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# Mapping Surface Segregation of Single-Atom Pt Dispersed in M Surfaces (M = Cu, Ag, Au, Ni, Pd, Co, Rh and Ir) Under Hydrogen Pressure at Various Temperatures

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## Abstract

Single-atom alloys (SAAs) are emerging materials containing isolated metal atoms dispersed on host metal surfaces, exhibiting unique reactivity compared with the corresponding monometallic counterparts. However, the stability of the isolated atoms in the host metal has hardly been studied, although, metal segregation has been commonly observed in bimetallic nanoparticles under reaction conditions. In this work we focus on single-atom Pt anchored on various metallic support surfaces. Density Functional Theory (DFT) calculations coupled with environmental segregation energy analysis are performed to map the segregation trends of 22 different Pt-SAA surfaces under various hydrogen conditions. The results show the high stability of single-atom Pt in Ni, Co, Rh and Ir host metallic surfaces while no stability is predicted on Au and Ag surfaces. For Pd and Cu host supports, the single-atom Pt is found to be stable on specific surface facets and within definite temperature and pressure conditions. This work brings an important understanding of SAA systems through the prediction of

surface atomic ordering changes under operating conditions which related to the reactivity will ultimately allow the design of more efficient catalysts.

## **Introduction**

Single-site heterogeneous catalysts containing atomically dispersed active metal species are attracting growing attention as they have shown unprecedented activity and selectivity toward various reactions [1-2]. Single site atomically dispersed Pd in metallic copper host catalyst has been shown to be effective for selective hydrogenation reaction [3-5], whereas isolated Au in metallic Ni has been shown to considerably suppress carbon deposition in steam reforming of methane [6]. Moreover, in attempt to find an alternative way for reducing the amount of Pt as a scarce nobel metal and potentially enhancing its catalytic selectivity, Pt-based single-atom alloys (SAAs) have generated significant interest. The Pt single-atom alloys were created by depositing isolated Pt atoms on various metal surfaces [7-8]. Copper nanocatalysts with single-site Pt dispersed in the surface has been found to exhibit high activity and selectivity for butadiene hydrogenation to butenes under mild reaction conditions. In such a system, the isolated Pt atom geometries are found to enable hydrogen activation and spillover but being incapable of C–C bond scission leading to loss of selectivity and to catalyst deactivation [9]. Pt single site dispersed in Pd octahedral nanoparticle surfaces prepared a priori to form a Pt/Pd SAA has shown remarkable hydrogen evolution reaction (HER) activity compared to a commercial Pt/C, as well as an ultrahigh mass activity that was much higher than the latter [10]. This strong activity was attributed to the high unoccupied density of Pt 5*d* orbitals, in line with a Pt single atom site on other supports [7].

Controlling the dispersion of single-atom sites in suitable host materials opens unique opportunities for catalyst design, but also faces many challenges. Indeed, similar to bimetallic systems the surface of these SAA catalysts is subject to changes under working conditions. In

presence of gas or solvent, and depending on the reaction temperature, the surface composition may change and segregation and/or sintering phenomena may occur. The segregation process leads to an enrichment of one of the alloy components at the surface or into the bulk, while the sintering, governed by the high surface mobility and diffusion of atomically dispersed metal species results in the aggregation of SAAs to form clusters of few atoms on the surface [11-15]. The sintering of singly dispersed metal atoms into clusters and nanoparticles has been observed for many SAAs [16-17]. In addition, under specific reaction conditions either in reductive or oxidative atmospheres, the different chemical potential between both elements and reactants may cause the segregation of the isolated metal sites [17]. In other word, depending on the affinity of the metal in the surface with the interacting gas, surface or bulk segregation may increase. Although, metal segregation has been commonly observed in bimetallic nanoparticles under reaction conditions [18-22], the segregation and the stability of the isolated atoms in the SAAs have been rarely studied [23]. Considering Pt, in spite of the large number of works devoted to the single-atom Pt dispersed in various surface types, the study of its stability under gas atmosphere and reaction temperature has never been undertaken. In a recent work, Gong et al. [24] have reported important results about stable Pt/Cu single atom alloys as effective catalysts for propane dehydrogenation. In this work, DFT calculations have been performed to study the thermodynamic stability of exposed isolated surface Pt atoms within facets of Pt/Cu SAA nanoparticles. The reported results show the better stability of single-atom Pt within Cu(111) facet compared to other types of Pt species. As it will be demonstrated in this paper, the single-atom Pt remain stable in this latter surface under a wide range of hydrogen pressure and temperature conditions which confirm the reported speculation on catalytic performances of this system.

In this work, we investigate the effect of hydrogen on the stability of single-site Pt in Pt-based SAAs. The choice of hydrogen was motivated by the fact that it is ubiquitous in many

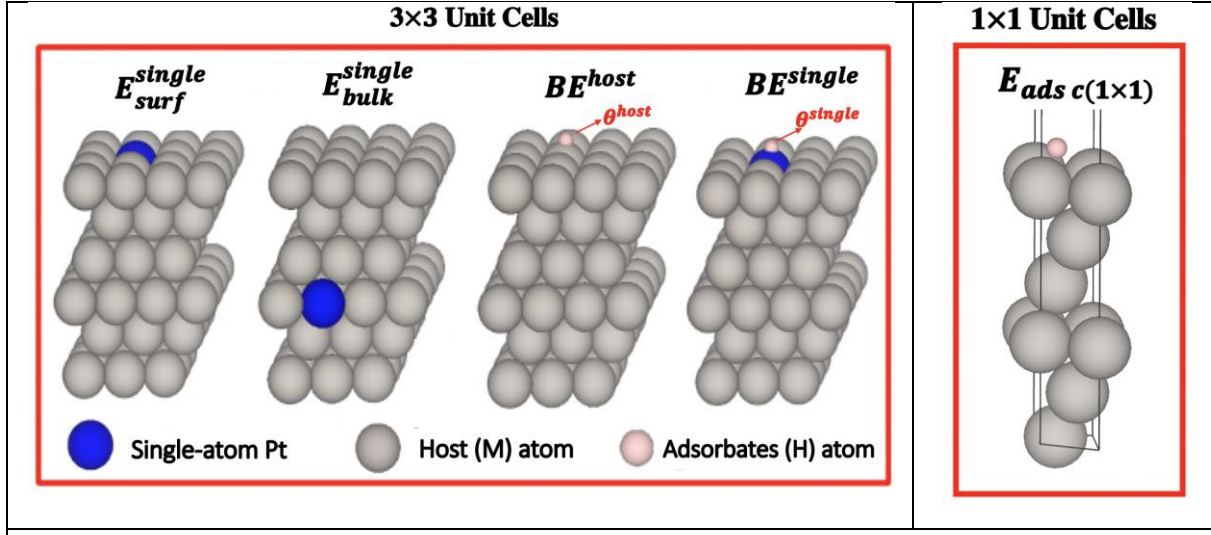
reactions catalyzed by single-site heterogeneous catalysts and particularly Pt. We focused here on the segregation phenomena leaving the sintering effect for a near-future scope. We mapped, for the first time the environmental surface segregation ( $E_{eseg}$ ) trends of Pt single-atom dispersed in host metal surfaces M (Pt/M, with M = Cu, Ag, Au, Ni, Pd, Co, Rh and Ir) under various hydrogen gas pressures and temperatures. This environmental segregation energy model has been shown to predict the surface composition evolution of binary alloys in reaction conditions [25-29]. In addition, the effects of surface orientations on hydrogen induced segregation were also analyzed by considering three low index surfaces: (111), (100) and (110). As these surfaces are the dominant facets of stable catalytic metallic nanoparticles, the conditions under which the Pt single atom remains stable on a given metallic nanoparticle surface under hydrogen pressures are revealed. This work may serve as a guide to high throughput pre-screening the desired SAAs under optimal conditions, permitting to break with the empirical trial-error experimental approach and gain in performances in the design of new materials.

