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# C<sub>2</sub>H<sub>2</sub>-Induced Surface Restructuring of Pd-Ag Catalysts: Insights from Theoretical Modelling

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**ABSTRACT:** In this paper, the influence of acetylene chemisorption on the equilibrium distribution of atoms in the (111) surface layer of Pd-Ag alloys is studied. All possible surface layer compositions are considered from a statistical mechanics based model with parameters determined from first principles computations. Surface restructuring is investigated at three different temperatures. In conditions relevant for the catalytic acetylene selective hydrogenation, the equilibrium surface distribution of alloy atom type strongly deviates from the smooth binomial random case and specific ensembles are favored, with sharp transition zones between them as a function of Ag content. Indeed, the chemisorption energy of acetylene on Pd rich ensembles provides a contribution to the free energy that counterbalances the entropic gain from the random alloy distribution. The molecule coverage and the associated energetic term are weakened by thermal effects and lateral interactions between adsorbates.

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## Introduction

Acetylene selective hydrogenation is one of the most prominent catalytic processes in the petrochemical industry. It purifies ethylene streams prior to polymerization, granting both a high quality product and an extended life cycle of the polymerization catalyst. Palladium is the key catalytic metal in selective hydrogenation catalysts. Supported Pd catalysts have been commercialized for decades, thanks to their high activity and high selectivity towards ethylene.<sup>1</sup> Nonetheless, a sound assessment of their performance has only recently been achieved, with the advent of more advanced characterization

techniques, such as X-ray Photoelectron Spectroscopy and Prompt Gamma Activation Analysis, that allow an *in situ* analysis of the catalyst structure.<sup>2,3</sup> These studies demonstrate that dissociative adsorptions of acetylene and hydrogen give rise to carbon and hydrogen diffusion through the uppermost surface layers, driven by the gas-phase chemical potential. This results in the formation of a carbide and a hydride phase and the interplay between these phases has been theoretically investigated. The carbide phase acts as a kinetic barrier to the hydrogen resurfacing.<sup>4</sup> It also facilitates ethylene desorption, hence increasing the selectivity towards ethylene.<sup>5</sup>

Even though palladium catalysts are still frequently studied materials in the chemical research community, Pd-based alloys generally exhibit a higher performance:<sup>6</sup> Addition of an ancillary metal, inactive for hydrogenation, improves the selectivity of the process at the expense of activity. The origin of this synergy is still a matter of scientific debate. It is recognized that alloying causes isolation of surface palladium atoms, but also alters the surface electronic structure; the former being usually referred to as the *geometric (or ensemble) effect* while the latter is known as the *electronic effect*. Pd-Ag alloys are among the most selective ones and, commonly used in industrial applications, are still subject of active research.<sup>7</sup> The bulk Pd-Ag alloys adopt a random configuration, implying that a lattice site's occupation probability is only related to the alloy composition. Experimentally identifying the relative importance of the geometric and electronic effect is highly challenging. Both Temperature Programmed Desorption (TPD)<sup>8</sup> and Infra-Red (IR) spectroscopy<sup>9</sup> of

CO provided evidence in favor of the geometric effect, and this was also supported by Density Functional Theory (DFT) calculations.<sup>10,11</sup> On the other hand, theoretical studies highlighted a noteworthy change in the d-band location and shape<sup>12</sup> for alloyed Pd atoms, and ascribed the same electronic effect to Ag as observed with surface carbide, i.e., improve the competition between ethylene desorption and its further hydrogenation at the surface of the catalyst.<sup>13</sup>

It is customary to describe an alloy surface in terms of ensembles or multiplets on which adsorption primarily takes place.<sup>14</sup> In the case of the Pd (111) plane, acetylene adsorbs preferably on the hcp hollow site,<sup>15</sup> which contains three surface atoms. For Pd-Ag alloys, the (111) surface can be paved with trimers forming hcp and fcc hollow sites, including Pd<sub>3</sub>, Pd<sub>2</sub>Ag, PdAg<sub>2</sub> and Ag<sub>3</sub> ensembles. The distribution of these ensembles in vacuum as a function of the Ag surface content was recently measured by Engstfeld *et al.* by means of Scanning Tunneling Microscopy (STM).<sup>16</sup> Multinomial distributions are adopted to a large extent, thus reflecting the random nature of the alloy. However, as these STM studies were performed in high vacuum conditions, the influence of adsorbates on the surface structure is excluded.<sup>17</sup> In the presence of an adsorbed molecule the expected surface ensemble distributions minimize the free energy, including the energetic contribution due to adsorption, and hence the surface distribution of metal atoms could dramatically change. These deviations from high vacuum conditions could be assessed from an *in situ* atomically resolved study, but this has, at present, not been accomplished. A theoretical evaluation of the ensemble distributions constitutes an attractive alternative, since it sheds light on the contribution of the ensemble effect, i.e., on the nature and molar fractions of active ensembles, defined here as the surface metal trimers that provide a stable adsorption of acetylene.

