Tuning the chemical activity through PtAu nanoalloying: a first principles study

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The electronic structure and adsorption properties of 1.5 nm sized Pt, Au, and PtAu nanoclusters are studied by density functional theory. We explain the recent experimental finding that 20% Au content in PtAu nanoparticles is optimal to induce a dramatically different catalytic behavior. Our results show that the *d*-band center together with the density of states at the Fermi energy can be used as an indicator of the chemical activity of PtAu nanoclusters. The most favorable adsorption sites on the cluster surfaces as a function of the Pt/Au ratio are identified using atomic H as a probe.

I Introduction

The catalytic properties of bimetallic nanoparticles have been investigated extensively both theoretically and experimentally in the field of core-shell heterogeneous nanocatalysis.^{1–5} This is connected to the fact that the catalytic reactions occur primarily on the nanoparticle surface, whereas the core markedly affects the entire nanoparticle performance. However, recent results show that the lowest energy structures of PtAu nanoclusters with different Pt/Au ratios display alloy-type complex surface patterns with a variety of chemically active binding sites.^{6,7} Experiments performed by Schrinner and coworkers⁸ using 1 to 10 nm PtAu nanoparticles immobilized on spherical poly-electrolyte brushes have shown that the chemical activity or turnover rate for the oxidation of alcohols to their respective aldehydes as a function of the Pt/Au ratio goes through a maximum at 20% Au content. A maximum activity at 20% Au content has also been found by Petkov and coworkers⁶ by resonant high energy X-ray diffraction. However, both studies could not explain why 20% Au content is optimal to enhance the catalytic behavior.

As a matter of fact, alloying causes multiple changes in the physicochemical properties of the metallic components. Concerning the catalytic properties, two effects are important: (i) the ensemble effect, *i.e.*, a finite number of atoms in a specific geometric orientation required for enhancing a particular catalytic process and (ii) ligand effects, *i.e.*, a modification of the electron density distribution as a consequence of the formation of mixed bonds. Ensemble and ligand effects are usually simultaneously present and produce a combined effect on the catalytic activity in bimetallic catalysts. The purpose of the present study is to systematically investigate the dependence of

the chemical activity on the underlying alloy electronic structure and adsorption site energetics of atomic H on Pt, Au, and PtAu nanoclusters. H is one of the most simple adsorbates and its interaction with PtAu nanoclusters is a vital step towards understanding the general trends of the chemisorption properties of bimetallic PtAu nanocatalysts.

II Simulation details

The structure and chemical ordering of 201 atom PtAu clusters can be obtained by a combination of a symmetry orbit approach and density functional reoptimization. The symmetry orbit approach exploits the full point group symmetry of a cluster by partitioning the atoms into atomic shells. Thus, for a given geometrical structure, the number of in-equivalent homotops can be reduced from 2^T , where T is the total number of atoms in a given cluster, to 2^S , where S is the number of atomic shells. The 201 atom clusters have truncated octahedral structures and therefore specific properties, in particular a unique arrangement of the atomic shells that simplify the implementation of the symmetry orbital technique. As a consequence, the necessary computation time is drastically reduced, so that first principles simulations become possible even for large clusters. We investigated the full range of homotops of the 201 atom PtAu clusters. However, for the purpose of the present study we focus on the most stable configurations.

Calculations for the H adsorption are performed using the Vienna *Ab initio* Simulation Package,¹⁴ employing a projected plane-wave basis set and the generalized gradient approximation in the Perdew–Burke–Ernzerhof flavor.^{15,16} All calculations take into account possible spin-polarization, where the wave functions are expanded up to a kinetic energy cut-off of 500 eV. Since clusters are non-periodic systems, the reciprocal space summation is restricted to the Γ point. Moreover, the Kohn–Sham energy levels are broadened using a Gaussian smearing of 0.02 eV width. We consider a simple cubic supercell of size

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$a = 32 \text{ \AA}$, which is found to be sufficient to neglect the interaction of the cluster with its periodic images. The self-consistency convergence criteria are set to $10^{-5} \text{ eV \AA}^{-1}$ for the energy gradient and $5 \times 10^{-4} \text{ \AA}$ for the atomic displacements. The computational strategy employed here has been successfully used to study similar alloy clusters in ref. 17 and 18.

III Results and discussion

In the following we address the electronic structure and adsorption properties of Pt, Au, and PtAu nanoclusters as a function of the Pt/Au ratio. In Section III(A) we explain the puzzling experimental finding that the 20% Au content in PtAu nanoparticles is optimal to display a dramatically different catalytic behavior. Section III(B) outlines a scheme to find the nonequivalent adsorption sites of atomic H on Pt, Au, and PtAu nanoclusters and Sections III(C) and (D) deal with the H adsorption energies and their site dependence by analyzing the local density of states and the underlying charge transfer process.

