

# Theoretical Study of the Catalytic Activity of Bimetallic RhCu Surfaces and Nanoparticles toward H<sub>2</sub> Dissociation

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First principles based density functional methods and theoretical models have been used to investigate the reactivity of different RhCu alloys toward molecular hydrogen dissociation. For pure Rh(111), it is predicted that H<sub>2</sub> can either dissociate spontaneously or be physisorbed as molecular hydrogen. These predictions agree with recent experimental findings. The simple addition of a Cu atom to a Rh-rich environment is enough to eliminate the presence of the energy minimum associated with molecularly adsorbed hydrogen and to convert H<sub>2</sub> dissociation in an activated process. From the present results it is concluded that increasing the Cu content may lead to a change in the active site and permits us to speculate about the enhancement on the irreversible hydrogen uptake on going from Rh to RhCu alloys with a small Cu content.

## I. Introduction

Bimetallic systems constitute a broad class of catalysts that takes advantage of the different chemical activity of the two metals toward a given chemical reaction.<sup>1–5</sup> The resulting catalyst has special features and does not always display evidence of a chemical reactivity that can be anticipated by a simple interpolation of the reactivity of the constituents. In particular, bimetallic catalysts may exhibit interesting properties such as improved selectivity and activity. These enhanced qualities of bimetallic systems are being currently exploited in several industrial processes, particularly in hydrocarbon reforming in the oil industry.<sup>6–8</sup> The superiority of bimetallic catalysts has activated a large amount of research, both of applied and basic character. A simple explanation of the different behavior of the bimetallic system as compared to the pure components makes use of the so-called structural (ensemble) and electronic (ligand) effects. Structural effects correspond to the geometrical changes introduced by alloying the metals; these changes can induce or remove certain active sites and hence be responsible for a different chemistry. Electronic effects are more subtle and are a consequence of the heterometallic bonding that may induce changes in the surface states and consequently on the surface work function and other related properties.

A type of bimetallic system that exhibits interesting chemical properties that are frequently exploited in industrial processes contains Pt-group (Pt, Pd, Rh) metals and host metals such as Cu. This is the case of PdCu bimetallic-based catalysts, which are active in the NO reduction by CO<sup>9</sup> and thus are of specific and practical interest in the automotive industry. Likewise, PdCu is efficient in alkene oxidation,<sup>10</sup> ethanol decomposition,<sup>11</sup> and in several hydrogenation processes; among them we quote CO,

benzene, and toluene hydrogenation.<sup>11–14</sup> Because of these peculiarities PdCu alloys have also been the subject of detailed experimental studies<sup>15</sup> and also of several theoretical investigations.<sup>16–20</sup> In particular, in a series of previous papers the electronic structure<sup>17,18</sup> and chemical activity of PdCu bimetallic systems toward probe molecules<sup>16,17,19</sup> and H<sub>2</sub> dissociation<sup>20</sup> has been studied in detail by means of density functional methods and cluster models. An important conclusion derived from the theoretical modeling is that a single Pd atom in a Cu surface is able to dissociate H<sub>2</sub>, whereas the Cu surface is inactive.<sup>20</sup> However, the necessary condition for this single Pd atom to be active is that it is surrounded by other Pd atoms in the second layer of the bimetallic surface. This is a clear indication that electronic effects are dominant, at least for H<sub>2</sub> dissociation on PdCu surfaces. Therefore, it is important to investigate whether this behavior is characteristic of PdCu alloys or is it more general and appears in other bimetallic systems.

RhCu alloys provide another example of bimetallic systems where Cu is used essentially to dilute the active metal. The interest in this particular bimetallic catalyst goes back to the earlier seventies,<sup>21</sup> although it has been the object of a renewed interest in recent studies.<sup>22–25</sup> In the PdCu binary system the phase diagram shows the existence of substitutionally disordered fcc (face centered cubic) alloys and indicates that solid solutions between both elemental components can exist over the full composition range.<sup>26</sup> However, in RhCu the two components are only partially miscible and the corresponding phase diagram exhibits two well-defined phases, one rich in Cu (with  $X_{\text{Cu}} \geq 0.8$ ) and another one rich in Rh (with  $X_{\text{Cu}} \leq 0.2$ ).<sup>27,28</sup> Here it is worth mentioning that these considerations apply to macroscopic systems and that small particles of nanoscopic or even smaller size may exhibit a different behavior due to the important contribution of the particle surface to its total energy. We will come back to this point in the forthcoming discussion. The electronic structure of the RhCu system is to a large extent unknown. Fernández-García et al. have interpreted the results