The present study requires a sound theoretical base to describe surface ordering phenomena in binary alloys. Mezey *et al.*<sup>18</sup> developed a model to calculate the equilibrium concentration of the alloy-adsorbate interface based on macroscopic material properties. They extended the approach to subsurface layers<sup>19</sup> and proposed corrections to include deviations from ideal mixtures.<sup>20</sup> Alternatively, atomistic thermodynamics<sup>21</sup> is conceptually well suited to be based on DFT calculations. Indeed, all the thermodynamic parameters are formulated in terms of periodic boundary conditions, and the free-energy is easily assessed. Creuze *et al.*<sup>22</sup> recently suggested the use of DFT calculations to parametrize Ising-type Hamiltonians and calculate effective pair interactions. This model

allows interpreting the origin of the segregation enthalpy. The reader is referred to the review of Liao *et al.*<sup>23</sup> for a more exhaustive discussion on segregation theories. Unfortunately, all of these studies focus on segregation and reverse segregation, along the axis perpendicular to the surface plane, while surface ordering and 2D-island generation are much less considered. An exception is the chemically oriented approach of Soto-Verdugo and Metiu,<sup>24</sup> in which the adsorbate-catalyst interaction is accounted for in the surface plane directions. Central to their discussion is the concept of the chemical equilibrium between alloy components in the bulk and at the surface, and the island formation of the solute upon adsorption of a species binding strongly to only one of the components.

The present paper estimates the ensemble distributions in the top layer of a Pd-Ag (111) surface based on the surface chemical equilibrium between these ensembles. Since (reverse) segregation is likely to be important in three dimensional models, the ratio of Pd to Ag we consider herein refers to the surface layer and not necessarily to the bulk alloy composition. The chemical equilibrium of trimer ensembles generates multinomial distributions in the absence of adsorbates, in agreement with the experimental data. Ensemble distributions at equilibrium in the presence of adsorbed acetylene are then studied for all values of Ag fraction in the surface layer. Realistic acetylene pressures and temperatures are used.

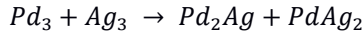
## Computational Details

Energies and geometries were calculated at the DFT level of theory, using the Vienna Ab Initio Simulation Package (VASP) code. The exchange-correlation functional of Perdew, Ernzerhof, and Burke<sup>25</sup> was employed to self-consistently solve the Kohn-Sham equations, using a plane wave basis set with a 400 eV kinetic energy cut-off. The dDsC dispersion correction<sup>26</sup> was adopted to address van der Waals interactions. This scheme proved to be accurate to describe small organic molecules interacting with metallic surfaces.<sup>27</sup> Gas phase molecule models were computed in a 14x15x16 Å<sup>3</sup> cell, and at the  $\Gamma$ -point. Adsorption energies were calculated from 6-layers surface models of the fcc structure (111) plane, spaced by 15 Å of vacuum along the axis normal to the surface plane. Acetylene coverage of 0.11, 0.25, 0.33, 0.44, and 0.50 monolayers (ML) were obtained by using the following supercells: p(3x3), p(2x2), R30°xR30°, p(3x3) with four molecules and p(2x2) with two molecules. All acetylene molecules were placed on hcp hollow sites (further specification is provided in the

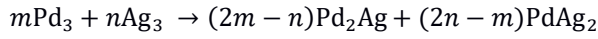
Supporting Information). Accurate Brillouin zone integration was performed by using a  $6 \times 6 \times 1$ ,  $\Gamma$ -centered  $k$ -points grid. The Methfessel – Paxton<sup>28</sup> smearing scheme was employed in all calculations.

## Theoretical Background

When mapping a (111) surface layer of a Pd-Ag fcc alloy with triangles with apexes defined by three neighboring metal nuclei, each metal atom is shared by six triangular sites. Atom exchange is allowed between triangular sites, as a fictitious diffusion process to drive the system towards an equilibrium distribution. The typical surface exchange between triatomic sites is then written as follows



and in general reads



subjected to the constraint that all the stoichiometric coefficients need to be positive integers. Our model for computing the equilibrium distributions of covered and un-covered surface sites is based on the two separated processes (ensemble distributions and adsorption), which are, of course, coupled. Note, that we use “ensemble” and “sites” synonymous, since we assume adsorption to only occur on sites built from 3 atoms (see Figure 1).