## Computational details

Periodic DFT calculations were carried out using density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP) [30] and the Perdew, Burke, and Ernzerhof (PBE) functional [31]. The spin polarized calculations were applied to all systems. The valence electrons were treated explicitly, and their interactions with the ionic cores were described by the projector augmented-wave method, which allowed the use of a low energy cut off equal to 400 eV for the plane-wave basis. As shown in Schema 1, two sizes of unit cells of selected facets ( $hkl$ ) were created: (3×3) and (1×1) unit cells, which are both separated by 15Å of vacuum space containing 6 atomic layers from which the bottom

two layers are fixed on the bulk atom positions. The Brillouin zone integrations were performed with a Monkhorst–Pack  $(3 \times 3 \times 1)$   $k$ -point mesh for the  $(3 \times 3)$  unit cells and  $(6 \times 6 \times 1)$   $k$ -point mesh for the  $(1 \times 1)$  unit cells.

**Segregation Energy ( $E_{seg}$ ) and Environmental Segregation Energy ( $E_{eseg}$ )**



**Figure 1:** DFT surface models considered in this work to calculate the total energies of SAAs including single-atom Pt in the surface ( $E_{surf}^{single}$ ) and in the bulk ( $E_{bulk}^{single}$ ), the binding energies of hydrogen with host surface ( $BE^{host}$ ) and with single atom ( $BE^{single}$ ).

The segregation energy  $E_{seg}$  under vacuum is the energy difference between a system where the single-atom Pt may be located the topmost host surfaces ( $E_{surf}^{single}$ ) and the system where the single atom Pt may be located in the bulk geometry ( $E_{bulk}^{single}$ ) of host surfaces, i.e. in the 4<sup>th</sup> layer:

$$E_{seg} = E_{surf}^{single} - E_{bulk}^{single} \quad (1)$$

Furthermore, the hydrogen induced environmental segregation energy  $E_{eseg}$  is described as below:

$$E_{eseg} = E_{seg} + (E_{ads}^{single} \theta_H^{single} - E_{ads}^{host} \theta_H^{host}) \quad (2)$$

Where the  $E_{ads}^{single}$  and  $E_{ads}^{host}$  are the average adsorption energy of atomic hydrogen on the single-atom site and on the surface of host metals, and  $\theta_H^{single}$  and  $\theta_H^{host}$  are the coverage of adsorbed hydrogen on the single sites and host sites, respectively.

According to the definition, if  $E_{eseg}$  or  $E_{seg}$  is sufficiently negative, the single-metal atom is stable in the surface, conversely, it segregates to the bulk when  $E_{eseg}$  or  $E_{seg}$  is sufficiently positive. The different systems studied are summarized in Figure 1.

In this work, Pt atom is selected as the single atom site to the host surfaces (M), on the M (111), M (100) and M (110) facets, except for cobalt host surface, where only the hexagonal close-packed Co (0001) surface is considered. Indeed, the (0001) surface is the main surface orientation of Co nanoparticles with hexagonal close-packed (HCP) bulk structure [32] which have been shown to have much higher intrinsic activity than the face centered-cubic (FCC) one [33].

### **Binding Energy $BE^{host}$ and $BE^{single}$**

The  $E_{ads}^{single}$  and  $E_{ads}^{host}$  are coverage-dependent due to the lateral interaction ( $w$ ) between the neighboring adsorbed hydrogens:

$$E_{ads}^{host} = BE^{host} - zw\theta_H^{host} \quad (3)$$

and

$$E_{ads}^{sol} = BE^{single} - zw\theta_H^{host} \quad (4)$$

With  $z$  representing the number of nearest neighboring adsorbates.  $BE^{host}$  is the adsorption energy of the isolated hydrogen on the most stable adsorption site of the respective host

surface, FCC site for M(111)/Co(0001), bridge site for M(110) and M(100).  $BE^{single}$  is the hydrogen adsorption energy on the top site of the single atom (Pt) inserted in the host surface. The lateral interaction ( $w$ ) is evaluated as the energy difference in adsorption energy of a hydrogen atom on the  $(3 \times 3)$  M host surface ( $\theta_H^{host} = \frac{1}{9}ML$ ) and on the  $(1 \times 1)$  M host surface ( $\theta_H^{host} = 1ML$ ). Negative value of  $w$  indicates repulsion between adsorbed hydrogen atoms and positive value indicates attraction.

**Fowler-Guggenheim (F-G) Theorem: gas coverage ( $\theta_H^{single}$ ,  $\theta_H^{host}$ ) and Entropy ( $S_{gas}$ ,  $S_{ads}$ )**

The F-G adsorption isotherm is applied to describe  $\theta_H^{single}$  and  $\theta_H^{host}$  as the gas coverage  $\theta$  is at temperature ( $T$ ), and pressure ( $P$ ), and adsorption energy dependent:

$$PK = \frac{\theta_H^{host/single}}{1 - \theta_H^{host/single}} e^{-c\theta_H^{host}}, \quad c = \frac{z\omega}{RT} \quad (5)$$

$$K = \exp\left(-\frac{BE^{host/sol} - T(S_{ads} - S_{gas})}{RT}\right) \quad (6)$$

Where the adsorbed gas is assumed to stick on the surface, so  $S_{gas}$  is considered to be equal to zero. The  $S_{ads}$  is dependent on  $T$  and  $P$ :

$$S_{gas} = S_{gas}(T, P^0) - R \ln\left(\frac{P}{P^0}\right) \quad (7)$$

$S_{gas}(T, P^0)$  is the gas entropy at 1 atmosphere pressure ( $P^0$ ) as a function of  $T$ , which is fitted based on the data from the NIST-JANAF Thermochemical Tables [34].

