyst’ surfaces, has been studied by high-resolution X-ray photoelectron spectroscopy using synchrotron radiation. Since CO does not chemisorb on V oxide surfaces at room temperature, the adsorption of CO reflects the reactivity of the free Pd sites of this inverse catalyst surface. The C 1s and Pd 3d core level spectra have been monitored to follow the CO surface coverage as a function of CO exposure and V oxide coverage and to investigate the CO adsorption sites. The results indicate that the adsorption of CO on V-oxide/Pd(111) surfaces is kinetically influenced by the V oxide phase via spill-over of CO molecules from a mobile physisorbed precursor state on the oxide surface on to Pd sites. As a result of this spill-over effect the initial sticking probability of CO per free Pd site increases beyond unity with increasing oxide coverage. The analysis of C 1s binding energies as a function of CO and oxide coverage suggests that the distribution of CO adsorption sites is altered by the V-oxide/Pd phase boundary. © 2000 Elsevier Science B.V.

Keywords: CO adsorption; Inverse catalyst; Pd(111) surface; Spill-over effect; Synchrotron radiation; V oxide; X-ray photoelectron spectroscopy

1. Introduction

The use of well-characterised catalyst model systems to study the elementary steps of a catalytic reaction is a well-established procedure to obtain a better comprehension of industrial catalytic processes [1]. Model catalysts with defined particle sizes and morphologies have recently been prepared by the deposition of metals on specially designed oxide supports, which consist of thin film oxide layers on single crystal metal substrates [2]. These systems allow charged probe surface science techniques to be applied for the characterisation at the microscopic level, because the charging induced by the probe particles may be dissipated by the underlying metal substrate. An alternative route towards the fabrication of catalytic model systems is the generation of small oxide island structures on single crystal metal surfaces. These oxide-on-metal structures have particular advantages if the interest of study is focused on the properties of the metal–oxide interface. In view of the complementary nature to real catalysts the latter systems may be regarded as ‘inverse catalysts’, although, of course, it is not suggested that the latter will be of the same practical relevance as the real systems.

The design of inverse catalysts has several appealing technical features compared with model
systems based on the real catalyst concept. The technique of preparing clean metal single crystal surfaces is well established and the metal substrate is conducting. The characterisation of the growth properties of oxides on metals is an interesting scientific problem in itself, and the oxide formation process can be controlled or at least microscopically characterised. From a conceptual viewpoint, the oxide-on-metal system also allows one to model the promotion effect, which some metal oxides seem to exert on metallic catalyst components: at the perimeter of the oxide islands new, catalytically active sites may be created at the metal-oxide phase boundary, which can be studied with surface science techniques.

The inverse catalyst model system chosen for this work is vanadium oxides on Pd(111). This choice is motivated by the so-called strong metal support interaction effect, which was originally reported by Tauster et al. [3]. Despite numerous studies on this subject the true nature of this effect is still somewhat obscure (see e.g. Refs. [4–7]), but it appears that the metal-oxide phase boundary plays an important role. An interesting aspect of the strong metal support interaction effect in the present context is the fact that the metal oxide involved has to exist in different oxidation states. Vanadium oxides are well suited for this purpose, since many V oxides are known, with cation oxidation states ranging from V$^{2+}$ (VO) to V$^{5+}$ ($\text{V}_2\text{O}_5$).

We have fabricated V oxide island structures on a Pd(111) single crystal surface by reactive evaporation of V metal in an oxygen atmosphere. By choosing low oxide coverages, ranging from submonolayer to 1–2 monolayers, we obtained oxide islands of nanometre lateral dimensions and of monolayer heights, while free Pd areas also remain at the surface. The investigation of the adsorption properties of the Pd sites in the presence of the metal-oxide phase boundary in the vicinity constitutes the principal aim of this study. Here we describe the adsorption of CO on the V-oxide/Pd(111) inverse catalysts. CO is particularly well suited to probe the free Pd sites, since it does not adsorb on V oxides at room temperature under ultrahigh vacuum conditions. We employed high-resolution X-ray photoelectron spectroscopy (HR-XPS) with the use of synchrotron radiation to monitor the CO adsorption as a function of the V oxide coverage. HR-XPS is a powerful tool for such studies because of the high surface sensitivity and the atomic selectivity of the technique. In addition, if performed at high resolution it allows information to be obtained on the chemical state of the adsorbate and on the adsorption geometry.