Introducing  $x_i$  as the molar fraction of the  $Pd_{3-i}Ag_i$  ensemble, and  $\theta_i$  as its covered fraction, the following reaction constant  $K_{surf}$  then describes the surface ensemble equilibrium for the uncovered sites

$$\frac{(x_1 - \theta_1)(x_2 - \theta_2)}{(x_0 - \theta_0)(x_3 - \theta_3)} = K_{surf} = \frac{\omega_1\omega_2}{\omega_0\omega_3} = 9$$

Since experimentally the Ag-Pd alloy is found to be random, we assume that there is no enthalpy term associated with the equilibrium constant for the ensemble distribution of uncovered sites. Hence, the ratio between the products and reactants partition functions of surface ensembles is given by the ratio of the sites multiplicities  $\omega_i$  which are given by the non-

equivalent permutations (3 for  $Pd_2Ag$  and  $PdAg_2$  and 1 for  $Pd_3$  and  $Ag_3$ ). The adsorption isotherms for each site, which not only depend on  $x_i$ , but also contain the entire temperature dependence of the global equilibrium is given by

$$\theta_i = x_i \frac{Z_t Z_r p e^{-\frac{\Delta \varepsilon_i}{kT}}}{1 + Z_t Z_r p e^{-\frac{\Delta \varepsilon_i}{kT}}} \equiv x_i k_i$$

where  $T$  is the temperature,  $\Delta \varepsilon_i$  the adsorption energy,  $p$  is the pressure of acetylene in the gas phase, and  $Z_t$  and  $Z_r$  represent the translational and the rotational partition function, respectively. In terms of fundamental constants and microscopic parameters, these two functions are determined from the following expression assuming a rigidly rotating linear molecule

$$Z_t Z_r = \left( \frac{2\pi M k T}{h^2} \right)^{\frac{3}{2}} k T^{\frac{1}{2}} \frac{8\pi^2 I k T}{\sigma h^2}$$

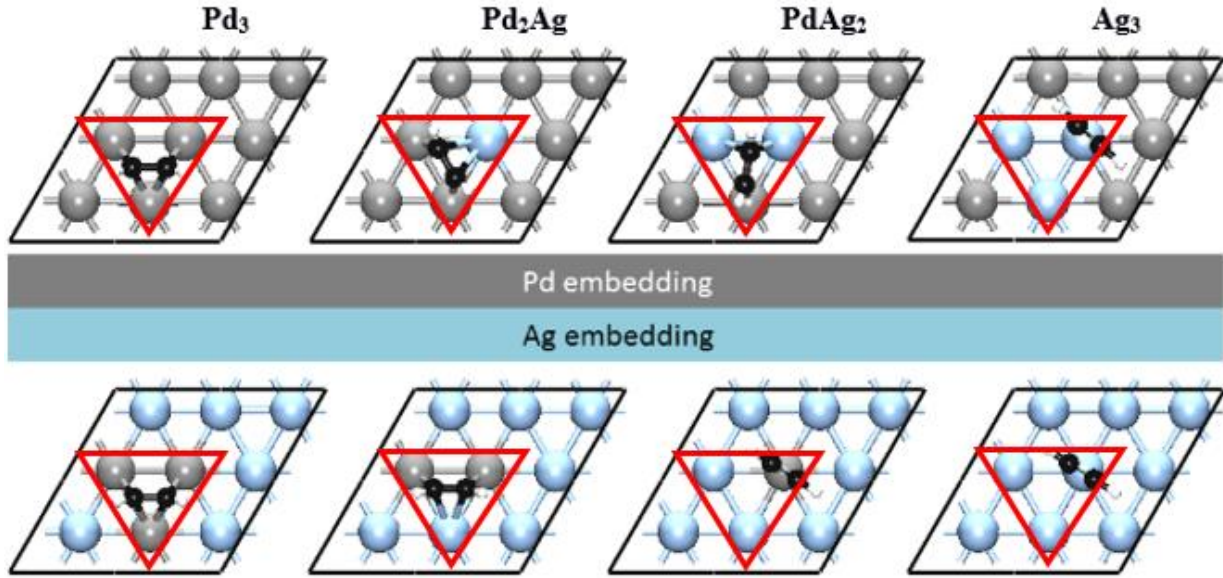
where  $M$ ,  $\sigma$ , and  $I$  are the total mass, the symmetry factor, and the moment of inertia of acetylene. Apart from vibrations, hindered rotations for the chemisorbed molecule are also excluded for simplicity.

The resulting system consists of  $4n+1$  equations in  $4n+4$  unknowns,  $n$  being the number of gaseous species. Two mass conservation expressions are introduced which relate the weighed sum of Ag and Pd ensembles to the surface Ag ( $\varphi$ ) and Pd fractions ( $1-\varphi$ ):

$$\begin{cases} \frac{(x_1 + \theta_1)}{3} + \frac{2(x_2 + \theta_2)}{3} + x_3 + \theta_3 = \varphi \\ x_0 + \theta_0 + \frac{2(x_1 + \theta_1)}{3} + \frac{(x_2 + \theta_2)}{3} = 1 - \varphi \end{cases}$$

