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A high pressure X-ray photoelectron spectroscopy study of oxidation and reduction of Rh(100) and Rh nanoparticles

S. Blomberg [a,*], R. Westerström [a], N.M. Martin [a], E. Lundgren [a], J.N. Andersen [a], M.E. Messing [a,b], J. Gustafson [a]

[a] Division of Synchrotron Radiation Research, Lund University, Box 118, SE-221 00, Sweden
[b] Solid State Physics, Lund University, Box 118, SE-221 00 Lund, Sweden

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ABSTRACT

We have studied the oxidation and reduction of Rh(100) and SiO_2 supported Rh particles using high pressure X-ray photoelectron spectroscopy. We show that the formation and reduction of Rh bulk oxide can be followed in situ in O_2 and CO pressures in the range of 0.1 Torr. In general, the oxidation/reduction processes are similar on Rh(100) and the nanoparticles, but there are significant differences in temperature dependence. Already at a sample temperature of 140 °C, the particles show clear signs of a thin bulk oxide, while an ultra-thin so-called surface oxide covers the single crystal at the same temperature. Both of these oxide films, however, hinder further oxidation, and a thick oxide is only found at a temperature of at least 300 °C, for both samples. The reduction, in contrast, starts at a higher temperature on the particles as compared to the single crystal, but once started the particles are completely reduced at lower temperatures.

1. Introduction

Driven mainly by its importance for catalysis, the interaction between Pt-group metals and different gases has been extensively studied within the field of surface science. The result is a deep understanding of the adsorption processes as well as catalytic reactions between co-adsorbed molecules. Traditionally, however, these studies are performed on simplified model systems, such as perfect single crystal surfaces in Ultra High Vacuum (UHV) compatible pressures. Such conditions are obviously different from those found for industrial catalysts that generally consist of nanoparticles of the active metal, dispersed inside a porous oxide support, which functions at atmospheric pressure or above. Consequently, much effort has been devoted recently to bridge these so-called pressure and material gaps between surface science measurements and industrial catalysis.

Due to its relative simplicity, in combination with industrial relevance, the most studied reaction in this context is the oxidation of CO through $CO + \frac{1}{2}O_2 \Rightarrow CO_2$. The major potential energy barrier for this reaction, when not catalyzed, is the dissociation of O_2, but if oxygen is adsorbed on a suitable catalytic surface, the dissociation is spontaneous. Hence, if CO and oxygen are co-adsorbed, the result is an active catalyst, following the Langmuir–Hinshelwood mechanism, where all the reactants need to be adsorbed on the catalytic surface. A layer of chemisorbed oxygen usually leaves enough space for CO to adsorb, keeping the surface active [1–3]. As O_2 needs to dissociate, however, it needs more space in order to adsorb. A CO covered surface therefore hinders the O_2 adsorption and poisons the catalyst. Similarly, it has been found that CO does not adsorb on most oxide surfaces. This has led to the general belief that the active phase of a CO oxidation catalyst is a metallic oxygen dominated surface [4–7].

Since more than a decade, several studies have shown that, under more realistic conditions, a thin oxide film forms on Ru, Pt, Pd and Rh in conjunction with a switch from low (CO poisoned) to high activity, suggesting that the active phase is oxidized rather than metallic [8–17]. Although this question is far from settled, it is clear that the oxidation and reduction of these surfaces under more realistic conditions are of major importance for understanding CO oxidation catalysis on a fundamental level [18–28].

In this paper we report on an in situ high pressure X-ray photoelectron spectroscopy (HP-XPS) study of the oxidation and reduction of Rh(100) and 21 nm sized Rh particles. We show that we can follow the formation of an ultra-thin so-called surface oxide, as well as the subsequent bulk oxidation at higher temperatures on the crystal. The particles, however, show a formation of a bulk oxide at significant lower temperature. While CO does not adsorb on Rh oxides at room temperature and low pressures, in CO pressures in the range of 0.1 Torr we can identify a CO induced surface core level shift of the top oxygen layer in the oxide. At elevated temperatures, we can follow the gradual reduction of the oxide resulting in a CO covered metallic surface.

