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Š Pick

J Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic

Abstract. Experiments on CO chemisorption at the transition-metal alloy Pt₃Ti(111) find the molecule bound more weakly than at Pt(111). There was, however, disagreement in experimental interpretation supporting either the bulk termination or pure platinum surface. A recent LEED study strongly supports the latter possibility. We have performed extended self-consistent tight-binding calculations for bulk and surface electronic structure of the alloy and for CO chemisorption at selected adsorption sites. For the bulk we get in the initial-state approximation a good agreement with the measured core-level shifts. For CO we find for both the surface models sites at which the adsorption energy is reduced in agreement with measurements, but also sites at which the adsorption energy practically coincides with that at Pt(111). The calculated core-level shifts at Pt sites in both models are close to experimental values. We predict, however, a distinct CLS for Pt atoms at Ti sites in the Pt overlayer which is not reported experimentally. The possible enrichment of the subsurface layer by titanium might reconcile the experimental and theoretical findings. Correlations between surface core-level shifts and reactivity are also discussed.

1. Introduction

One of the central problems of contemporary surface science is to prepare new bimetallic surface systems with specific technological, and particularly with specific catalytic, properties. Numerous experimental and theoretical investigations have been devoted to ordered alloys of early transition metals (TMs) with late TMs. Such materials are known also as alloys or intermetallic compounds with split d bands. Their surface properties have been studied less frequently. Significant experiments have been done mainly for Pt₃Ti(111) [1–6] with an fcc-like Cu₃Au (Ll₂) structure. Theoretical studies are scarce [7, 8].

Invaluable information on bimetallic systems is provided by core-level shifts (CLSs). In alloys with split d bands considerable positive CLSs (shifts to higher binding energies) are common [9, 10] for both constituting atoms. For Pt₃Ti the experimental bulk CLS values for the Pt(4f₇/₂) and Ti(2p₃/₂) core levels are 0.4–0.6 eV and 1.3 eV, respectively; at the (111) surface the Pt CLSs are lower by 0.4–0.5 eV but no different value is resolved for Ti [2, 6]. Adsorption of CO induces an additional positive contribution to the surface platinum CLS (0.6 eV) [2] which is smaller than for Pt(111) (1.3 eV) [11].

For CO chemisorbed at Pt₃Ti(111) [1, 3, 4] the intensity of the thermodesorption signal is halved and the binding energy is smaller by about 0.2 eV per molecule as compared with Pt(111). In [1] a feature in thermodesorption spectra has been ascribed to the predissociated

CO at a surface Ti atom [1, 7]—one of the arguments corroborating the ideal surface termination. Experiments by other authors support the Pt surface overlayer [3, 6]. Also the recent tensor LEED analysis [5] points strongly to the fully segregated epitaxial Pt(111) overlayer with negligible rumpling due to the two nonequivalent surface sites. The ideal stoichiometry in subsequent layers gives the best R-factor value although an enrichment of the subsurface layer by Ti cannot be ruled out.

A few years ago we completed tight-binding calculations [8] for the bulk and ideal-surface electronic structure of Ti alloys including Pt_3Ti. The CLS values were evaluated in a simplified initial-state approximation and agreed well with the available data. Recently, we have generalized [12] the semiempirical model of [13] to describe CO chemisorption. It is the aim of the present paper to apply these models to $Pt_3Ti(111)$, with both ideal and Pt-segregated surface structure, and to CO adsorption on it.

## 2. Model

We use a tight-binding self-consistent s, d-electron model. To obtain the local electronic density of states (LDOS) the recursion method is employed. Since details of the approach are described in [14] for metallic systems without adsorbate and in [12] for CO chemisorption, respectively, we give only brief information here.