The results of this study demonstrate that the kinetics of CO adsorption on V-oxide/Pd(111) is significantly influenced by a mobile precursor state on the oxide surface, from which ‘spill-over’ on to Pd sites occurs. We also obtain indications that the CO adsorption site distribution on Pd areas may be altered by the presence of the adjacent metal-oxide interface.

2. Experimental

The HR-XPS experiments were performed at beamline 22 at the Swedish synchrotron radiation facility MAX I in Lund. The setup contains a modified SX-700 monochromator in conjunction with a large hemispherical electron energy analyser of the Scienta type. The C 1s and Pd 3d spectra were recorded with a photon energy $h\nu = 400$ eV with a total resolution of ~250 meV.

The Pd(111) surface was cleaned by a standard procedure, i.e. by Ar ion bombardment and annealing at 750°C; LEED and XPS were used to check surface order and cleanliness. The V oxide structures were prepared by reactive evaporation of vanadium from an electron beam evaporator in 2×10$^{-7}$ mbar O$_2$ onto the Pd(111) substrate, which was heated to 250°C. This procedure has been established in previous work to yield a V$_2$O$_3$-type oxide phase [9]. The evaporation rate employed was ~0.2 ML min$^{-1}$ as measured by a quartz crystal microbalance. The oxide coverages cited in this paper are given in nominal monolayer coverages (ML) of V, i.e. they correspond to the evaporated amount of V, which for convenience has been converted into monolayers based on the atomic density of the Pd(111) surface (1 ML = 1.52×10$^{15}$ V atoms cm$^{-2}$). CO was dosed from the system ambient via a leak valve and the
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Fig. 1. (a) V 2p\textsubscript{3/2} XPS peak of 0.5 ML V oxide on Pd(111), displaying the typical core level signature of a V\textsubscript{2}O\textsubscript{3}-type oxide phase. (b) Constant-current STM image of the 0.5 ML V-oxide/Pd(111) surface (tunnelling conditions: +1.9 V sample bias; 0.7 nA current). The free Pd (dark areas), first layer oxide (1) and second layer oxide (2) regions are marked on the image. (c) Schematic drawing of the morphology of the V-oxide/Pd(111) inverse catalyst surface. Numbers 1 and 2 correspond to first and second layer oxide regions, as in (b).

exposures are given in Langmuir (1 L = 1×10^{-6} Torr s). To check on the consistency of our experimental parameters we measured the initial sticking coefficient \( S_0 \) of CO on the clean Pd(111) surface, using the XPS C 1s peak areas as a function of CO exposure with a room temperature saturation coverage of 0.5 as calibration value, as reported in the literature [10]. We obtained \( S_0 = 1.05 \), in good agreement with the accepted literature value of \( \sim 1.0 \) [11,12].

The V-oxide/Pd(111) inverse catalyst surfaces were characterised by XPS and scanning tunnelling microscopy (STM). Fig. 1 shows, as a typical example, XPS and STM results for the 0.5 ML V\textsubscript{2}O\textsubscript{3}/Pd(111) system, together with a schematic illustration of the morphology of this surface. The V 2p\textsubscript{3/2} XPS spectrum (Fig. 1a) displays a spectral structure at a binding energy of 515.6 eV. This binding energy is consistent with a V\textsubscript{2}O\textsubscript{3} stoichiometry as discussed in previous work [9,13–15]. The width [half width at half-maximum (FWHM)] of the V 2p core level peak is 2.9 eV, which is also consistent with a single phase oxide layer [9].

