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The effect of alloying on the H-atom adsorption on the (100) surfaces of Pd-Ag, Pd-Pt, Pd-Au, Pt-Ag, and Pt-Au. A theoretical study

Research Article

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Abstract: The effect of alloying on the adsorption of atomic hydrogen was studied using density functional theory (DFT). In the study the (100) surfaces of Pd-Ag, Pd-Pt, Pd-Au, Pt-Ag, and Pt-Au alloys were considered by means of a cluster model. The structural and energetic properties of the H atom adsorbed on the Pd_4Me (Me = Ag, Pt, Au) and Pt_4Me (Me = Pd, Ag, Au) clusters were calculated and compared with the H-atom adsorption on monometallic clusters. The effect of alloying on the H-atom adsorption is evident for all the investigated bimetallic systems. However, it strongly depends on the second metal atom, Me, is placed in the surface layer or in the subsurface one. In general, the H atom adsorbed in a site containing the second metal exhibits different properties from those characteristic of its adsorption on Pd(100) and Pt(100). Hence, the modified interaction between atomic hydrogen and the alloyed surfaces may increase the selectivity of the catalytic hydrogenation reactions on such surfaces.

Keywords: *Hydrogen • Adsorption • Noble metal alloys • DFT*

1. Introduction

Palladium and platinum are considered to be two of the most important metals in heterogeneous catalysis [1,2]. These two metals play a central role as catalysts in reactions involving hydrogen. Reactions such as hydrogenations of unsaturated hydrocarbons proceed after the dissociation of hydrogen molecules and the adsorption of the formed H atoms on the metallic surface. According to the Langmuir-Hinshelwood mechanism, the hydrogenation reactions occur between unsaturated hydrocarbon and atomic hydrogen that are both adsorbed on the surface. Moreover, the interactions between hydrogen and the surface often have a dominating influence on the rate of the whole catalytic hydrogenation reaction and they can be a rate determining step [3].

The addition of a second metal to pure palladium or platinum, that is, alloying Pd or Pt, may improve the properties and performance of the catalysts [4,5]. In the last two decades, the binary alloys containing Pd or Pt have attracted much attention (see reviews [6-8]), although they have been known since the 1960s. The combination of Pd or Pt with a neighboring metal, such as Ag or Au, leads to the bimetallic catalysts that have properties different from the pure metals alone. While Pd and Pt adsorb dihydrogen dissociatively without any activation barrier, Ag and Au are inactive in the reactions with H_2 molecules. However, the adsorption of atomic hydrogen on silver and gold remains possible. Hence, the mixing of Pd or Pt with Ag or Au is used for tailoring the properties of the catalyst to enhance stability and/or selectivity in a given hydrogenation reaction.

The literature on theoretical investigations of the interaction between atomic hydrogen and the surfaces of the binary alloys of Pd or Pt with Ag or Au is rather scarce [9-12], in contrast to numerous publications dealing with the H-adsorption on various monometallic Pd and Pt surfaces, *e.g.* [13-20]. The majority of the reported studies of the H-atom adsorption on the alloyed surfaces concern the (111) surface of Pd-Ag [9-11] and the results presented therein were obtained from periodic slab DFT calculations. Løvvik and Olsen [9] found that the threefold hollow sites with as many neighboring Pd atoms as possible were preferred for the H-atom adsorption on

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the Pd-Ag(111). The same preference of adsorption sites with the maximal number of neighboring Pd atoms was observed by González *et al*. [10]. The results of the calculations performed by Sheth *et al*. [11] designated the bridging Pd-Pd site for the H-atom adsorption on the Pd(50%)-Ag(50%)/Pd(111) surface, as opposed to the threefold hollow site on Pd(111). However, the change in the binding energy for the atomic hydrogen in moving from Pd(111) surface to the bimetallic one turned out to be only ca. 0.05 eV. The adsorption of H atoms on the Pd-Au surface was investigated by Mei *et al*. [12] in the context of ethylene hydrogenation. To our knowledge, no theoretical studies have so far been performed for the H-atom adsorption on the (100) surfaces of such alloys.

