TAILORING THE SURFACE REACTIVITY: COMPARISON OF Pd/Nb(110) AND Rh/Nb(110)

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Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

Ni, Pd and Pt overlayers deposited on many metallic surfaces show properties resembling those of noble metals. We pose the question whether a similar trend might occur also for other transition-metal overlayers. To this goal, we perform first-principles density-functional theory calculations for Pd(111), Rh(111) surfaces, Pd and Rh epitaxial monolayers deposited on Nb(110), and for CO chemisorption on these systems. Density functional calculations indicate that the behavior of the two overlayers is quite different. Whereas the Rh overlayer on Nb(110) resembles the Rh(111) surface, for the Pd overlayer the electronic structure around the Fermi level is strongly affected by hybridization with Nb electrons, which accounts for unique properties of the overlayer. We expect that the latter mechanism may be of importance just for Pd, Pt, Ni and not for other transition metals with lower d-electron occupation.

Keywords: Adsorption; Density functional calculations; Surface chemistry; Niobium; Palladium; Rhodium.

Bimetallic surface systems are a highly popular topic in catalysis and other branches of surface science. The reason is that they give hope to tailor important surface properties and/or to find materials that are less expensive. The present study is devoted to a specific class of metallic overlayers within this family. As an example, we have chosen the Pd monolayer deposited at the Nb(110) surface and compared it with the Rh overlayer.

At surfaces of transition metals from the right half of the Periodic System, negative surface core-level shifts (CLS; the shifts are evaluated with respect to the core-level value in the bulk) are frequently measured, which correlate well with displacement of the local density of d-electron states (LDOS) towards lower binding energies. The trend is rationalized[1,2] by the surface

band-narrowing effect: due to the narrowing, vacant electronic states would be transferred below the Fermi level E_F if not opposed by the repulsive Coulomb potential. Just opposite behavior was discovered[3] for epitaxial Pd monolayer deposited upon Nb(110). Namely, a pronounced shift to higher binding energies is found for valence Pd d-electron states as well as for palladium CLS, and the overlayer resembles thus rather a noble-metal surface. The phenomenon attracted considerable attention and the very same trend has been discovered for a number of bimetallic systems; also clear correlation between d-band shift and positive CLS (shifts to higher binding energies) has been proven. The reviews[4–8] offer detailed information especially on the experimentally observed properties of Pd, Pt and Ni overlayers or surface alloys with transition metals with a lower electronic occupation, and also in contact with some other metals (Al, Sn, Zn). Similar situation takes place also for Au deposition. It is important to mention that an analogous situation arises[9,10] also for (bulk) alloys of Pd, Pt and Ni. All these findings prove that the effect is robust and does not depend critically on tiny details such as a specific geometry, stoichiometry, etc. Yet more important is the correlation between the magnitude of the above mentioned shifts and drop in the reactivity of the surface (in particular variation of desorption temperature for chemisorbed CO has been studied in detail). The latter fact is quite natural if the quantum-chemical HOMO-LUMO concept is invoked, which has been widely used in various forms to elucidate chemisorption. In our case, the almost occupied d-electron band of Pd, Pt or Ni plays the role of HOMO and the energetical position of this "effective orbital" can be represented by a mean value – center of gravity (CG) of the corresponding LDOS. In such a picture a CG shift away from E_F accounts for lowered overlayer reactivity. A detailed analysis of this point is given in ref.[11]. Another well-kown indicator of reactivity lowering is a marked lowering of the LDOS at E_F, $\rho(E_F)$. As a rule, it correlates well with the CG shift. Recently, it has been suggested[12] that by watching $\rho(E_F)$, one can refine the analysis based on the CG positions. Hence, becauuse of the hope to control the surrace reactivity, bimetallic surfaces of this kind still attract attention[12–20]. The problem is of interest in electrochemistry[21] as well.

