DFT study of adsorption of hydrogen and carbon monoxide on Pt$_x$Bi$_{1-x}$/Pt(111) bimetallic overlayers: correlation to surface electronic properties

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Analysis of the electronic properties of Pt$_x$Bi$_{1-x}$/Pt(111) bimetallic overlayers was performed by DFT calculation. The positions of the d-band centers and band widths were correlated using a triangular band model. In addition, the adsorption of hydrogen atoms as well as CO tolerance of selected Pt$_x$Bi$_{1-x}$/Pt(111) bimetallic overlayers were analysed. Excellent correlation was obtained of the adsorption energies of H and CO with d-band centers of platinum atoms on the studied surfaces. The red shift of Pt–H stretching vibration of adsorbed hydrogen, and decrease of work function upon adsorption of H were predicted. Analysis of hydrogen and CO chemisorption by means of the difference of the projected density of states was performed in order to identify d-states involved in bonding. The results obtained by calculations were compared with the experimental ones, where available.

1. Introduction

In order to reduce the consumption of platinum in catalysts and electrocatalysts (in electrolysers, fuel cells *etc.*) various platinum alloys have been investigated, both experimentally and theoretically.[1–7] One can divide these alloys into two groups: platinum alloyed with transition metals and platinum alloyed with elements located in the p block of the Periodic Table of Elements (PTE). It is important to note that the first group has been studied much more extensively than the second one, both experimentally and theoretically. As a nice illustration of this statement, one can mention either the review by Stamenkovic *et al.*[1–3] or the computational high-throughput study performed by Greely *et al.*[4] In the mentioned studies the authors combined experimental and theoretical methods in order to understand and improve the activity of electrocatalysts.

From the point of view of electrocatalysis, two platinum bimetallic systems, Pt–Bi[4] and Pt–Sn,[5] are of particular interest. Two most commonly reported forms of Pt–Bi catalysts are bulk intermetallic PtBi and PtBi$_2$ and irreversibly adsorbed bismuth, usually designated as Bi$_{ir}$–Pt. These systems were studied as catalysts in many electrochemical reactions and a detailed review can be found in the work of Markovic and Ross.[6] It is interesting to mention that Bi$_{ir}$–Pt displays significantly reduced activity for hydrogen evolution reaction (HER) compared with pure platinum surface.[7] It is also important to mention that pure Bi is an extremely poor electrocatalyst for HER. On the other hand, by means of computational high-throughput screening, Greely *et al.*[4] predicted that Pt$_3$Bi/Pt(111) and Pt$_2$Bi/Pt(111) bimetallic overlayers show enhanced activity for HER compared to pure

platinum. This was indeed proven experimentally by careful electrochemical synthesis of Pt–Bi bimetallic overlayer with nominal composition Pt$_{1.00}$Bi$_{0.95}$ and examination of its electrochemical properties.

During theoretical investigation of alloys, several parameters have been recognized as important from the point of view of surface characterization and catalysis. The modification of electronic and chemical properties induced by alloying of platinum was found to be a function of various variables. One of them is the density of states at the Fermi energy (ρ_F) of surface atoms and it was correlated with the adsorption energy of simple adsorbates. Hammer and Nørskov[8] have shown that the value of PDOS at single energy cannot represent the entire d-band. They pointed to an application of the mean energy of the d-band, commonly denoted as the d-band center (E_{d-band}). A number of studies published later confirmed the so-called d-band model that predicts the correlation of E_{ads} and E_{d-band}. The d-band centers were found to depend on both strain and ligand effects. Ruban *et al.*[9] concluded that compressive and tensile strains lead to downshift and upshift, respectively, of the d-band center. The ligand effect was analysed by Kitchin *et al.*,[10] by a triangular d-band model. By a simple assumption of the triangular shape of the band, they correlated the d-band center and the mean-squared band width (RMS^2), calculated as the second moment of the band:

$$\text{RMS}^2 = \frac{1}{3}\left(\frac{1}{0.5 - f_d}E_{d-band}\right)^2(1 - 3f_d + 3f_d^2) \qquad (1)$$

where f_d is fractional filling (presumed to be constant) of the d-band. This rather simple model was found to hold for the d-bands of the surface platinum atoms with one subsurface layer composed of 3d elements. From the DOS profiles presented in the mentioned paper[10] it follows that d-bands of surface Pt atoms are rather symmetrical and spanning over a relatively narrow energy window, approximately 7 eV in

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width. An Explanation for observed behavior was found in the interatomic matrix element which describes bonding interactions between d-orbitals of both platinum and subsurface 3d metals. This theory was elaborated by the same authors for a large number of d-metal systems showing that interactions between d-orbitals of various metals give rise to observed changes in the d-band center and d-band width.[11]

In this paper, using DFT calculations, we analysed the effects of alloying of the platinum surface with p element bismuth, in order to investigate the electronic and chemisorption properties of such type of surfaces. First of all, the study of the electronic properties of ordered $Pt_xBi_{1-x}/Pt(111)$ bimetallic overlayers was carried out, focused on the analysis of d-band shape and basic characteristics. Furthermore, detailed analysis of H adsorption on ordered $Pt_3Bi/Pt(111)$ and $Pt_2Bi/Pt(111)$ bimetallic overlayers as well as on pure Pt(111) was carried out. After that, the tolerance of the same surfaces towards poisoning by CO was analysed. These results were compared with the experimental ones, if available in the literature.