In the present paper the results of the DFT calculations of the interaction between the H atom and the (100) surfaces of the Pd-Ag, Pd-Pt, Pd-Au, Pt-Ag, and Pt-Au alloys are reported. The bimetallic surfaces have been considered using a cluster model and the binding energy of the H atom adsorbed on the Pd_4Me (Me = Ag, Pt, Au) and Pt_4Me (Me = Pd, Ag, Au) clusters has been determined. By providing a detailed structural and energetic description of the H-atom adsorption on the alloyed surfaces and by comparison with the adsorption on the monometallic surfaces, the effect of alloying is established and quantified.

2. Calculation Details

A series of calculations on diatomic molecules was performed to select the most appropriate density functional for calculations of the interaction between the H atom and the alloyed surfaces. The equilibrium bond lengths, r_e, dissociation energies, D_0, and harmonic vibrational frequencies, ω_e, of diatomic molecules containing H, Pd, Ag, Pt, and Au, that is, homo- and heteronuclear metal dimers and metal hydrides, were calculated and compared with the available experimental data (see Table 1). A broad range of hybrid and pure non-local exchange-correlation functionals implemented in Gaussian 98 [35] was considered and all these functionals are listed in Table 2. Their commonly accepted abbreviations have been explained and referenced in many books, *e.g*. [36,37], and in the software documentation available *via* the Internet. The DFT methods were combined with the LANL2DZ basis set [38]. This basis set ascribes the Los Alamos effective core potentials with the valence double-ζ basis to Pd, Ag, Pt, Au and the full double-ζ D95 basis [39] to H. The basis-set superposition error (BSSE) correction [40] and the zero-point energy were incorporated into the D_0 values in the calculations.

Table 1. Experimental bond lengths, r_e, dissociation energies, D_0, and harmonic vibrational frequencies, ω_e, of 11 diatomic molecules used to assess accuracies of the density functionals. The values quoted after [21], unless stated otherwise

Molecule	r_e (Å)	D_0 (eV)	ω_e (cm^{-1})
PdH	1.534 [22]	2.42 [23]	2036 [24]
AgH	1.618	2.28	1759.9
PtH	1.528 [25]	3.44	2378 [25]
AuH	1.524	3.22	2305
Pd_2	2.48	1.03 [26]	210 [27]
Ag_2	2.530 [28]	1.65 [29]	192.4
Pt_2	2.333 [30]	3.14 [31]	222.5 [32]
Au_2	2.472	2.29	190.9
PdAu		1.44	
PdPt		1.94 [33]	
AgAu	2.496 [32]	2.06 [34]	198.2 [32]

For each density functional considered, its reliability for predictions of the diatomic properties was assessed in a statistical manner. The standard deviations in the calculated bond lengths, $\sigma(r_e)$, dissociation energies, $\sigma(D_0)$, and harmonic vibrational frequencies, $\sigma(\omega_e)$, with respect to the corresponding experimental data were computed to express the accuracy of each functional quantitatively. As shown in Table 2, the smallest $\sigma(r_e)$ and $\sigma(\omega_e)$ are obtained with the BH&H hybrid functional, while the G96P86 non-local one yields the minimal value of $\sigma(D_0)$. On the basis of the superior accuracies of these two functionals for the predictions of the properties of the diatomic molecules, it can be assumed that these functionals are the most suitable for larger systems containing H, Pd, Ag, Pt, and Au with the LANL2DZ basis set assigned. As a result, energetic aspects of such systems are analyzed in this paper by means of G96P86, whereas BH&H provides structural properties with the greatest accuracy.