A final equation is introduced assuming that uncovered ensembles are randomly distributed. This implies that the uncovered  $Pd_3$  molar fraction is equal to the cube of the fraction of uncovered palladium, the uncovered  $Pd_2Ag$  molar fraction is equal to the square of the fraction of uncovered palladium times the fraction of total silver, and so on. This gives rise to the following expressions

$$\begin{cases} y_0 = \left[ x_0 - \theta_0 + \frac{2(x_1 - \theta_1)}{3} + \frac{(x_2 - \theta_2)}{3} \right]^3 - x_0 + \theta_0 = 0 \\ y_1 = 3 \left[ x_0 - \theta_0 + \frac{2(x_1 - \theta_1)}{3} + \frac{(x_2 - \theta_2)}{3} \right]^2 \left[ \frac{(x_1 - \theta_1)}{3} + \frac{2(x_2 - \theta_2)}{3} + x_3 - \theta_3 \right] - x_1 + \theta_1 = 0 \\ y_2 = 3 \left[ x_0 - \theta_0 + \frac{2(x_1 - \theta_1)}{3} + \frac{(x_2 - \theta_2)}{3} \right] \left[ \frac{(x_1 - \theta_1)}{3} + \frac{2(x_2 - \theta_2)}{3} + x_3 - \theta_3 \right]^2 - x_2 + \theta_2 = 0 \\ y_3 = \left[ \frac{(x_1 - \theta_1)}{3} + \frac{2(x_2 - \theta_2)}{3} + x_3 - \theta_3 \right]^3 - x_3 + \theta_3 = 0 \end{cases}$$



**Figure 1.** Optimized geometries of acetylene adsorbed on different Pd<sub>3-i</sub>-Ag<sub>i</sub> (i=0-3) trimers on a (111) surface. Sites are embedded in Pd (top) and Ag (bottom). Pd atoms are colored in grey, Ag in light blue, C in black, and H in white. The periodic cell is indicated by black lines. All the represented structure are drawn with the MAPS software.<sup>36</sup>

The sum of these equations should equal to 0, which provides the last constraint. Note that in this first model approach without lateral interactions, all fcc and hcp sites can be occupied, leading to a high maximum coverage value of two. Lateral interactions will be considered in the subsequent step in this paper. Apart from very simple cases, an analytic solution to this set of equations is non-existing and numerical procedures are required to obtain approximate solutions. Herein, the described scheme was implemented into a FORTRAN90 program. Mass balance and ensemble equilibrium equations are solved for the molar fractions of three ensembles as a function of the molar fraction of the fourth one. The last equation, the randomness assumption is then expressed as a function of the only remaining free variable. Whenever the randomness ansatz is violated, the algorithm minimizes the deviation.

## Results and Discussions

**1. Quantum Chemical Modeling of Acetylene Adsorption on Pd-Ag Alloys.** The adsorption energy of acetylene depends on three factors. The first corresponds to the interaction between a single

acetylene molecule and a tri-metallic site. The second is the embedding of the site-molecule complex into the surface environment, and the third takes interactions between molecules into account. Embedding the molecule-three metal atoms unit in a disordered Pd-Ag alloy surface causes a change in adsorption energy due to strain and electronic effects. This change is, in principle, specific to the surface configuration, and is rather a statistical property of the system than a fixed property of the active site. However, since reliably sampling surface configurations would be computationally expensive, we limit the sampling to the two extreme cases: The active site (3 surface atoms) is either embedded in a p(3x3) Ag or Pd environment, abbreviated by Ag<sup>embed</sup> and Pd<sup>embed</sup>, respectively. The average adsorption energies and the deviation between the two models are taken as the representative adsorption energy and the embedding error, respectively. In order to increase the accuracy of our model, the environmental effect could, as proposed

**Table 1.** Adsorption Energies of Acetylene on Triangular Sites of Different Composition, in Two Different Embeddings. Energies are in eV

Site	Pd <sup>embed</sup>	Ag <sup>embed</sup>	Average	Error
Pd <sub>3</sub>	-2.37	-1.90	-2.14	0.24
Pd <sub>2</sub> Ag	-1.82	-1.37	-1.60	0.23
PdAg <sub>2</sub>	-1.00	-0.75	-0.88	0.13
Ag <sub>3</sub>	-0.36	-0.09	-0.23	0.14

by Boes *et al.*<sup>29</sup> be cast into a strain effect that depends on the bulk lattice constant of the given alloy. Corresponding results, which do not qualitatively differ from the simpler model, are presented in the SI, in addition to the distributions based on PBE instead of PBE-dDsC.

Acetylene is known to show multiple adsorption modes on a Pd(111) surface with dynamic transitions observed between them at room temperature.<sup>15</sup> Similarly, acetylene can adsorb in various modes on mixed Pd<sub>3-i</sub>Ag<sub>i</sub> sites; the most stable mode for each site was selected and shown in Figure 1. For Pd<sub>3</sub> and Pd<sub>2</sub>Ag sites embedded in Pd, acetylene chemisorbs flat on a triangular site, and is oriented parallel to the Pd-Pd bond, while it lies perpendicularly to the Ag-Ag bond in the PdAg<sub>2</sub> site embedded in Pd. For the Pd-embedded Ag<sub>3</sub> site acetylene is adsorbed on top of one Ag atom. The same structures are also observed when the subsurface environment is changed to silver, except for the PdAg<sub>2</sub> site where the energetically favored mode is acetylene on top of the Pd atom.