2. Calculation methods

DFT calculations were performed using PWscf code which is a part of the Quantum ESPRESSO package for *ab initio* calculations.[12] The Perdew–Burke–Ernzerhof (PBE) functional within general gradient approximation (GGA) was used.[13] Ultrasoft pseudopotentials (USPP) were generated through the Vanderbilt scheme.[14] For platinum, USPP was generated with 10 valence electrons in $5d^96s^16p^0$ configuration. For the Bi configuration that we used it was $6s^26p^35d^{10}5f^0$ with 15 valent electrons. As a smearing scheme Marzari–Vanderbilt smearing[15] was used with broadening of 0.5 eV. Kinetic energy cutoff was 272 eV (charge density cutoff was 10 times higher) and for Brillouin-zone integration Monkhorst–Pack set of 9 special k-points was used.[16] Convergence with respect to cutoff energies and the number of k-points was used as criteria for the correctness of the procedure. The Pt(111) surface and ordered Pt(111) bimetallic overlayers were constructed using a supercell with a thin metal (alloy) slab separated from its periodic images by a layer of vacuum. In all cases seven-layer slabs and 20 Å thick vacuum layer separating the surfaces, were used. This was found to provide convergence of the total energy and work function toward stationary values. We used one layer for all $Pt_xBi_{1-x}/Pt(111)$ bimetallic overlayers which were set on both sides of the slab in order to prevent electronic coupling of the slabs. For (111) surfaces a hexagonal cell with an interlayer spacing of $a_0/\sqrt{3}$ and an ABCABC stacking was used, where a_0 is the platinum equilibrium lattice parameter. For the composition of bimetallic overlayers corresponding to $x = 0.75$ and $x = 0.5$, (2×2) unit cell was used, while for all the other compositions $(\sqrt{3} \times \sqrt{3})R\text{-}30°$ unit cell was used. As a platinum equilibrium lattice parameter we used the value of 4.01 Å obtained by structural optimization of the platinum bulk. In all calculations, ideal bulk truncated positions were considered in order to capture the electronic factors arising from alloying the surface and adsorption. This was justified by previous test calculations on selected surfaces that revealed small buckling of the solute atoms, followed by modest stabilization of the d-band. In addition, by relaxation of the first substrate layer it was found that E_{ads} is changed by less than 0.05 eV. For the purpose of structural relaxation of adsorbate we used the Broyden–Fletcher–Goldfarb–Shanno method.[17] Geometrical optimizations have been preformed until all force components on the adsorbate atoms were below 0.05 eV Å^{-1}.

For the work function calculations we employed two different methods. The first one is based on definition of work function and it uses following equation:

$$W = V(+\infty) - E_F \tag{2}$$

where $V(+\infty)$ is the electrostatic potential in the middle of the vacuum region, and E_F denotes the Fermi energy of the slab. We also applied a method based on the macroscopic average[18] by which the work function is calculated as:

$$W = \Delta V + V_{bulk} - E_{F,bulk} \tag{3}$$

where ΔV, V_{bulk} and $E_{F,bulk}$ are potential steps across the surface, the mean electrostatic potential in the bulk and the Fermi energy of the bulk metal, respectively. The last two quantities are obtained in separate calculations on clean platinum bulk. The d-band density of states was determined by projection of the plane waves onto spherical harmonic orbitals. Additional test performed on selected surfaces, revealed that the increase of kinetic energy cutoff up to 476 eV gives values of adsorption energy within 0.05 eV around the ones calculated with a lower kinetic energy cutoff.

3. Results and discussion

3.1 Electronic properties

Using the proposed models of surface overlayers for the sake of computing, we disregarded the question of their actual stability. In fact, it is likely that M atoms may diffuse inside the surface layers of Pt(111), Pt atoms may segregate on the surface, islands or clusters could be formed on top of the surface, the Pt_xM_{1-x} overlayer may become rumpling or even reconstructed, and these phenomena may affect the position and the width of the d-band of $Pt_xBi_{1-x}/Pt(111)$. Thus far, only Greeley *et al.*[4] considered these topics, in part. Namely, by computing methods, they identified $Pt_3Bi/Pt(111)$ and $Pt_2Bi/Pt(111)$ overlayers as possible electrocatalysts for HER, and predicted their stability against the segregation events, intrasurface transformations and surface de-alloying. The stability of the considered overlayers at the compositions out of the above mentioned ones remains a matter of future considerations.

The results for d-band centers, band widths (root mean square (RMS), calculated as the second moment of the band), and densities of states at Fermi energy (ρ_F) are listed in Table 1. As one can easily see, d-bands of platinum atoms are stabilized with an increased amount of solute element in the surface layer. This stabilization indicates that Pt atoms bind more efficiently to the solute Bi atoms than to the other Pt atoms. Based on the observed d-band stabilization, one can conclude that Pt atoms in studied bimetallic overlayers have increased effective coordination, compared to pure platinum surface. Increased stabilization of the band leads to the
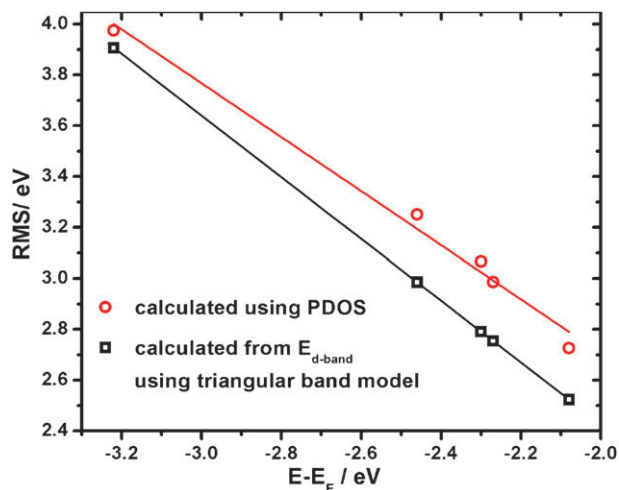
Table 1 Obtained values of d-band centers (E_{d-band}), band widths (mean squared band width calculated as the second moment of the band) and the densities of states at Fermi energy (ρ_F) for surface Pt atoms in the studied pseudomorphic bimetallic overlayers with different composition

