Reactivity of bimetallic systems studied from first principles

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Bimetallic systems are of special interest in the field of heterogeneous catalysis since they offer the possibility to tailor the reactivity by preparing specific surface compositions and structures. The reactivity of bimetallic substrates is governed by an interplay of electronic and geometric effects which are hard to disentangle experimentally. It will be shown that electronic structure calculations allow to identify the microscopic factors underlying the reactivity of bimetallic systems. Recent first-principles investigations of the reactivity of bimetallic systems will be presented and the general principles that can be derived from these studies will be discussed.

Keywords: electronic structure calculations, heterogeneous catalysis, electrocatalysis, chemisorption, bimetallic surfaces

I. INTRODUCTION

One of the main goals of the rational approach towards heterogeneous catalysis is to understand the main principles underlying the reactivity and selectivity of a catalyst and to use this knowledge for the systematic design of better catalysts [1]. There are basically two possibilities for the modification of a catalyst, namely to alter its structure or its composition (or both). For a detailed microscopic analysis of the dependence of catalysts on both types of modifications, structured bimetallic surfaces are particularly well-suited. They are simple enough so that the relationship between their microscopic structure and their catalytic activity can be systematically studied. On the other hand, a broad variety of possible structures and compositions of bimetallic substrates can be prepared with an increasing degree of complexity. It should also be noted that many bimetallic systems are well-known catalysts in their own right [2, 3].

Because of the advances in electronic structure theory and the increase in computer power [4], bimetallic substrates can nowadays be routinely addressed by first-principles total energy calculations yielding microscopic insights into the fundamental factors underlying their reactivity. In this brief review, I will present some of the recent theoretical studies on the reactivity of bimetallic systems and discuss the general principles that can be derived from these studies.

The activity of bimetallic catalysts is often discussed using the concept of the *ensemble* versus the *ligand* effect [2, 5]. The term ensemble effect refers to the fact that for many reactions a certain number of active sites is required for a particular reaction to occur. By blocking a large ensemble of active sites certain reactions can be suppressed thus increasing the selectivity towards reactions that only need a small ensemble of active sites. The modifications in the catalytic activity and selectivity caused by the electronic interactions between the components of a bimetallic system are described by the term ligand effect.

The size of the systems that can be handled by first-principles calculations is still too small to incorporate several active sites. Consequently, the ensemble effect is usually not addressed in detail in these studies. The ligand effect, however, can be well studied in electronic structure calculations. In addition to the pure electronic or ligand effect, the modifications of the interatomic distances in a bimetallic system can have a decisive influence on its catalytic activity, as will be shown in this review. Hence this *geometric effect* should also be considered together with the ensemble and ligand effects when the reactivity of bimetallic systems is discussed.

In this review, I will focus on three different types of bimetallic systems that have been addressed by first-principle electronic structure calculations: pseudomorphic overlayer systems, alloy surfaces and supported nanoparticles. These different types are illustrated in Fig. 1. This brief review is certainly not meant to give a complete overview over the whole field. I rather concentrate on studies which illustrate that there are a variety of effects that influence the electronic structure and thus the reactivity of the different bimetallic systems. It will be shown that there are bimetallic systems such as PtRu which exhibit properties that do not correspond to an intermediate behavior in between those of the pure components but that are rather beyond those of both components [6–8]. However, there are other bimetallic systems such as PdCu which act more like a novel metal with properties in between those of the single components [9, 10]. In order to analyse and categorize these effects, reactivity concepts are very helpful. I will predominantly use the *d*-band model by Hammer and Nørskov [11, 12] which is rather simple but still very successful for the interpretation of the reactivity of *d*-band metals.

As a probe of the reactivity of the bimetallic systems mainly the adsorption energies of hydrogen and CO will be used. However, one has to be cautious by identifying adsorption energies with reactivity. High catalytic activity usually is the consequence of a compromise. On the one hand, there should be a sufficiently strong interaction between the catalyst and the reactants in order to lead to, e.g., lower dissociation barriers than in the gas phase. On the other hand, this interaction should be relatively modest so that the products can desorb again. Still, the interaction strength of molecules with surfaces

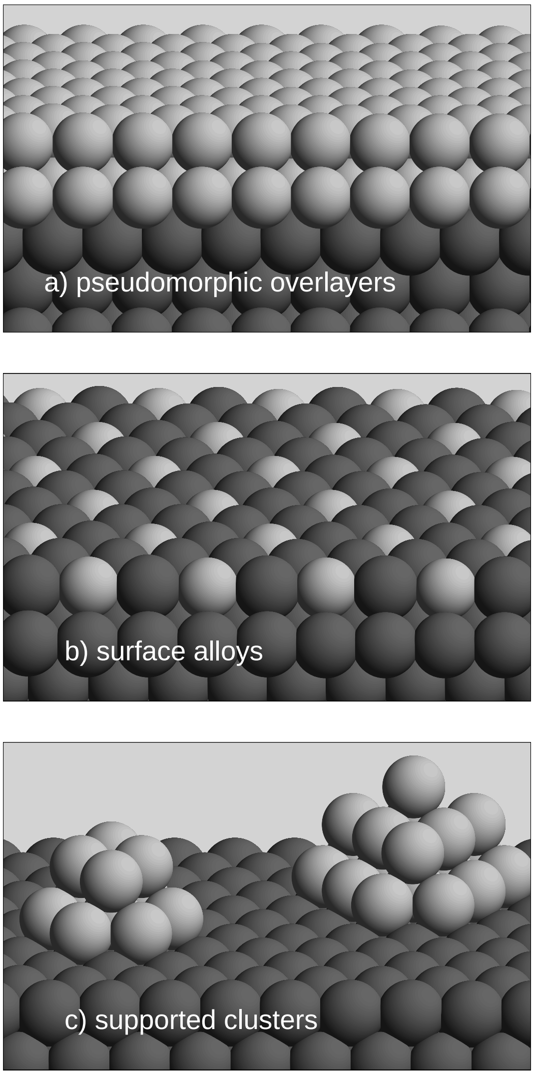

FIG. 1: Schematic illustration of the types of bimetallic systems discussed in this review.

is often closely correlated with the reactivity for a large class of catalytic reactions, for example via a Brønsted-Evans-Polanyi-type relation [13].