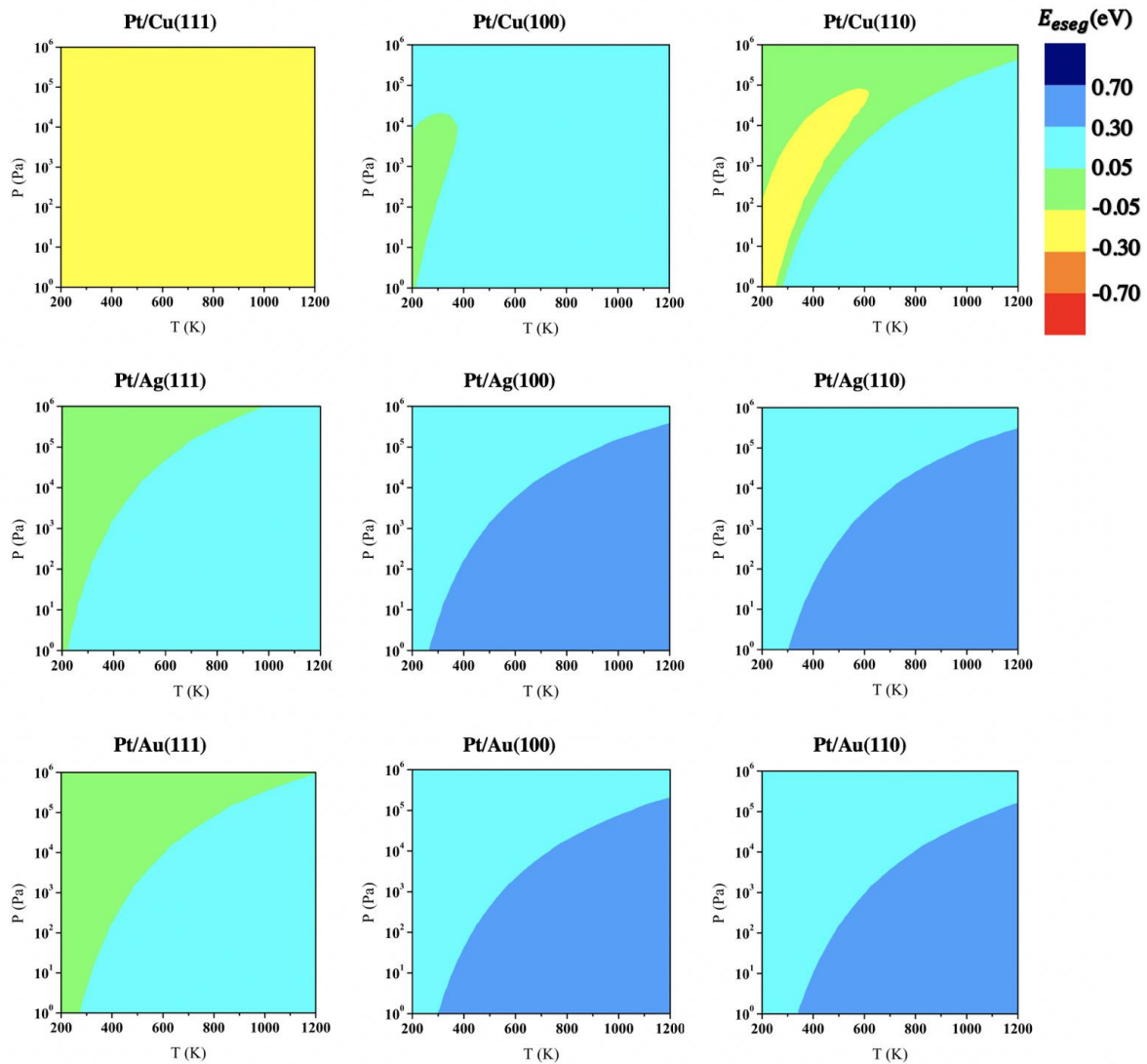


## Results and discussions

Considering hydrogen as the reactive gas, the segregation tendencies of single-atom Pt dispersed in metallic surfaces are studied under the pressure range of 1 Pa -  $10^6$  Pa and the temperature range of 200K - 1200K, which covers the common experimental working conditions. The counter plots of environmental segregation energy  $E_{eseg}$  of single-atom Pt as a function of temperature and hydrogen pressure evaluated in 22 SAA surfaces are reported in three Figures. The Figure 2 groups together host surfaces from coinage group (i.e. Cu, Ag, Au) while host surfaces form the nickel group (Ni, Pd) and from the cobalt group (Co, Rh, Ir) are gathered in Figure 3 and 4, respectively. The color code of the counter plots is defined as follows: positive values of  $E_{eseg}$  superior to +0.7eV (dark blue), between +0.7eV and +0.3eV (light blue) and between +0.3eV and +0.05eV (aqua) represent the ‘very strong’, ‘strong’ and ‘weak’ bulk segregation of single-atom Pt, respectively. The negative values of  $E_{eseg}$  inferior to -0.7 eV (red), between -0.3eV and -0.7 eV (orange) and between -0.05 eV and -0.3 eV (yellow) represent the ‘very strong’, ‘strong’ and ‘weak’ surface segregation of single-atom Pt, respectively. When  $E_{eseg}$  is between -0.05eV and +0.05eV (light green), single-atom Pt is considered as stable in the surface as in the bulk (no segregation preference).

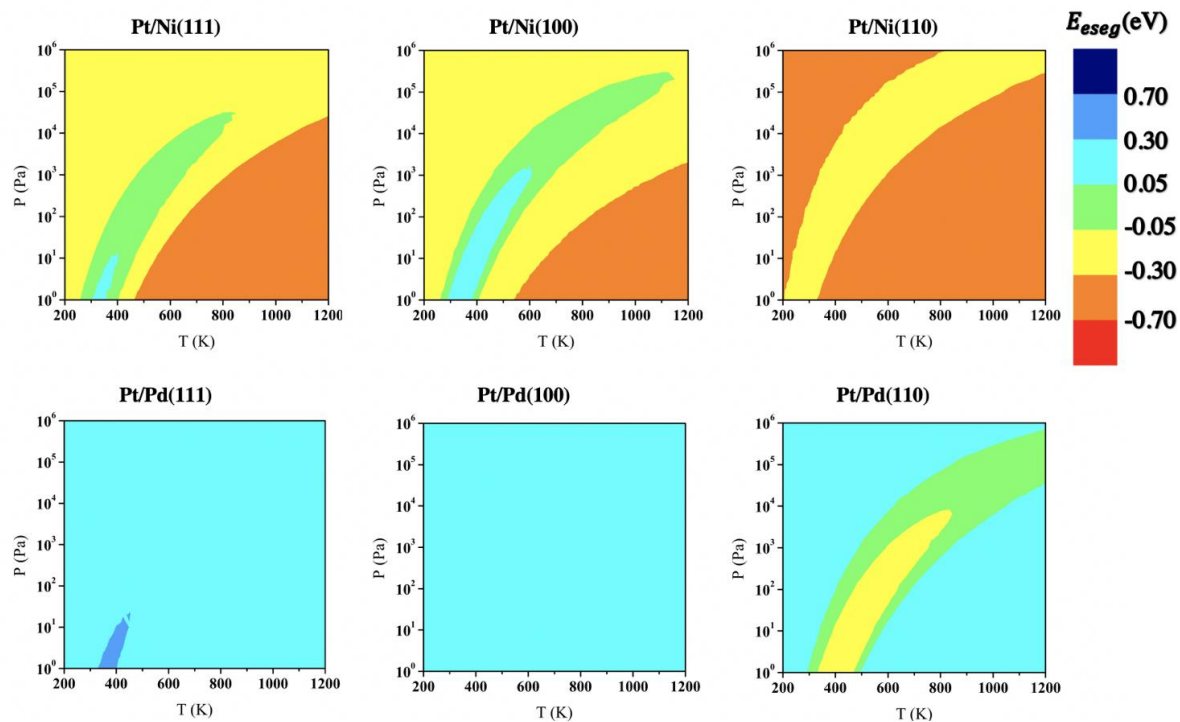
All calculated DFT energetic values issued from the 22 considered binary systems are depicted in **Table S1**.