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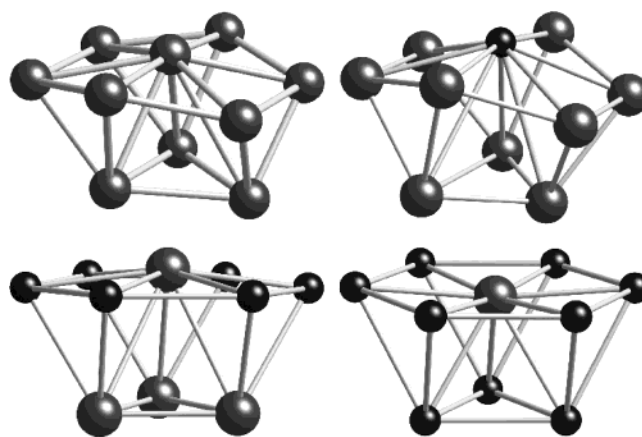
of Rh and Cu K-edge X-ray Absorption Near Edge Structure (XANES) in terms of the widely used charge-transfer model and concluded that Rh centers have a noticeable positive charge.<sup>25</sup> Similar conclusions based on similar arguments were used by Rodríguez et al. in their interpretation of X-ray Photoelectron Spectroscopy (XPS) obtained for the deposition of Rh on Cu(100).<sup>29</sup> We must point out that this naive interpretation of core-level shifts neglects many physical effects that contribute to the final measured shift. As a result, the simple charge-transfer picture can be even qualitatively incorrect, particularly in cases where moderate to low charge redistribution is involved in the hetero-metallic bond formation process.<sup>18,30</sup>

The reactivity of RhCu alloys toward hydrogen adsorption has been considered by Chou et al. in their study of bimetallic crystallites supported on alumina.<sup>31</sup> The crystallite sizes in these experiments are of 20 Å and thus contain ~ 50–100 atoms. These authors concluded that the composition of the crystallites formed upon introducing copper atoms into Rh/Al<sub>2</sub>O<sub>3</sub> are broadly compatible with that predicted from the phase diagram of the corresponding binary system, i.e., a Rh- or Cu-rich phase. In addition the authors interpret their results mostly in terms of the electronic effects, in fact, to explain the enhanced activity of the bimetallic system with a small copper content relative to bulk Rh particles, Chou et al. also suggested that new active sites are formed by the interaction of the two metals. They speculate that for values of  $X_{\text{Cu}} = 0.05$  the crystallites surface contains some Rh atoms surrounded by Cu, thus leading to a high capability for hydrogen chemisorption; upon increasing  $X_{\text{Cu}}$  the Cu atoms tend to occupy more surface sites and eventually segregate Cu islands which finally cover the whole surface. These are interesting hypotheses that are very difficult to prove by experiment but, on the other hand, can be explored by means of theoretical models. The present investigation aims to provide answers to some of these hypotheses by analyzing different possibilities by theoretical modeling.

In this work we explore the reactivity of several RhCu alloys of different composition toward hydrogen adsorption and dissociation. Following the strategy outlined in our previous work on PdCu,<sup>20</sup> we use cluster models representing either extended surfaces or microscopic particles and use density functional theory to study the interaction of molecular hydrogen with these surface models.

## II. Material Models

Cluster models have been employed to represent several compositions of the substitutionally disordered RhCu binary alloys. The choice of these disordered alloys comes from phase diagrams of the RhCu binary alloy which shows that these two metals are partially miscible and form two phases, i.e., a rhodium-rich phase and a copper-rich phase, at  $T < 1400$  K.<sup>27</sup> In a first series of models we attempt to mimic the structure of extended disordered alloys, whereas in a second series we consider genuine metal particles of microscopic size as a first step toward modeling of nanoparticles. The main difference between the two kinds of models concerns the geometric structure. In the first case one pretends that the model is representative of an extended surface and this is achieved, at least in part, by keeping the geometry of the cluster fixed at the bulk values. The main argument is that one of the effects of the extended system is precisely to provide a fixed structure; keeping the geometry of the cluster fixed provides a simple yet efficient mechanical embedding while neglecting the effect of the rest of the crystal in the electronic structure. This simple representation has no doubt important limitations, specially if

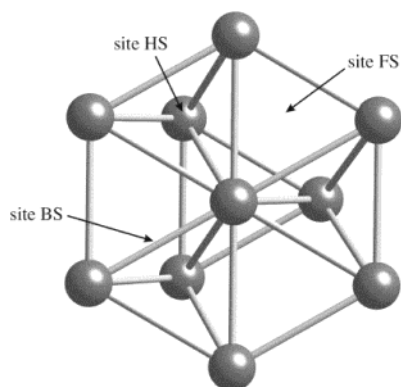


**Figure 1.** Optimized geometry of the different cluster models used to represent metallic Rh; Rh<sub>10</sub> (a), and bimetallic RhCu; Rh<sub>9</sub>Cu (b), Rh<sub>4</sub>Cu<sub>6</sub> (c), and RhCu<sub>9</sub> (d).

one pretends to describe properties that depend on the long-range electronic structure. However, the cluster approach provides an excellent model to study local properties, chemisorption and dissociative adsorption being among them.<sup>32–35</sup> In the second type of models one aims to represent an isolated metallic or bimetallic particle. Therefore, the geometry of the metal cluster is fully optimized to allow it to reach the optimum structure corresponding to a microscopic metal particle. This is also useful to represent the structure and reactivity of small supported metal clusters. In fact, it has been shown that the metal–support interaction is in many cases rather small and hence not enough to distort the cluster geometry.<sup>36–38</sup> Obviously, cases where epitaxial growth of the metallic phase occurs are out of this simplification.