This paper is structured as follows. Some aspects of the electronic structure theory and the d-band model will be very briefly addressed in the next section. The following sections are devoted to the presentation of *ab initio* studies covering the three different types of bimetallis systems shown in Fig. 1. The paper will end with some concluding remarks.

II. THEORETICAL BACKGROUND

The field of first-principles calculations for surface science problems is dominated by electronic structure calculations based on density functional theory (DFT)[14, 15]. In practical applications, the many-body Schrödinger equation is replaced by a set of coupled effective one-particle equations, the so-called Kohn-Sham equations [16] which makes present-day DFT implementations numerically very efficient [17–19]. All many-body effects are contained in the so-called exchange-correlation functional which is unfortunately not known. For many surface science problems, a sufficient accuracy can be obtained within the so-called generalized gradient approximation (GGA) [20]. Note that we report both adsorption energies and binding energies in this paper. While adsorption energies have a negative sign for stable adsorption, binding energies have a positive sign.

In order to interprete the results of the electronic structure calculations, qualitative concepts are needed that allow an fundamental analysis of the electronic structure. A rather simple but still very useful reactivity concept was derived by Hammer and Nørskov [11], the so-called d-band model which is related to the frontier orbital concept [21, 22]. In this model, the whole d-band is replaced by an effective level located at the center of the d-band ε_d. This level plays the role of the substrate frontier orbitals, i.e. of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

The d-band model is particularly useful for comparing the reactivity of relatively similar systems which only differ in the position of the d-band center. Then there is a linear relationship between the d-band center shift and the change in the interaction strength [12, 23] which means that there is a stronger interaction or larger energy gain upon an upshift of the d-band.

III. OVERLAYER SYSTEMS

The electronic and chemical properties of pseudomorphic overlayers are modified mainly because of two effects, the electronic interaction between the substrate and the overlayers and the strain in the overlayers induced by the lattice mismatch between substrate and the overlayers. Experimentally, it was demonstrated for CO and oxygen adsorbed on Ru(0001) that the expansion of the substrate lattice leads to a preferential adsorption while compression causes a depletion of the adsorbate layer [24, 25]. These results were confirmed in DFT calculations [26] and explained in terms of the d-band model. Upon expansion of the substrate lattice, the width of the d-band decreases because of the reduced overlap between the atomic orbitals. If the d-band is more than half-filled, charge conservation leads to an up-shift of the d-band and to larger adsorbate binding energies.

For pseudomorphic overlayer systems it is experimentally usually very hard to disentangle the strain effects from the influence of the electronic interaction between overlayer and substrate. As far as the theory is concerned, Shubina and Koper have calculated the change in the CO adsorption energies on a Pt monolayer deposited on a number of different d-band metals with respect to clean Pt(111) [7]. In particular the Pt/Ru system is of

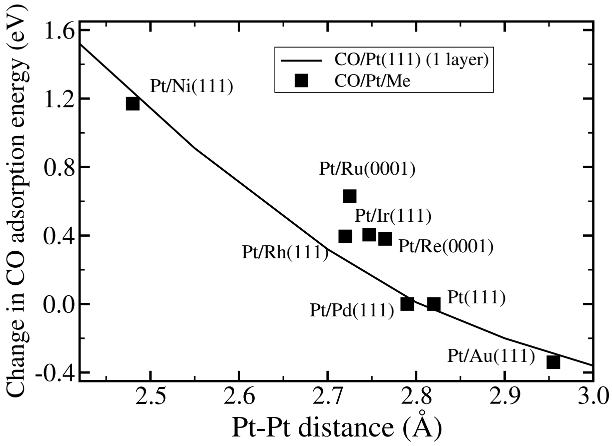

FIG. 2: Calculated change in CO adsorption energy with respect to CO/Pt(111) at the most stable adsorption site as a function of the Pt-Pt distance. A positive change in the adsorption energy means a reduced binding. The solid line corresponds to the CO adsorption energy in the hollow site of a Pt(111) one-layer slab (after [7]).

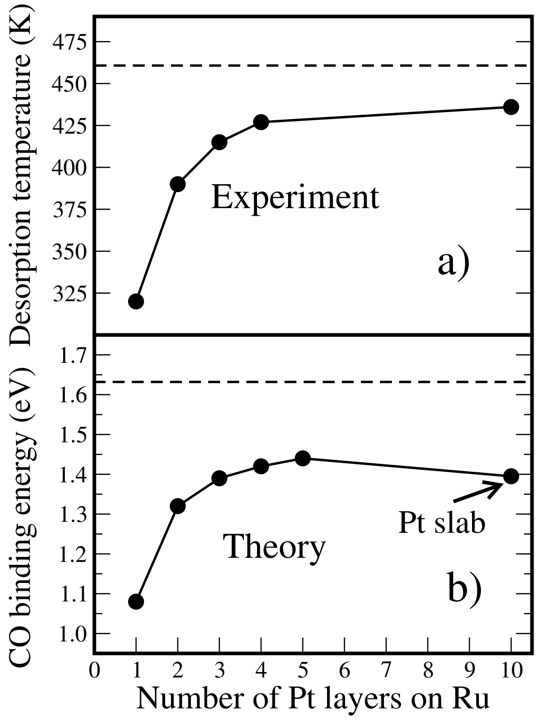

FIG. 3: CO interaction with Pt/Ru(0001) overlayer. a) experimentally determined desorption temperature; b) calculated CO binding energies. The dashed line denotes the corresponding result for pure Pt(111). The theoretical result for the largest number of Pt layers on Ru has been obtained by a calculation with a pure Pt slab with the lateral lattice constant of Ru (after [8]).

strong current interest in the context of CO tolerant fuel cell catalysts. CO binds so strongly to many catalysts that they become poisoned because all catalytic active sites are blocked by CO. The results of the calculations are shown in Fig. 2 as a function of the Pt-Pt distance in the pseudomorphic overlayer systems. A positive change corresponds to a weaker binding. It is obvious that the CO binding energies are reduced on most of the overlayer systems.