For (bi)metallic crystals the hopping matrix elements of the electronic Hamiltonian are based on the literature LMTO band-structure calculations whereas the Coulomb integrals (diagonal matrix elements) follow from a self-consistent procedure yielding the prescribed charge distribution. The model is not sensitive to the assumptions concerning the s electrons but their inclusion improves the description of low-density LDOS tails (see below) which appear near the Fermi level E_F for late-TM atoms such as Pt. (Throughout the paper, only the d-electron LDOS is considered.) Particularly, we suppose identical d-electron occupation as in the bulk of the corresponding elemental crystal. For Pt_3Ti alloy a Ti→Pt charge transfer of mainly s, p electrons is reported in [6] and we accept this value for s electrons. However, we introduce no charge transfer at the Pt overlayer on $Pt_3Ti(111)$ since the surface atoms have no or only one Ti neighbour. Besides that, we omit the negligible surface rumpling suggested by experiment [5].

It is supposed that the CO adsorption at TM surfaces can be rationalized in terms of the CO 5σ and $2\pi^*$ orbitals. This idea has been employed in the simple 'classical' molecular-orbital models [13, 15, 16]. The recent first-principles studies [17, 18] support it; note that especially the role of the $2\pi^*$ orbitals is stressed (see also [19, 33]). Other molecular states of CO are not relevant until a kind of predissociation takes place which might cause the orbital rehybridization. Hence we represent CO merely by 5σ and $2\pi^*$ orbitals. These orbitals are decomposed into atomic ones and the carbon–metal hopping elements are fitted by literature values. To allow some ionicity we use a Hubbard-like method in which the molecular (atomic) Coulomb integrals of CO and its first and second substrate nearest neighbours, respectively, are changed. The self-consistent correction is proportional to the local charge. Since the results can violate slightly the global charge neutrality, special measures are to be taken in which our model [12] differs from that of [13]. Namely, Andreoni and Varma [13] introduce an *ad hoc* intraatomic Coulomb term to ensure the system global charge neutrality. This strategy leads sometimes to unreasonably large ionicity especially for dense (1×1) adsorbate overlayers [33]. Instead of this, we believe that the above charge-transfer values that can violate the charge conservation reflect nevertheless the true ability of particular atoms to participate in the charge transfer. For this reason we redistribute the charge that is necessary to restore the system charge neutrality among particular atoms proportionally

to these charge-transfer values. Generally, a major problem in semiempirical models is self-consistency formalism yielding the values of Coulomb integrals. In systems with only TM atoms, all models keeping the d-electron occupation near the bulk value give similar results. In the presence of adsorbate the situation is more involved. As we have discussed previously, there are fortunately not many parameters to which the results are sensitive [12]. The condition that the model does not predict highly unreasonable results (position of the 5σ feature, value of $2\pi^*$ backdonation) for a test system (CO on Pd or Pt(111)) helps to avoid an erroneous choice and suppresses the uncertainty. We note that the self-consistency procedure we have sketched leads to a considerable stability of the calculated results with respect to the input Coulomb integrals.
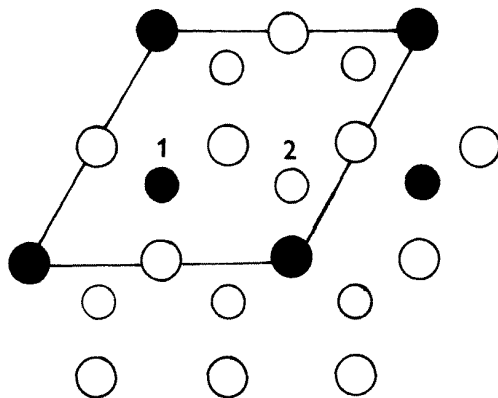
Figure 1. The geometry of the hexagonal (111) surface and subsurface (smaller circles) layer of Pt₃Ti(111) with the elementary cell are shown. The P and T sites are represented by empty and filled circles, respectively. The nonequivalent bridges PP₁, PP₂ are distinguished by numbers 1 and 2. See text for details.