2. Experimental

The single crystal Rh(100) surface was cleaned by cycles of Ar^+ sputtering and subsequent anneals. By annealing the crystals in an O_2

* Corresponding author.

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pressure of 10^{-7} Torr carbon contaminations could be removed, and any remaining oxygen could be removed by flashing to 800 °C in UHV. The metallic surface was confirmed by XPS.

The nanoparticles studied herein are produced by an aerosol deposition technique. A spark discharge process between two Rh electrodes generates agglomerate aerosol particles by evaporation of electrode material followed by cooling of the vapor [29]. The agglomerate particles are then fed into an aerosol nanoparticle setup where they are reshaped into compact particles by heating and subsequently size selected by a differential mobility analyzer, which is a common tool in aerosol science. After size selection, a known number of the particles are deposited onto a substrate by means of an electric field. The production process is described in more detail in Ref. [30]. The generated Rh particles in this study have a diameter of 21 nm and are evenly distributed on a Si substrate covered by a native oxide. As can be seen from Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images of the particles (Fig. 1a) and b)), the particles have a hexagonal shape and a narrow size distribution. Measurements of lattice fringes from high-resolution TEM images in combination with X-ray energy dispersive spectroscopy (XEDS) measurements (not shown) confirm that the particles are indeed pure Rh particles. Fig. 1c) shows overview XPS spectra of pristine SiO_x substrates with and without the Rh nanoparticles. The spectra show carbon contamination, which likely originates from hydrocarbons in the air when the samples are transferred between the experimental set-ups in open air. The particle samples are therefore cleaned in an oxidation/reduction cycle where the sample is heated rapidly from room temperature to 450 °C in 1 Torr O_2, and subsequently reduced with CO [20].

The high pressure XPS studies were performed at the Molecular Science beamline 9.3.2 at the ALS in Berkeley [31], USA and at the ISISS endstation at BESSY at Helmholtz-Zentrum Berlin, Germany. Both endstations have an XPS set-up with a differential pumping system and electrostatic lenses, focusing the photoelectrons in the analyzer. This enables in situ XPS measurements in gas pressures up to 1 Torr. The Rh $3d_{5/2}$, C 1s and O 1s core levels were probed and the spectra were deconvoluted using a Doniach–Šunjić lineshape [32] convoluted with a Gaussian lineshape. The Gaussian FWHM was varied due to the different experimental set-ups utilized. A linear background was subtracted from the spectra and the energy scales were calibrated against the Fermi edge. The formation of the bulk oxide made the sample less conductive and in the absence of a clear Fermi edge, the spectra were instead calibrated against the photoelectron binding energy of a known emission peak.

3. Oxidation of Rh(100)

Fig. 2 shows the results from in situ HPXPS measurements of the oxidation of Rh(100) in 0.1 Torr O_2 and stepwise increasing temperature. Starting from the bottom of Fig. 2b), the spectrum acquired at 30 °C in vacuum reveals a metallic surface, characterized by a single peak at 307.1 eV which is in good agreement with previous reported binding energy of the Rh bulk [33]. The lack of a surface component is most probably due to contamination from the residual gas in the HP chamber, which is the origin of the small peaks (gray) at the high energy side in O 1s.

In the second spectrum, the chamber is filled with 0.1 Torr O_2 and the sample is heated to 140 °C. This starts the oxidation process, as shown by the appearance of one component in the Rh $3d_{5/2}$ level with a surface core level shift of +0.79 eV relative the bulk, and two components in O 1s separated ~0.8 eV. This is recognized as the surface oxide,