The (100) surfaces of Pd or Pt alloyed with Ag, Au, or Pt and Pd were represented within the framework of a bare-cluster model by two kinds of the Pd_4Me (Me = Ag, Pt, Au) and Pt_4Me (Me = Pd, Ag, Au) clusters. The first kind takes a square shape with Pd or Pt atoms at the corners and with an atom of the second metal, Me, in the same plane in the center of the square (see Fig. 1). The second kind exhibits a pyramidal geometry and is composed of four Pd or Pt atoms located in a plane and the fifth subsurface Me atom lies beneath the plane in the vertex of the pyramid. The distances between the atoms in the clusters refer to the face-centered cubic (fcc) structure of Pd-Ag, Pd-Pt, Pd-Au, Pt-Ag, and Pt-Au substitutional alloys. The lattice constant, a, of each alloy was approximated as an arithmetic average of the lattice constants of two neat components (see Table 3). The distances in the

Table 2. Standard deviations in calculated bond lengths, $\sigma(r_e)$, dissociation energies, $\sigma(D_0)$, and harmonic vibrational frequencies, $\sigma(\omega_e)$, with respect to the corresponding experimental values for the diatomic molecules listed in Table 1. The diatomic properties calculated by means of the hybrid (the first seven rows) and non-local (the next twelve rows) functionals

Method	$\sigma(r_e)$ (Å)	$\sigma(D_0)$ (eV)	$\sigma(\omega_e)$ (cm^{-1})
B1LYP	0.070	0.45	90.0
B3LYP	0.065	0.35	86.8
B3P86	0.041	0.24	65.0
B3PW91	0.048	0.35	72.5
BH&H	0.027	0.37	57.2
BH&HLYP	0.069	0.78	88.6
MPW1PW91	0.047	0.40	70.1
BLYP	0.075	0.21	101.1
BP86	0.047	0.21	77.8
BPW91	0.050	0.22	79.5
PW91LYP	0.072	0.23	93.9
PW91P86	0.045	0.31	72.1
PW91PW91	0.048	0.25	73.5
MPWLYP	0.074	0.21	97.4
MPWP86	0.047	0.25	74.8
MPWPW91	0.049	0.23	76.4
G96LYP	0.064	0.23	85.0
G96P86	0.037	0.19	72.0
G96PW91	0.039	0.25	73.4

Table 3. Experimental lattice constants, a, of the fcc metals and estimated lattice constants of the investigated fcc alloys

Metal/alloy	a (Å)
Pd	3.891 [41]
Ag	4.085 [42]
Pt	3.924 [43]
Au	4.078 [44]
Pd-Ag	3.988
Pd-Pt	3.907
Pd-Au	3.984
Pt-Ag	4.005
Pt-Au	4.001

Pd_4Pt and Pt_4Pd clusters were assumed to be the same. The clusters model the characteristic adsorption sites that are composed of four Pd or Pt atom and one atom of the second metal. The positions on the central atom of the planar clusters and above the subsurface atom of the pyramidal ones correspond to atop and hollow adsorption sites on the (100) surface (see Fig. 1).

In addition, the H-atom adsorption on the (100) monometallic surfaces was investigated. The Pd_5, Ag_5, Pt_5, and Au_5 clusters exhibited the planar and pyramidal structures with the distances equal to those of the neat metals (see Table 3).

The H atom was adsorbed in the atop and hollow adsorption positions on the mono- and bimetallic clusters. The distance, h, of the H atom from the (100) plane was optimized and then the total energy of the whole system containing the cluster and the adsorbed H atom was calculated. In the process of optimization, the geometry of the cluster did not change. After the subtraction of the energies of the separated cluster and single H atom from the total energy of the cluster with the hydrogen adsorbed in a given adsorption position, the binding energy, BE, of the H atom adsorbed in this position was evaluated. The BSSE correction was included into the BE values.