Bimetallic overlayer	E_{d-band}[19]/eV	Mean squared band width/eV^2	ρ_F/a.u.
Pt	−2.08	7.43	1.622
Pt$_3$Bi	−2.27	8.91	1.013
Pt$_2$Bi	−2.30	9.40	0.934
PtBi	−2.46	10.57	0.725
PtBi$_2$	−3.22	15.80	0.347

conclusion that the chemical reactivity of the surface is going to be reduced, resulting in lowered adsorption energies. In addition, the observed downshift of the d-band center is in good agreement with the model proposed by Ruban *et al.*[9] which analyses the effects of strain on the position of the d-band center.

The other important parameter is the width of the d-bands, for which, compared to E_{d-band}, much less literature reports exist. If one assumes that d-band filling keeps unchanged after bimetallic overlayer formation, the shift of the d-band center can be easily related to the band width. Namely, in order to conserve d-band occupancy, the band must become narrower in energy when the d-band center is shifted-up. For the same reason, the band becomes broader in energy when the center is shifted down. This was illustrated by Kitchin *et al.*[10] for the case of modification of the electronic properties of platinum with 3d atoms subsurface. Fig. 1 presents the comparative plots of band widths calculated either from PDOS of surface Pt atoms, or from the triangular band model using eqn (1), *versus* the d-band center.
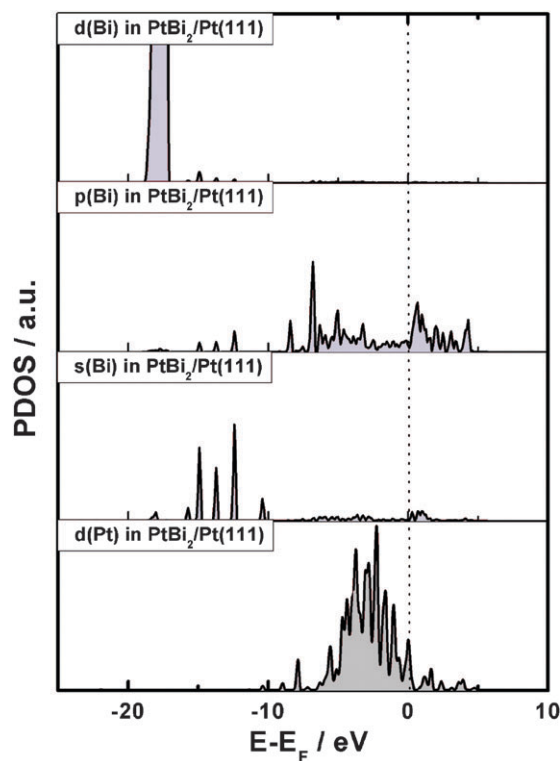
These plots demonstrate a linear relationship between E_{d-band} and RMS. The obtained slope amounts to −1.06 ± 0.07, which is rather similar to that obtained for the triangular band model for fractional d-band filling $f_d = 0.92$ (amounting to −1.21). Although the values of RMS are systematically higher than the ones predicted by the model, the linear fit of calculated RMS was performed on a high confidence level ($P < 0.0001$). One should keep in mind that the value used for

fractional filling is the average one obtained by integration of all PDOS's of the studied alloys from the lowest available energy (in theory, from −∞) to the Fermi energy (in practice, this is equal to zero). The obtained slope is quite close to the one obtained by Kitchin *et al.*[11] In addition, we also obtained a nonzero intercept that can be considered as an artifact of Gaussian broadening used in the projection of the density of states onto atomic orbitals to account for the finite number of k points.[11] In addition, this can also be considered as the reason why the values calculated from PDOS are systematically higher than the ones predicted by the model. One can see that the triangular band model holds for platinum alloyed with sp metals, although the interaction of Pt with the solute elements occurs through the d–p hybridization[20] (Fig. 2).

In addition, the calculated ρ_F values decrease when d-band centers shift down, which agrees with the qualitative picture afforded by the triangular band model. However, previously

Fig. 1 Comparison of the d-band widths calculated from PDOS (circles) and triangular band model (fractional filling $f_d = 0.92$ (eqn (1)), squares) *versus* the d-band centre. Solid lines are the results of a linear fit.

Fig. 2 PDOS calculated for PtBi$_2$/Pt(111) bimetallic overlayer. The d states of Bi are strongly bonded and localized, having practically no contribution in bonding. On the other hand, the s and p states of Bi atoms are highly delocalized and interact with the d-states of the platinum atoms.

published studies[10] demonstrated that ρ_F may not represent satisfactorily the chemical activity of the surface, due to the fact that, unlike d-band center, it depends sensitively on the states located around the Fermi energy.

In the introductory section we outlined the literature data where PDOS of platinum atoms adjacent to the transition metal layer are rather symmetrical and narrow in energy, due to the d–d interaction in these systems.[10] From Fig. 2 it follows that there are some high bonded states originating from the sp–d interaction. We tried to estimate the contribution of these low lying states in overall d-PDOS using the skewness coefficient, γ, defined as:[21]

$$\gamma = \frac{\mu_3}{\mu_2^{\frac{3}{2}}} \qquad (4)$$

where μ_2 and μ_3 are the second and the third central moments of the band ($\mu_2 = \sigma^2$). This quantity is commonly used in mathematical statistics in order to measure the asymmetry of density distribution. The more symmetrical the distribution, the closer to zero is the value of the skewness coefficient. The results are depicted in Fig. 3.