The acetylene adsorption energies are reported in Table 1 along with the average values and associated errors. The adsorption energy clearly decreases with the silver content of the ensemble and we will see that this affects the type of acetylene covered site as a function of temperature. The change in adsorption energy with the embedding varies between 0.25 and 0.47 eV, and is hence significant. To assess this influence of the environment on the surface equilibrium, it is important to evaluate the error propagation in the mathematical model. The error in site coverage is given by the differential of the adsorption isotherm

$$\delta k_i(p, T) = \frac{pe^{-\frac{\Delta\varepsilon_i}{kT}} e^{\frac{\mu^0}{kT}}}{\left(1 + pe^{-\frac{\Delta\varepsilon_i}{kT}} e^{\frac{\mu^0}{kT}}\right)^2 kT} \delta\varepsilon_i$$

The prefactor of  $\delta\varepsilon_i$  goes rapidly to zero whenever  $\frac{\Delta\varepsilon_i}{kT}$  strongly differs from one, implying that the error propagation is only substantial in the vicinity of the desorption temperature.

Lateral interactions between molecules chemisorbed on a metal surface are described by direct through-space interactions or indirect ones mediated by the surface. Expressing the detailed dependence of these through-surface interactions on the disordered alloy concentration would represent a formidable task, due to the compositional heterogeneity of the catalytic material. Therefore, we approximate the lateral interactions on all sites and alloy compositions by

those determined as a function of coverage for pure Pd. First, the coverage dependent adsorption energy of acetylene was computed (see Table 2). Then, we identified a suitable mathematical function to parameterize the data as a function of the overall coverage. We found an exponential expression most

**Table 2. Coverage dependent acetylene adsorption energy on Pd(111)**

Coverage (ML)	$E_{\text{ads}}(\text{DFT})/\text{eV}$	$E_{\text{ads}}(\text{fit})/\text{eV}$
0.11	-2.37	-2.34
0.25	-2.32	-2.27
0.33	-2.18	-2.16
0.44	-1.65	-1.73
0.50	-1.34	-1.30

convenient:

$$E(\theta) = E(0.11) + 0.01e^{9.34\theta}$$

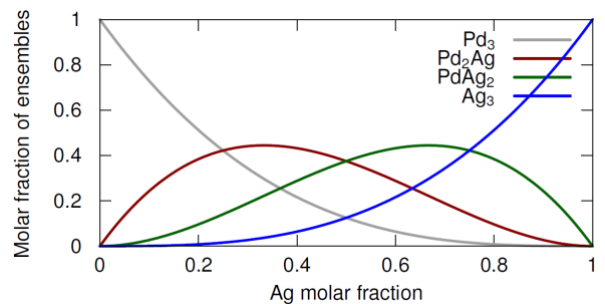
where  $\theta$  is the total molecular coverage of all ensembles expressed in ML. Note that the adsorption energy variation for the other ensembles is obtained by replacing  $E(0.11)$  by the corresponding adsorption energy.

**2. Pd-Ag surface layer structure in absence of adsorbed molecules.** Assuming operation under vacuum, i.e.,  $\theta_i = 0$ , leads to the following set of equations

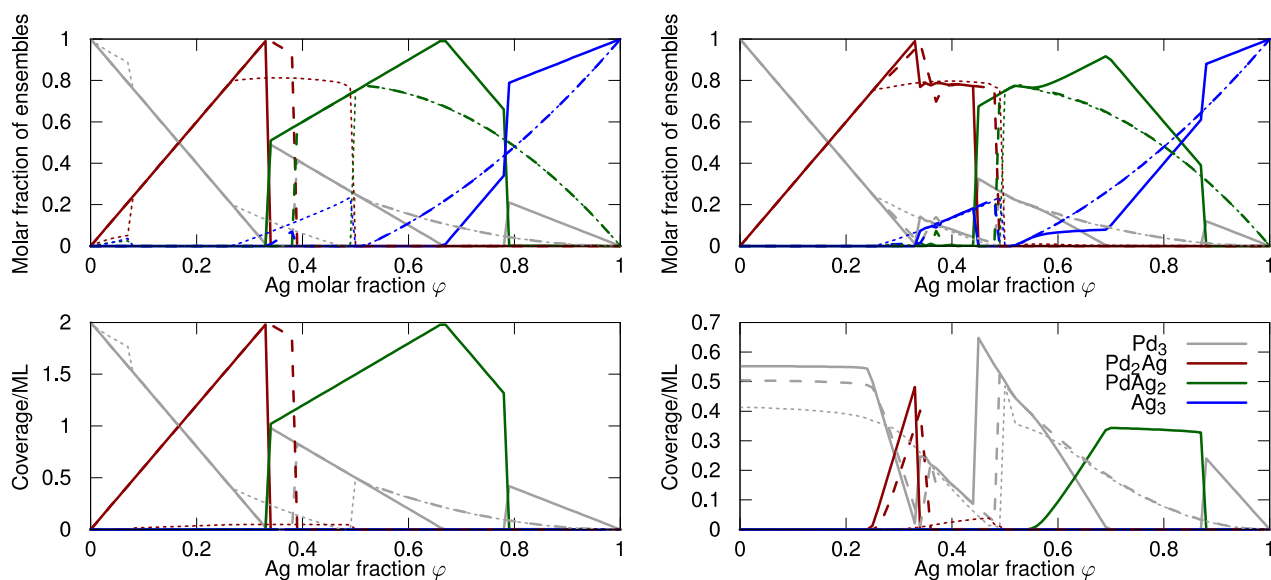
$$\begin{cases} \frac{x_1 x_2}{x_0 x_3} = 9 \\ \frac{x_1}{3} + \frac{2x_2}{3} + x_3 = \varphi \\ x_0 + \frac{2x_1}{3} + \frac{x_2}{3} = 1 - \varphi \\ \sum_{i=0}^3 y_i = 0 \end{cases}$$