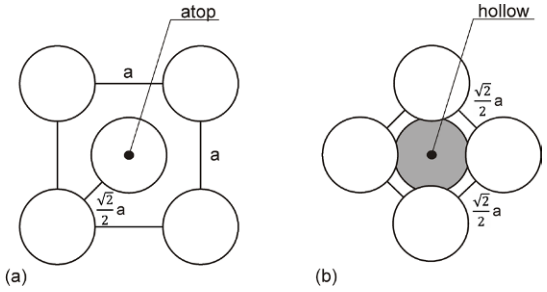

Figure 1. Schematic illustration of the investigated (a) planar and (b) pyramidal clusters that model the (100) surfaces of the alloys and the neat metals. Light circles represent the atoms of the surface layer, while dark circle marks the subsurface atom. The lattice constant, a, taken from Table 3. Two characteristic positions of the H-atom adsorption also denoted

3. Results and Discussion

3.1. The effect of the second metal

The effect of the second metal, Me, in the Pd_4Me and Pt_4Me clusters on the H-atom adsorption can be established by comparison of the h and BE values of the H atom adsorbed in the atop and hollow positions on the bimetallic clusters with the corresponding values on Pd_5 and Pt_5. The h and BE values of the H atom for the pure and alloyed clusters are listed in Table 4. The h values obtained from BH&H and the BE values calculated by means of G96P86 will be discussed below.

The h value of the H atom adsorbed in the atop position on the planar Pd_5 cluster is equal to 1.504 Å. The higher values of h were found for the planar Pd_4Me clusters. In the case of Pd_4Ag, the increase of the distance of atomic hydrogen from the surface is the highest. Compared to the h value on Pd_5, it is higher by over 0.1 Å. The h values of the H atom adsorbed in the hollow position on the pyramidal Pd_4Me clusters vary quite significantly depending on the Me metal. Atomic hydrogen adsorbs at the height of ca. 0.26 ÷ 0.3 Å above the (100) surface layer of the pyramidal Pd_4Ag and Pd_4Au, while its migration beneath the surface can be observed for the Pd_5 and

Table 4. Distances, h, of the H atom from the (100) surface of the mono- and bimetallic clusters and binding energies, BE, of the H on this surface in two characteristic adsorption positions

Position of the H atom on the cluster	BH&H		G96P86	
	h (Å)	BE (eV)	h (Å)	BE (eV)
Pd_5				
atop	1.504	-3.37	1.522	-2.45
hollow	-0.172	-5.52	0.115	-4.35
Pd_4Ag				
atop	1.614	-1.70	1.607	-1.50
hollow	0.267	-4.42	0.432	-3.78
Pd_4Pt				
atop	1.516	-4.04	1.534	-3.31
hollow	-0.265	-4.52	0.344	-3.14
Pd_4Au				
atop	1.546	-2.17	1.566	-1.83
hollow	0.301	-2.81	0.484	-2.57
Pt_5				
atop	1.507	-7.21	1.531	-2.96
hollow	0.451	-4.82	0.610	-3.40
Pt_4Ag				
atop	1.585	-2.19	1.593	-0.92
hollow	0.383	-4.59	0.583	-3.44
Pt_4Pd				
atop	1.480	-6.71	1.509	-2.60
hollow	0.394	-5.33	0.552	-3.43
Pt_4Au				
atop	1.535	-2.85	1.562	-1.49
hollow	0.438	-2.25	0.616	-3.38
Ag_5				
atop	1.567	-0.23	1.586	-0.76
hollow	-0.081	-1.03	-0.012	-1.23
Au_5				
atop	1.519	-1.52	1.545	-1.85
hollow	0.100	-1.54	0.251	-1.84

Pd_4Pt clusters. The negative sign of the h values means that the H atom crosses the surface layer, for which h = 0 Å, and approaches the subsurface layer in the hollow position. In this position the h value crucially depends on which group of the periodic table the subsurface atom belongs to, and, in general, the h value is higher for Pd_4Ag and Pd_4Au than for Pd_5 and Pd_4Pt. This finding remains valid for the planar and pyramidal clusters.

The BE values show that the exoenergetic effect of the H-atom adsorption is decreased when the central atom of the planar Pd_5 cluster is replaced by Ag and Au. Similarly, the decrease of the exoenergetic effect occurred for the (111) surfaces of Pd-Ag [9] and Pd-Au [12]. On the contrary, the binding of the H atom in the atop position on Pd_4Pt is by 0.86 eV stronger than that on Pd_5. The energetic effect for the adsorption in the hollow site on Pd_4Me reveals an inhibiting role of the second metal occupying the subsurface layer toward the H-atom adsorption. Surprisingly, the subsurface platinum brings about a larger decrease of exoenergetic effect of BE than the subsurface Ag atom. The relationship between h and BE is found for the Pd_5 and Pd_4Me (Me = Ag, Au) clusters of both geometries. The higher the H atom is adsorbed above the central atom, the weaker it is bound by the cluster, that is, the BE values become less negative.