One can see that PDOS of Pt atoms in Pt–Bi bimetallic overlayers has a much higher skewness coefficient in comparison to pure platinum. In addition, the skewness coefficient decreases in an approximately linear manner if the mole fraction of the solute in the surface layer increases. The decrease of γ most probably correlates with the density of s and p states that increase together with the increase in the mole fraction of solutes in the surface layer.

3.2 Adsorption of H atoms on Pt_xBi_{1-x} bimetallic overlayers

In this section, we describe the results of DFT energy calculations of hydrogen dissociative adsorption on both a clean Pt(111) surface and two selected bimetallic overlayers, Pt_2Bi/Pt(111) and $PtBi_2$/Pt(111). The only one coverage degree

Fig. 3 Asymmetry of Pt d-band in Pt–Bi bimetallic overlayers measured through the skewness coefficient. Graphics regarding the ordering of the surface bimetallic layers are also inserted. For the three-dimensional presentation please refer to Fig. 2 in the work of Greeley et al.[4]

of adsorbed hydrogen is preferred, in order to avoid the consideration of the adsorbate–adsorbate interactions with the variation of coverage.

For the purpose of calculation, hydrogen was adsorbed on both sides of the 7-layer slab. Adsorption was studied in the atop adsorption site which is, according to Ford et al.,[22] the preferential site for hydrogen adsorption on Pt(111). In addition, no multi-coordinated hydrogen was detected spectroscopically in electrochemical conditions.[23] In addition to hydrogen adsorption, the atop site was found experimentally to be preferential for CO adsorption on Pt(111) surface (see section 3.3). Other adsorption sites were not analysed, as we wanted to compare the effects of modification of the electronic structure of the substrate on equivalent sites on all of the three studied surfaces. The Pt_2Bi/Pt(111) surface does not possess Pt3-fcc and hcp hollow sites, while $PtBi_2$/Pt(111) does not possess Pt2-bridge sites). The adsorption energy (E_{ads}) was calculated using the following equation:
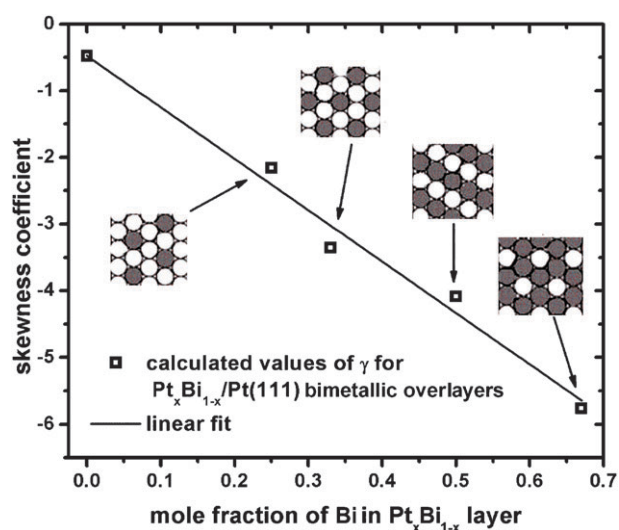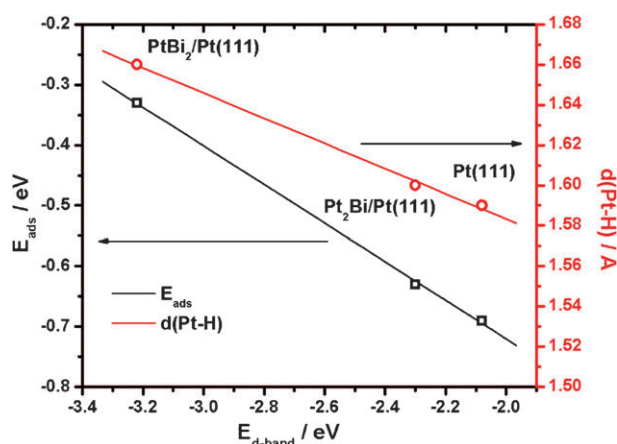
$$E_{ads} = \tfrac{1}{2}(E_{slab+2H} - (E_{slab} + E_{H_2})) \qquad (5)$$

where $E_{slab+2H}$, E_{slab} and E_{H_2} are the total energy of the slab with two hydrogen atoms adsorbed, the total energy of the Pt slab and the total energy of the isolated hydrogen molecule, respectively. Table 2 shows the calculated values of adsorption energies, lengths of Pt–H bonds and the wavenumbers of H–Pt stretching vibrations. The last quantity was calculated using harmonic approximation, fitting distance–energy curve with a second order polynomial function.

For pure Pt(111), the calculated value of the adsorption energy of H agrees well with both the experimental and calculated values published elsewhere.[6,22–24] In addition, calculated wavenumbers of stretching vibration of H adsorbed on Pt(111) as well as the Pt–H distances agree well with the ones given by Ford et al.[22] (amounting to 2223 cm^{-1} and 1.57 angstroms, respectively).

Let us comment on the adsorption trends in the studied alloys. One can see that the adsorption energy decreases linearly with the d-band center, as presented in Fig. 4. This is in excellent agreement with the d-band model given by Hammer and Nørskov.[8] The decrease of adsorption energy is accompanied by both red shift of Pt–H stretching vibration and increase of Pt–H bond length.