(A) Center of the *d*-band and density of states at the Fermi energy

The interaction strength of atoms or molecules with metal surfaces to a large extent is controlled by the location of the *d*-band center.^{9,10} Therefore, we have calculated the position of the *d*-band center relative to the Fermi energy for different clusters. Frontier orbital theory establishes that the states of a metal that is directly involved in electron transfer with the adsorbate are closest to the Fermi energy.¹¹ Therefore, the *d*-band center and the density of states at the Fermi energy give rise to indicators of the chemical activity. We have calculated and tabulated these parameters for different Pt/Au ratios in Table 1. The calculated *d*-band centers of Pt₂₀₁ and Au₂₀₁ are -2.20 and -3.21 eV , respectively, which is in good agreement with the Hammer-Nørskov *d*-band model.^{12,13} This model predicts higher chemical activity for Pt than Au, since the Pt *d*-band center is closer to the Fermi energy. In addition, the density of states at the Fermi energy of Pt₂₀₁ shows a huge enhancement (nearly 14 times) as compared to that of Au₂₀₁.

We next answer the question why 20% Au content yields the maximal activity in experiments. Table 1 indicates that the *d*-band center shifts progressively closer to the Fermi energy and the

density of states at the Fermi energy is significantly enhanced when the Au content is reduced towards 20%. We now focus our attention to PtAu clusters with low Au content. In the cases of 20% and 12% Au contents, we notice that the *d*-band center remains almost unchanged with respect to that of Pt₂₀₁. On top of that, the density of states at the Fermi energy is maximal for low Au content, more exactly for the Au₄₂Pt₁₅₉ cluster, which corresponds to almost exactly 20% Au content. For this reason, the maximum of the catalytic activity observed for 20% Au content is to be attributed to a maximal charge transfer in this case, induced by the unique surface atomic arrangement. Specifically, we find that Au atoms occupy all the sites of the 100 facets, which significantly modifies the charge distribution in the cluster.

(B) H adsorption on Pt, Au, and PtAu nanoclusters

Starting with the pure Pt and Au clusters, we have considered 16 nonequivalent positions for the H adsorption, 6 on the 100 facet and another 10 on the 111 facet. The adsorption sites are named as follows: the atop position refers to a H atom situated directly above the center of a surface Pt or Au atom. There are a number of atop sites; however, they can be classified into two categories: those on the 111 facet (atop111) and those on the 100 facet (atop100), see Fig. 1. The bridge position refers to a H atom situated in the middle of PtPt, AuAu or PtAu dimers. The bridge sites again can be classified into two categories according to the facet (bridge111 and bridge100). Moreover, there are fcc sites where H occupies a hollow site, triangulated by three Pt or Au atoms or a combination of Pt and Au atoms.

We have considered the full multitude of active sites on PtAu cluster surfaces and shown in Fig. 1 the five most favorable sites for the Pt/Au ratios under consideration. The procedure for identifying the different adsorption sites is more complicated in the case of PtAu cluster surfaces, since more details have to be taken into account, such as the facet and types of atoms involved in an adsorption site. For example, a bridge site can be of bridge111PtPt or bridge111AuAu type, where the H atom is located midway between two Pt or Au atoms on the 111 facet. In addition, the bridge111PtPt site, for example, may be at the edge of a 111 facet (bridge111PtPt-outer) or in the inner region (bridge111PtPt-inner).

(C) Adsorption energies

The strength of the interaction or in other words the adsorption energy of atomic H with Pt, Au, and PtAu nanoparticles has been quantified and is shown in Fig. 1. Apparently, one can notice a systematic increase in the adsorption energy in the order of 0.08 eV as a function of increasing Pt/Au ratios having a lowest value of 0.43 eV corresponding to Au₂₀₁H and a highest value of 1.11 eV corresponding to Pt₂₀₁H. The adsorption energy obtained for Pt₂₀₁H from this work is apparently higher (nearly three times) than that of the bridgePtPt site on a Pt111 surface reported in ref. 19. The experimental values of H adsorption on Pt111 scatters between 0.30 and 0.99 eV . The most favorable adsorption site we obtained is brigePt100-outer and the most weakly adsorbed site is atopPt111-outer (not shown in Fig. 1). Whereas for the Au₂₀₁H cluster, the most favorable adsorption

Table 1 Center of the *d*-band and density of states at the Fermi energy for various Pt_mAu_{201-m} clusters

