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A valence band photoemission study of Pb adsorption on Rh(1 0 0) and Rh(1 1 0)

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Abstract

We have studied the adsorption of Pb on the Rh(1 0 0) and (1 1 0) surfaces by photoemission and low energy electron diffraction (LEED), and tested the chemical properties by adsorption of CO. Pb forms two distinct $c(2\times2)$ phases on Rh(1 0 0), according to the temperature of the substrate. The phase formed below about 570–620 K, denoted α-$c(2\times2)$, reduces the coverage of adsorbed CO but does not affect the valence band spectrum of the molecule. The phase formed above this temperature, denoted β-$c(2\times2)$, also reduces the coverage of adsorbed CO but the valence band spectrum of the adsorbed CO is strongly affected. The two phases are also characterised by a slightly different binding energy of the Pb $5d_{5/2}$ level, 17.54 eV for the α phase and 17.70 for the β phase. The Pb/Rh(1 1 0) surface shows two ordered Pb induced phases, $c(2\times2)$ and $p(3\times1)$. CO adsorbs on the first with reduced heat of adsorption and with a valence band spectrum that is strongly altered with respect to CO adsorbed on clean Rh(1 1 0), but does not adsorb on the $p(3\times1)$ structure at 300 K. We compare the present results with previous results from related systems.

Keywords: Rhodium; Lead; Photoemission; Adsorption; Bimetallic surface alloys

1. Introduction

Two-dimensional metal alloy systems exhibit a range of interesting physical and chemical properties; for example systems that are immiscible in the bulk may form solid solutions or ordered compounds, or the chemical properties may be different from those of both the components [1]. The alloying may modify the activity towards the adsorption of third species, such as gases. This feature is attractive for catalysis design, as the existence of two metals in a bimetallic catalyst gives an extra degree of freedom in tuning properties.

Lead is often regarded as a potent poison of catalysts because of its notorious role in automotive catalysis. However its adsorption on late transition metals represents an interesting case study for surface science because of the difference between Pb and the substrate. Pb is a sp metal which is rather inert, while transition metals have open d shells and are catalytically active. A general formulation of the interaction of transition metals with adsorbates has been given by Nørskov and co-workers [2]. They view poisoning interactions as being due to a lowering in energy of the centroid of the valence d-band. An alternative approach is to focus on the "frontier orbitals", since these are the most likely to be involved in chemical bonding. In metals the frontier orbitals correspond to the states at the Fermi level.

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We are not aware of any published work on the adsorption of Pb on Rh single crystals although there has been an investigation of Sn, which is chemically related, adsorbed on Rh(1 1 1) [3]. In the present work, we examine the way in which Pb interacts with two Rh surfaces, Rh(1 0 0) and Rh(1 1 0), and compare the results with our previous studies of related systems [4–7].

2. Experimental

The experiments were performed at the Materials Science Beamline, operated by the Academy of Sciences of the Czech Republic, the Charles University of Prague and Sincrotrone Trieste, at the Elettra synchrotron light source in Trieste; further details are given elsewhere [8]. The photoemission spectra were recorded using a PHOIBOS analyser (SPECS, Berlin) at normal emission from the surface. The spectra were taken at photon energies of 49.6 eV, 72.4 eV and 100–130 eV. At the lower two energies, we expect the valence band to be dominated by Rh 4d states, while at 100–130 eV, which corresponds to the Cooper minimum of the Rh 4d valence band, the spectra are more sensitive to other states, such as adsorbate valence states.

The total resolution (analyser + photons + natural width) was determined on another sample by measuring the width of the Fermi level at a temperature of 120 K and was equal to or better than 130 meV for all energies. The spectra were normalised to the drain current from a gold mesh. This allowed comparison of the intensity of spectra taken at the same photon energy, but not at different photon energies, since the relative efficiency of the mesh is not known as a function of photon energy.

The rhodium crystals were discs of 10 mm diameter and 3 mm thickness, oriented to within 0.2° of the (1 0 0) and (1 1 0) planes. The cleaning procedure was similar to that described previously [10], with many cycles of sputtering, annealing and heating in oxygen. The lead adlayers were deposited from a home-made evaporator consisting of a ceramic tube heated by a molybdenum wire, and with a thermocouple placed close to the Pb.