In order to disentangle strain effects from electronic interaction effects between overlayer and substrate, CO adsorption energies on a Pt(111) one-layer slab were also calculated as a function of the Pt-Pt distance (solid line in Fig. 2). The deviations for many systems between the overlayer and the one-layer slab calculations indicate that pure strain effects are not sufficient in order to explain in general the modified reactivity of pseudomorphic overlayers.

Recently, the first experimental study was performed that allowed a direct identification of the lattice strain effects versus the electronic interaction effects [8]. In this study, the binding energy of CO on Pt/Ru was determined as a function of the number n of Pt layers on Ru. The Pt lattice constant is 2.5% smaller than the Ru lattice constant. Still, compressed Pt layers retain their pseudomorphic structure up to a film thickness of at least 10 layers. In Fig. 3, the measured CO desorption temperature has been plotted as a function of the number of Pt layers on Ru. The desorption temperatures are directly related to the binding energy of CO, but the exact value depends on the prefactor of the desorption rate which is not really known.

On one Pt overlayer on Ru(0001), the CO binding is strongly reduced compared to the clean Pt(111) surface, and then there is a rapid increase of the CO bond strength for $n = 1-4$ while for $n > 4$ the CO binding energy E_B remains almost constant. Assuming a prefactor for desorption adequate for on-top bonded CO of $k_0 = 10^{15}\ 1/s$, CO binding energies of 0.99 eV (1st layer), 1.21 eV (2nd layer) and about 1.30 - 1.35 eV for higher layers are obtained [8]. Still, even for $n = 10$, the CO binding on the Pt/Ru system is lower than on pure Pt(111) (dashed line in Fig. 3). Since for ten layers Pt on Ru no direct electronic interaction between the uppermost Pt layer and the substrate is to be expected, the lower binding energy is a consequence of the compressive strain in the pseudomorphic Pt overlayer, in qualitative agreement with theoretical predictions [26]. The experimental findings are nicely reproduced by DFT calculations [8]. The results for the largest number of Pt layers on Ru in Fig. 3b are in fact obtained for a five-layer slab of Pt(111) with the lateral lattice constant of Ru. The slight decrease of this energy with respect to the results for four and five Pt layers on Ru is within the numerical accuracy of the calculations.

These results show that both the electronic interaction and the strain induced by the lattice mismatch can contribute significantly to the modified reactivity of a bimetallic overlayer system, as already found by Shubina and Koper (see Fig. 2). The strong interaction of Ru

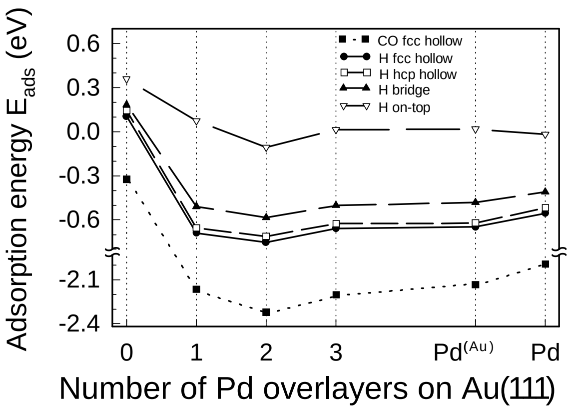

FIG. 4: CO and hydrogen adsorption energies as a function of the number of Pd overlayers on Au(111) for different adsorption sites on the surface at a coverage of $\theta = 0.25$. The pure Pd substrates with the lateral lattice constant of Au ($a = 4.18$ Å) and Pd ($a = 3.96$ Å) are labeled by $\mathrm{Pd}^{(\mathrm{Au})}$ and Pd, respectively (after [27]).

with Pt leads to a downshift of the local d-band center which together with the compressive strain reduces the CO binding energy on one Pt layer on Ru by more than 0.5 eV compared to pure Pt. As far as the electronic interaction is concerned, one could say that Pt is so strongly interacting with Ru that it cannot bind adsorbates as well as pure Pt. Thus depositing a less reactive metal (Pt) on a more reactive metal (Ru) makes the overlayer even less reactive.

Now it is of course interesting to investigate an overlayer system with opposite properties: a more reactive metal deposited pseudomorphically on an inert metal with a larger lattice constant. In fact, there is such a system that has been studied in detail experimentally, namely the Pd/Au system [28–32]. This system is of particular interest in the field of electrocatalysis because of its catalytic activity in the oxidation reactions of methanol, formic acid and carbon monoxide.

In order to assess the reactivity of this system, the CO and hydrogen adsorption energies were determined as a function of the number of pseudomorphic Pd overlayers on Au(111) and Au(100) [27, 33]. The results for Pd/Au(111) are shown in Fig. 4. Pseudomorphic Pd overlayers on Au are expanded by about 5%. The pure strain effects in the adsorption energies can be deduced by comparing the adsorption energies on equilibrium Pd(111) and strained Pd(111) with the lateral lattice constant of Au which is denoted by $\mathrm{Pd}^{(\mathrm{Au})}$ in Fig. 4. There is a considerable increase in the H and CO binding energies on Pd(111) upon the lattice expansion by 5% which is agreement with the predictions of the d-band model given above. However, the binding energy of the H atom to the ontop site in fact decreases upon lattice expansion. A similar non-uniform trend as a function of the lattice strain has also been found for the H adsorption energies on Cu [34]. An analysis of the electronic structure suggests that this behavior is caused by the strong perturbation of the Pd $d_{3z^2-r^2}$ orbital upon ontop adsorption so that the d-band model is no longer appropriate [27, 34].