## Copper group

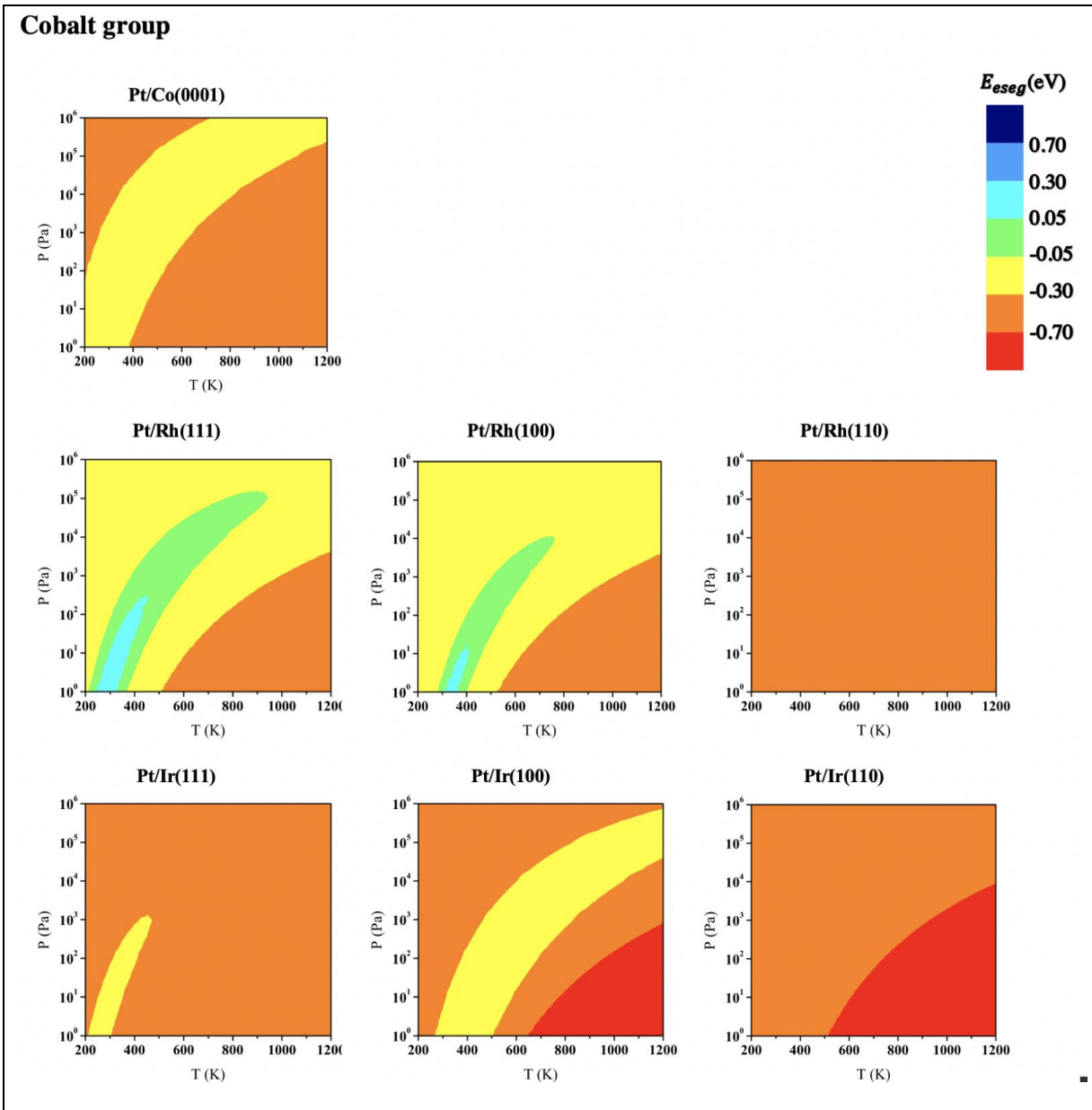


**Figure 2:** Color mapped environmental  $E_{eseg}$  of single-atom Pt as function of temperature ( $T$ ) and  $H_2$  pressure (Pa). Single-atom Pt is hosted by metal surface from coinage group (Cu, Ag and Au). Negative segregation energies (dark red, orange and yellow) indicate surface segregation of single-atom Pt and its stability on the topmost layers of the host surface. Positive values (dark blue, light blue and aqua) indicate that single-atom Pt prefers to segregate toward the bulk. Light green color indicates the absence of segregation.

### Nickel group



**Figure 3:** Color mapped environmental  $E_{eseq}$  of single-atom Pt as function of temperature ( $T$ ) and  $H_2$  pressure (Pa). Single-atom Pt is hosted by metal surface from Nickel group (Ni and Pd).



**Figure 4:** Color mapped environmental  $E_{eseg}$  of single-atom Pt as function of temperature (T) and H<sub>2</sub> pressure (Pa). Single-atom Pt is hosted by metal surface from Cobalt group (Co, Rh and Ir). For Co host surface, only the most stable (0001) surface orientation is considered.