The cluster models have been designed to represent either the Rh- or Cu-rich alloys predicted by the phase diagram. These are Rh<sub>9</sub>Cu and RhCu<sub>9</sub> with seven atoms in the first layer, three in the second, and arranged as in an (111) face. This is usually the one encountered in real situations because for a fcc structure this crystal termination exhibits the smallest surface energy. In addition, we have considered an intermediate composition, Rh<sub>4</sub>Cu<sub>6</sub>, not existing in the RhCu phase diagram, but similar to that encountered in PdCu alloys. There are two reasons for this choice, one is of academic and the other of scientific character. The first reason is simply to compare RhCu to PdCu in similar compositions although the former could not exist in macroscopic samples. The second reason is that even if this intermediate composition does not appear at the macroscopic level it may well occur for small metal particles of nanoscopic size. To compare the reactivity of the RhCu alloy models to that of the pure components, a Rh<sub>10</sub> cluster model has been used to represent the Rh(111) surface whereas for Cu(111) we will use the data already published for the Cu<sub>10</sub> cluster.<sup>20</sup> For the clusters with fixed geometry the metal–metal distances are as follows:  $d(\text{Rh–Cu}) = 2.59$  Å and  $d(\text{Rh–Rh}) = 2.67$  Å; the first one corresponds to a weighted interpolated value between Cu and Rh bulk and the second one to Rh bulk and have been extracted from the literature.<sup>28,39</sup>

Taking the structures above-described for Rh<sub>10</sub>, Rh<sub>9</sub>Cu, Rh<sub>4</sub>Cu<sub>6</sub>, and RhCu<sub>9</sub> as a starting point, a geometry optimization procedure has been carried out to allow the metal particles to relax and adopt the minimum energy conformation closest to that of a (111) phase. The optimum configurations are displayed in Figure 1 and show that in all cases the final structure is fairly



**Figure 2.** Schematic representation of the BS, FS, and HS active sites considered for H<sub>2</sub> dissociative chemisorption. The M<sub>10</sub> cluster model depicted in the figure can represent any of the systems studied.

close to the one of the fixed cluster used to mimic the extended alloys. The details of these structures will be discussed later on.

Following our previous work on the H<sub>2</sub>/PdCu system,<sup>20</sup> the interaction of molecular hydrogen with each of the cluster models described above has been studied by placing the hydrogen atoms pointing toward the high-symmetry surface sites (Figure 2). Therefore, one may have the two hydrogen atoms pointing toward open fcc sites (FS), toward eclipsed or hcp (hexagonal close packed) sites (HS), and, finally, both pointing toward bridge sites (BS). From these initial geometries a complete optimization procedure was carried out to find the different possible stable physisorbed or dissociatively adsorbed situations. Details about the energy calculation and geometry optimization procedures are given in the next section.

In the RhCu active sites for H<sub>2</sub> dissociation described above there are still several different possibilities as compared to those exhibited by the pure metal, Rh or Cu, (111) surfaces. The active sites modeled in this work involve either a single-surface Rh or Cu atom. In the first case, two different electronic environments are considered. The first one is represented by the RhCu<sub>9</sub> cluster model where the Rh surface atom is completely surrounded by Cu atoms and the second one by the Rh<sub>4</sub>Cu<sub>6</sub> cluster in which the surface Rh atom is surrounded by Cu atoms in the first layer and Rh atoms in the second layer. Notice that the later may be regarded as a tetrahedral Rh<sub>4</sub> unit embedded in Cu atoms. The third active site involves a Cu atom surrounded by Rh atoms, this corresponds to the Rh<sub>9</sub>Cu cluster and represents a Rh-rich alloy.