Now let us comment on the change in electronic properties of the bonding platinum atoms caused by chemisorption of hydrogen. Table 3 shows Löwdin charges of adsorbed H atoms, calculated work functions and d-band centers of Pt atoms after adsorption of H.

Upon hydrogen adsorption, work functions go down uniformly for each of the studied surfaces (Fig. 5). For the sake of comparison, Lewis and Gomer reported that they measured the drop in work function of Pt(111) after

Table 2 Adsorption energies, equilibrium bond lengths and wavenumbers of H–Pt stretching vibrations

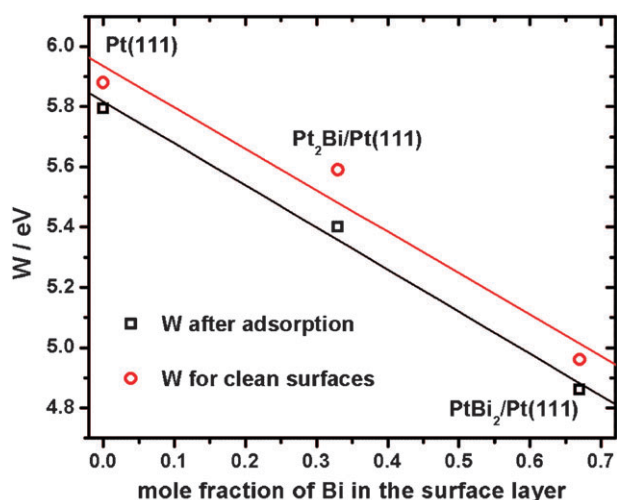| System	E_{d-band}/eV	E_{ads}/eV	v/cm^{-1}	d(Pt–H)/Å
Pt(111)	−2.08	−0.69	2160	1.59
Pt_2Bi/Pt(111)	−2.30	−0.63	2145	1.60
$PtBi_2$/Pt(111)	−3.22	−0.33	1897	1.66

Fig. 4 Adsorption energies and equilibrium bond lengths, as the function of d-band center.

Table 3 Löwdin charges located on adsorbed H atoms (spilling parameter), W functions by means of (eqn (2) (eqn (3)) after adsorption and d-band centers after adsorption (shift of the d-band center)

| System	Q/eV	W/eV	E_{d-band}/eV
Pt(111)	0.8154	5.72	−2.42
	(0.0012)	(5.80)	(−0.34)
Pt$_2$Bi/Pt(111)	0.8740	5.36	−2.72
	(0.0016)	(5.40)	(−0.42)
PtBi$_2$/Pt(111)	0.9614	4.82	−3.67
	(0.0021)	(4.86)	(−0.45)

Fig. 5 Work functions of studied Pt–Bi bimetallic overlayers prior to and after adsorption of hydrogen (the work functions of clean surfaces were taken from ref. 19).

adsorption of H, which amounted to −0.15 eV at 250 K.[25] Two methods of calculation of W applied in the present study, afford similar results, although the method based on macroscopic averages delivered values somewhat higher from the ones obtained by eqn (2). The decrease of the work function indicates that a certain amount of charge is transferred from the adsorbed hydrogen atoms to the substrate. The Löwdin charges (Table 3) of adsorbed hydrogen atoms whose dipoles are oriented perpendicular to

the surface confirm this assumption. The amount of charge transferred from hydrogen to slab decreases with the decrease of adsorption energy and the increase of Pt–H distance.

As expected, the d-band center shifts down upon adsorption of H atoms, which indicates certain stabilization of the band. We expected that the order of the downshift of the band is going to be opposite to the position of the d-band center prior the adsorption, but the actual order of stabilization of the d-band was found to be: Pt(111) < Pt$_2$Bi/Pt(111) < PtBi$_2$(111). Following the work of Liu and co-workers[26] we performed the analysis of modification of electronic states of binding atoms by means of the difference of projected densities of states (Δd-PDOS). Fig. 6 shows the changes in PDOS of binding a Pt atom after and prior to the adsorption of the H atom. From the presented plots it is obvious that PDOS close to the Fermi energy (in the energy window of a few eV) is significantly reduced upon adsorption of H in all of the three cases studied. This is a clear indication that these d-states of clean surfaces are predominantly involved in hydrogen binding. As the hydrogen atom is an extremely simple adsorbate, the resulting picture is also quite simple. For all cases, Δd-PDOS is preferably positive for $E > E_F$, contributing to the unoccupied states. Δd-PDOS is strongly negative for energies ranging from approx. −4 eV to the Fermi one. For the energies below −4 eV, there is a wide region of positive Δd-PDOS which contributes to the occupied states. These two regions of positive Δd-PDOS, the first one above the Fermi energy, and the second one below −4 eV, may be identified as the main antibonding and bonding regions between hydrogen s-states and platinum d-states. The region
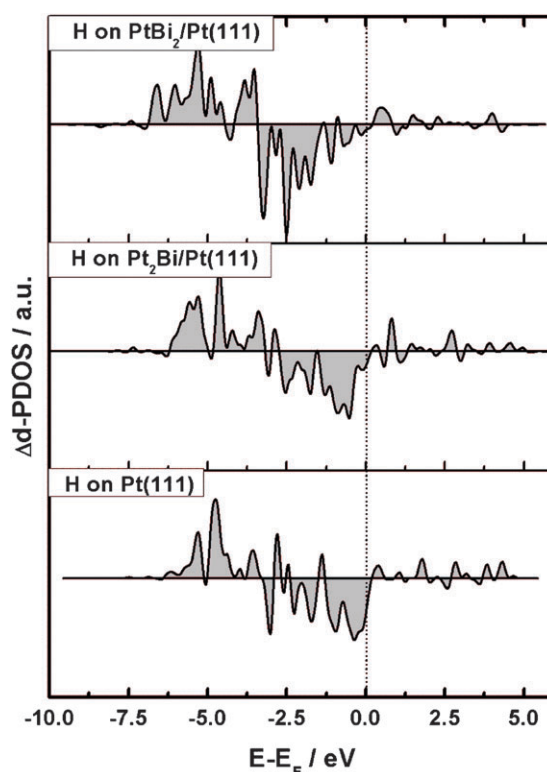
Fig. 6 Δd-PDOS of surface platinum atoms calculated for the studied surfaces in the case of hydrogen adsorption (according to ref. 26).