At Pt(111) CO chemisorbs upright by its carbon end, initially in the atop position and as the coverage grows also in the bridge geometry. We consider these sites also for the alloy surface with the same carbon–platinum distance as at Pt(111). At the ideally terminated (111) surface there are (figure 1) Pt and Ti atoms with the bulk stoichiometry 3:1 referred to below as P and T sites, respectively. The same notation, P and T, is used for Pt atoms at corresponding sites in the Pt overlayer. For CO at bridge geometry one can envisage the bridge formed by PT or PP substrate dimers. Actually, there are two non-equivalent surface PP dimers that we denote as PP₁ and PP₂, respectively. In the former case the two Pt atoms have a common subsurface Ti neighbour (figure 1) whereas each Pt atom in PP₂ interacts with a distinct subsurface Ti atom. The two PP dimers occur at the surface with the same frequency. There is little doubt [7, 13] that the interaction of CO with a Ti atom—if the latter are really present at the surface—is much stronger than that at pure Pt sites. Since the CO molecule would be probably strongly perturbed at such sites, and we have no reference data on undissociated CO at pure Ti, we do not consider the chemisorption at T and PT sites for the ideal Pt₃Ti(111) termination.

To calculate CLSs we start from the initial-state approximation [10]. Although the model is not rigorous it is known to provide, as a rule, semiquantitatively or even quantitatively correct results in metallic systems. The problem has been studied thoroughly mainly for TM surfaces [20, 21] but calculations for more complicated TM systems also exist, see e.g. [22, 23]. The transition-state concept is well justified [24] to evaluate CLSs. It gives

values half-way between the initial-state and $Z + 1$ (equivalent-core) approximations. The two above approximations arrive at identical results within a simplified model [23] and the approximate validity of this rule has been checked for a number of TM systems, see, e.g., [24]. For elemental TM surfaces the final-state effects at the surface and in the bulk, differ usually by less than ∼0.2 eV [20]. The first-principles LMTO analysis for Mo(001) and Pd(001) shows that within a similar accuracy (∼0.02 Ryd), the CLS, the shift of the LDOS centre of gravity, and the potential in the centre and on the surface of the muffin-tin sphere, respectively, are equal [21]. In tight-binding models the LDOS centre-of-gravity shift is exactly equal to the change of the local Coulomb integral and one recovers the assumption [23] that the core electrons are subject to similar electrostatic potential changes as the d electrons. Hence, we identify the CLS (up to the change of sign) with the Coulomb integral shift we calculate.

Let us briefly explain on the basis of our model [8, 14] why in bimetallic systems positive CLSs can appear for both constituent atoms. There is a correspondence between the local charge distribution and value of the Coulomb integral. An important point is to realize that, with Coulomb integrals adjusted at the same value with respect to E_F as in the elemental crystal, a charge deficit on both types of atom can appear: the charge flows from the more electropositive atoms to the more electronegative ones as expected. However, simultaneously a low-density tail is formed in the LDOS of the late-TM component above E_F due to hybridization with electronic states in the early-TM d band that is situated higher in energy. Into this tail some charge tends to be displaced. Since the correct charge distribution maintains the global charge neutrality and avoids exaggerated ionicity, the potential on both kinds of atom must be more attractive, inducing thus positive CLSs. It is observed experimentally that for many atomic and simple molecular adsorbates of very different electronegativity the chemisorption-induced contribution to the substrate CLS is positive as well. Our previous calculations [12, 25] offer a picture analogous to that just described. An unoccupied or partly occupied antibonding feature in the LDOS is formed due to the adsorbate–substrate interaction. If the Coulomb potential (or the LDOS centre of gravity) were kept at the clean-surface value, too much of the d-electron states would fill this new empty feature, leading thus to an unphysically large depletion of d states. In other words, the substrate potential must be again more attractive. Previously, the CLS trends at TM surfaces have been explained by supposing that the change of the Coulomb potential compensates the surface 'band-narrowing' effect [10, 23, 21]. The formation of the low-density LDOS tail or of antibonding states can be viewed as an asymmetric 'band widening' at the low-binding-energy side with consequences opposite to the band narrowing [8, 12, 14]. At surface sites, the band widening due to the hybridization and the band narrowing due to the lower atom coordination compete mutually.