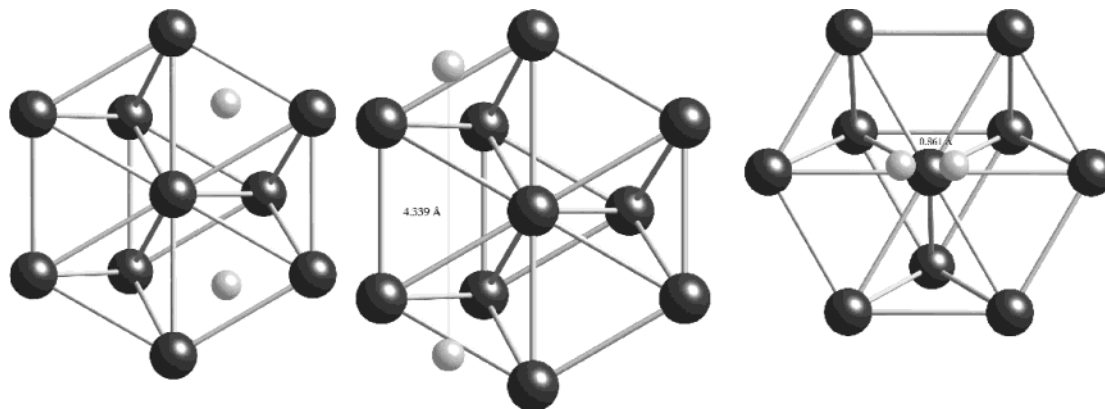
### III. Computational Details

To study the interaction of molecular hydrogen with the different surface cluster models we use a first principles density functional based method. In particular, we have chosen the widely used B3LYP<sup>40</sup> functional as implemented in the Gaussian98 suite of programs.<sup>41</sup> The B3LYP is an hybrid functional that combines different functionals to achieve the best fit to experimental thermochemical data of a series of molecules. In particular, the B3LYP functional combines the exact Fock exchange with the gradient corrected exchange functional proposed by Becke,<sup>42</sup> and with the nonlocal expression of the correlation functional proposed by Lee, Yang, and Parr<sup>43</sup> (BLYP), based on the original work of Colle and Salvetti on the correlation factor.<sup>44,45</sup> It is worth pointing out that quite surprisingly, the B3LYP hybrid functional is able to reproduce the thermochemistry of molecules containing transition metal atoms although no transition metal compounds were included in the data set used in the fit.<sup>46–49</sup>

To represent the electron density of the metallic clusters we use relatively extended Gaussian Type Orbitals, GTO, and the relativistic small-core effective core potentials, ECP, derived by Hay and Wadt.<sup>50</sup> These ECPs, commonly referred to LANL2, leave explicitly the 3s, 3p, 3d, and 4s electrons of Cu atoms and the 4s, 4p, and 4d electrons of Rh. The standard GTO double- $\zeta$  basis set also reported by Hay and Wadt,<sup>50</sup> and denoted usually as LANL2DZ, was used to expand the electron density arising from the valence electrons of Cu and Rh whereas the electron density of the hydrogen atoms was described with a standard 6-31G\*\* basis set.

Following the strategy outlined in a previous work,<sup>20</sup> we use a step by step geometry optimization procedure to characterize the energy profile of the H<sub>2</sub> dissociative chemisorption with these binary alloys. In this procedure the H–H and the perpendicular distance of H<sub>2</sub> to the surface are optimized with the cluster geometry fixed at the bulk values. The H<sub>2</sub> molecule is placed above the surface with the H atoms pointing each toward a BS, FS, or HS, surface site, cf. Figure 2. The initial perpendicular approach has not been considered because, as found for other substrates,<sup>51</sup> this is either repulsive or lead to a parallel orientation.<sup>20</sup> The geometry search starting from the BS, FS, and HS and with a value for the H<sub>2</sub> internuclear distance close to that for the gas phase molecule attempts to find possible physisorbed states which can be considered as precursors for dissociation. At this geometry optimization step, the position of each H atom is allowed to vary but always maintaining a symmetry plane. To study the FS and HS sites the symmetry plane is such that the H atoms are symmetric and to study the BS site the two H atoms are contained in the symmetry plane. The use of a symmetry constraint is introduced to avoid the hydrogen atoms flipping from one active site to the other. Hence, the presence of the symmetry plane permits us to have the two hydrogen atoms above the same site. Starting from each one of the conformations above-described permits us to ensure that the configuration space is sufficiently scanned. Depending on the final H–H internuclear distance one can decide whether physisorption or dissociative chemisorption of H<sub>2</sub> occurs on the various surfaces. In fact, in some optimized geometries, the H–H distance is only slightly elongated with respect to the equilibrium gas-phase value. This is indicative of a physisorption process where the H<sub>2</sub> molecule preserves, in part, its identity. In other cases, the final geometry corresponds to well separated H atoms placed above the surface model and quite far from the cluster edge. This is interpreted as the fingerprint of H<sub>2</sub> dissociation. Finally, there are situations in which the final geometry also corresponds to separate H atoms but interacting with the cluster edge. This final structure reveals limitations of the cluster model but does also indicate that H<sub>2</sub> will not dissociate in the regular sites of that surface. In all cases the main focus lies in the energy profile and final structure. Here it is worth pointing out that since physisorption energies are in the range of weak interactions, it is not obvious that they can be properly described with the current exchange–correlation functionals.<sup>52–54</sup> This should not introduce any problem because the main goal of the present approach is not a detailed description of physisorption but instead a comparison of the reactivity of different RhCu bimetallic alloys. In a final step, the geometry of the whole system is allowed to vary but the symmetry plane is maintained for convenience. This final step permits us to check the stability of the cluster models with respect to distortion and also to investigate the effect of H<sub>2</sub> dissociative chemisorption on the optimized structure of the naked cluster. The comparison of the energy profile obtained