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Phys. Chem. Chem. Phys., 2009, **11**, 6225–6233 | 6229

of negative Δd-PDOS is more pronounced for $PtBi_2$ alloy compared to pure Pt and Pt_2Bi alloy. As the d-band centers of the Pt atoms in $PtBi_2$ bimetallic overlayers are shifted toward much lower values compared to the one in a clean Pt and Pt_2Bi alloy, Δd-PDOS decrease close to the lower edge of this region. For a pure Pt and Pt_2Bi alloy, the lower values of Δd-PDOS are close to the Fermi energy, the upper limit of negative part of Δd-PDOS.

3.3 CO tolerance of Pt_xBi_{1-x} bimetallic overlayers

According to Markovic and Ross,[6] the adsorption of carbon monoxide has been investigated in the greatest details with modern UHV systems. From the standpoint of electrochemistry, CO serves as a "model fuel" for electrocatalysis of C_1 molecules. Another important fact is that the oxidation of C_1 molecules provides the formation of one particular intermediate: adsorbed CO. Having in mind all these facts, the literature regarding CO chemisorption is vast. Before reporting the obtained results, some important issues should be commented upon. As already well documented in the literature, low energy site for CO adsorption on Pt(111) in DFT is not the atop site, but rather the three fold fcc-hollow site. This problem, know as the "CO/Pt(111) puzzle", was first discussed by Feibelman et al.[27] These qualitative errors cast some doubts on the applicability of DFT for analysis of reactions involving CO on Pt(111) surface and a lot of effort was made in order to resolve these problems. For example, Dabo et al.[28] analysed the performance of the PBE-GGA approach on the adsorption of CO on Pt(111) and Pt–Ru surfaces. The authors demonstrated excellent agreement of the calculated vibrational frequencies of adsorbed CO with experimentally determined ones, invoking vibrational recognition of the CO adsorption site, rather than recognition of the preferred adsorption site as the one with the lowest adsorption energy.

According to the most widely accepted Blyholder model[29] of CO chemisorption on transition metal surfaces, the two main interactions dominate the bonding: the donation of electrons form 5σ filled levels of CO to the metal, and the back-donation from metal into CO π^* orbitals, which are empty in isolated molecule. As pointed out by Oana and co-workers[30] there are certain doubts whether σ interaction is net repulsive or indirect. They also emphasized the importance of occupancy and the d-band position of the particular system under the study. The same authors have studied the CO tolerance of Pt–Bi intermetallic alloys using the tight-binding extended Hückel (eH) method. Although the eH method does not allow structural relaxation and cannot give important d-band characteristics necessary to predict surface behavior, qualitative understanding of increased CO tolerance of PtBi and $PtBi_2$ intermetallic alloys has been offered. It should be clear that the intermetallic alloys reported in the literature are much different than the systems studied here. Obviously, there is a different lattice constant that is a function of alloy composition. This resulted in different adsorbate–adsorbate interactions at identical coverages, while the alloys studied here have the same lattice constant for all compositions. This allows us to treat the changes of both electronic and chemical

properties as a function of different electronic environments, separated from the changes of bond distances and other geometrical effects. In this part of the paper we briefly summarize the study of the CO tolerance of $Pt_2Bi/Pt(111)$ and $PtBi_2/Pt(111)$ bimetallic overlayers.

The calculation parameters described in section 3.2 were used here, too. To calculate CO adsorption energy, we applied a different approach than in the case of H chemisorption. The adsorption energies were calculated using the following equation:

$$E_{ads} = \tfrac{1}{2}(E_{slab+2adsCO} - E_{slab+2CO}) \qquad (6)$$

In this equation $E_{slab+2adsCO}$ is the energy of the slab with two CO molecules adsorbed in the Pt atop site (on both sides of the slab) and $E_{slab+2CO}$ is the energy of the slab with two CO molecules distanced 5 Å from both sides of the slab. In the later case, it is assumed that the separation is large enough to prevent any covalent interaction between CO molecule and the surface. The relaxations of CO molecule in these cases rendered the C–O bond length of 1.134 Å for all studied surfaces. The obtained value is in good agreement with both the experimental value of C–O bond length in isolated CO molecule, and the result of HF calculations, being equal to 1.128 and 1.137 Å, respectively.[31] Table 4 summarizes the obtained results for bond lengths and adsorption energies.

The experimentally determined adsorption energy of CO on Pt(111) at atop sites was reported elsewhere to amount to -1.50 eV.[32] This value agrees excellently with the value calculated in this study. The Pt–C and C–O distances, calculated here, also agree very well with the experimentally determined values amounting to 1.85 ± 0.1 and 1.15 ± 0.05 Å, respectively.[33] In addition, Hammer et al.[34] obtained -1.45 eV for the adsorption energy of CO on Pt(111) by means of DFT, and found Pt–C and C–O bond lengths to be 1.88 and 1.15 Å, respectively.