3. Results and discussion

For the bulk and the ideal (111) surface of the alloy the results are quite similar to those we obtained in [8]. For the platinum LDOS the small peak found previously (figure 4 of [8]) at E_F drops slightly down, thus now placing the Fermi level in an LDOS dip in agreement with other calculations [6, 26]. We again find an upward shift of LDOS near E_F for surface Pt atoms indicating the presence of a surface state which represents, however, a rather weak feature. For the Pt overlayer on the alloy (111) surface the LDOS is a bit unusual. There is a large peak with the centre about 1 eV below E_F (figure 2) at the T site which might suggest an enhanced reactivity of Pt atoms at the T site. It would be interesting to clarify a possible relation of this feature to a photoemission peak close to E_F at off-normal angles
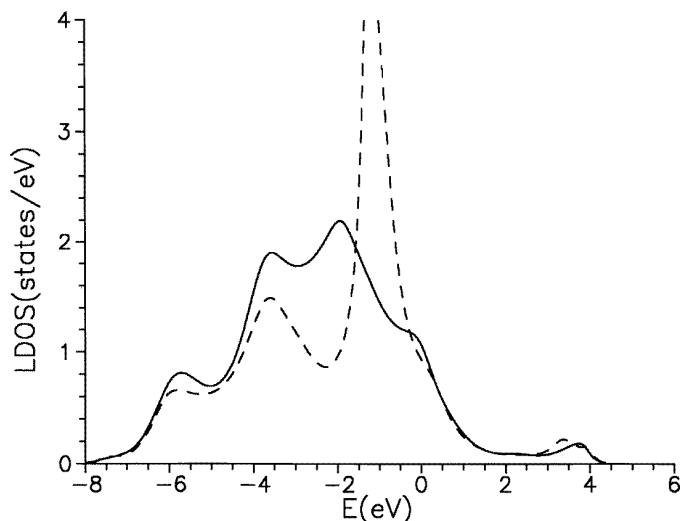
Figure 2. Local density of electronic states for the epitaxial Pt overlayer on the Pt₃Ti(111) surface. The full (dashed) line corresponds to states at the P (T) site; see text for definition.

Table 1. Core-level shifts calculated in the initial-state picture. The values are given with respect to the bulk of elemental Pt or Ti crystal, respectively. The experimental values (Expt. CLS) are also shown. The subscript *s* (*b*) stands for a surface (bulk) atom. P denotes a platinum atom, T a titanium atom or a platinum atom at the Ti site for the Pt overlayer on Pt₃Ti(111). CLSs on subsurface atoms are close to bulk values with the exception of the second-layer Pt atoms in the Pt/Pt₃Ti(111) system with CLS equal to 0.4 eV.

System	Atom	CLS (eV)	Expt. CLS (eV)
Pt(111)	P_b	0.0[a]	0.0
	P_s	−0.4	−0.4 [11]
Pt₃Ti(111)	P_b	0.5	0.6 [2], 0.4 [6]
	T_b	1.4	1.3 [2, 6]
	P_s	0.0	0.1 [2], 0.0 [6]
	T_s	1.4	[b] [2, 6]
Pt/Pt₃Ti(111)	P_s	−0.2	0.1 [2], 0.0 [6]
	T_s	−0.6	0.1 [2], 0.0 [6]

[a] Reference level.

[b] No specific surface peak found.

found in [2].

The calculated CLSs we gather in table 1 are to be compared with experimental values. For Pt₃Ti bulk there is a fair agreement. The shift of surface Pt core levels to lower binding energies as compared to the bulk can be explained by the band-narrowing mechanism. There is a reasonable accord with measurement for the ideal surface model as well as for P sites at the Pt overlayer. For the latter structure, however, a distinct value is predicted for Pt atoms at T sites.

