The surface oxide as a source of oxygen on Rh(1 1 1)

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Abstract

The reduction of a thin surface oxide on the Rh(1 1 1) surface by CO is studied in situ by photoemission spectroscopy, scanning tunneling microscopy, and density functional theory. CO molecules are found not to adsorb on the surface oxide at a sample temperature of 100 K, in contrast to on the clean and chemisorbed oxygen covered surface. Despite this behavior, the surface oxide may still be reduced by CO, albeit in a significantly different fashion as compared to the reduction of a phase containing only chemisorbed oxygen. The experimental observations combined with theoretical considerations concerning the stability of the surface oxide, result in a model of the reduction process at these pressures suggesting that the surface oxide behaves as a source of oxygen for the CO-oxidation reaction.

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1. Introduction

Because of the importance for commercial applications, the catalytic activity of the late transition metals has been studied for many years. By using model systems, such as single crystal surfaces under ultra high vacuum (UHV) conditions, and carefully controlling the reactant gas abundance on the surface, significant progress has been made in the understanding of adsorbate–adsorbate and adsorbate–metal interactions. A common model system to study has been the CO reactivity with O chemisorbed on close-packed late transition metal surfaces. In recent years however, it has been discussed in the literature that on Ru, Pt and Pd surfaces [1–3], it is not the chemisorbed atomic oxygen adsorbed on the surface, but rather the oxides formed on the surfaces under such conditions, that are the most efficient phase in oxidizing CO. In the case of Ru, it has been shown that whereas metallic Ru is not active in CO oxidation, RuO2, which forms under high partial O pressure on the Ru(001) surface, is the most active catalyst known for this reaction. The reason for the high activity could be shown to be due to the details of the surface structure of the RuO2 (1 1 0) surface, indicating that the formed oxide also provide one of the reactant species, namely oxygen (Mars-van-Krevelen mechanism). The RuO2 (1 1 0) surface provides catalytically active sites, so-called coordinatively unsaturated sites (CUS), onto which impinging molecules readily adsorb and later react [4]. Thus, on Ru the mechanism for the increased CO-oxidation activity due to the geometrical details of the formed RuO2 is in general understood, in contrast to the situation for Pd, Pt and Rh which are not as thoroughly investigated on the atomic scale at or after exposure to higher O partial pressures. One reason for the difference in knowledge is the higher partial oxygen pressures needed to form the bulk oxides on the latter materials. Another reason is that on Pd and Rh, the formation of thicker oxides has turned out to be more complicated than initially believed. On several of these surfaces, at intermediate O partial pressures, so-called tri-layer surface-oxides form [5–8] prior to the onset of the growth of thicker oxides. Some of these thin, intermediate oxides display properties which are not found in the corresponding bulk oxides [6], 0368-2048/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
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and in the case of Rh(1 1 1) as well as on Pd(001) [89], the presence of a surface oxide kinetically hinders the formation of the respective bulk oxides.

The role of the surface oxides in the catalytic activity of these metals is at present not clear. This statement is in particular valid at pressures and temperatures approaching those found in a more realistic environment of a catalyst. It is however clear that the surface structure on the atomic scale of the surface oxides does not exhibit any obvious CUS sites (see, e.g., inset in Fig. 1), suggesting a different interaction with an impinging or adsorbed reducing molecule than in the RuO$_2$(1 1 0) case. Therefore, it is of interest to study the interaction of a tri-layer surface oxide and a reducing molecule, and eventually try to elucidate the importance of this interaction in a more realistic environment.

In the present contribution we have investigated the reduction by CO of the (9 × 9) tri-layer surface-oxide formed on Rh(1 1 1) at elevated O partial pressures and sample temperatures. We show that CO does not adsorb on the (9 × 9) surface oxide. The reduction of the (9 × 9) phase is initially slower than the CO reduction of the p(2 × 1) chemisorbed phase, however the reduction speed is observed to increase as more of the metal surface is exposed. We propose a model explaining the observed behavior using experimental evidence as well as theoretical considerations based on density functional theory. The observed CO-oxidation behavior of the surface oxide is in good agreement with previous experiments [10], in which the onset of oxidation of Rh reduces rather than stops the reactivity.

2. Experiment and theory

The PES measurements were performed at beam line I311 at MAX II in Lund, Sweden [11]. All spectra were recorded using a normal emission angle using photon energies of 625 eV (C 1s) and 400 eV (C 1s). Scanning tunneling microscopy (STM) measurements were done in Vienna at room temperature using the same instrument as in Refs. [6,8]. The cleaning procedure of the Rh(1 1 1) surface has been described elsewhere [8]. The p(2 × 1) (θ = 1/2 ML, Monolayers, 1 ML equals the number of atoms in one Rh(1 1 1) layer) oxygen induced structure could be formed by exposing the Rh(1 1 1) surface to 100 L of oxygen at a temperature of 300 K, while the (9 × 9) phase at this temperature. The inset displays a side view of the (9 × 9) structure.