As shown by Mei *et al*. [12], the weakening of the strength of the hydrogen-metal bond for the Pd-Au alloy has an influence on the kinetics of ethylene hydrogenation. However, the influence is evident for higher compositions of Au in the alloy. For Au compositions below 25%, there are two opposite kinetic effects compensating one another, and thus the ethylene hydrogenation is not affected by alloying. The first effect increases reactivity because the growing number of surface Au atoms binds the H atoms more weakly compared to the H-Pd bond strength. The simultaneous decrease of the hydrogen surface coverage is responsible for the second effect that lowers reactivity.

The effect of alloying is also evident for the adsorption on the Pt_4Me clusters (see Table 4). Similarly to the Pd_4Me clusters, the increase of h is associated with the substitution of Ag or Au for platinum in the center of the planar Pt_4Me clusters. Moreover, the highest h value is yielded in the atop position on Pt_4Ag. However, some differences with respect to the Pd_4Me clusters occurred. The h value in the atop position of the Pt_5 cluster is almost the same as it is for Pd_5, but the Pt_4Me (Me = Ag, Au) clusters exhibit smaller h values than the corresponding Pd_4Me. While the planar Pd_4Pt cluster follows the increasing trend in h, the Pt_4Pd one does not and its h value is by 0.027 Å lower than that of Pt_5. In the case of the hollow position on the pyramidal Pt_4Me clusters, the H atom is always adsorbed above the (100) surface layer. The subsurface Me atom lowers the h value compared to that of the pyramidal Pt_5 cluster, but the H atom does not cross the surface layer.

The Ag and Au atoms located in the center of the planar Pt_4Me clusters cause a considerable increase of BE toward positive values with respect to the BE in the atop position on Pt_5. The presence of palladium in the surface layer also weakens the binding of atomic hydrogen in the atop position, but the unfavorable effect of Pd is minor to that of Ag and Au. The Me atom in the pyramidal Pt_4Me clusters exhibits a very interesting behavior with respect to atomic hydrogen. The results of the calculations show that the BE values in the hollow position on all the Pt_4Me clusters remain very close to that on Pt_5 despite the differences in the h values. It may indicate that the surface Pt atoms govern the adsorption of the H atom in this position and they determine the exoenergetic effect of the adsorption to the greatest extent.

3.2. The effect of the surroundings

By comparing pairs of clusters containing the same central atom, Me, but different four neighboring corner atoms, it is possible to determine the influence of the Pd and Pt surroundings on the ability of the Me atom to bind the H atom. In order to establish the influence of the surroundings on the Ag and Au atoms, it was necessary to calculate the h and BE values of the H atom adsorbed on the monometallic Ag_5 and Au_5 clusters and the results of such calculations are added at the bottom of Table 4.

Palladium atoms influence the adsorption properties of the Ag atom lying in both layers of the investigated clusters. The Pd surroundings make the H atom adsorb higher above the Ag atom compared to the h values on the monometallic Ag_5 cluster. The ability of the Ag atom to adsorb the H atom is increased by the neighboring Pd atoms and thus the surroundings play a promoting role. Furthermore, the adsorption ability of Ag is promoted more strongly when the Ag atom sits in the subsurface layer and therefore the occupation of the subsurface position by Ag seems to be favorable for Pd-Ag(100) in the presence of hydrogen. It is in line with the observation of González *et al*. [10] that the increasing coverage of adsorbed H atoms on Pd-Ag(111) is accompanied by the migration of the Ag atoms from the surface to the subsurface region. In our work a strong promoting effect of the neighboring Pd atom is also seen for Pd_4Au, but it is limited to the Au atom placed in the subsurface layer. The BE of the H atom adsorbed on the Au atom present in the surface layer of the alloyed cluster is almost the same as in the atop position on Au_5. In the case of the Pd_4Pt cluster the effect of the Pd surroundings depends on the location of the Pt atom. When the Pt atom is placed in the surface layer, the promoting effect of the surroundings on its ability to adsorb atomic hydrogen can be observed. By contrast, the Pd surroundings diminish the ability of the subsurface platinum. It is worth noting that the poisoning effect of the Pd surroundings is not strong enough to suppress the migration of the H atom beneath the surface layer in the hollow position on the Pt atom.