3. Results

The samples were examined by LEED and gave sharp diffraction patterns for the clean surfaces. Adsorption of sub-monolayer quantities of Pb on Rh(1 0 0) at low (130 K) and room temperature gave rise to a $c(2\times2)$ pattern. Since this pattern occurred at low temperature where diffusion of Rh is inhibited, we conclude that it consists of Pb atoms adsorbed on the surface without reconstruction of the substrate. Heating this surface to 470 K produced a sharper LEED pattern, indicating the elimination of defects, with no significant changes in the Pb 5d core levels or the valence band. An obvious structure model for this LEED pattern is for the Pb atoms to be located in fourfold hollow sites, with $c(2\times2)$ periodicity: this implies a Pb–Pb distance of 3.8 Å, compared with the distance in bulk Pb of 3.50 Å. The coverage was calibrated to 0.5 ML (monolayer) for this model structure, where 1 ML refers to the number of surface Rh atoms per unit area.

On adsorption of 0.5 ML of Pb at 300 K, the valence band decreased in intensity but showed only minor changes in shape, Fig. 1. By measuring at more than one photon energy, we aim to avoid spectral changes that are due simply to Umklapp effects, that is, electrons scattered into the normal emission direction by the changed surface periodicity. The spectrum of the shallow Pb 5d core levels is shown for one photon energy only, as the binding energy remains the same, and only the intensity changes with photon energy. Adsorption of more than 0.5 ML of Pb at room temperature led to complicated LEED patterns which we do not discuss here.

On heating the $c(2\times2)$ structure formed at room temperature, the LEED pattern remained $c(2\times2)$. However between 570 and 620 K, the Pb core levels shifted by 160 meV from 17.54 to 17.70 eV binding energy, Fig. 2. The core levels also broaden and become more symmetric; the width of the $5d_{5/2}$ level increases from 0.36 to 0.46 eV. The valence band also showed some changes, and the intensity near the Fermi level increased slightly. This is interpreted as surface alloying, probably with the Pb atoms in the surface plane as in Ni(1 1 1)$(\sqrt{3}\times\sqrt{3})R30°$–Pb [9], to form a new structure: we denote this structure β-$c(2\times2)$, and the structure formed below 570–620 K as α-$c(2\times2)$.

Space does not permit us to show all data, but the Rh $3d_{5/2}$ core level also showed shifts due to Pb adsorption. The clean surface was found to have a surface core level shift of 0.64 eV, in good agreement with literature values of 0.62 [10] and 0.64 eV [11]. On formation of the α phase, the shift was reduced to about 0.44 eV, as the surface peak moved towards bulk binding energy values. The β phase had a similar shift, but different bulk-surface intensity ratio, reflecting the different structure of the phase.

These structures were tested for their chemical properties by exposure to CO. Fig. 3 shows photoemission spectra

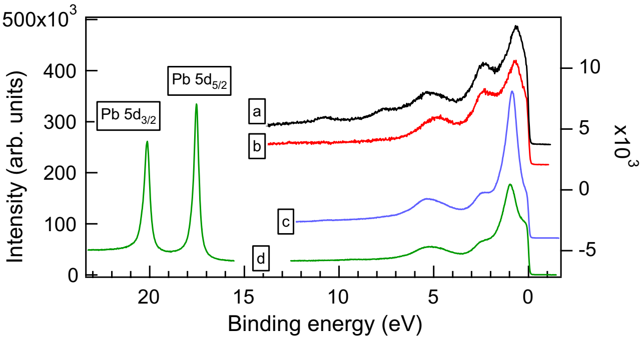

Fig. 1. Photoemission spectra of Rh(1 0 0), and Rh(1 0 0)$c(2\times2)$–Pb, annealed to 473 K. (a) Photon energy 130 eV, clean surface (a trace of CO is present, indicated by weak peaks at 10.6 and 7.8 eV). (b) Photon energy 130 eV, Rh(1 0 0)$c(2\times2)$–Pb. (c) Photon energy 72.4 eV, clean surface. (d) Photon energy 72.4 eV, Rh(1 0 0)$c(2\times2)$–Pb, showing Pb 5d peaks and valence band.