The STM image (Fig. 1b) shows that at the nominal oxide coverage of 0.5 ML besides bare Pd areas and first layer oxide phases (marked 1 on the image) a second oxide layer (marked 2) also begins to grow. This is also illustrated in the schematic drawing in Fig. 1c. We note therefore that multilayer oxide growth starts before the completion of the first monolayer, but that the intended coexistence of free Pd areas and V oxide phase, as required for the inverse catalyst concept, is well established.

3. Results

Fig. 2 displays a sequence of C 1s core level spectra of CO on 0.5 ML V-oxide/Pd(111) as a
function of CO exposure. The spectral intensities have been normalised to a constant background level at a few electronvolts higher kinetic energy to the C 1s peak. The C 1s binding energy (BE) is observed at 285.60 eV at low CO coverage and it increases to 285.72 eV for CO saturation coverage, whereas the peak widths remain approximately constant, with a FWHM = 0.55 eV. Similar C 1s spectral sequences have been recorded as a function of the V oxide coverage, and peak positions and peak areas have been evaluated quantitatively. The inset to Fig. 2 shows a plot of the C 1s areas versus CO exposure for the spectra in Fig. 2, which gives the CO uptake curve for the 0.5 ML V-oxide/Pd(111) surface.

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The Pd 3d core level spectra are of interest for adsorption studies because they provide additional information on the adsorption site via their adsorption induced shifts of the surface core level binding energies [8]. In Fig. 3, Pd 3d_{5/2} core level peaks are shown for clean Pd(111) (curve a), and for 0.5 ML V-oxide/Pd(111), in the latter case for the pristine (curve b) and the CO covered surfaces (curve c). The experimental spectra have been decomposed into bulk (B), surface (S), and interface (I) components using asymmetric Voigt lines to model the core level emission from the individual components [16]. Shirley-type backgrounds have been considered as indicated on the figure. For the clean Pd(111) surface a good fit of the experimental spectrum is obtained with two components, a bulk component at 335.06 eV and a surface component at 334.78 eV; here we have used a surface core level shift (SCLS) of −280 meV in the decomposition as reported by Andersen et al. [17] for the Pd(111) surface. The Pd 3d spectrum of the Pd(111) surface is difficult...
to decompose, because the SCLS is small and the raw experimental spectrum has no specific spectral feature (such as a shoulder) to assist in the decomposition analysis. This is unfortunately also true for the Pd 3d spectra of some of the adsorbate covered surfaces, and the analysis has to be performed therefore with due caution.

The decomposition of the Pd 3d<sub>5/2</sub> spectrum of the pristine 0.5 ML V-oxide/Pd(111) surface shows three components in a good fit: the bulk component B, the clean surface component S, and a component marked I<sub>O</sub> at 335.4 eV BE. The latter is due to oxygen, which is adsorbed on parts of the bare Pd surface areas during the preparation procedure of the inverse catalyst (V evaporation in an O<sub>2</sub> atmosphere at 250°C). The adsorption of oxygen on Pd(111) and the surface reaction with CO has been studied recently by HR-XPS, HREELS, and kinetic measurements in a separate study, which is reported elsewhere [18].

The CO adsorption results discussed here are therefore virtually uninfluenced by the O precoverage, which is introduced in the catalyst preparation step. An interesting point in the spectrum of Fig. 3b is that the component of the Pd/V-oxide interface surfaces within the experimental error of ±0.05 eV; and (ii) the CO stretching frequency as measured by high-resolution electron energy loss spectroscopy, which is sensitive to the density of CO molecules at the surface [20,21], is the same at saturation on clean Pd(111) and on V-oxide/Pd(111) [22]. In Fig. 4a the CO surface coverage at saturation is plotted against the nominal V oxide coverage: there is an approximately linear decrease of θ<sub>CO</sub> with the V oxide coverage. Since CO does not chemisorb on V oxides at room temperature [23], the decrease of the CO saturation coverage is the result of the blocking of Pd sites by the V oxide phase. It is worth noting that at a nominal coverage of 1 ML oxide CO still adsorbs at the surface, indicating the presence of
free Pd sites. This is consistent with STM observations, where areas of free Pd sites are still detected for 1 ML oxide coverage [9]. According to Fig. 4a, the entire surface is covered with V oxide at a nominal coverage of 1.4 ML.