This set has one physically meaningful solution, being

$$\begin{cases} x_0 = (1 - \varphi)^3 \\ x_1 = 3\varphi(1 - \varphi)^2 \\ x_2 = 3(1 - \varphi)\varphi^2 \\ x_3 = \varphi^3 \end{cases}$$



**Figure 2. Probability of Pd<sub>3</sub> (grey) Pd<sub>2</sub>Ag (magenta), PdAg<sub>2</sub> (green) and Ag<sub>3</sub> (blue) triplets present on the clean Pd-Ag surface as a function of the Ag concentration.**



**Figure 3.** Probability of presence (top) and coverage (bottom) for Pd<sub>3</sub> (grey), Pd<sub>2</sub>Ag (magenta), PdAg<sub>2</sub> (green) and Ag<sub>3</sub> (blue) triplets on the clean Pd-Ag surface as a function of the Ag concentration  $\phi$ . Left: Ideal model without interaction between molecules; right: Including lateral interactions. Solid (resp. dashed, dotted) lines are solutions as obtained at 300 K (resp. 500 K, 700 K). All lines are based on numerical solutions spaced by 0.01.

These are multinomial distributions, as shown in Figure 2. The catalyst surface layer is thus portrayed as a random two dimensional alloy, in agreement with the results of Engstfeld *et al.*<sup>16</sup>

### 3. Pd-Ag surface layer structure under acetylene adsorption.

Ensembles distributions subjected to an acetylene gas pressure of 1 bar were numerically determined for a wide range of temperatures, namely from 300 K to 700 K, while spanning the whole surface Ag molar fraction range of the alloy. The temperatures of 300 K, 500 K, and 700 K are discussed specifically. Note, that we only consider molecular adsorption, although in the real system acetylene would decompose at these temperatures. The resulting equilibrium involves hydride and carbide phases that are beyond the scope of the present manuscript. Above 900 K acetylene completely desorbs, restoring multinomial distributions. The ideal case where acetylene molecules do not laterally interact is first discussed. Lateral interactions are treated afterwards.

In comparison with the cubic dependence in the multinomial distributions (Figure 2), the linear dependence of Pd<sub>3</sub> ensemble concentration on the surface Ag fraction,  $\phi$  in Figure 3 clearly highlights changes in the driving force for surface organization: where multinomial solutions result from entropic terms

only, the system's free energy in the presence of acetylene is given by both entropic and energetic contributions. The abrupt changes in concentration profiles are reminiscent of phase transitions, as pointed out by Mussardo<sup>30</sup>. Pd atoms play a key role in this restructuring, since they interact much more strongly with acetylene than Ag. At 300 K (Figure 3, top-left, full lines), the Pd<sub>3</sub> ensemble is the most common ensemble if  $\phi$  is in the range 0.00 – 0.18. From 0.18 on, the Pd<sub>2</sub>Ag triplet starts to dominate the surface up to  $\phi=0.33$  where its molar fraction drastically drops. The bottom panel of Figure 3 shows the acetylene coverage on these ensembles, which are fully covered by acetylene molecules at that point, and therefore considered active.<sup>31</sup> Compared to the multinomial distributions in Figure 2, we see in this 0-0.33 range a strongly enhanced contribution of Pd<sub>2</sub>Ag ensembles, which represent the best compromise between energetic (adsorption) and entropic (configuration) contributions to the free energy. This is, of course, at the expense of Ag-rich sites (PdAg<sub>2</sub> and Ag<sub>3</sub>) which are not formed. At  $\phi=0.33$  Pd<sub>2</sub>Ag sites fully saturate the surface, and a further increase in Ag content above that point provokes an abrupt switch in the optimal distribution, with a disappearance of Pd<sub>2</sub>Ag ensembles, transformed into covered PdAg<sub>2</sub> and Pd<sub>3</sub> triplets, again a case far from the random situation. Pd<sub>3</sub> sites decrease in importance with increasing Ag surface content and PdAg<sub>2</sub> dominates up to  $\phi=0.80$ , where a second sudden transition is seen. PdAg<sub>2</sub> ensembles are transformed into mainly Ag<sub>3</sub>, and a small fraction of acetylene covered Pd<sub>3</sub> sites. Acetylene adsorption is too weak on the Ag<sub>3</sub> site to compensate entropy loss induced by

adsorption at 300 K. As a summary, all sites but  $\text{Ag}_3$  are covered by acetylene at 300 K, and the differential adsorption energy results in a strong deviation of ensemble distribution from the random case. A clear trend towards ordering is emerging, with consecutive domination of  $\text{Pd}_3$ ,  $\text{Pd}_2\text{Ag}$ ,  $\text{PdAg}_2$  and  $\text{Ag}_3$  trimers upon increasing Ag content.