As far as the direct interaction between Pd and Au is concerned, it leads to a further increase in the binding strength. The relative weak interaction between Pd and Au makes the Pd overlayer more reactive which is also reflected by a further upshift of the d-band compared to the expanded pure Pd(111) surface. These findings are in agreement with the enhanced CO binding found on Pt/Au(111) (see Fig. 2). Thus depositing a more reactive metal on a less reactive metal makes the overlayer even more reactive. Interestingly enough, for Pd/Au there is a maximum in the binding energies for two Pd overlayers on Au at all adsorption sites. This can be related to second nearest neighbor interaction effects. For just one layer of Pd on Au(111) there is an indirect repulsive interaction between the adsorbates and Au which reduces the binding [27].

In the examples presented so far, the electronic interaction and the strain have the same effect: either both lead to a weaker (Pt/Ru) or to a stronger (Pd/Au) interaction with adsorbates. For PdCu systems, the electronic interaction and the lattice mismatch should cause opposing effects since the supposedly more inert metal, Cu, has a lattice constant that is 8% smaller than the one of Pd. In fact, because of this strong suppression pseudomorphic Pd overlayers on Cu do not exist, they rather form alloys [35, 36], as will be discussed in more detail in the next section. In contrast to the Pd/Cu(111) system, at room temperature Cu/Pd(111) has been found to grow in a layer-by-layer fashion for at least the first two layers [37]. Furthermore, underpotential deposition of Cu on Pd(111) in sulfuric acid solution has been observed [38, 39].

In order to establish chemical trends, it is still interesting to calculate adsorption energies on pseudomorphic Pd/Cu(111) and Cu/Pd(111) overlayer systems and on the corresponding strained pure substrates. This has been done using periodic DFT calculations for hydrogen adsorption [10]. The results are shown in Fig. 5. In contrast to the Pd/Au system, there is a strong interaction between Pd and Cu. Pd atoms are in fact more strongly bound to Cu(111) by 0.3 eV than Cu atoms, and conversely, Cu atoms are more strongly bound to a Pd(111) surface than Pd atoms. This strong interaction is reflected in the lower hydrogen binding energies on the Pd/Cu(111) overlayer compared to the pure compressed Pd surface. The Pd/Cu(111) overlayer shows adsorption properties similar to Cu(111). A corresponding result has also been found for CO adsorption on a Pd/Cu(111) overlayer in DFT-GGA calculations [9]. The Cu/Pd(111) properties, on the other hand, are closer to those of Cu(111) than Pd(111). This is mainly caused by the fact that the geometric strain hardly influences the adsorption energies on Cu [34] while it has a large effect on Pd. But overall, both Pd/Cu(111) and Cu/Pd(111)

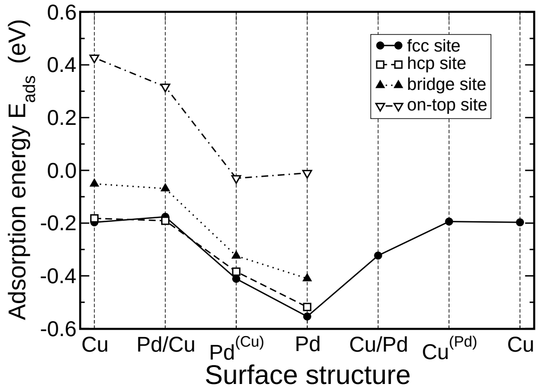

FIG. 5: Calculated atomic hydrogen adsorption energy on bimetallic PdCu surfaces for a quarter monolayer hydrogen coverage, namely on pure Cu(111), on a pseudomophic Pd overlayer on Cu(111) (Pd/Cu), on pure Pd(111) with the lateral Cu lattice constant ($Pd^{(Cu)}$), on pure Pd(111), on a pseudomophic Cu overlayer on Pd(111) (Cu/Pd), and on pure Cu(111) with the lateral Pd lattice constant ($Cu^{(Pd)}$) (after [10]).

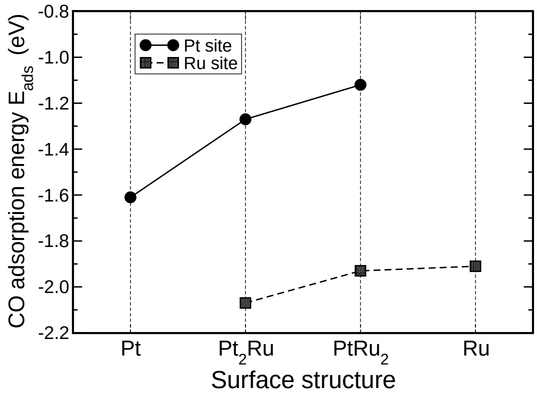

FIG. 6: Calculated CO adsorption energies at the top sites of Pt(111), $Pt_2Ru(111)$, $PtRu_2(0001)$ and Ru(0001) [6].

exhibit an intermediate behavior between pure Cu(111) and pure Pd(111) which is caused by the strong interaction between Pd and Cu.

IV. ALLOY SURFACES AND SURFACE ALLOYS

In the preceding section, we have seen that the chemical properties of bimetallic overlayer systems can be strongly modified with respect to those of the single components. Still, bimetallic overlayer systems exhibit homogeneous surfaces. The variety of possible modifications is strongly enhanced if one considers surfaces of bimetallic alloys. Even is some metals are immiscible in the bulk they may still be able to form alloys at the surface. Then two different species are present on surfaces. This offers for example the possibility of bifunctional mechanisms [40] where one species may adsorb one reactant and the other species the other reactant for a desired reaction.

This bifunctional mechanism has be invoked as a possible explanation for the fact that PtRu catalysts are among the most stable and active CO tolerant catalysts under practical conditions [41]. In this mechanism, CO molecules adsorbed on Pt atoms are preferentially oxidized by an oxygen-containing surface species located above Ru atoms. This bifunctional mechanism has been addressed in DFT calculations by Koper *et al.* [6, 7]. They have calculated the CO adsorption energies on a number of different PtRu systems. The results for the adsorption on top of the Pt and Ru atoms of $Pt_2Ru(111)$ and $PtRu_2(0001)$ are compared to the corresponding results for pure Pt(111) and Ru(0001) in Fig. 6. Both alloy surfaces are stochiometric with a $(\sqrt{3} \times \sqrt{3})$ structure.