Cluster	Au%	Center of the <i>d</i> -band relative to the Fermi energy (eV)	Density of states at the Fermi energy (1/eV)
Au ₂₀₁	100	-3.21	24
Au ₁₇₆ Pt ₂₅	88	-2.75	75
Au ₁₅₁ Pt ₅₀	75	-2.67	80
Au ₁₀₂ Pt ₉₉	51	-2.41	201
Au ₅₀ Pt ₁₅₁	25	-2.30	320
Au ₄₂ Pt ₁₅₉	20	-2.22	353
Au ₂₅ Pt ₁₇₆	12	-2.19	344
Pt ₂₀₁	0	-2.20	330

Fig. 1 Adsorption site energetics of H on $\text{Pt}_m\text{Au}_{201-m}$ clusters with different Pt/Au ratios.

site has changed with respect to the Pt_{201}H and is bridgeAu100-inner. Interestingly, we found that the differences in the adsorption energies for the most favorable adsorption site and most weakly adsorbed site is less than 0.01 eV regardless of the two different facets and different adsorption sites.

Let us start our discussion on the adsorption site energetics of H on PtAu clusters. In the case of a small Pt concentration ($\text{Pt}_{25}\text{Au}_{176}\text{H}$), the most favorable adsorption site is found to be bridge111AuAu-outer. In the case of nearly 25% of Pt concentration ($\text{Pt}_{50}\text{Au}_{151}\text{H}$), the most favorable adsorption site is found to be atop111Pt situated at the middle of the 111 facet and the adsorption energy shows an increase of 0.08 eV compared to that of $\text{Pt}_{25}\text{Au}_{176}\text{H}$.

(D) Density of states and charge redistribution

The preference for specific adsorption sites on PtAu cluster surfaces can be demonstrated by analyzing the density of states projected onto the H 1s state, yielding insight into the charge redistribution mechanism as a result of the H adsorption. As an example, we consider the $\text{Pt}_{50}\text{Au}_{151}\text{H}$ cluster and its three most favorable H adsorption sites, which are displayed in Fig. 2. Apparently, there are significant shifts in the H 1s peaks between the different adsorption sites. To understand the origin of these shifts, one has to consider in detail the interaction process of atomic H with the PtAu cluster surface. In both Pt and Au the 6s valence state is only half occupied and very broad, whereas the 5d states are localized and therefore narrow. The interaction of the H 1s state with the PtAu alloy states can be considered as a two level process. In the first step, the H 1s state interacts with

Fig. 2 H 1s partial density of states and charge density isosurface of the most and second most favorable H sites on the $\text{Pt}_{50}\text{Au}_{151}\text{H}$ cluster, see Fig. 1(c). Blue and yellow colors represent electron accumulation and depletion, respectively. The isosurface charge density is taken as 0.01 electrons per $\text{\AA}^3$.

the 6s valence state of the PtAu alloy. This broadens the H 1s state and gives rise to a single resonance band below the Fermi energy, which results in a weak H–PtAu bond. In the second step, the H 1s state interacts with the 5d states of the PtAu alloy. This results in strong chemisorption by splitting of the H 1s state into H 1s–PtAu 5d bonding and antibonding states, thus inducing a strong hydride–alloy bond. It is well known that strong chemisorption occurs if the number of empty antibonding states increases, see Fig. 2 for comparison.

The energetical position of the H 1s–PtAu 5d bonding state in the H density of states for adsorption site 1 is significantly shifted towards the Fermi energy as compared to the adsorption sites 2 and 3. In addition, the number of H 1s–PtAu 5d anti-bonding states is larger for site 1, which is due to the unique geometric position of this site. The H atom occupies the atop111Pt position (bonded to 6 Au surface atoms), which enhances the PtAu–H bond formation. This conclusion is confirmed by a Voronoi charge transfer analysis,²⁰ see Fig. 2. An interesting result of the charge transfer from Pt to Au is that the transferred charge will shift the Au *d*-band center away from the Fermi energy, which leads to weaker (stronger) interaction between H and Au (Pt) atoms.

IV Conclusion

The electronic structure and adsorption site energetics of atomic H on 1.5 nm sized Pt, Au, and PtAu nanoclusters have been studied using density functional theory. The *d*-band center and density of states at the Fermi energy are found to correlate with the chemical activity observed in experiments. First principles results thus can provide a consistent explanation of recent puzzling experimental findings on PtAu nanoparticles. The local electronic structures of Pt and Au atoms, especially those forming direct bonds with the H atom, are significantly modified by a combined effect of a sizable charge transfer from the Pt to the Au atoms and the formation of covalent H–PtAu bonds. Systematic and continuous changes are observed in the adsorption energies, which opens the possibility of tuning the catalytic properties *via* PtAu nanoalloying.

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