The Pt surroundings cause the increase of the h values when the H atom is adsorbed on the Ag and Au atoms. The increase is particularly significant for the hollow position. For this position the Pt surroundings produce a strong promoting effect on the adsorption properties of Ag and Au. The Ag atom in the surface layer of the Pt_4Ag cluster experiences the weaker promoting influence of the surroundings compared to the subsurface Ag atom. By contrast, the Pt surroundings decrease the binding of the H atom adsorbed on the surface Au atom by 0.36 eV, which is rather surprising. The poisoning effect can also be observed for the subsurface Pd atom. On the other hand, the ability of the surface Pd atom to adsorb the H atom is promoted by the Pt neighboring atoms. Within the framework of the cluster model used in this paper, the atom of the other group 10 metal, that is, Pd in Pt_4Pd and Pt in Pd_4Pt, is subjected to two opposite

effects, depending on its location. When it is placed in the surface layer, the neighboring atoms promote its ability to adsorb the H atom, but when it occupies the position in the subsurface layer, its ability is inhibited by the surroundings.

4. Conclusions

The effect of alloying on the H-atom adsorption was investigated using DFT. The structural and energetic properties of the H atom adsorbed on the (100) surfaces of the Pd-Ag, Pd-Pt, Pd-Au, Pt-Ag, and Pt-Au alloys were determined within the framework of the cluster model.

The results of the calculations indicate that the Ag and Au atoms, present in the (100) surface layer of the alloyed palladium and platinum, adsorb the H atom less exoenergetically than the Pd and Pt surface atoms. The distance at which the H atom is adsorbed by Ag and Au in the alloyed surface layer is higher than that in the atop position on neat Pd(100) and Pt(100). The adsorption of atomic hydrogen on the subsurface second-metal atom in the Pd-Me alloys is less exoenergetic than on the subsurface Pd atom. However, the presence of the second metal in the subsurface layer of the Pt-Me alloys influences negligibly the energetic effect of the H-atom adsorption compared to the BE of the H atom on the subsurface Pt atom. On the surfaces alloyed with Pd or Pt, the strongest binding of the H atom occurs on the surface Pt and subsurface Pd atoms.

The Ag atom in the Pd-Ag and Pt-Ag alloys experiences a promoting effect on its ability to adsorb the H atom, since the more exoenergetic values of BE are observed when moving from neat Ag(100) to the alloyed surfaces. In the case of the surfaces alloyed with Au, the role of the surroundings depends on the location of the second-metal atom in the adsorption site. The Au atom occupying the subsurface position is promoted, whereas in the surface layer it is subjected to the inhibiting effect.

Relating the effect of alloying to the catalytic hydrogenation reactions, the results of the calculations have shown that Ag and Au generally act as poisoning reagents to the H-atom adsorption when Pd and Pt are alloyed with them. The BE of the H atom becomes less exoenergetic on such alloyed surfaces. Hence, the (100) surfaces of the Pd-Ag, Pd-Au, Pt-Ag, and Pt-Au alloys can exhibit enhanced selectivity in the catalytic hydrogenation reactions. By contrast, alloying with Pd or Pt leads to the surfaces that keep strongly adsorbing atomic hydrogen and, thus, their utilization in the selective hydrogenation seems to be rather limited.

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Supplementary material

The properties of the diatomic molecules calculated by means of seven hybrid and twelve non-local density functionals and some details concerning the statistical approach used to assess the accuracy of each functional.

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