At first sight a paradox might seem to arise. Whereas palladium is more electronegative than niobium, the sign of Pd CLS seems to indicate depletion of charge at Pd. Such an idea is, however, simplistic[5]. A formal mathematical analysis also shows that similar reasoning applies only with caution: Let us consider, for example, a simple tight-binding Hamiltonian H for an extended transition-metal system. For a selected atom, j, let us make the local potential less attractive for d-electrons by introducing a lo-

cal perturbation (orbital indices are omitted for the sake of simplicity) $\Delta H_{ij} = \delta > 0$, without changing any other matrix elements. For a nearest neighbor i of the atom j, let us consider the resulting change $\Delta Q_i(E_F)$ of the local d-electron charge considered as a function of E_F. As usual, one defines the k-th local moment of the Hamilatonian[22,23] as $\mu_k = \mathrm{Tr}_i H^k$, where the trace is taken over all d-electron orbitals localized on the the atom i. Clearly, the above perturbation does not change the first and second moment, whereas the third moment increases due to terms of the form $H_{ij}\delta H_{ji}$. A mathematical theorem[24] (Hadamard theorem) employed some time ago several times to enlighten general trends in solid-state physics and chemistry[22,23,25] now leads to the conclusion, that $\Delta Q_j(E_F)$ changes its sign twice at least, when E_F varies between the d-band bottom and top, whereas straigthforward electronegativity arguments would suggest $\Delta Q_i \geq 0$. Intuitively, the "anomalous" ΔQ_i sign might be expected for a very small or almost complete d-band occupation at the atom i; one can anticipate also accompanying "anomalous" self-consistent corrections working against the charge transfer. Such a situation correlates with the behavior of Ni, Pd and Pt described above.

Let us also note that a simple tight-binding model assuming the same d-electron occupation for transition-metal atoms in pure-metal crystals and in bimetallic systems arrives at conclusions[26,27] that are in accord with observations. Analysis of charge transfer in related systems has been performed in refs[28,29] on the first-principles level showing that, e.g., in Pd–Nb systems, the charge transfer has the "right" sign but the Pd d-electron count practically does not differ from Pd metal. The authors argue that one of the mechanisms playing the role is the tendency to deplete the d-electron band of the metal from the right part of the Periodic System by hybridization with the d-band of the second metal that extends well above E_F. However, they do not offer explanation why this mechanism is not operative for a wider set of metals with more than half-filled d-band. In ref.[30], the electronic structure of Pd overlayer on several substrates is calculated. The results indicate the presence of a polarized bond with electron concentration between the unlike atoms. The authors conclude that electrons feel a more attractive potential explaining thus the shifts described above.

It is clear that the situation in the described bimetallic systems has been thoroughly studied both experimentally and theoretically and that there remain no serious puzzles. On the other hand, it seems that there is no answer why the "surprising" shifts are observed only for Pd, Pt, Ni and partly for noble-metal overlayers or alloys. To shed more light on this problem, we compare in this note the calculated electronic structure of Pd and Rh

epitaxial overlayers on Nb(110). Since the (110) surface of body-centered cubic (BCC) crystals can be viewed as a distorted hexagonal two-dimensional structure, we compare selected results with the (111) surfaces of face-centered cubic (FCC) crystals Pd and Rh, respectively.