Fig. 7 shows Δd-PDOS for bonding Pt atoms of the studied surfaces. Guided by the results of Kresse and co-workers,[35] a brief analysis of the presented profiles can be performed. The region of positive Δd-PDOS below -4 eV can be attributed to 5σ–d_{z^2} interaction which leads to the bonding states in this region and the antibonding states slightly above the Fermi energy. This shift of antibonding states above the Fermi energy ensures that 5σ–d_{z^2} interaction is not pure Pauli-like repulsion. The interaction of d_{yz} and d_{xz} states of Pt atoms with 1π orbital and $2\pi^*$ CO LUMO leads to depletion of PDOS between -4 and 0 eV (-5 and 0 according to ref. 35) due to the back donation of electrons from substrate to initially empty $2\pi^*$ orbital. At energies higher than 2 eV, the states arising from $2\pi^*$–d_{yz}/d_{xz} antibonding interaction are clearly visible, although they have a low density. An identical qualitative picture holds for all three surfaces studied. As one

Table 4 Adsorption energies and bond lengths for CO chemisorption on the studied surfaces
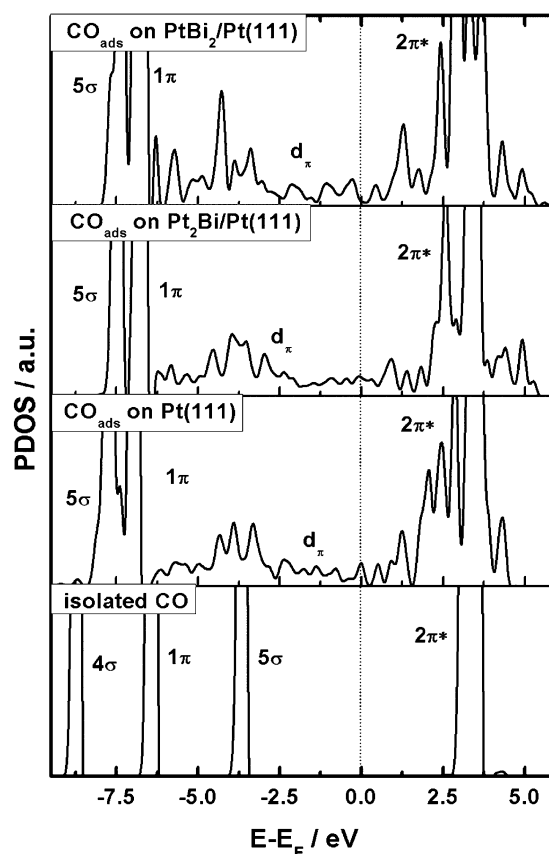
System	E_{ads}/eV	$d(Pt–C)$/Å	$d(C–O)$/Å
Pt(111)	−1.48	1.879	1.146
$Pt_2Bi/Pt(111)$	−1.17	1.882	1.153
$PtBi_2/Pt(111)$	−0.45	1.908	1.163
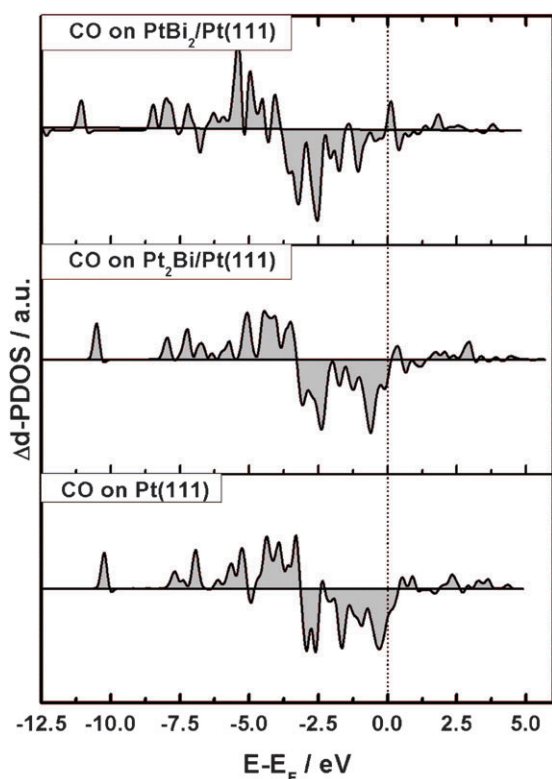
Fig. 7 Δd-PDOS of surface platinum atoms in the case of CO adsorption on the studied surfaces (the vertical scale is the same on all three graphs).

Fig. 8 PDOS of CO molecule, isolated (bottom) and adsorbed on Pt–Bi surfaces.

might conclude from the presented Δd-PDOS profiles, additional stabilization of the d-band due to adsorption occurs, likely to the case of hydrogen adsorption. For a clean Pt(111) surface, the d-band center of bonding Pt atom shifts down to -3.31 eV, while E_{d-band} of bonding Pt atoms in $Pt_2Bi/Pt(111)$ and $PtBi_2/Pt(111)$ alloys are located at -3.55 and -4.43 eV, respectively.