3. Results and discussion

The CO adsorption at 100 K on the clean Rh(1 1 1) surface and on the (9 × 9) structure is shown in Fig. 1. While on the clean surface a strong C 1s peak is observed indicating the existence of suitable adsorption sites, no such peak is discernible after an even higher CO exposure onto the (9 × 9) surface. The measurements in Fig. 1 indicate that there is only an extremely small number of sites on the (9 × 9) phase onto which the CO can adsorb with an adsorption energy comparable to the clean surface. In catalytic reactions based on the usual Langmuir–Hinshelwood mechanism the activity is closely related to the adsorption ability of the gas phase reactants onto the surface. In this picture, Fig. 1 suggests a low CO oxidation reactivity of the surface oxide. However, a high activity also requires low barriers resulting in that intermediate adsorption energies are desirable [16]. Thus, in order to study the reactivity of a particular structure, the interaction between the adsorbed CO and O should be studied. Co-adsorbing CO at room temperature with chemisorbed O such as the p(2 × 1) structure, results in a mixed layer in which the CO preferably takes the on-top sites and the O the fcc-hollow sites [17]. Thus, also in the presence of chemisorbed oxygen, the adsorption ability of CO is significantly higher than that on the (9 × 9) structure, indicating a lower reactivity for the (9 × 9) structure.

More information about the in situ CO interaction with a chemisorbed oxygen phase such as the p(2 × 1) and a surface oxide such as the (9 × 9) structure can be obtained by previous DFT-GGA calculations (a$_0$ = 3.83 Å, e.g. Ref. [15]). The Rh substrate was modelled by six layer thick slabs, and the Brillouin zone integration was performed with grids corresponding to 24 × 24 k points in the primitive surface cell.

![Fig. 1. Comparison of CO adsorption (1 L at 100 K) on the clean Rh(1 1 1) surface and on the (9 × 9) surface oxide (30 L at 100 K). No CO is observed to adsorb on the (9 × 9) phase at this temperature. The inset displays a side view of the (9 × 9) structure.](image)
the measurements shown in Fig. 2. Fig. 2a shows the reduction of the \( p(2 \times 1) \) structure in a CO partial pressure of \( 2 \times 10^{-8} \) mbar and a sample temperature of 375 K. The left panel of Fig. 2a shows a two-dimensional plot of the O 1s region compiled from spectra recorded during the CO exposure with one spectrum per 24 s. The O 1s component at a binding energy of around 530 eV corresponds to the chemisorbed O atoms in fcc hollow sites, while the component at 532.4 eV reflects the O in the CO adsorbing in on-top sites. In the right panel of Fig. 2a, some selected O 1s spectra during the reduction are shown. The area underneath the chemisorbed O component directly reflects the reduction rate. The corresponding measurements from the reduction of the \( (9 \times 9) \) structure using the same sample environments as in the \( p(2 \times 1) \) is shown in Fig. 2b. The O 1s fingerprint from the \( (9 \times 9) \) structure is somewhat more complicated due to the two components at 529 eV (surface component) and 530 eV (interface component) from the two different oxygen layers in the tri-layer structure of the \( (9 \times 9) \) structure, yielding a ratio between the area underneath each component of 1:1. Nevertheless, the reduction can be monitored, and although CO does not adsorb to a high degree on this surface as was shown above, eventually, the structure can be reduced.

By performing a fit of the recorded PES spectra shown in the left panel of Fig. 2 using the components as shown in the right panel, we can extract details on the reduction process of the two different oxygen prepared samples. The result from this procedure is shown in Fig. 3. Starting with the reduction of the \( p(2 \times 1) \) structure in Fig. 3a, it can be seen that the amount of chemisorbed O decreases immediately when the sample gets exposed to the CO gas, indicating that the O on the surface in the \( (2 \times 1) \) structure reacts with the impinging CO forming CO\(_2\). It can be seen that the rate of the decrease of the chemisorbed O 1s signal is reduced in a decreasing fashion with time, i.e. the CO-oxidation reaction rate decreases linearly. The reason for this is presumably simply due to the reduced number of O atoms on the surface, yielding a progressively lower probability for the CO-oxidation reaction. The behavior observed is in good agreement with that expected from a Langmuir–Hinshelwood mechanism, in which the reactants adsorb on the surface either molecularly or dissociatively, diffuse on the surface and react occasionally on the surface. It should also be noted that each coincidence not necessarily leads to a reaction. The complete disappearance of the chemisorbed O 1s signal also indicates that neither the Eley–Ridal mechanism (in which gas phase molecules should react directly with molecules adsorbed on the surface, in this case the oxygen atoms in the \( (9 \times 9) \) structure) nor the Mars-van-Krevelen mechanism is of a significant importance on the surface of the \( (9 \times 9) \) structure at these pressures and sample temperatures. We would have expected a more immediate response in the decrease of the O 1s signal in both cases.