The inspection of Fig. 6 reveals that mixing of Pt by Ru leads to a weaker binding of CO while mixing of Ru by Pt causes a stronger binding of CO. Thus the difference in the CO adsorption energies between Pt and Ru sites *increases* when Pt and Ru are mixed. This means that the mixing does not lead to an intermediate behavior for both components but rather enhances the differences. The weakening of the Pt-CO bond due to the presence of Ru is in agreement with the qualitative findings for the Pt/Ru overlayer system [8]. Because of the strong interaction between Pt and Ru, Pt atoms bind adsorbates less strongly. At the Ru sites, it is the other way around. The Pt-Ru interaction is weaker than the Ru-Ru interaction, therefore the Ru atom becomes more reactive due to the presence of neighboring Pt atoms. This explanation has in fact been backed up using the *d*-band model [6].

For OH adsorption, the same qualititative trend has been found in the adsorption as for CO. OH also favors the Ru sites. However, a good CO oxidation catalyst should combine a weak binding to CO with a strong affinity for OH [6] so that CO can easily be oxidized. Motivated by experimental studies [42], the CO and OH adsorption has also been addressed on $Pt_2Mo(111)$ and $PtSn_3(111)$ surfaces [7]. Both systems are apparently better CO oxidation catalysts than PtRu. On PtMo, OH binds much more strongly to Mo than to Pt whereas CO does not exhibit a clear site preference. On PtSn, CO only binds to Pt while OH shows a preference for the Sn sites. Hence both PtMo and PtSn can act as real bifunctional catalysts, with one element binding preferentially the first reactant, and the other element the second reactant.

In the last section we had seen that PdCu overlayer exhibit intermediate characteristics between Pd and Cu. For the CO adsorption on Cu-Pd(111) alloys, in fact similar results have been found in electronic structure calculations [9, 43]. Using DFT, different Cu-Pd(111) bulk and surface alloys have been studied [9]. $Cu_3Pd(111)$ is a stoichiometric surface corresponding to a $p(2 \times 2)$ unit cell. The $Cu_{50}Pd_{50}$ alloy has a bcc structure; along the (111) direction pure Cu and pure Pd layers are stacked

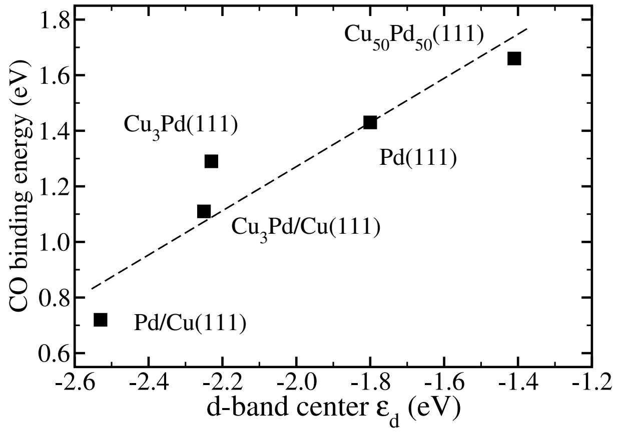

FIG. 7: Calculated CO binding energies on top of Pd atoms as a function of the local d-band center ε_d. The dashed line is plotted as a guide to the eye (after [9]).

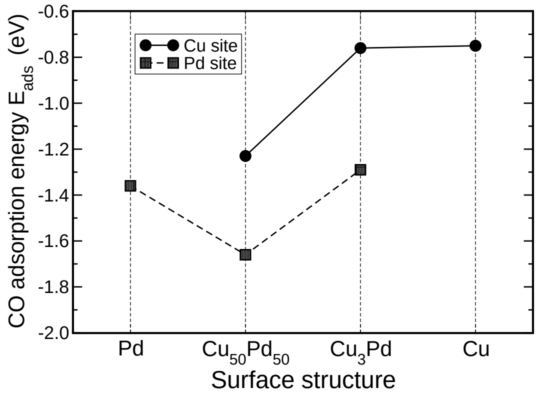

FIG. 8: Calculated CO adsorption energies at the top sites of Pd(111), $Cu_{50}Ru_{50}(111)$, $Cu_3Pd(111)$ and Cu(111) [9].

consecutively. Hence for $Cu_{50}Pd_{50}(111)$ both an Pd-terminated and a Cu-terminated surface exists. Furthermore, a Cu_3Pd surface alloy on a Cu(111) slab has been considered. In addition, the results for the alloy surface have been compared to those for the clean surfaces and pseudomorphic overlayer systems.

The CO binding energies on top of Pd sites are plotted as a function of the local d-band center in Fig. 7. The top sites are not the energetically most favorable CO adsorption sites on Pd and Cu, these are rather the higher coordinated sites, but the on top adsorption on different substrates is easier to compare. First of all, an approximate linear correlation between binding energy and d-band center is obvious, giving credibility to the d-band model. Second, the calculations show that the presence of the inert component, Cu, reduces the CO binding energies. The Pd-terminated $Cu_{50}Pd_{50}(111)$ surface is exceptional because of the rather open structure of the bcc(111) surface which leads to a better binding. On the other hand, the CO binding on Pd/Cu(111) is most strongly surpressed because of the strong compression of the Pd overlayer, in agreement with the results for hydrogen adsorption (see Fig. 5).

The Pd-Cu interaction in the alloys does not only lead to a weaker CO binding to Pd, it also causes a stronger CO interaction with Cu. At the Cu fcc site of $Cu_3Pd(111)$, e.g., the CO binding energy is increased to 1.11 eV from 0.9 eV for the pure Cu(111) surface. And on the top site of the Cu-terminated $Cu_{50}Pd_{50}(111)$ the CO binding energy is 1.23 eV while it is only 0.75 eV on the top site of Cu(111) [9]. It should, however, be noted that on the $Cu_3Pd/Cu(111)$ surface alloy the CO binding energy to the Cu sites is lower than on the pure Cu(111) surface indicating that there are subtle geometric and electronic effects which are not necessarily easy to reveal.