### *Single-atom Pt anchored in coinage group metal surfaces*

In Figure 2, the  $E_{eseg}$  of single-atom Pt anchored in coinage group surfaces show interesting changes with increasing hydrogen pressure and/or decreasing temperature. The stability

trends of single-atom Pt in Au and Ag host surfaces are very similar and evolve monotonically whereas non-monotonic changes were found for single-atom Pt in Cu (100) and Cu (110) host surfaces. For Au and Ag host surfaces (111), (100) and (110), the Pt has a positive segregation energy under vacuum (see Table S1), which means that single-atom Pt could not be present on these host surfaces and prefers to stabilize in the bulk. This is an expected result as the surface energies of Au ( $1.5 \text{ J/m}^2$  [35]) and Ag ( $1.32 \text{ eV/atom}$  [35]) are much lower than Pt surface energy ( $2.37 \text{ J/m}^2$  [36]). Interestingly, hydrogen exposure seems not to alter this tendency. Indeed, the color changes in the counter plots from strong (light blue) to weak (aqua) bulk segregation and non-existing (light green) segregation with decreasing temperature and increasing hydrogen pressure, show that the probability to find single-atom Pt on these surfaces (Au and Ag) is negligible. In contrast, in Cu (111), the surface segregation of single-atom Pt is found to be quite favorable under vacuum ( $E_{seg} = -0.06 \text{ eV}$ ) and could be preserved (yellow color) for the entire pressure and temperature considered ranges. When inserted in Cu(110), which for nanoparticles represents edges, the single-atom Pt could be only stabilized in the surface within a small temperature window of 300-500K at  $10^4 \text{ Pa}$  of hydrogen pressure or at very low temperatures and pressures (lower than 300K and  $10^2 \text{ Pa}$ ). These temperature/pressure domains are governed by a competition between coverage of hydrogen on host Cu surface and on single Pt sites as illustrated by Figure S3. These results agree with the reported experimental work of Lucci et al. [9] showing the high activity, under mild conditions, of copper nanocatalysts with single-site Pt dispersed in the surface toward the selectivity for butadiene hydrogenation to butenes. Moreover these authors reported that under realistic pressures (1 bar) and at low loadings, Pt exists as individual isolated (substituted) atoms in the Cu(111) surface, species ensuring stable activity and 100% selectivity. Several other recent works demonstrated the stability of Pt/Cu SAAs under hydrogen pressure [37] and in many selective hydrogenation and

dehydrogenation reactions [38-41] and the herein results bring a molecular picture of the surface under selected experimental conditions.

### ***Single-atom Pt anchored in nickel group metal surfaces***

Under vacuum conditions, the segregation behaviors of single-atom Pt in nickel and palladium surfaces are found to be opposite. Indeed, Pt surface segregation toward topmost surface nickel is favored whereas bulk segregation is predicted in Pd bulk. This behavior is in line with the surface energies order increasing from Pd (2 J/m<sup>2</sup> [35]) to Pt (2.37 J/m<sup>2</sup> [36]) and Ni (2.44 J/m<sup>2</sup> [36]).

Figure 3 shows that hydrogen pressure and temperature may affect the stability of single-atom Pt in Ni. This former remains stable in the surface for a wide range of temperatures and pressures except within a narrow window of temperature between 300K and 600K and very low hydrogen pressure (below 10<sup>3</sup> Pa.), where Pt is found to segregate into the bulk of Ni(111) and Ni(100). To explain the changes within these narrow domains, we followed at fixed temperature of 400K, the evolutions of E<sub>seg</sub> of Pt in Ni(100), the hydrogen coverage on surface host site  $\theta_H^{host}$  and single-atom Pt  $\theta_H^{single}$  as a function of hydrogen pressure (see Figure S4). At 1 Pa. pressure, the calculated E<sub>seg</sub> in Pt/Ni(100) is -0.01 eV. For this low pressure, the hydrogen already covers almost 0.6ML of Ni surface sites. However, the coverage of single-atom Pt by hydrogen is near to zero. At this stage, the hydrogen has a negligible effect on the segregation behavior of single-atom Pt. With the pressure increases from 1 Pa to 10 Pa, the E<sub>seg</sub> increases monotonically. At 10 Pa, it reaches a maxim positive value of 0.13 eV. The coverage of hydrogen on the host surface and on single atom sites is 0.9ML and 0.10 ML, respectively. The Hydrogen prefer to adsorb on the surface Ni atoms instead of Pt atoms (see table S1). Such difference of adsorption preference prevented the segregation of the single-atom atoms Pt. The E<sub>seg</sub> starts to decreases with the further

increase in pressure. This is because the hydrogen on the Ni atoms reaches its maximum. Further increasing the pressure only increases the coverage on the single-atom Pt, which reduces the coverage difference, and consequently, the hydrogen adsorption effects on the segregation energy. Near  $10^6$  Pa, Eeseg decreases to -0.14 eV, which is higher than Eeseg at 1 Pa.

Recently, Peng et al. [42] have reported the high activity of Pt single atoms embedded in the surface of Ni nanocrystals toward the selective hydrogenation reaction of nitro compounds. The reactions were conducted at low temperature (313K) and hydrogen pressure as high as 1-3 bar, conditions allowing the stabilization of single-atom Pt in the Pt/Ni SAAs.

In contrast with nickel, single-atom Pt could not be found in the surface of Pd under hydrogen pressure. Located in the bulk of Pd matrix under vacuum, it may remain stable for a wide range of temperatures and hydrogen pressures, except for the Pd(110) surface. In this latter, single-atom Pt is found to segregate toward the surface at a very narrow window of intermediate temperature and pressure (around  $10^2 - 10^3$  Pa and 400K - 600K). These results are in contradiction with the recent published work of Zhang et al. [10] who reported the fabrication of Pt/Pd SAA catalysts through an ALD method. According to these authors Pt atoms were successfully deposited on Pd nanoparticles with (100) and (111) surfaces, respectively. The as-prepared Pt/Pd SAA catalysts have been reported to exhibit much higher hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities than other types of ALD-prepared Pd/Pt catalysts. However, despite the thorough characterization work (XANES, EXAFS and XAS) showing the stabilization of such single-atom Pt in octahedral Pd nanoparticle surfaces, no evidence of its stability in the surface under operating conditions was demonstrated.