We believe that the reason for observing a slow decrease of the signal at all—despite that we know that CO does not adsorb on the surface—is defects. A small number of defects on the \( (9 \times 9) \) structure exposing oxygen undercoordinated Rh atoms will be attractive adsorption sites for CO molecules. From these sites, the CO may react with the O atoms in the nearby oxide, resulting in CO\(_2\) and a larger area of the unreconstructed surface. From our measurements, this process seems to be initially rather slow. The process however eventually leads to an increase of the unreconstructed oxide O 1s signal.

The extracted area underneath the O 1s components as a function of time during the reduction after a fitting procedure from (a) the p(2×1) structure with components due to the chemisorbed O and the CO. (b) The (9×9) structure with components due to the (9×9) bulk oxygen component, chemisorbed oxygen, and CO. In the fit of the (9×9), the ratio of the surface and the bulk oxygen area was locked as 1:1 as obtained by spectra prior to CO exposure.

Fig. 4. Room-temperature STM images (50 nm × 50 nm) of a Rh(1 1 1) surface completely covered by the O–Rh–O (9 × 9) surface oxide after reduction for 1300 s at 375 K in 2×10−8 mbar CO. Frame (a) shows two reduced areas (arrows) within a large terrace still fully covered by the surface oxide (appearing as a hexagonal network–like pattern). At the same time, the surface oxide is completely absent on many of the terraces in the more stepped parts of the sample (white arrows), as shown in frame (b).
where approx. twice as much adsorbed O as CO is found [Fig. 3(b)].

To understand the increased catalytic reactivity of the surface oxide the theoretical phase diagram, shown in Fig. 5, is helpful. Below a chemical potential of $-1.2$ eV, oxygen is simply chemisorbed on the otherwise unreconstructed surface either in a low coverage $p(2 \times 2)$-1O phase or in the higher coverage $p(2 \times 1)$-1O phase; at more oxidizing conditions ($\mu_O > -1.2$ eV) the surface oxide is stable. For finite temperatures, instead of sharp boundaries between the three domains smoother transitions with intermediate disordered phases may occur, but the picture remains essentially the same. When the surface oxide is now reduced by carbon monoxide, patches of the surface oxide and the unreconstructed surface—covered partly by atomic oxygen—must be simultaneously present at the surface. This is oxygen and CO—must be simultaneously present at the surface. Ignoring the more weakly bound CO, this is only possible if the chemical potential of oxygen is exactly $-1.2$ eV, i.e. at the crossing point of the energy lines of the $p(2 \times 1)$-1O phase and the surface oxide. This behavior is similar to a temperature driven melting transition in a solid, where the liquid and the solid coexist only at one specific temperature (at a given pressure). In the present case the chemical potential plays the role of the temperature and remains constant, as long as both phases coexist on the surface. Microscopically we can understand the behavior as follows (see Fig. 6): carbon monoxide and oxygen coexist at patches which are not covered by the surface oxide. Eventually they react, decreasing the oxygen and CO content locally. But at the boundaries of these patches the surface oxides immediately decomposes in order to increase the oxygen content in the depleted areas. Therefore, the surface oxide indeed acts as an efficient source for atomic oxygen keeping the chemical potential of oxygen essentially constant, until it has entirely “evaporated”. On the unreconstructed surface, however, the chemical potential of oxygen is progressively reduced, as oxygen reacts with carbon monoxide. Since the driving force for oxidation is directly proportional to the chemical potential of oxygen on the surface, the reaction is faster on the oxide precovered surface (at least once sufficient surface area is available to adsorb carbon monoxide).

After around 1500 s, the reduction rate seen in Fig. 3(b) becomes roughly constant. Simultaneously the amount of chemisorbed oxygen on the Rh(111) surface continues to increase, but finally starts to disappear without a noticeable decrease of the reaction rate. At this stage, the major difference between the two initial surface preparations is most likely the number of defects on the surface. Since the Rh density in the ($9 \times 9$) layer is 19% smaller than in a Rh(111) plane, reduction of the oxide results in a metal surface with a high density of defects, such as steps, kinks and corners. These sites could be responsible for the observed differences at the final reduction stage, since they
are known to be favorable sites for adsorption and reactions [18–20].

4. Summary

In summary we have shown that CO does not easily adsorb on the \((9 \times 9)\) surface oxide at 100 K, and argued that the reason for this is the low availability of suitable adsorption sites. The CO reduction process at a CO pressure of \(2 \times 10^{-8}\) mbar and sample temperature of 375 K of the \((2 \times 1)\) and the \((9 \times 9)\) oxygen induced structures on the Rh(1 1 1) surface was studied by in situ time-resolved PES. The measurements demonstrate significant differences in the reduction rate; for the \((2 \times 1)\) a traditional Langmuir–Hinshelwood mechanism was observed while for the \((9 \times 9)\) a more complicated reduction process was observed, involving both defects and the stability of the \((9 \times 9)\) structure with respect to the clean surface, as calculated by DFT.

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