Still the general picture is valid. Because of the strong interaction between Cu and Pd, Cu-Pd alloys do not act as bifunctional catalysts. They rather form a relatively homogeneous new metal with intermediate properties between those of the single components. This is demonstrated in Fig. 8 where the CO on top adsorption energies on Pd(111), $Cu_{50}Ru_{50}(111)$, $Cu_3Pd(111)$ and Cu(111) are plotted. There is some variation in the adsorption energies as a function of the surface structure because of additional geometric effects, in particular for $Cu_{50}Ru_{50}(111)$, but the difference between the CO on top adsorption energies at the Pd and Cu sites *decreases* as Pd and Cu are mixed, in contrast to the results for PtRu alloys (see Fig. 8). Again, the $Cu_3Pd/Cu(111)$ case (not shown in Fig. 8) is exceptional because here the difference in the on top CO adsorption energies for Pd and Cu is larger than on the pure surfaces.

Finally I would like to demonstrate that the theoretical insight from electronic structure calculations [45, 46] can contribute to the design of more efficient bimetallic catalysts [47]. Ni-based catalysts have been usually employed in order to promote the steam-reforming process in which hydrocarbon molecules (mainly CH_4) and water are converted into H_2 and CO. Industrially, this is a very important process since it is the first step for several large scale chemical processes such as ammonia synthesis, methanol production or reactions that need H_2 [47]. However, during the catalyzed reaction also an unwanted by-product, namely graphite, is formed. The graphite overlayer on the Ni surface blocks the active sites of the Ni-based catalyst and thus poisons the reaction. This is very costly since the time the catalyst can be used is reduced and a more frequent maintenance of the reactor unit in the chemical plant is required.

In order to suppress the graphite formation, the carbon interaction with the Ni surface should be reduced. One possible way is to alloy Ni with Au. While Ni and Au are immiscible in the bulk, they still form alloys at the surface. And since Au is a noble metal, its presence on the surface reduces the chemisorption energy of C on Ni significantly by almost 2 eV, if the C atom is located close to the Au atom, but also next-nearest neighbor sites become significantly destabilized, as DFT calculations have

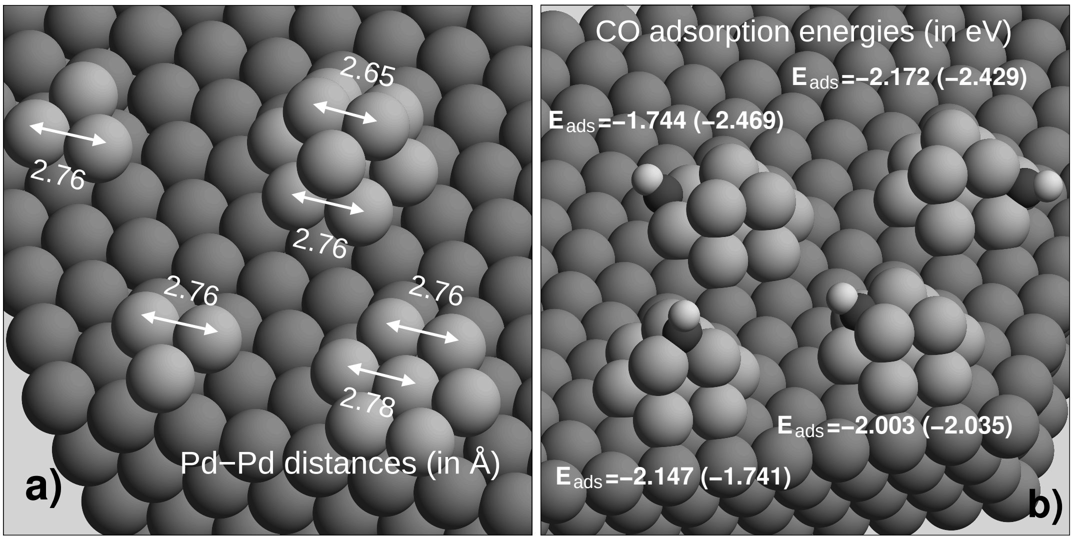

FIG. 9: Pd_n cluster supported on Au(111) studied by DFT calculations. a) calculated nearest-neighbor Pd-Pd distances in Å of the Pd_n cluster; b) CO adsorption positions and energies in eV on the Pd_{10}/Au(111) cluster. The energies in parentheses correspond to the adsorption energies on free Pd_{10} clusters in exactly the same configuration as the supported clusters (after [44]).

shown [45]. An analysis of the calculated electronic structure revealed that the presence of neighboring Au atoms leads to a downshift of the d states at the Ni atom which weakens the interaction with the carbon atoms. Thus the formation of CO becomes more likely which prevents the building up of a graphite layer.

The presence of Au has of course also other consequences. The dissociation of CH_4 into CH_3 and H is the rate-limiting step in the steam-reforming process on Ni. According to DFT calculations by Kratzer *et al.* this process is hindered by a relatively high barrier of 1.1 eV on pure Ni(111) [46]. If a Ni atom on the (111) surface has one or two Au atoms as neighbors, this barrier is increased by 165 meV and 330 meV, respectively. The CH_4 dissociation barrier directly over the Au atom is even much higher [45].

Hence alloying a Ni surface with Au atoms leads to a reduced activity of the catalyst. However, for the industrial catalyst the lowering of the C chemisorption energy by alloying Ni with Au is much more relevant than the increase of the CH_4 dissociation barrier. The NiAu catalyst is slightly less reactive but much more robust and stable due to its higher resistance to graphite formation. Fundamental theoretical results together with experimental studies have thus led to the design of a new catalyst that has been patented [47].

V. SUPPORTED CLUSTER

So far we have only be concerned with flat surfaces. However, small supported metal particles are currently studied in great detail because of their strongly modified chemical properties compared to extended structures [48]. In heterogeneous catalysis, the catalytically active metal particles are usually deposited on an oxide support, but again, in electrochemistry transition metal cluster supported on inert noble metals are of particular interest [49, 50] since the substrate has to be conductive so that supported nanostructures can act as electrodes. Using an electrochemical scanning tunneling microscope, highly ordered arrays of metal clusters containing of the order of only one hundred atoms can be generated [49, 51, 52].