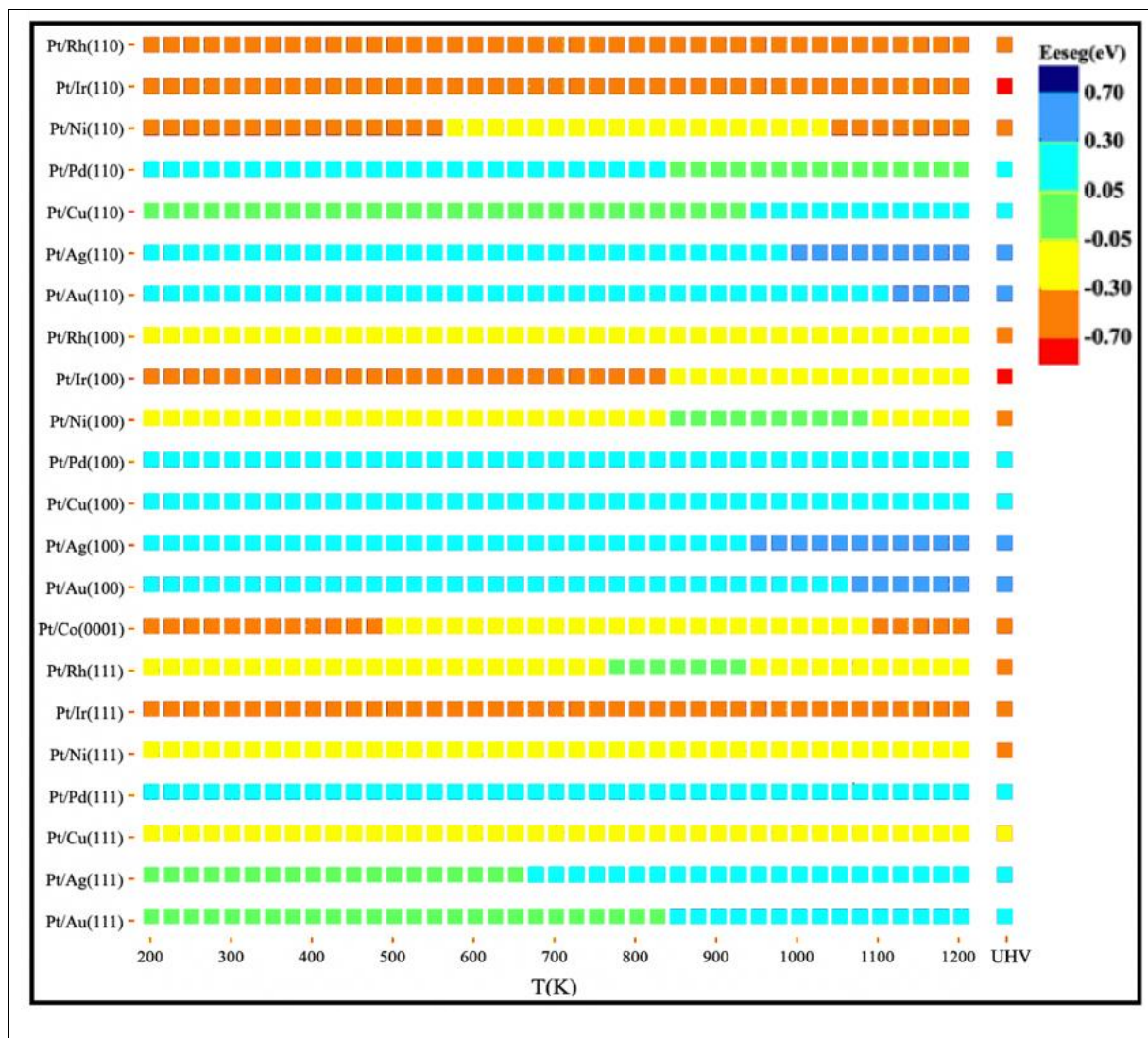
### ***Single-atom Pt anchored in cobalt group metal surfaces***

Under vacuum conditions, the segregation energies  $E_{seg}$  of single-atom Pt in Co(0001), Rh(111) and Ir(111) are predicted to be of -0.63 eV, -0.32 eV and -0.53 eV, respectively. These negative values indicate the strong stability of Pt on the top surface of these alloys. In Figure 4, the contour plots of  $E_{seg}$  evolutions of single-atom Pt in Pt/Co, Pt/Rh and Pt/Ir SAAs are presented. From a general point of view, the hydrogen pressure and temperature do not seem to strongly alter the stability of Pt surface site. Except a very small window at very low pressure (less than  $10^2$  Pa) and around 300K where single-atom Pt in Rh(111) and Rh(100) seems to prefer bulk segregation, the single-atom Pt is predicted to remain stable on the cobalt group metal surfaces. For Ir (100) and (110) surfaces, the surface segregation of Pt is predicted to be strongly favored for high temperature. The high stability of single-atom Pt in cobalt group surfaces was recently demonstrated experimentally. Jiang et al. [43] have reported single-atom Pt decorating nanoporous cobalt selenide as efficient electrocatalysts for HER. Using Operando X-ray absorption spectroscopy technics, these authors show that single-atom Pt significantly reduce energy barriers of water dissociation and improve adsorption/desorption behavior of hydrogen.

To the best of our knowledge, no results are yet reported on single-atom Pt anchored in Rh or Ir metallic supports. Here we present the evidence of the high stability of these SAAs under hydrogen pressure and temperature conditions.

To compare the general behavior of single atom Pt in all considered SAAs at the most common working pressure, we report in Figure 5, the typical segregation trends that change with temperature under the hydrogen pressure of  $10^5$  Pa. Results obtained for lower pressures ( $100$  Pa and  $10^2$  Pa) are reported in Figure 1S.





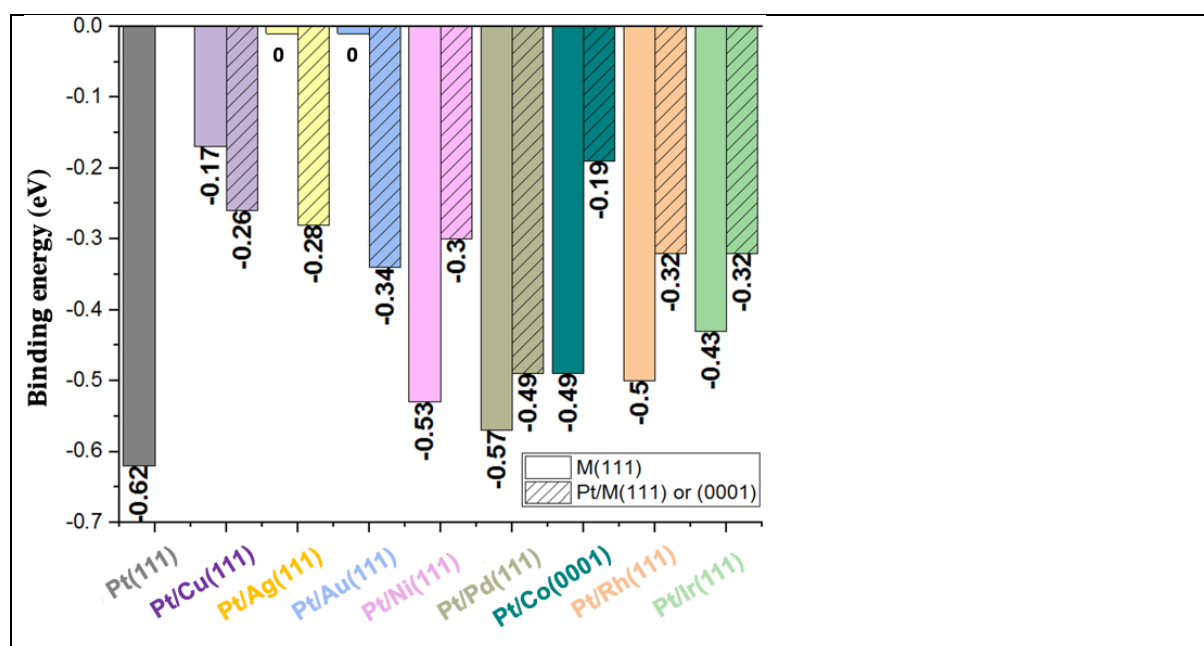
**Figure 5:** Evolution of the environment segregation energy  $E_{eseg}$  of single-atom Pt in M host metallic surfaces (Pt/M) as function of temperature under  $10^5$  Pa of Hydrogen gas pressure, compared with  $E_{seg}$  under vacuum (UHV).