Consider now the CO adsorption. The results are reproduced in table 2. We shall spare the reader from a parade of LDOS figures since they mostly resemble the published results [12] for CO on Pd (111): a considerable amount of LDOS at metal atoms in direct contact

Table 2. Results of calculation for an isolated CO molecule at Pt(111) [12], Pt$_3$Ti(111) surface terminated ideally and the same surface with a Pt overlayer. The adsorption at atop or bridge position, respectively, is specified by showing the nearest platinum neighbours of CO (P or T, see the text; the atoms on the Pt(111) surface are denoted as P). $-\epsilon_\sigma$ is the position of the 5σ feature below E_F, ΔN_σ (ΔN_π) is the change of the 5σ ($2\pi^*$) occupation, ΔE_a is the change of the chemisorption energy as compared to the analogous adsorption site at Pt(111), and ΔCLS is the additional core-level shift induced by the chemisorption at the CO nearest-neighbour atoms.

For the convenience of the reader we gather here also the known experimental data: $-\epsilon_\sigma \sim 9$ eV both for Pt(111) and the alloy (111) face [2], $\Delta E_a \sim -0.2$ eV for the alloy [1, 4], ΔCLS $= 1.3$ eV for Pt(111) [11] and 0.6 for the alloy [2].

System	Site	$-\epsilon_\sigma$ (eV)	ΔN_σ (eV)	ΔN_π (eV)	ΔE_a (eV)	ΔCLS (eV)
Pt(111)	P	9.1	−0.21	0.49	0.0	1.2
	PP	8.0	−0.14	0.37	0.0	0.2
Pt$_3$Ti(111)	P	9.3	−0.13	0.35	−0.3	0.7
	PP$_1$	8.1	−0.09	0.36	0.0	0.2
	PP$_2$	7.9	−0.10	0.28	−0.2	0.2
Pt/Pt$_3$Ti(111)	P	9.2	−0.15	0.38	−0.2	0.7
	T	9.2	−0.17	0.45	0.0	1.1
	PP$_1$	7.9	−0.12	0.35	0.0	0.3
	PP$_2$	8.0	−0.11	0.28	−0.1	0.1
	PT	8.0	−0.09	0.32	−0.1	0.2[a]

[a] ΔCLS on P and T sites are almost the same.

with the adsorbate is transferred from the E_F vicinity to the lower part of the d bands, the effect being more pronounced for the atop chemisorption. An exception is represented by the Pt atom at the T site at Pt/Pt$_3$Ti(111). The prominent peak below E_F described above is reduced but represents still a dominating feature for CO in the atop position.

Photoemission spectra of CO on Pt$_3$Ti(111) [1] show a 5σ feature 9 eV below E_F that conforms to our result for atop adsorption. Let us turn to additional CLS induced by the adsorption. Similarly as in [12] we get values a good deal higher for the less coordinated atop site. Our result for the atop position on Pt(111) is very close to the experimental one [11]. The reduced additional CLS and adsorption energy observed experimentally [1, 4] for the alloy agree with our results for atop adsorption at Pt atoms at the ideal surface as well as at the P site at the Pt overlayer. At the Pt overlayer, however, the T site is somewhat more reactive, with a large CLS which is not reported in the experiment. On the other hand, we find that for the PP$_1$ bridge position the chemisorption energy is almost the same in both the surface models as for the twofold site at Pt(111). One should clarify whether this fact does not contradict the thermodesorption experiment [1, 3]. Since interpretation of the measurement is not unambiguous and some surface sites can be blocked [3] it is difficult to comment upon this question. Our analysis that is done for isolated admolecules might be modified for higher coverage and even for the Pt(111) surface the coverage dependence of CO chemisorption is perhaps not well understood [27]. Another suggestion will be given later.