**Figure 3.** Schematic representation of the three final geometries of  $H_2$  above the  $Rh_{10}$  cluster model: (a) dissociated  $H_2$  with the hydrogen atoms almost above the FS active sites at a perpendicular distance to the surface of 0.91 Å; (b) dissociated  $H_2$  with the hydrogen atoms on the cluster edge; (c) physisorbed  $H_2$  involving the hydrogen atoms interacting almost with a surface atom, the perpendicular distance to the surface is 1.65 Å and the H–H distance 0.86 Å.

with the rigid and optimized cluster will also provide useful information about similarities and differences between the reactivity of alloys extended surfaces and that of small bimetallic particles that are often encountered in the real catalysts. The optimization geometry strategy just described does not pretend to find all the possible local minima of these cluster models. In fact, since the final optimization is carried out by allowing all atoms to move keeping only a symmetry plane it is likely that the minimization algorithm will reach the energy minimum in the potential energy hypersurface that is closest to the starting geometry.

Finally, it is worth pointing out that the present calculations have all been carried out by deliberately choosing a singlet closed-shell electronic structure for the different cluster models. This choice may seem inadequate since the present study involves dissociation processes that, in principle, lead to an open shell electronic structure. However, the dissociation process takes place above a metal surface and metal–hydrogen bonds are formed, meanwhile the hydrogen–hydrogen bond breaks. Following previous work, only the final structures are of interest and no attempt has been made to locate the possible transition states corresponding to dissociative chemisorption.<sup>20</sup> The use of a closed-shell electronic structure to locate the transition state may be questioned, although this is also a common practice in periodic density functional calculations.<sup>55</sup> Last, we note that although Rh and Cu are nonmagnetic metals, small clusters do not necessarily have a nonmagnetic ground state. However, the electronic states of small metal clusters are very close in energy, even for magnetic metals such as Ni and Co.<sup>36</sup> Moreover, Ricart et al.<sup>56</sup> have shown that the choice of the electronic state does not largely affect the basic bonding mechanisms. Since the models used in this work attempt to simulate extended alloys that do not possess net magnetic moments, the choice of a closed-shell electronic structure constitutes the natural reference.

#### IV. Results and Discussion

To facilitate the discussion, the complete set of results will be described in three subsections. In the first section we focus on the interaction of  $H_2$  with Rh(111), whereas the remaining two sections are devoted to the bimetallic models—depending on whether the substrate aims to represent the (111) surface or a bimetallic particle.

**(a) Interaction of  $H_2$  with the Rh(111) Surface.** The interaction of  $H_2$  with the  $Rh_{10}$  cluster model leads to three different structures which are stable with respect to the separated systems: two of these structures arise from a dissociative

**TABLE 1: Summary of Results for the Interaction of Molecular Hydrogen with the Cluster Models Representing the Rh (111) and Bimetallic RhCu Surfaces<sup>a</sup>**

site	$d_{H-H}$ (Å)	$d_{\perp}$ (Å)	$E_{ads}$ (kcal/mol)
$Rh_{10}$			
FS	2.98	0.91	−15.1
edge	4.34	1.01	−27.9
physisorption	0.86	1.65	−7.96
$Rh_9Cu$			
FS	2.75	1.00	+4.4
edge	3.86	1.10	−6.0
$Rh_4Cu_6$			
BS	1.93	1.29	−15.8
$RhCu_9$			
BS	1.93	1.26	+21.6

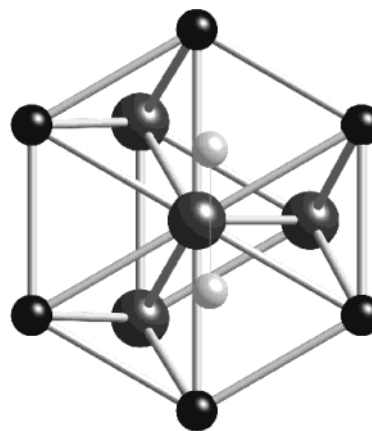
<sup>a</sup> Reported in the table are the active site where a stable structure is found, the H–H distance,  $d_{H-H}$ , the H–surface distance,  $d_{\perp}$ , and the interaction energy,  $E_{ads}$ .

adsorption process and one corresponds to physisorption. One of the two structures implying  $H_2$  dissociation has the two hydrogen atoms placed almost above the FS site and well inside the cluster region (Figure 3a). In the second structure the H atoms are almost in the cluster edge; cf. Table 1 and Figure 3b. A third mode involves molecularly adsorbed hydrogen, Figure 3c. Accordingly, only the first structure can be actually considered as the final step of molecular hydrogen dissociation on Rh(111), whereas the second one could be related to the final state for a small particle; we will come back to this point in the next subsection. The fact that the present calculations predict  $H_2$  dissociation on Rh(111) is in agreement with experiment.<sup>57</sup> Moreover, the existence of physisorbed molecular hydrogen at a perpendicular distance of 1.65 Å to the metallic surface with the  $H_2$  atoms nearly above the central Rh atom (Figure 3c) may help to explain the sudden change in sticking probability with (beam) energy found in recent molecular beam experiments.<sup>57</sup> The claim for a physisorbed state is supported by the internuclear H–H distance that appears to be 0.86 Å or ~16% larger than the corresponding value for the gas-phase molecule. It is worth pointing out that at this level several differences appear with respect to pure Pd. First, Pd(111) prompts  $H_2$  dissociation with no evidence of any physisorbed precursor and, second, FS and HS sites appear to have similar stability whereas for Rh(111) only the FS site seems to be occupied. However, the  $H_2$  adsorption energy on  $Rh_{10}$  is very similar but smaller than the one computed for  $H_2$  on  $Pd_{10}$  on the FS site using the same quantum chemical approach, 15.1 versus 18.0 kcal/mol. Although both metals (Rh and Pd) are