Three classes of SAAs could be distinguished but not related to the position of the host metal group on the periodic table. Exposed to hydrogen pressure, single-atom Pt anchored in Au and Ag could not be stabilized in the surface and will segregate into the bulk. For copper and Pd supports, surface segregation of Pt could be optimum only for definite orientations and under specific conditions. For Co, Rh, Ir and Ni, single-atom Pt is found to be stable in the surface in the quasi-totality of the pressure and temperature ranges, with exception for Rh and Ni where Pt is predicted to segregate into the bulk within a narrow window of low temperature

and pressure. In order to understand this puzzling behavior of single-atom Pt in these metal supports we analyzed the effect of hydrogen from binding energies and from electronic density of states (DOSs).

### ***Binding hydrogen energies and electronic density of states***

In Figure 6, are represented in one graph, the binding energies of hydrogen on pure host metallic (111) surfaces (free from single-atom sites) and on single-atom Pt anchored in these surfaces. The binding energy of hydrogen atom on pure Pt (111) surfaces is added for valuable comparison. Two other graphs gathering computed hydrogen binding energies on (100) and (110) surfaces are provided in Figure S2.



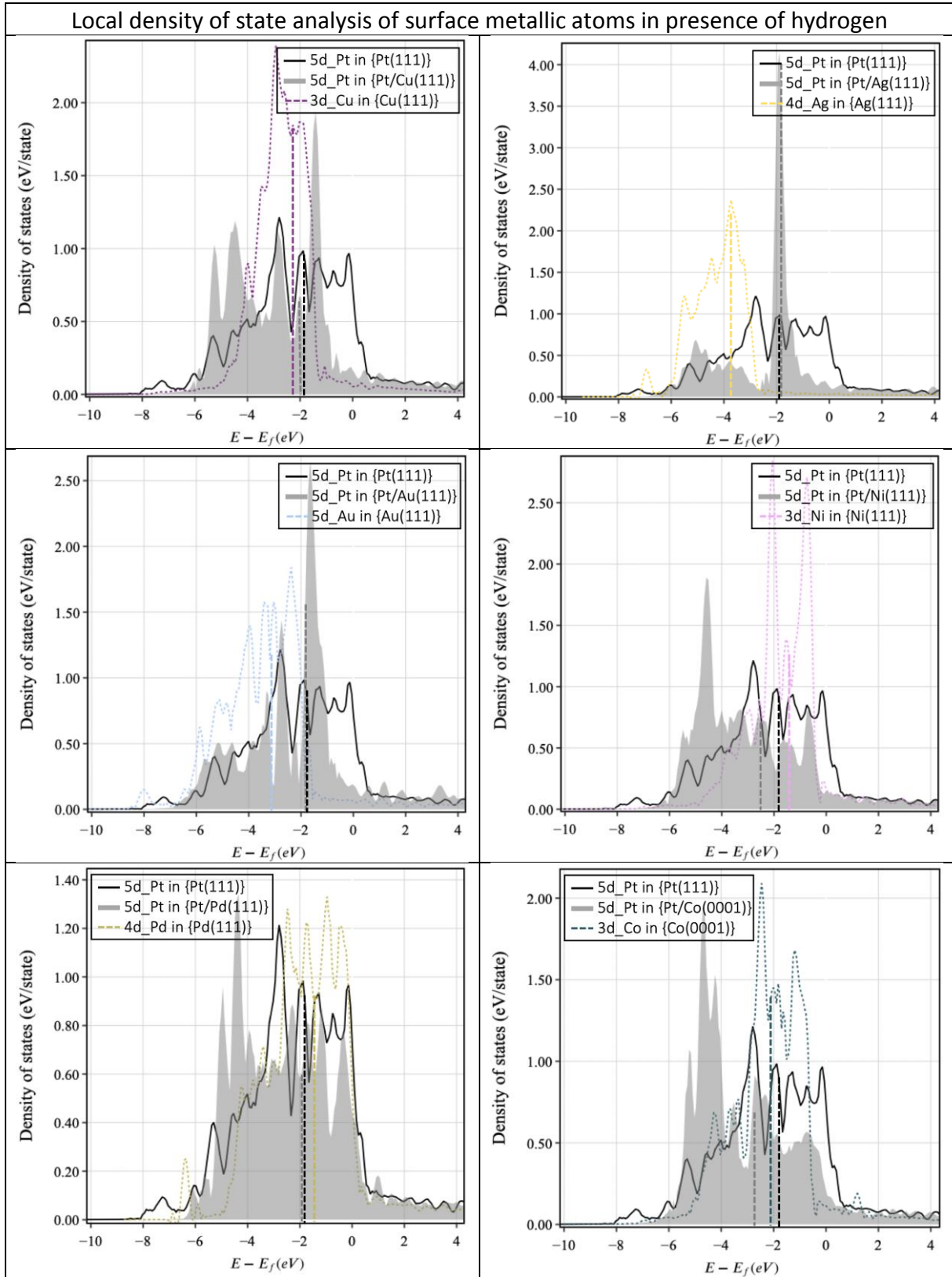
**Figure 6:** Binding energy comparison between pure M(111) host surfaces  $BE_{ads}^{host}$  and M(111) surfaces anchoring single-atom Pt atom  $BE_{ads}^{single}$ . For comparison, the binding energy of hydrogen on pure Pt(111) surfaces is indicated.