It has been shown [28, 29] on extensive experimental material mainly for CO chemisorption at late-TM films deposited on electropositive substrates that the overlayer atoms with more positive (less negative) CLSs are less reactive. The correlation takes place also for other systems [30, 31] and one might expect it to work also for Pt$_3$Ti. Let us give non-rigorous but simple arguments elucidating the trend.

In the above bimetallic systems photoemission spectra indicate for the late-TM

component an apparent shift of the occupied LDOS to higher binding energies as compared with the elemental metal. This shift is usually larger than the positive CLS value which, in our picture, is associated with the centre of gravity of the full (occupied and empty) LDOS. The difference comes from the (mainly) unoccupied states that move into the higher-energy region of the electropositive TM d band (cf the low-density LDOS tail discussed in section 2). The effect for the occupied part of the LDOS comes mainly from the hybridization and repulsion between the d bands of the two kinds of atom, in analogy to level repulsion in the elementary quantum mechanics of two-level systems. Of course, the change of the local Coulomb potential contributes as well. Intuitively, the magnitudes of both CLS and LDOS changes reflect the intensity of the hybridization and they should correlate. This is, as a rule, confirmed by experiments [28] and theory [14, 22]. Now, one can try to rationalize [12] the reactivity trend by common quantum-chemical HOMO–LUMO (highest occupied–lowest unoccupied molecular orbital) arguments. Since the proper LUMO orbitals are the CO($2\pi^*$) pair one must supply an *occupied* metal orbital. We have just seen, however, that the occupied part of the LDOS drops down (away from E_F) in energy which renders its interaction with the LUMO orbitals less effective. According to the arguments from the previous section, the variation of the $2\pi^*$ backdonation should be another quantity reflecting the variation of the chemisorption energy. Let us glance at tables 1 and 2. The above correlations are partly valid although not completely reliable. For example, for the atop site the relation between ΔE_a, CLS before the chemisorption and ΔN_π holds true. On the other hand we fail to explain the difference in chemisorption energy between the bridge sites PP$_1$ and PP$_2$ and at variance with our results it predicts the T site at Pt/Pt₃Ti(111) to be more reactive than Pt atoms at the Pt(111) face. The former example also shows that a simple counting of Pt–Pt and Pt–Ti bonds does not give an answer on the local reactivity. The main reason for the imperfect correspondence between quantities we compare is probably that for the Pt₃Ti(111) system the differences are often too small to be explained by simple rules. In such a situation the 'input' properties of the clean surface can be too crude to predict the chemisorption results accurately [12, 32]. Also the rather complicated geometry (steric factors) has not been considered in the heuristic frontier-orbital reasoning.

It follows from the previous discussion that our model for both the ideally terminated surface and the Pt overlayer agrees approximately with most of the experimental observations. The only exception is the Pt atom at the Ti-like site in the Pt overlayer for which we find a specific CLS value and somewhat higher reactivity. Since the modern LEED techniques provide reliable results especially for the first surface layer our predictions call for an explanation. One can suggest that the signal from minority surface T sites (25%) has not been resolved. The speculation is reinforced by the argument that a surface contamination would affect primarily the T sites. However, there is another possibility that seems to be logical. Namely, the LEED experiment [5] does not exclude enrichment of the subsurface layer by titanium. It is obvious from the preceding that the result would be a downward shift of surface core levels accompanied by a drop in surface reactivity. Note that any Ti→Pt substitution in the subsurface layer brings about a Ti neighbour to the surface Pt at the T site (figure 1).

To summarize, we present results of tight-binding calculation of the electronic structure of the Pt₃Ti(111) surface and CO chemisorption on it. If the most likely model of the pure Pt surface is adopted the results agree only partly with the experimental data. However, the agreement is undoubtedly better if enrichment of the subsurface layer by Ti is supposed. We believe that the problem is rather interesting and deserves further investigation.

Acknowledgment

Note added in proof. New calculations of the Pt_3Ti bulk electronic structure have recently been published (Chen W, Chulkov E and Paul J 1996 *Phys. Scr.* **54** 392).

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