very efficient toward H<sub>2</sub> dissociation, the present data give support to the idea that Pd would have a superior activity. This conclusion is also consistent with the final distance of the H atoms above the surface, 0.91 Å, significantly larger than that reported for H<sub>2</sub> above a Pd<sub>10</sub> cluster model, 0.76 Å.

**(b) Interaction of H<sub>2</sub> with RhCu Alloys.** The discussion above has disclosed some features of the interaction of molecular hydrogen with a Rh(111) surface. Indeed, these are in agreement with experiment, thus validating the present approach, at least for the present purposes. Next, we analyze the changes in reactivity induced by the presence of Cu atoms in the substrate leading to bimetallic systems of different composition. Relevant results are summarized in Table 1. First, we consider the effect of a single Cu atom completely surrounded by Rh atoms, i.e., the Rh<sub>9</sub>Cu cluster (Figure 1b). The geometry optimization leads to two structures with large H–H separation which are closely related to those described for Rh<sub>10</sub>. One is representative of H<sub>2</sub> dissociation on a Rh-rich RhCu alloy and has the H atoms near the FS sites while in the other structure the H atoms are in the cluster edge. For the former structure, the H–H distance is 2.75 Å, ~8% shorter than for Rh<sub>10</sub>, and the vertical distance to the surface is 1.00 Å, significantly larger than for Rh<sub>10</sub>. The decrease in H–H distance is clearly a consequence of the shorter metal–metal average distance in the surface model while the larger vertical one is related to the more delocalized nature of the Cu one-electron states. These structural parameters already indicate a smaller chemical activity toward H<sub>2</sub> dissociation, the H–H distance is less elongated and the molecule is farther from the surface than for H<sub>2</sub> on Rh<sub>10</sub>. This is consistent with a relative decrease in the chemisorption energy which now becomes endothermic by 4.4 kcal/mol. No evidence for H<sub>2</sub> physisorption has been found for this bimetallic cluster. In the second minimum energy structure the H atoms are once more in the cluster edge, the final energy is 6 kcal/mol below the energy of the separated systems. This structure can only be assigned to dissociative adsorption on a small bimetallic particle. No evidence for physisorbed H<sub>2</sub> has been found for this bimetallic cluster. Therefore, we can conclude that the presence of a single Cu atom in a Rh-rich environment has two fundamental effects. First, it seems to avoid the formation of physisorbed H<sub>2</sub>, this is a clear structural effect and rather easy to understand, the active site has simply disappeared. Second, there is a decrease in the catalytic activity of Rh toward H<sub>2</sub> dissociation but maintaining FS as the active site.

Next we consider the case of Rh<sub>4</sub>Cu<sub>6</sub> where the surface Rh is surrounded by Cu atoms in the first layer while maintaining its coordination to other Rh atoms in the second layer. The presence of Cu atoms on the first layer induces a considerable change on the reactivity toward molecular hydrogen, there is only one optimal structure and it has the H atoms in the bridge site (Figure 4). It is worth mentioning that the same active site has been found in a similar cluster model of bimetallic PdCu. Hence, the difference coordination of the central Rh atom induces a change in the active site; again, this can be viewed as a structural effect. Moreover, the H–H distance is 1.93 Å, significantly smaller than the one found in the interaction of molecular hydrogen with both Rh<sub>10</sub> (2.98 Å) and Rh<sub>9</sub>Cu (2.75 Å). This is consistent with a larger distance to the surface 1.29 Å, although the interaction energy is 15.8 kcal/mol, close to that corresponding to a pure Rh surface model. This is also consistent with the Rh–H distance which for Rh<sub>4</sub>Cu<sub>6</sub> is 1.63 Å, whereas for Rh<sub>10</sub> the shortest Rh–H distance is 1.72 Å. Therefore, this bimetallic system can be a useful catalyst for some hydrogenation reactions, the H–H bond is almost broken



**Figure 4.** Schematic representation of the final geometry H<sub>2</sub> above Rh<sub>4</sub>Cu<sub>6</sub>. Notice that the hydrogen atoms are situated in BS sites, the perpendicular distance to the surface is 1.29 Å, and the H–H distance 1.93 Å.

but since the distance to the surface is larger it will provide an excellent precursor for hydrogenation reactions.