In Fig. 4b the CO saturation exposure, i.e. the exposure necessary to reach saturation adsorption conditions, is plotted as a function of the V oxide coverage. The saturation exposure decreases with increasing oxide coverage. This is unexpected, since the saturation exposure for adsorption on the free Pd areas should not be a function of the oxide coverage, unless the oxide phase plays a kinetic role in the CO adsorption process. This, however, seems to be the case, and the results of Fig. 4b indicate that CO adsorbed on the V oxide surface in an intermediate mobile precursor state, spills over the oxide–metal phase boundary and diffuses onto free Pd sites.

Fig. 5a displays the initial sticking coefficient $S_0$ of CO as a function of V oxide coverage. The $S_0$ values in Fig. 5a have been derived from the initial slopes of the experimental CO uptake curves, i.e. the $\theta_{CO}$ versus exposure curves (see e.g. Fig. 2, inset), for the different V oxide covered surfaces. They correspond therefore to the values per unit area of the composite metal–oxide surfaces, and have been normalised to $S_0 = 1.0$ on the clean Pd(111) surface [11,12] (see also Section 2). As seen in Fig. 5a, $S_0$ remains close to unity for low oxide coverages, but decreases linearly from about 0.5 ML V oxide to zero at ~1.4 ML V oxide coverage. It has to be kept in mind in assessing this plot that the active Pd surface area also decreases with increasing oxide coverage. A more instructive diagram is therefore obtained, if the data of Fig. 5a are renormalised to the number of free Pd sites by using Fig. 4a. Fig. 5b shows that $S_0$ per free Pd site increases with the V oxide coverage and reaches a value of ~2 at 1 ML.
shown in Fig. 4b. The C 1s binding energies at CO saturation are displayed as a function of the V oxide coverage in Fig. 6b. The C 1s BE at saturation decreases smoothly with oxide coverage, the range of variation being \( \sim 200 \) meV. The C 1s binding energy is dependent on the specific adsorption site, e.g. on-top, bridge, or hollow site; as a general rule it appears that the higher the coordination of the adsorbate, the lower the C 1s BE [24–26]. In Section 4 we will consider whether the observed C 1s BE changes with oxide coverage reflect a different site distribution of the adsorbed CO species induced by the presence of the oxide phase boundary.

4. Discussion

The most conspicuous result of this study is the influence of the V oxide phase on the adsorption kinetics of CO on the V-oxide/Pd(111) surface. The data presented in Fig. 5 show that the initial sticking coefficient per free Pd site increases beyond unity with increasing V oxide coverage. This indicates that the oxide surface provides a source of CO in addition to the CO molecules which impinge directly from the gas phase on to the Pd surface. The CO molecules on the V oxide surface are physisorbed in a mobile precursor state, from where they can diffuse over the oxide-metal boundary to reach Pd sites, where they chemisorb. Thus the inverse catalyst here mimics supported catalyst systems where diffusion of CO on an oxide support to reach metal particles has also been observed, e.g. for Pd and Rh on Al₂O₃, Pd on mica, or Pd on MgO [27]. The sticking coefficient of CO on V-oxide/Pd(111) in Fig. 5b reaches a saturation level at an oxide coverage of \( \sim 0.6–0.7 \) ML. This saturation effect is most naturally explained using the concept developed by Boudard et al. [28], who described the contribution of the surface diffusion to the sticking coefficient for CO on Pd on alumina in terms of capture zones on the oxide, which surround the active metal particles. CO physisorbed on the oxide within a given capture zone may reach the metal by diffusion over the oxide surface before it desorbs. The radius of the capture zones is therefore defined by the
mean surface diffusion length of CO at a given temperature. For the present oxide-on-metal system the spill-over of CO from the V oxide surface to the Pd areas saturates, if the mean oxide island size exceeds the size of the capture zones. This appears to occur for $\theta_{\text{oxide}} \approx 0.6-0.7$ ML. In principle the diffusion length of CO could be estimated from these data in combination with STM, as it will be strongly dependent on the details of the oxide morphology. However, as is apparent in Fig. 1b, the oxide islands form such a complicated network that a quantitative evaluation is not possible.