Results from simulations at 500 K (dashed lines in Figure 3 top left) confirm the previous trends. The abrupt first transition, this time at the critical silver fraction of 0.39, is followed again by a region dominated by  $\text{PdAg}_2$  ensembles, with smaller amount of  $\text{Pd}_3$ ; however, inspection of Figure 3, bottom-left, shows that those  $\text{PdAg}_2$  sites are not covered by acetylene at this temperature. This regime, where adsorption only takes place on a minor number of  $\text{Pd}_3$  ensembles, represents a transition between ordered (adsorption energy driven) and disordered (entropy driven) situations. Trends in the Ag-rich domain of the catalyst compositions at 500 K are smoother than those calculated at 300 K, and this tendency increases at the higher temperature of 700 K. Here (dotted line in Figure 3 top left), the  $\text{Pd}_2\text{Ag} \rightarrow \text{PdAg}_2$  transition threshold is further shifted to the silver fraction value of 0.50, which is also the crossing point of multinomial  $\text{Pd}_2\text{Ag}$  and  $\text{PdAg}_2$  distributions. The reason for this change is found in the competition between thermal effects (entropy) and the adsorption process (energy). Only  $\text{Pd}_3$  sites are covered by acetylene at 700 K.  $\text{Pd}_2\text{Ag}$  sites are entropically favored compared to  $\text{Ag}_3$  and  $\text{Pd}_3$  until the transition at 0.5, where  $\text{PdAg}_2$  sites suddenly dominate with the reformation of a fraction of occupied  $\text{Pd}_3$  ensembles.

Implementation of lateral interactions in the model does not qualitatively change the previous picture in terms of ensemble distributions (Figure 3, top right). The main difference is that lateral interactions markedly decrease the acetylene coverage, bringing it to a more realistic value (Figure 3, bottom right). The combined coverage of  $\text{Pd}_3$  and  $\text{Pd}_2\text{Ag}$  or  $\text{PdAg}_2$  ensembles never exceeds 0.70 per surface atom. At low Ag content, only  $\text{Pd}_3$  sites are covered with  $\sim 0.5$  ML. For a pure palladium surface this is equivalent to 1/4 of all  $\text{Pd}_3$  sites occupied. However, at  $\phi = 0.25$ , all  $\text{Pd}_3$  sites present on the surface are occupied in order to attain 0.5 ML as no other types of sites contribute to acetylene adsorption.  $\text{Pd}_2\text{Ag}$  sites become covered only when the fraction of  $\text{Pd}_3$  sites is too low to withstand this value of coverage. The reason is that the  $\text{Pd}_3$  ensembles are clearly preferred for adsorption until their saturation, at the expense of  $\text{Pd}_2\text{Ag}$ . These  $\text{Pd}_2\text{Ag}$  sites return to an uncovered state at  $\phi \sim 0.35$  but remain at a high concentration for

$T = 300\text{--}500$  K until  $\phi \sim 0.5$ , with a behavior similar to that occurring at 700 K in the absence of lateral interactions. Indeed repulsive interactions between acetylene molecules reduce the acetylene coverage and hence the energetic driving force towards ordering: features from the entropically favored multinomial distributions occurs at lower temperature. At this value of  $\phi \sim 0.5$  an abrupt switch of population again occurs, with disappearance of  $\text{Pd}_2\text{Ag}$ , major formation of  $\text{PdAg}_2$  and minor reformation of covered  $\text{Pd}_3$ . At 300 K, these  $\text{PdAg}_2$  ensembles are not acetylene covered right after their formation, and, as seen before for  $\text{Pd}_2\text{Ag}$  sites, get populated only at a higher Ag content, where the fraction of  $\text{Pd}_3$  is low enough.

In summary, the probability distributions exhibited by the alloy under acetylene pressure in the catalytically active temperature range (300 K – 350 K) strongly deviate from random distribution presented in Figure 2 and favor the formation of specific ensembles. In the following, we discuss the cases of two widely studied alloys,  $\text{Pd75\%Ag25\%}$  and  $\text{Pd25\%Ag75\%}$ , in view of previous results from the literature.