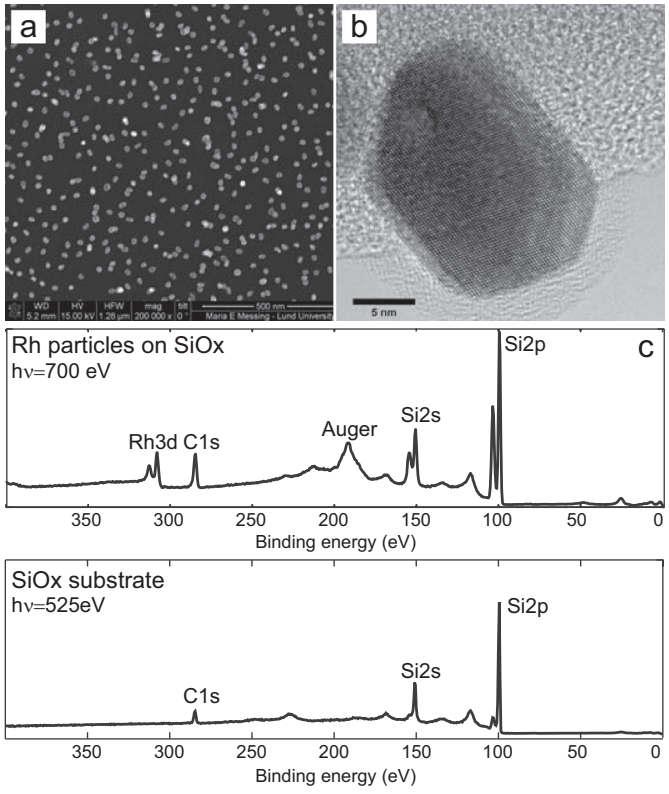

Fig. 1. a) The SEM image shows a narrow size distribution of the particles over the SiOx substrate. b) TEM image of the hexagonal shaped 21 nm Rh particle. c) The XPS spectra of two pristine samples. The upper spectrum originates from 21 nm Rh particles distributed on a SiOx substrate measured with photon energy of 700 eV. The spectrum below is recorded with photon energy 525 eV of a bare SiOx substrate. Both spectra are measured in vacuum and at room temperature.

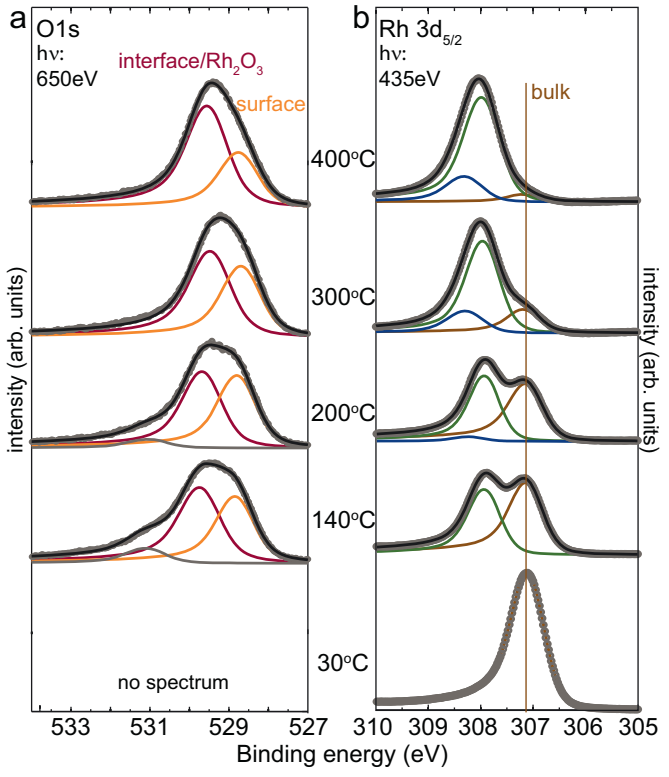

Fig. 2. a) In situ Rh $3d_{5/2}$ and b) O 1s spectra of the oxidation of Rh(100) in 0.1 Torr O_2 with the temperature increasing upwards in the figure. At room temperature, a metal bulk peak (brown) is observed. Already at 140 °C, a surface oxide is formed and by increasing the temperature further, a thicker oxide is observed. At 400 °C, the metal bulk component is almost vanished. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)