METHOD OF CALCULATION

In the present study, we perform electronic-structure calculations for epitaxial Pd and Rh monolayers deposited upon the Nb(110) surface as well as for the Pd(111) and Rh(111) surfaces. Besides we study also the ordered CO overlayer forming the superstructure $p(2 \times 2)$ (CO coverage $\theta = 1/4$) above the (110) surfaces, and the CO overlayer with the $(\sqrt{3} \times \sqrt{3})R\,30°$ geometry ($\theta = 1/3$) above the (111) faces. The separation between the molecules is large enough to describe adsorption in the low coverage limit. The CO molecules are placed upright above a surface atom (top position) and oriented with the carbon atom towards the surface. We employ the ab initio density-functional code DACAPO [31,32]. It is a code employing Vanderbilt ultrasoft pseudopotentials and a plane-wave basis set to investigate periodic structures. The exchange-correlation gradient-corrected functional in the Perdew–Wang (PW91) form ref.[33] is used. The supercell approach with crystals modelled by periodically repeating six metallic-layer films separated by vacuum ca. 14 Å wide layer is utilized. The input structures are based on bulk calculations that yield lattice constants of 3.31, 3.99 and 3.83 Å for BCC Nb and FCC Pd and Rh, respectively. The geometry is further optimized for three upper metallic layers and for CO molecules if the latter are present. The absence of magnetization is assumed, other calculation details are essentially the same as in ref.[34]. Local electronic properties such as LDOS and CG are evaluated for the crystal Wigner–Seitz spheres. The corresponding radii R_{WS} are 1.56 Å (FCC Pd), 1.50 Å (FCC Rh) and 1.63 Å (BCC Nb and Pd or Rh overlayers on Nb(110)).

RESULTS AND DISCUSSION

Let us start with some simplified considerations that can be easily understood in an elementary quantum mechanical two-level model. Since CG of the Pd (or Rh) d-band lies below CG of the niobium LDOS, the hybridization tends to push the Pd states below E_F enhancing thus the band-narrowing trend with respect to Pd crystal surface. On the other hand, some Pd states will appear in the Nb d-band region[28] extending well above E_F, with the tendency to depopulate Pd states; in ref.[35] the effect is denoted

as asymmetric band widening. Usual arguments suggest that to avoid exaggerated charge transfer, a band narrowing should make the surface potential more repulsive. By the same reasoning, the band widening introduces attractive correction. Intuitively, the widening effects can prevail over the narrowing ones if d-electron LDOS in some energy interval below E_F is higher than above E_F, i.e. when LDOS is quickly decreasing with energy at E_F. This is the case of Pd, Pt and Ni; for noble metals the criterion is unclear because of low and slowly decreasing LDOS at E_F. (The band narrowing probably always dominates for atoms with very low coordination such as an isolated adatom.)

The calculated quantities are shown in Tables I and II for clean and CO-covered surfaces, respectively, and LDOS in Figs 1 and 2. It is convenient to define two somewhat different CGs: The first one, denoted as g, is evaluated by integrating over the whole range of d-electron states; for the other one, g^o, only the occupied part of LDOS is taken into account. Changes of g reflect the local electrostatic potential changes felt by the d-electrons and, if the initial-state approximation[36] is accurate enough, they should be close to changes of CLS. On the other hand, g^o can be assessed, from the occupied part of valence bands seen in photoemission experiments. As seen in Table I, the changes of g and g^o, respectively, are very similar in particular for Pd. By the simplified method (differences between g's) just described, we predict CLS –0.31 eV for Pd(111) and –0.37 eV for Rh(111). (Let us remind that the measured CLS [36,37] for Pd(111) and Rh(111) are –0.28 and –0.50

TABLE I
Calculated centre of gravity of the local surface or bulk d-electron band with respect to the Fermi level g, its analogue g^o evaluated for the occupied d-states only, local density of d-electron states at the Fermi level $\rho(E_F)$, and electronic work function ϕ

System	g, eV	g^o, eV	$\rho(E_F)$, states/eV	ϕ, eV
Pd bulk	–1.95	–2.22	1.73	
Pd(111)	–1.64	–1.88	1.58	5.27
Pd/Nb(110)	–2.29	–2.54	0.34	4.44[a]
Rh bulk	–2.05	–2.87	1.15	
Rh(111)	–1.68	–2.34	1.68	5.20
Rh/Nb(110)	–1.64	–2.12	1.58	4.56

[a] 4.61 eV for Nb(110) surface.