Neurock and coworkers<sup>10</sup> have studied acetylene adsorption on the  $\text{Pd}_3$  fcc site of an ordered  $\text{Pd75\%Ag25\%}$  model surface. The adsorption energies on the other ensembles, relevant for a random alloy, have not been reported. In our work, for an Ag molar fraction of 0.25, acetylene-induced organization drives the surface towards a mixed state containing 25 % of  $\text{Pd}_3$  and 75 % of  $\text{Pd}_2\text{Ag}$  sites. When taking into account the lateral interactions, the majority ensemble ( $\text{Pd}_2\text{Ag}$ ) is not covered, despite an intrinsically exergonic adsorption of acetylene, indicating the catalytic importance of  $\text{Pd}_3$  ensembles. It is to be noted that the assumption of equal bulk and surface silver compositions implies that segregation effects perpendicular to the surface are not taken into account. It was shown, both by experiments<sup>32</sup> and by theory,<sup>33,34</sup> that the Pd-Ag alloy undergoes reverse segregation (enrichment in Pd at surface) when in contact with a large variety of adsorbing species. Therefore, the  $\text{Pd75\%Ag25\%}$  bulk composition is likely to correspond to a surface Ag fraction below 0.25, which suggests an even more important role for  $\text{Pd}_3$  sites and less inactive "spacers" in our model. Hence, in agreement with the choice from Neurock and coworkers, we identify  $\text{Pd}_3$  as the active ensembles for the  $\text{Pd75\%Ag25\%}$  alloy.

The situation for the  $\text{Pd25\%Ag75\%}$  alloy is somewhat more complex. Lopez and Vargas-Fuentes<sup>12</sup> studied acetylene hydrogenation on this alloy in the absence of a dispersion correction, an approximation where acetylene binds only very weakly to the



PdAg<sub>2</sub> sites (see SI). They propose that reverse segregation from bulk to surface would create Pd<sub>2</sub>Ag ensembles on the surface which would strengthen acetylene adsorption and play a major role for the catalytic reaction. However, even for a Ag content lower than 0.75, the surface equilibrium calculated in our work does not show any Pd<sub>2</sub>Ag ensemble but suggests a mixture of Ag<sub>3</sub> and PdAg<sub>2</sub> instead. Formation of Pd<sub>2</sub>Ag ensembles requires a much lower Ag content at the surface (<0.35) which is very far from the bulk content. Although explicit alloy surface configurations cannot be obtained from our ensemble equilibrium approach, the absence of Pd<sub>2</sub>Ag trimers can only be explained by the formation of single Pd atoms embedded in a Ag surface. Such isolated Pd sites could explain the low activity of the catalyst for unwanted oligomerization reactions, which we presume to require neighboring Pd atoms that strongly bind acetylene. Further increasing the Ag content beyond 0.75 first corresponds to a reduction of the amount of PdAg<sub>2</sub> ensembles and increase of Ag<sub>3</sub>. At very high silver content ( $\phi \sim 0.9$ ) the entropic contribution that favors these isolated Pd sites however stops to dominate and the remaining Pd atoms merge to form acetylene covered Pd<sub>3</sub> sites. Counter intuitively a more Pd-like catalysis on few Pd<sub>3</sub> ensembles would hence be predicted at such very high Ag-fraction alloys.

Though the present model offers important insights on surface reconfiguration at relevant reaction conditions, the model could be refined in two aspects. First, an extension to a three-dimensional model including segregation perpendicular to the surface could be developed. The possibility to modulate the Pd content in the surface could affect the discontinuities in Figure 3. In the framework of the surface chemical equilibrium approach, such an extension could be realized by implementing an additional equilibrium constant. Second, both the coverage dependent adsorption energy and the coupling between different ensembles are based on averages and not on instantaneous interactions. Approaches based on real-space Monte Carlo simulations combined with energy cluster expansions<sup>35</sup> of the energy would increase our insight in surface alloy restructuring.

## Conclusions

In this paper, the surface equilibrium between tri-atomic ensembles of Pd-Ag alloys was studied by means of a model coupling acetylene adsorption and ensemble rearrangements, in order to determine and understand the surface equilibrium states under realistic conditions.

Our results demonstrate that acetylene adsorption drives Pd-Ag surface reordering, with a single ensemble dominating the structure in each interval of Ag content and sharp transitions between these intervals. The obtained ensemble distribution hence strongly deviates from the entropy driven random distribution, relevant to bare alloy surface in UHV conditions. The effect is decreased at large surface Ag content, leading to a weak interaction with the adsorbate, and more random-like distributions. The differences in acetylene adsorption energy of tri-atomic sites embedded in Pd compared to the Ag embedding, illustrates the significant electronic effect for this system. The deviation in adsorption energy due to the environment of the 3 atom ensembles has, however, consequences on the ensemble distribution only at temperature close to adsorbate desorption.

The methodology presented in this work is not restricted to PdAg alloys, but can be easily extended to other bimetallics. It gives key insights on the origin of the enhanced selectivity for the industrially relevant Ag-rich formulations, linking it to the isolation of single Pd atoms by Ag domains. It shows in addition that too much Ag is not beneficial, since Pd atoms counter-intuitively tend to reform Pd islands in these conditions.

## Supporting Information available

Embedding energies, results with the PBE exchange correlation functional and all geometries are provided.

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