Finally, we discuss the reactivity of RhCu<sub>9</sub> which is representative of a Cu-rich alloy. Moreover, comparison with Rh<sub>4</sub>Cu<sub>6</sub> permits us to separate structural and electronic or ligand effects because both clusters have the same active site, a Rh surface atom surrounded by Cu atoms, but differ in the coordination in the cluster second layer. For RhCu<sub>9</sub> only a final optimized structure is found and this is indeed very close to that encountered in Rh<sub>4</sub>Cu<sub>6</sub>. The H atoms sit nearly above the BS site, with H–H and perpendicular distances to the surface almost indistinguishable from those predicted for Rh<sub>4</sub>Cu<sub>6</sub>. The only significant difference appears in the interaction energy which now is endothermic by 22 kcal/mol with respect to the separated systems. Therefore, H<sub>2</sub> dissociation on Cu-rich bimetallic surfaces appears to be an activated process. This is a rather obvious example of electronic effects. There is no change in the active site and final structure of almost-dissociated molecular hydrogen, but surprisingly enough the process is energetically less favorable. It is worth pointing out that this is in line with the conclusions reached in a previous study of the PdCu bimetallic system.<sup>20</sup>

**(c) Interaction of H<sub>2</sub> with Rh and RhCu Microscopic Particles.** The optimized geometries of the different surface cluster models have already been introduced in Figure 1. Essentially, the clusters maintain their structure, and the final geometry is reminiscent of that used to mimic extended bimetallic surfaces. This is consistent with the fact that the energy gain associated to the geometry relaxation is relatively small; 39.2 kcal/mol for Rh<sub>10</sub> and 23.9, 10.8, and 4.7 kcal/mol for Rh<sub>9</sub>Cu, Rh<sub>4</sub>Cu<sub>6</sub>, and RhCu<sub>9</sub>, respectively. It is important to point out that although the geometry optimization has been carried out by keeping a symmetry plane a re-optimization with no symmetry restrictions does not introduce appreciable changes. Consequently, the symmetry plane has been conserved in the calculations with molecular hydrogen to make sure that the two hydrogen atoms occupy equivalent sites.

For the H<sub>2</sub> interaction with the optimized Rh<sub>10</sub> two different structures are found, one with the H atoms well separated and in the cluster edge and the other one close to the physisorption minimum already found for the fixed Rh<sub>10</sub> cluster, Table 2. Hence, the only effect of substrate relaxation is the disappearance of the structure with the H at the FS site. The FS site is precisely the preferred adsorption site for chemisorbed atomic hydrogen on the (111) surface of transition metals<sup>58</sup> including

**TABLE 2: Summary of Results for the Interaction of Molecular Hydrogen with the Cluster Models Representing Rh and RhCu Particles<sup>a</sup>**

site	$d_{\text{H-H}}$ (Å)	$d_{\perp}$ (Å)	$E_{\text{ads}}$ (kcal/mol)
Rh <sub>10</sub>			
edge	6.07	0.17	+11.4
physisorption	0.86	1.65	-12.3
Rh <sub>9</sub> Cu			
FS	2.73	0.43	+13.0
HS	2.81	0.62	+3.8
Rh <sub>4</sub> Cu <sub>6</sub>			
BS	1.70	1.33	-18.0
RhCu <sub>9</sub>			
BS	1.73	1.37	+27.6

<sup>a</sup> Reported in the table are the active site where a stable structure is found, the H-H distance,  $d_{\text{H-H}}$ , the H-surface distance,  $d_{\perp}$ , and the interaction energy,  $E_{\text{ads}}$ .

Rh(111).<sup>59</sup> The disappearance of this adsorption mode upon geometry optimization is clearly a consequence of the distortion of the surface. This fact provides also some validation of the cluster model representation of Rh(111) because this adsorption site is properly predicted by a fixed cluster model. The physisorbed structure is further stabilized by 4 kcal/mol. For the minimum with the H atoms in the cluster edge it is not possible to have a meaningful comparison because the H atoms are well outside the cluster region. From these results one would infer that the reactivity of small Rh particles is perhaps likely enhanced, leading to dissociated H<sub>2</sub> with the H atoms well in the cluster edge but without loosing the characteristic feature of the Rh(111) surface of adsorbing molecular hydrogen in a non dissociative way as well.