(–0.49) eV, respectively.) For the overlayers, we predict positive CLS 0.34 eV for Pd, and for Rh/Nb(110) yet a slightly more negative CLS –0.41 eV than for the Rh(111) surface. The positive CLS agree well with the measurement[38] for Pd on polycrystalline Nb where, however, a rigorous comparison is problematic because of the presence of the Pd–Nb alloying; for iso-electronic Pd/Ta(110) the Pd(3d) CLS is[4] +0.5 eV with respect to the Pd bulk. Let us compare the LDOS presented in Figs 1 and 2. The high-density region below and just above E_F existing for Pd(111) LDOS is transformed

TABLE II
Calculated adsorption energy E_{ads}, C–O and C–M (M = Pd, Rh) separation d, and the electronic work function ϕ for CO adsorbed on various surfaces

System	E_{ads}, eV/molecule[a]	d_{CO}, Å	d_{CM}, Å	ϕ, eV
Pd(111)	1.67	1.17	1.90	5.57
Pd/Nb(110)	1.45	1.17	1.98	5.06
Rh(111)	2.13	1.17	1.82	6.13
Rh/Nb(110)	2.07	1.17	1.87	5.55

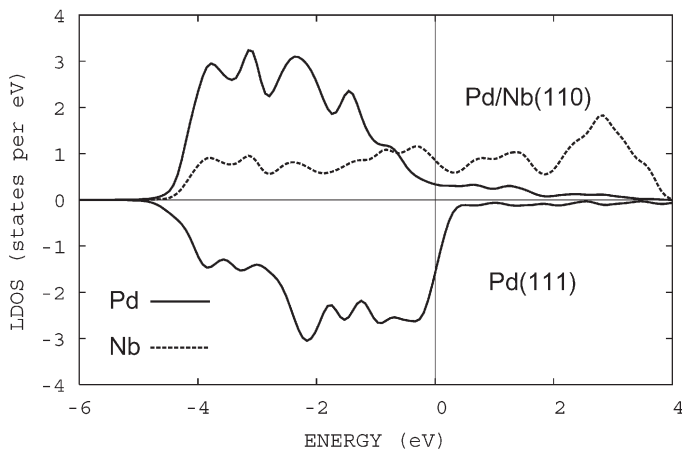[a] 1 eV/molecule = 96.4853 kJ/mol = 23.0605 kcal/mol.

FIG. 1
Local density of d-electron states (LDOS) at Pd and Nb atoms at the Pd/Nb(110) interface (positive values) and at the Pd(111) surface atom (negative values). The Fermi level lies at the energy zero

into a rather low-density tail of Pd d-electron states which, however, extends far on both sides of E_F (see also ref.[39]) due to hybridization with electronic states of Nb. The effect can be viewed as the asymmetric band widening introduced above. Simultaneously, $\rho(E_F)$ is drastically lowered for the Pd overlayer. In other words, a decisive factor is a quick change from high to low LDOS close to the Fermi level as illustrated for Pd(111) in Fig. 1. An interaction with atoms like Nb which offer considerable LDOS above E_F will tend to deplete the occupied electronic Pd states. In metals which avoid, as a rule, any marked ionicity, the effect must be compensated by a more attractive electrostatic potential at Pd atoms. For Rh, such a modification takes place only at higher energies, the situation in the vicinity of Fermi level being less perturbed. The comparison suggests that the very specific behavior observed for Ni, Pd and Pt overlayers cannot appear for metals with a lower d-electron occupation, i.e. with E_F positioned well inside the local d-electron band. By invoking the electron-hole analogy, however, one can speculate whether "inverse" effects (negative CLS, higher reactivity) do not appear for Sc overlayers deposited on appropriate metal surfaces. In our tables we show also the calculated electronic work function ϕ. For single crystals, the values agree reasonably well with measurements which, however, show non-negligible scatter[40]. The lowering of Nb(110) work function due to the Pd overlayer (Table I) is also in accord with experimental[5] observation.
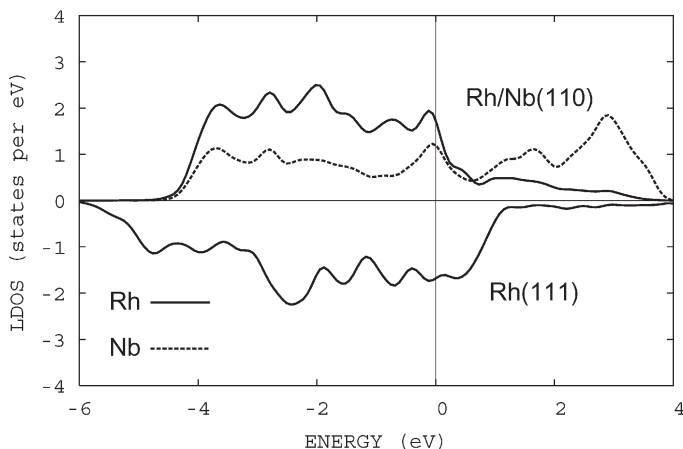