Similar to the case of hydrogen adsorption, there is also an excellent correlation between the E_{ads} and the position of the d-band center. Along with the downshift of E_{d-band}, we observed the increase of both Pt–C bond length and C–O bond length. The slope of E_{ads} vs. E_{d-band} for CO chemisorption is -0.87, while the same relationship for H adsorption gave a slope of -0.32. This difference indicates that CO binding is more affected by the d-band shift than H adsorption. A comparison of the values of H adsorption energy on $Pt_2Bi/Pt(111)$ and Pt(111) leads to the conclusion that on $Pt_2Bi/Pt(111)$ H binds weaker by 0.06 eV. This is five times less than the change of CO adsorption energy on $Pt_2Bi/Pt(111)$ as compared to clean Pt(111) surface, so $Pt_2Bi/Pt(111)$ surface binds H almost as strongly as clean Pt(111) but has a much higher CO tolerance than the Pt(111) surface. These observations correspond to the model of adsorption proposed by Hammer and co-workers,[8,34] where the changes in adsorption energies are interpreted in terms of the coupling matrix elements, energies of renormalized adsorbate states and the position of the d-band center of the surface metal atoms. The demonstrated effects of modification of electronic structure of clean surfaces on their chemical reactivity might

have some practical importance in searching for new electrocatalysts. According to the calculated binding energies of H and CO some improved catalytic performance of surfaces with low content of Bi might be expected. In addition, some attention should be paid to the sensitivity of different adsorbates on the modification of the electronic structure of the surfaces, essentially described through the theory of Hammer and Nørskov.[8] Different effects of modification of the electronic structure on the adsorption trends of different species might also be extended to spectator (blocking) species (for the importance of this issue see ref. 1). Detailed knowledge on the trends of different species to adsorb on solid surfaces might lead to the discovery of low-cost electrocatalysts with good performance, which would not be (highly) sensitive to the presence of spectator species, or at least to point out on the conditions of its practical application.

Since the Pt–Bi bimetallic overlayers studied here present rather a new system, which has not been studied experimentally elsewhere, we would like to compare the obtained results with those reported by Fukutani et al.,[36] who analysed CO adsorption on the Pt(111)–Ge bimetallic overlayer by means of angle-integrated photoemission spectroscopy (PES). We justify this comparison by (a) similarity in the electronegativity of Ge (2.01) and Bi (2.02), and by these experimental findings following the alloying of the Pt surface with Ge: (b) the d-band filing of platinum surface atoms increases and (c) the band undergoes stabilization. The same

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Phys. Chem. Chem. Phys., 2009, **11**, 6225–6233 | 6231

holds for the case of Pt–Bi bimetallic overlayers, studied here. As found by Fukutani *et al.*[36] CO chemisorption energy on Pt–Ge alloy is reduced by approximately 25 KJ mol^{-1} compared to the one on a clean Pt surface. This is close to the reduction of CO chemisorption energy on the Pt$_2$Bi bimetallic overlayer found here to amount to approx. 30 KJ mol^{-1}. Furthermore, the analysis of PES data revealed that the binding energies of the occupied states of CO adsorbed on Pt(111) and Pt(111)–Ge bimetallic overlayer are almost the same. We analysed PDOS of CO adsorbed on the studied surfaces and these results are presented in Fig. 8. Parts of PDOS are labeled as 4σ, 5σ, 1π and $2\pi^*$ according to ref. 35. It can be seen that the overall structure of CO PDOS is the same for all three studied surfaces, in accordance to experimental findings of Fukutani and co-workers.[36] On the basis of the obtained results, we can use the same arguments as in ref. 36 and conclude that CO chemisorption energy is dominated by interaction of the d-states of platinum atoms in the studied surfaces (described through position of E_{d-band}) and $2\pi^*$ states of CO.

4. Conclusions

In the present paper we firstly analysed the electronic properties of ordered Pt$_x$Bi$_{1-x}$/Pt(111) bimetallic overlayers of various compositions. The triangular band model, proven to be able to explain the changes of the d-band width in a d-metal upon alloying, was successfully applied. In the studied alloys, the d-orbitals of platinum atoms were found to interact with s and p-orbitals of bismuth, thus an additional effort was needed to put the observed behavior in an appropriate theoretical framework. In addition, the analysis of the shape of PDOS of surface Pt atoms revealed that the Pt d-bands in Pt–Bi bimetallic overlayers are highly asymmetric due to the high-bonded states introduced by alloying.

In the second part of the paper, the results of analysis of adsorption of hydrogen atoms on a clean Pt(111) surface and Pt$_2$Bi/Pt(111) and PtBi$_2$/Pt(111) bimetallic overlayers were presented. It was shown that the adsorption energy of H decreases as the d-band center of binding platinum atom shifts down, due to the stabilization induced by alloying of the surface. Together with decreased adsorption energy, one observes the increase of the bond length, and the red shift of the stretching Pt–H vibration. The calculated values of the work functions show that there is a decrease of W upon hydrogen adsorption. The performed analysis indicates that the main bonding and antibonding d-states for hydrogen chemisorption are located beneath approximately −4 eV and above 0 eV, with respect to the Fermi energy. In addition to H chemisorption, the CO tolerance of the same Pt–Bi bimetallic overlayers was investigated. The states involved in CO bonding were analysed by means of difference of projected density of states. It was shown that the adsorption of CO is much more sensitive to the surface alloying effects as compared to hydrogen adsorption. For example, the Pt$_2$Bi/Pt(111) bimetallic overlayer binds H only 0.05 eV weaker than pure Pt(111), while for CO, analogous weakening amounts to even 0.30 eV. These observations fit the model of adsorption proposed by Hammer *et al.*[8,34] In addition, by analysis of

PDOS of adsorbed CO and guided by previously published data, CO chemisorption on the studied surfaces was found to be dominantly governed by interaction of the platinum d states and 2π states of CO.

The demonstrated effects of the modification of electronic structure of the surfaces could offer some directions in the search for new efficient low-cost catalysts. Some attention on different sensitivity of important reactive species on the modification of surface electronic structure should be paid as this can be a helpful tool in the development of highly specific electrocatalysts, and, if further extended, in the development of electrocatalysts which would be less sensitive to the presence of blocking species.

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Phys. Chem. Chem. Phys., 2009, **11**, 6225–6233 | 6233