The C 1s binding energy of CO adsorbed on a particular metal surface has been shown to be dictated primarily by the adsorption site [9,24–26]. On clean Pd(111) the C 1s BE varies from 285.60 eV at low coverage to 285.82 eV at room temperature saturation (see Fig. 6a). The adsorption site of CO on Pd(111) has been investigated by Bradshaw and Hoffmann [29] as a function of coverage using IR spectroscopy. up to 0.33 ML, a coverage characterised by a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern, the data indicated the threefold hollow positions as adsorption sites, whereas for higher coverages up to 0.5 ML the population of bridge sites has been invoked to account for the relatively strong shifts of the CO stretching frequency. More recently, Gießel et al. [21] have applied the photo-electron diffraction technique to the CO–Pd(111) system, showing that hollow sites are indeed occupied in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, but that CO adsorbs in a mixture of fcc and hcp hollows without bridge sites in the c(4 $\times$ 2) phase [30]. However, whereas the c(4 $\times$ 2) structure is easily observed in LEED for CO adsorption at low temperature, it is not obtained for room temperature adsorption, where a diffuse $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED structure with split spots is observed instead at saturation coverage (again 0.5 ML or close to it) [29,30]; this indicates that the ordering is poor in the room temperature CO adlayer and that many domain boundaries must be present. The C 1s XPS core level peaks for CO adsorption on Pd(111) at room temperature have been recorded during this work (not shown). Peak decomposition analysis revealed [30] that the C 1s 

peaks needed two spectral components for CO surface coverages in excess of 0.33 ML to obtain a good fit: one component at 285.60 eV as for $\theta_{\text{CO}} \leq 0.33$, which is associated with the threefold hollow adsorption positions, and a second component at 285.95 eV; the intensity of the latter component increases with increasing coverage thus producing the apparent overall shift of the C 1s line with coverage as seen in Fig. 6a. The C 1s peak of CO in the hollow positions ($\theta_{\text{CO}} \leq 0.33$) at 285.60 eV shifts only by $<0.1$ eV to higher BE with increasing coverage as a result of intermolecular repulsion effects. In view of the 0.35 eV BE difference to the hollow site component of the $\sqrt{3}$-CO surface the C 1s structure at 285.95 eV is more likely to be associated with CO adsorbed in bridged surface sites rather than in different hollow sites [24].

Very recently, Sautet et al. [31] have calculated the energetics of CO on Pd(111) by density functional theory (DFT). For the c(4 $\times$ 2)-CO structure the DFT calculations favour a model with CO occupying both fcc and hcp hollow sites, in agreement with recent experimental evidence [21]. However, a model with CO sitting in two bridge sites is only 0.06 eV per CO molecule higher in energy [31]. We therefore speculate that domains of a compressed $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (diffuse $\sqrt{3}$ LEED pattern with split spots) with CO in hollow and bridge sites might be present in the room temperature CO saturation layer; this would explain the presence of two different spectral components in our XPS results. We conjecture that the presence of domain boundaries in the poorly-ordered room temperature CO layer on Pd(111) might provide a kinetic stabilisation of this metastable adlayer.