For Rh<sub>9</sub>Cu, Rh<sub>4</sub>Cu<sub>6</sub>, and RhCu<sub>9</sub>, the effect of the substrate relaxation is even smaller. In Rh<sub>9</sub>Cu, the structures with the H atoms at the FS site and in the cluster edge coexist in both cases with a shorter H-H distance although in the former very close to the values obtained with the unrelaxed cluster whereas in the later this distance decreases to 2.8 Å and the H atoms nearly occupy HS sites. In both cases, the perpendicular distance to the surface decreases by ~0.5 Å. This can be understood easily from the final structure depicted in Figure 1b. The surface bends toward the second layer with a subsequent decrease of electron density near the FS and HS sites leading to a smaller Pauli repulsion and consequently a shorter distance to the surface. The adsorption energies become slightly more endothermic, 13.0 and 3.8 kcal/mol, respectively. Again, the introduction of a single Cu atom in a Rh environment leads to a decrease in the catalytic activity toward H<sub>2</sub> dissociation. Both relaxed Rh<sub>4</sub>Cu<sub>6</sub> and RhCu<sub>9</sub> maintain the BS site and as in the previous cases lead to shorter H-H distances, 1.70 and 1.73 Å, than for the fixed bimetallic clusters, 1.93 Å in both cases. The decrease in the H-H distance is a consequence of the larger stability of the cluster, decreasing the metal-metal repulsion in turn leading to a somehow less reactive cluster. Nevertheless, the energetic remains almost unchanged, the interaction energy becomes 18.0 kcal/mol for Rh<sub>4</sub>Cu<sub>6</sub>, only 2 kcal/mol more stable than on the unrelaxed substrate and endothermic by 27.6 kcal/ for RhCu<sub>9</sub>, only 6 kcal/mol less stable than in the fixed substrate.

The analysis above permits us to conclude that the reactivity of the different bimetallic cluster models discussed in subsection 4b is not qualitatively affected by the substrate relaxation. The only exception is perhaps for bulk Rh where the structure with the H atom at the FS site is not present for the relaxed cluster. In the remaining cases the substrate relaxation effects can be summarized as a decrease in the H-H distance and an accentuation of the overall trend, the exothermic structures

become slightly more exothermic and the endothermic ones also become more endothermic. In this respect, it looks as if the small clusters retain most of the chemical character of the extended surfaces. Obviously, small particles offer additional sites, specially those which are located at the cluster edges and between the different metallic layers. These have not been studied systematically in the present work. Nevertheless, one can anticipate a rather large number of structures in a narrow energy interval and it is likely that they do not lead to a different chemistry from that arising from the present results.

## V. Conclusions

In this work we have used first principles-based density functional methods and theoretical models to investigate the reactivity of different RhCu alloys toward molecular hydrogen dissociation. The present investigation is based on the structure and energy profile of reactants and products. Therefore it is important to point out that the conclusions outlined below should be corroborated by subsequent studies including the reaction path profile, energy barriers, and dynamical aspects.

For pure Rh(111), the present theoretical study predicts that H<sub>2</sub> can spontaneously dissociate although it can also be detected (before surface diffusion) as H<sub>2</sub> at the surface. These predictions both agree with recent experimental work based on molecular beam relaxation spectroscopy<sup>57</sup> and provide strong support to the conclusions reached in this work for the RhCu bimetallic clusters, where comparison to experiment is more difficult. It has been shown that the presence of a Cu atom in a Rh-rich environment is enough to eliminate the presence of the energy minimum associated with adsorbed molecular hydrogen and to convert H<sub>2</sub> dissociation in an activated process. This can be interpreted, to a first approximation, as a structural effect. However, in the optimum geometry the H atoms still occupy the FS sites as in pure Rh(111). Increasing the Cu content may lead to a change in the active site. In fact, Rh atoms surrounded by Cu atoms are still able to dissociate H<sub>2</sub> but the process is exothermic when the Rh atom is coordinated to subsurface Rh atoms and endothermic when is completely coordinated to Cu atoms. However, in both cases the final optimum structure corresponds to H atoms in the BS site. Here, one sees a mixture of structural and electronic effects. Nevertheless, the influence of electronic effects on chemical reactivity is clear; although the last two bimetallic systems mentioned have the same surface morphology only the former could spontaneously dissociate H<sub>2</sub>.

The change in active site predicted by the present cluster model calculations permits us to speculate about the enhancement on the irreversible hydrogen uptake on going from Rh to RhCu alloys with small Cu content.<sup>31</sup> These authors explain this rather surprising experimental result (not detected, for example, in PdCu alloys) by assuming that some extra sites must have been created upon addition of small Cu amounts to the monometallic Rh sample. This is consistent with the results reported in the present work. It is very possible that a Rh-rich alloy would have regions with isolated Cu atoms, as in Rh<sub>9</sub>Cu, and regions where Rh atoms will be coordinated to Cu atoms on the surface as in Rh<sub>4</sub>Cu<sub>6</sub>. In the former the H atoms would tend to occupy the FS sites whereas in the later the BS sites are preferred. At a given (111) surface the number of BS sites is superior to that of FS sites thus permitting an increase in the hydrogen uptake. Further increase of Cu will lead to Rh atoms completely coordinated to Cu with a concomitant decrease in the reactivity as experimentally found.

Finally, we stress the close similarity between the RhCu bimetallic systems and the PdCu systems studied in a previous



work. In particular, it is important to note that in both systems a single Pd or Rh atom can be active to dissociate molecular hydrogen but a necessary condition for single Pd or Rh atoms at the surface of the bimetallic system is to be coordinated to other Pd or Rh atoms below the surface, i.e., forming Pd or Rh microclusters that are surrounded by the other component of the binary alloy. This result stresses the importance of electronic or ligand effects in the activity of these bimetallic surfaces toward molecular hydrogen.

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