In order to contribute to the understanding of the chemical properties of these clusters, Pd_n clusters with $n = 3, 7, 10$ supported on Au(111) have been the subject of a DFT study [44]. The structure of these clusters is shown in Fig. 9a. The nearest-neighbor distances in Å are also indicated in the figure. The calculated value for Pd bulk is 2.80 Å, for Au bulk 2.95 Å. Although the Pd_n clusters are deposited on a gold substrate, all nearest-neighbor distances are even below the Pd bulk value. This is a consequence of the low coordination of the cluster atoms which makes the single Pd-Pd bonds stronger than in a bulk situation where every Pd atom is twelve-fold coordinated. At the second layer of the Pd_{10} cluster, the Pd-Pd distances are even further reduced to 2.65 Å. Note that for the free relaxed planar Pd_3 and Pd_7 cluster, the nearest neighbor distances are 2.50 Å and 2.64 Å, respectively.

The reduction in the interatomic distances results in a larger overlap of the d orbitals which leads to a broader local d-band and a down-shift of the local d-band center because of charge conservation according to the DFT calculations [44]. And indeed, the binding energies of CO adsorbed on different sites of Pd_{10} clusters supported by Au(111) are lower than those on pseudomorphic Pd/Au(111) overlayers (compare Fig. 9b with Fig. 4). The same results have also been found for atomic hydrogen adsorption energies. Naively one would expect that atoms and molecules bind more strongly to these clusters than to the corresponding flat overlayer surfaces because of the low coordination of the cluster atoms.

In order to better understand the reason for the reduced binding on the Pd_n/Au(111) cluster, the CO adsorption energies on free Pd_{10} clusters in exactly the same configuration as the supported clusters have also been calculated. They are included in Fig. 9b as the numbers in parentheses. These binding energies are in fact larger than on the supported clusters and also on flat [53] and stepped Pd surfaces [54, 55]. This shows that it is the electronic coupling to the Au substrate that together with the compression of the clusters contributes to the low binding energies. Isolated Pd_n clusters still interact more strongly with adsorbates than flat surfaces in spite of their compression.

Interestingly enough, at the top layer adsorption site of the Pd_{10} cluster, the CO binding energies on the free cluster are smaller than on the supported cluster. This surprising result is caused by the reactivity of the unsaturated hexagonal bottom layer of the free Pd_{10} cluster. An analysis of the energetics and the electronic structure of the free cluster shows that the free cluster binds the three topmost Pd atoms so strongly that the top layer becomes less reactive [44].

The electronic coupling of the Pd clusters to the metal substrate has been analysed by comparing the orbital resolved d-band local density of states (LDOS) for Pd_3 clusters deposited on Au(111) and on Pd(111) and for a free Pd_3 cluster (see Fig. 10). The LDOS of the free cluster consists of isolated discrete peaks corresponding to the localized orbitals of this isolated system. For the Pd_3/Pd(111) cluster, *all d* states in the cluster are considerably broadened. This demonstrates the strong coupling between the cluster and the substrate.

The supported Pd_3/Au(111) cluster shows an intermediate behavior. All d-band orbitals that are confined within the cluster layer, i.e. the d_{xy} and the $d_{x^2-y^2}$ orbitals, exhibit a rather discrete structure. This means that these orbitals are still well localised within the cluster. The LDOS of the other three orbitals that have a component along the vertical z-direction, on the other hand, is rather broad indicating that these states are already delocalized. Thus there is a significant electronic coupling between the Pd and Au states but it is not as strong as the coupling between the Pd states in the cluster and the substrate for the Pd_3 cluster.

It has been speculated that the unusual electrochemical stability of nanofabricated supported metal clusters [51] could be caused by quantum confinement effects [56] which would lead to a discrete electronic spectrum in the clusters. However, already for the small Pd_3 clusters the DFT calculations yield a continuous spectrum. For larger clusters, any quantum confinement effects would even be smaller. Thus these calculations do

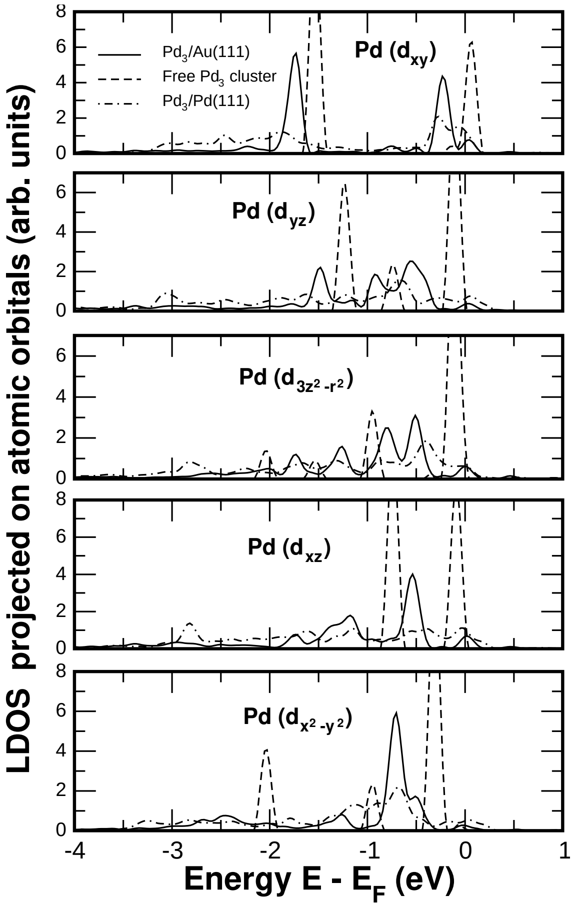

FIG. 10: Orbital resolved d-band local density of states (LDOS) of the supported Pd_3/Au(111) and Pd_3/Pd(111) clusters and the free Pd_3 clusters determined by DFT calculations (after [44]).

not support the speculation of Ref. [56].