Following this line of thought, we propose the following model to explain the results of Fig. 6, i.e. the reduction of the C 1s BE shift with increasing CO exposure as a function of oxide coverage. We suggest that the presence of the V oxide phase on the Pd(111) surface shifts the balance between bridge and hollow sites with increasing CO density at the surface. As the coverage of the oxide phase increases and the areas of free Pd sites decrease, the number of CO domain boundaries should be...
reduced because the metal–oxide interface provides new boundary conditions. The V-oxide/Pd interface may therefore remove the kinetic inhibition of the room temperature CO adlayer on Pd(111) to reach the thermodynamically stable CO adsorption configurations. It is expected that the two hollow adsorption sites of CO (fcc and hcp) should have a very similar C 1s binding energy, making them indistinguishable in XPS. The increasing population of hollow sites at the expense of bridge sites would then lead to the observed reduction (or absence) of a C 1s BE shift, as a function of CO coverage, with increasing oxide coverage (Fig. 6b). We realise that this proposed model is speculative at the present time, but further experiments to clarify the situation are planned, in particular, detailed vibrational spectroscopy investigations (HREELS) are presently under way.

Finally, the work of Hartmann and Knözinger [32] should be mentioned, who have investigated the adsorption of CO on a V-oxide/Rh(111) model catalyst by conventional low-resolution XPS. These authors reported two widely separated C 1s emissions after chemisorption of CO on a 0.3 ML V-oxide/Rh(111) surface, at 286.1 and 283.9 eV. The structure at 286.1 eV has been associated with molecular CO on Rh(111) sites, while the peak at 283.9 eV has been ascribed to surface carbon species originating from CO dissociation. It has been suggested that CO dissociation is induced on new sites, which are created at the metal–oxide interface along the perimeters of the V oxide islands. In the present study on V-oxide/Pd(111) surfaces evidence for CO dissociation has never been observed and the chemistry at the V-oxide/Pd boundary appears to be not so widely different from that on bare Pd surfaces. It is noteworthy to mention that the V-oxide/Pd system differs in this respect also from the Ti-oxide/Rh and Ti-oxide/Pt systems, where the formation of active cationic centres at the oxide–metal interface has been postulated [33,34].

5. Summary

The adsorption of CO on V-oxide/Pd(111) inverse model catalyst surfaces has been investigated to study the influence of the metal–oxide interface on the chemisorption properties of Pd sites on these multicomponent surfaces. We have employed HR-XPS with use of synchrotron radiation to monitor C 1s and Pd 3d core level emissions to obtain information on the CO adsorption sites; the C 1s intensities were used to determine quantitatively the CO surface coverage. Heterogeneous Pd(111) surfaces consisting of V₂O₃-type oxide island structures of nanometre dimensions and bare Pd areas have been prepared by reactive evaporation of V metal in oxygen atmosphere: the resulting inverse catalyst surfaces have been characterised by XPS, LEED, and STM [9]. The adsorption of CO has been followed as a function of CO exposure on surfaces with varying V oxide contents. Since CO does not chemisorb at room temperature on the V oxide components of the surfaces, the room temperature adsorption of CO is used to probe the reactivity of free metal sites.

The results obtained show that the CO exposure necessary to reach saturation adsorption conditions on the V-oxide/Pd(111) surfaces and the initial sticking coefficient of CO are a function of the oxide coverage, indicating a kinetic influence of the oxide phase on the CO adsorption on Pd sites. The decreasing CO saturation exposure and the increasing sticking coefficient per Pd site with increasing oxide coverage are interpreted as the result of a spill-over effect, where CO physisorbed in a mobile precursor state on the V oxide surface diffuses over the metal–oxide phase boundary to become chemisorbed at Pd sites. The course of the C 1s binding energy of adsorbed CO with CO coverage is dependent on the V oxide content of the surface: the overall C 1s peak energy shift to higher BE, which is observed with increasing CO coverage, decreases from 0.25 eV on the clean Pd(111) surface to ~0.05 eV for 1 ML nominal oxide coverage. This is discussed in a tentative model, where it is proposed that a shift of CO from bridge to hollow adsorption sites is mediated by the oxide phase boundaries.

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References