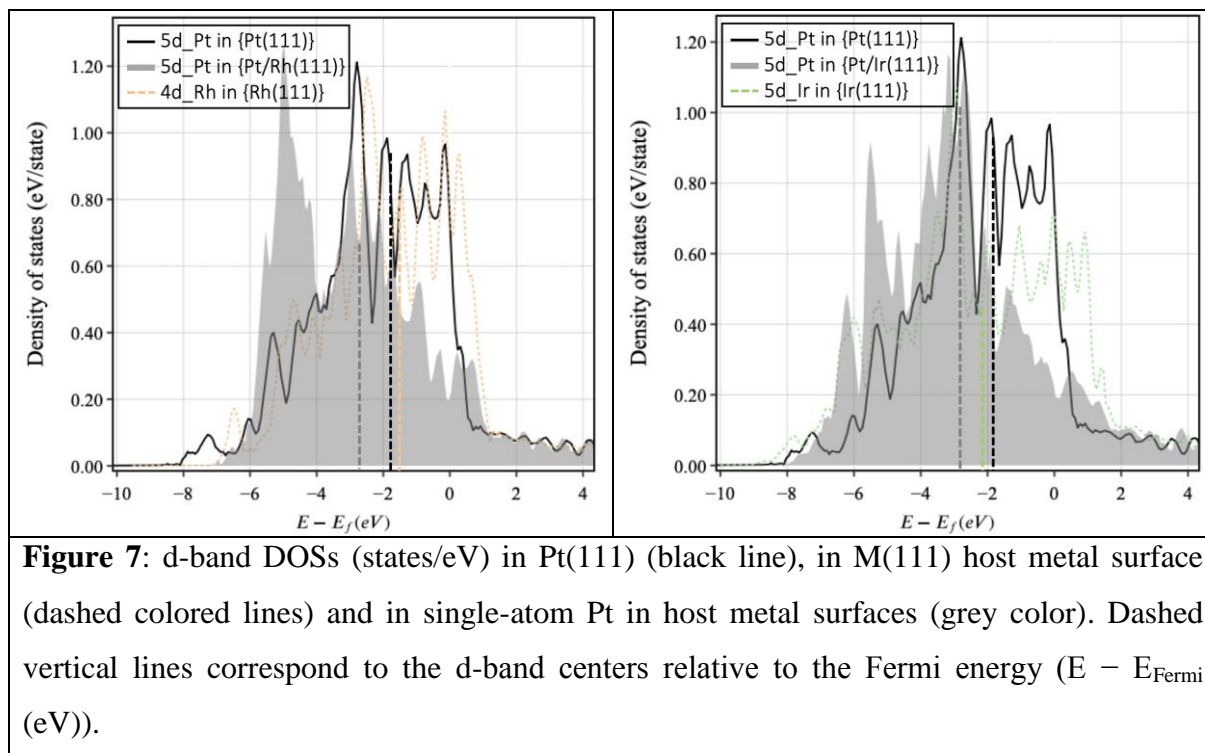
Generally, the expected response to adsorbates is that the more reactive alloy component (i.e., the one interacting strongly with the adsorbates) segregates to the surface [44-48].

Counterintuitive to this simplistic picture, the results on the considered SAAs show more complex behaviors. The results on Au (111) and Ag(111) surfaces, show that the most reactive component with hydrogen i.e. the single-atom Pt segregates toward the bulk. Indeed, the adsorption energy of hydrogen on Pt(111) is calculated to be of -0.62 eV while it is found to be endothermic on Au and Ag surfaces ). The analysis of local density of states in presence of hydrogen (see Figure 7) show that when single-atom Pt is located in the surface of Au(111) and Ag(111), its d-band is characterized by a pronounced narrow peak which lies below the Fermi level. Interestingly, the calculation of d-band centers (Table S2) show negligible shift between the 5*d*-band center of pure Pt(111) and single-atom Pt anchored in Au and Ag surfaces. For these latter nearly filled 1B metals, the position of the d-band centers is found to lie far away from the Fermi level in line with the calculated endothermic hydrogen binding energies. Thus, the non-stability of single-atom Pt could be explained by the fact that highly endothermic surface segregation under vacuum, could not be compensated by the mild binding energy of hydrogen on single-atom Pt of -0.28 eV and -0.34 eV in Ag(111) and Au(111), respectively.

The calculated binding energies of hydrogen on single-atom Pt in Cu(111) and Pd(111) compared with host surfaces are found to be competitive (0.09 eV in favor of single-atom Pt for the case of copper, and 0.08 eV in favor of host surface for the case of palladium). The calculated *d*-band centers of single-atom Pt vs. host surfaces are found to lie in the same energy ranges for the two systems, which is in agreement with the competitive binding energies. As the surface segregation of single-atom Pt in Cu(111) is slightly favored under vacuum, the better affinity of hydrogen to Pt increases the stability of this latter under a wide range of temperatures and pressures. In contrast, for Pd, the better affinity of hydrogen to Pd induces the better stability of single-atom Pt in the bulk. For these two systems, the interplay

between adsorption-driven surface segregation and surface orientation are found to induce different behaviors under reactive conditions.





**Figure 7:** d-band DOSs (states/eV) in Pt(111) (black line), in M(111) host metal surface (dashed colored lines) and in single-atom Pt in host metal surfaces (grey color). Dashed vertical lines correspond to the d-band centers relative to the Fermi energy ( $E - E_{\text{Fermi}}$  (eV)).

The binding energies of hydrogen interacting with single-atom Pt in the metallic Ni(111) (-0.3 eV), Co(0001) (-0.19 eV), Rh(111) (-0.32 eV) and Ir(111) (-0.32 eV) surfaces are found to be lower than on host surfaces (see graph in Figure 6). These results are in agreement with the calculated *d*-band centers of single-atom Pt found to lie much away from the Fermi level than the *d*-band centers of host metals. In spite of the lower reactivity of single-atom Pt toward hydrogen, this latter is found to be stable in the surface because of its highly exothermic surface segregation under vacuum. These identified single-atom properties (high stability under hydrogen pressure and temperature and lower interaction with hydrogen) may be of great interest for specific catalytic reactions.

## Conclusion

It is clear that the stability of single-atom Pt in Pt-based SAAs is changing under reactive conditions. In this study, using an environmental segregation model we provided a valuable picture of the surface stability of single-atom Pt within various metal host surfaces under different hydrogen pressures and temperatures. Three classes of SAAs could be distinguished.

The Au and Ag surfaces, in which single-atom Pt exposed to hydrogen pressure could not be found because this latter will prefer to segregate into the bulk. Copper and palladium supports, where the surface segregation of single-atom Pt could be optimum only for definite orientations (Cu(111) and Cu(110) for Pt/Cu and Pd(110) for Pt/Pd) and under specific hydrogen pressures and temperatures. Finally, Co, Rh, Ir and Ni supports in which single-atom Pt could remain stable in the surface within the quasi-totality of the pressure and temperature ranges studied (200K-1200K and 1Pa – 10<sup>5</sup> Pa)

These results are in contrast with the simplistic picture in which the response to adsorbates is that the more reactive alloy component (i.e., the one interacting strongly with the adsorbates) segregates to the surface. The reality is that the chemistry of diluted single atom Pt is completely different from what is known from the extended surfaces and from clusters and nanoparticle. Its stability in the surface is an interplay between different properties and depends either on its modified electronic structure within the host material, its geometric ensemble (surface orientation) and its affinity to the reactive gas.

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## TOC Figure