FIG. 2
Local density of d-electron states (LDOS) at Rh and Nb atoms at the Rh/Nb(110) interface (positive values) and at the Rh(111) surface atom (negative values). The Fermi level lies at the energy zero

Before considering the data in Table II for CO-covered surfaces, some explanation is necessary. Above Rh(111), CO adsorbs upright in the top position[41,42] and the same site seems most probable for Rh/Nb(110) because of similarity of both surfaces (Table I and Fig. 2). For Pd(111), the preferred adsorption site is the three-fold one. Such a position has no exact analogy on BCC (110) faces. According to a semiempirical model[35], CO is more destabilized by the presence of a second metal for chemisorption sites with higher coordination. Particularly, it was shown[43] for the isoelectronic system Pd/Ta(110) that CO resides in the top site, and a similar situation for Pd/Nb(110) seems to be thus likely.

A serious flaw of all density functionals used commonly in calculations for extended systems is an overestimation of binding energy for CO adsorbed on metal surfaces and the tendency to prefer adsorption sites with higher coordination. As discussed by several groups of authors, the reason is inaccuracy in the calculated HOMO-LUMO separation for CO or, equivalently, an inaccurate value of the excitation to the triplet state (inaccurate position of the $2\pi^*$ CO level). More details and references are given in refs[41,42]. Since the necessary energy corrections seem roughly the same for the sites with the same coordination[41,42], adsorption-energy differences rather than energies presented in Table II are to be considered. It appears that the Nb substrate destabilizes CO in the top position by 0.22 eV. The energy difference between adsorption in the three-fold and top sites above Pd(111) is[41,42] about 0.4 eV so that the total energy loss caused by the Nb(110) substrate is ca. 0.6 eV if our conjecture about the chemisorption geometry is right. The result agrees with the experimentally observed trends for Pd–Nb and related bimetallic surfaces. Particularly, for Pd/Ta(110), a comparable but somewhat higher value (~20 kcal/mol $\gtrsim$ 0.8 eV per molecule) was derived[43] experimentally. The change of the C–Pd separation (Table II) confirms the weakened C–Pd bond at Pd/Nb(110). The differences in the C–O distance are marginal. For Rh surfaces, the adsorption energy is not seriously affected by the Nb presence. The small changes of CG (Table I) might suggest a slightly stronger chemisorptive bond at the Rh/Nb(110) rather than at the Rh(111) surface. The reasoning[12] based on the LDOS value $\rho(E_F)$ at E_F, however, agrees (Tables I and II) with the calculated slightly stronger chemisorption above Rh(111).

To conclude, we have analyzed the situation when the position of the center of gravity of electronic states and core-level shifts at bimetallic surfaces differ qualitatively from the elemental metal surfaces. Such a behavior is known to occur for Pd, Pt, Ni and sometimes for noble metals in contact with a metal that provides extended density of electronic states above the

Fermi level. Hybridization with these states is the cause of the behavior we have mentioned. By calculating and comparing electronic structure and other properties for several surface systems, we illustrate relations between the local density of electronic states, core-level shifts, and surface reactivity. We argue that the effect is not likely to take place for other metals such as, e.g., Rh.

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