As an alternative explanation it has been proposed [57, 58] that the electrochemical nanofabrication of the clusters by the jump-to-contact method leads to an alloying of the clusters which causes their high electrochemical stability. account. Simulations based on the empirical embedded-atom-method (EAM) [59, 60] indicate that electrochemically stable clusters result only in those cases where the two metals that are involved form stable alloys [61]. In fact, DFT calculations yield that the Pd_{10} clusters on Au(111) [44] are stabilized by 0.1 eV if one of the Pd atoms at the base of the cluster is exchanged with an Au atom of the underlying substrate [62].

Intermixing or alloying is always an important issue in the case of bimetallic systems [2], as also recent experimental and theoretical studies on the electronic and chemical properties of Mo nanoparticles on Au(111) demonstrate [63–65]. These studies were motivated by the fact that the nanoparticles can act as precursors for the preparation of molybdenum sulfide and molybdenum oxide aggregates [66, 67] which are widely used catalyst materials in the chemical industry [68].

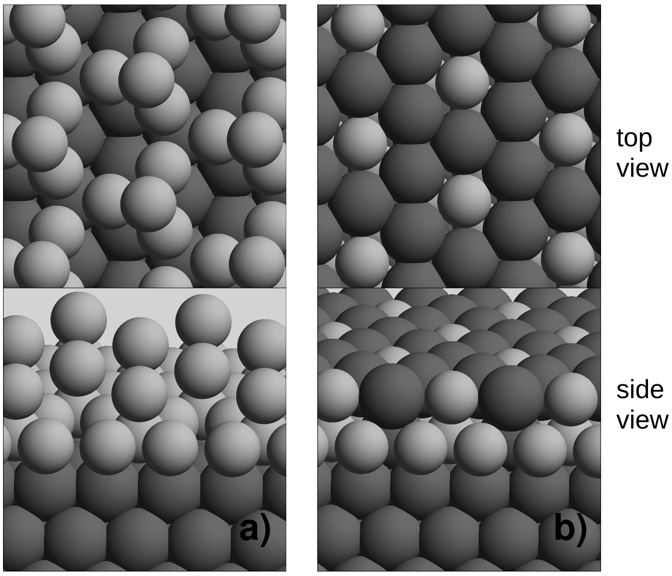

FIG. 11: Top and side view of two Mo/Au(111) structures studied by DFT calculations [65]. The dark and light balls represent Au and Mo, respectively.

The experiments indicated that CO does not adsorb on the Mo/Au(111) surface [63]. Since the exact structure of the Mo nanoparticles on Au(111) could not be determined experimentally several structural models of the Mo/Au(111) system were investigated within a (2×2) surface unit cell using DFT [65]. Two of them are shown in Fig. 11 which differ by the fact that the open Mo structure in Fig. 11a has been filled up with Au atoms in Fig. 11b leading to a flat (111) surface. The structure shown in Fig. 11b is by 0.3 eV/atom more stable than the one of Fig. 11a with respect to bulk Au and bulk Mo, i.e., Mo actually prefers to be embedded in the gold surface [64, 65]. One gains even another 0.01 eV/atom if the surface is fully covered by Au atom, i.e. if a Au-Mo-Au sandwich structure is formed.

CO binds relatively strongly to both structures shown in Fig. 11 is exothermic with binding energies of 2.22 eV and 1.03 eV for the structures a and b, respectively, which is at variance with the experimental findings that CO interacts very weakly with the Mo/Au(111) system. The binding energy of CO on one Mo monolayer on Au(111) is even larger, 2.79 eV [65]. The Mo/Au overlayer system behaves actually like the Pd/Au system [27] (see 4): The nearest-neighbor distance in Mo is 5% smaller than the one in Au so that the pseudomorphic Mo overlayer on Au is significantly expanded. This causes a significant upshift of the d-band center and consequently a stronger interaction with adsorbates. Similar trends have also been found for oxygen and sulfur adsorbed on the Mo/Au(111) system.

Since the calculated binding energies on the Mo/Au(111) structures are much larger than expected from the experiment, these structures are obviously not realized under the experimental conditions. Apparently, after the Mo deposition Mo-Au site exchange processes occur which lead to Au segregation at the surface. Two other admetals, Ni and Ru, were also considered in the DFT calculations [65]. And indeed, Ni and Ru also tend to mix with a Au substrate. In addition, the qualititative trends in the adsorption properties for Ni/Au(111) and for Ru/Au(111) resemble those found for Mo/Au(111). This means that Mo, Ni and Ru nanostructures on Au are obviously not stable. The metal nanoparticles become embedded in the Au matrix, and the resulting bimetallic system shows basically the chemical properties of a pure Au surface.

VI. CONCLUSIONS

Bimetallic systems show strongly modified chemical properties compared to those of their single components. These modifications are caused by the direct electronic interaction between the components together with geometric effects because of the different lattice constants. While it is hard (but not impossible) to disentangle these effects experimentally, electronic structure calculations are well-suited in order to allow a discrimination between these two effects.

As this review has shown, one can distinguish between two different classes of bimetallic systems. Either its properties are beyond those of the single components or they are in between. The list of bimetallic systems addressed by electronic structure calculations is certainly far from being exhausted. Still the available DFT studies suggest that if a more reactive metal with a smaller lattice constant is mixed with a more inert metal with a larger lattice constant, such as Ru and Pt or Pd and Au, then a bimetallic system will result that, e.g., binds adsorbates more strongly than any single component in a comparable structure. This is caused by the fact that in such a case both the direct electronic interaction as well as the lattice mismatch have the same qualitative effect. These bimetallic systems might be used a bifunctional catalysts.

If, on the other hand, a more reactive metal with a larger lattice constant is mixed with a more inert metal with a smaller lattice constant, such as Pd and Cu, and there is a strong mutual interaction between the two elements, then a bimetallic system may be formed that behaves as a new, almost homogeneous metal with intermediate properties. However, these guiding principles must still be checked using a larger database but they might already be helpful for the rational design of bimetallic catalysts.

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