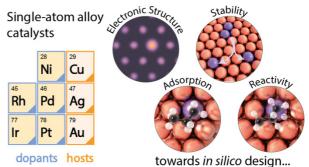# One decade of computational studies on Single-Atom Alloys: is *in silico* design within reach?

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Conspectus

Single-Atom Alloys (SAAs) are an emerging class of materials consisting of a coinage metal (Cu, Ag and Au) doped, at the single-atom limit, with another metal. As catalysts, coinage metals are rarely very active on their own, but when they are, they exhibit high selectivity. On the other hand, transition metals are usually very active but not as selective. Incorporating transition metals (guest elements) into coinage metals

(host material) is therefore appealing towards combining the activity and selectivity of each constituent in a balanced way. Additionally, first-principles calculations have shown that single-atoms embedded in the surface of a coinage metal can exhibit emergent properties. Here, we describe how computational studies based on Density Functional Theory (DFT) and kinetic Monte Carlo (KMC) simulations, often undertaken in close collaboration with experimental research groups, have shaped, over the last decade, the way we understand SAA catalysis.

This Account reviews our contributions in elucidating the stability of SAAs, their electronic structure, and the way adsorbates interact and react on SAA catalytic surfaces. By studying in detail the processes that affect the stability of the SAA phase, we have shown for instance, that, out of several bimetallic combinations of coinage metals with prominent Pt-group metals, only PtCu and PdCu are stable surface alloys under vacuum. More surface alloy structures are however possible in the presence of adsorbates, as the latter can stabilise, via strong binding, dopants in the surface of the material. More interestingly, a large number of these surface alloys are resistant to the aggregation of dopant atoms into clusters, thereby favoring the SAA structure. These major results from DFT calculations serve as a guide for experimentalists to explore new SAA catalysts. Further analysis has shown that SAAs have a unique electronic structure with a very sharp d-band feature close to the Fermi level, analogous to the electronic structure of molecular entities. This is one of the reasons why SAAs are particularly sought after: although they are metallic nanoparticles, they have properties akin to those of homogenous catalysts. In this context, we have contributed extensive screening studies, focusing on molecular fragments of catalytic relevance on a range of SAAs, which have driven the identification of new catalysts. We have also explored the rich chemistry of two-adsorbate systems via kinetic modelling, demonstrating how a spectator species with greater affinity for the dopant can modulate the reactivity of the catalyst via the so-called "(punctured) molecular cork" effect.

Since the first experimental characterization of SAAs about a decade ago, theoretical models have been able to support and explain various experimental observations. These models

have served as benchmarks for assessing the predicting capability of the underlying theoretical methods. In turn, the predictions delivered have guided and continue to guide the experimental research efforts in the field. These advancements show that the in silico *design of new SAA catalysts is now within reach.*

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Introduction

Alloys play a significant role in heterogeneous catalysis, since mixing metals offers the opportunity to transcend the structure-property constraints of monometallics and optimize the reactivity of catalysts.[5–8] However, it can be challenging to control the relative distribution of the different metals in the nanoparticle (NP) for optimal catalysis. Some NPs exhibit a core-shell structure and only expose one element at the surface, while other NPs show a surface distribution of their constitutive elements.[6] In the latter case, many surface configurations can be identified, ranging between two extremes: on the one end, the atoms are uniformly dispersed (like the black and white squares of a chessboard), while, on the other, the atoms form extended monometallic islands. This surface complexity is particularly prominent for alloys with similar amounts of constituent metals. However, when one of the two elements, for bimetallic alloys, is exceedingly less abundant than the other, entropy favors the formation of isolated small surface clusters. In 2005, the pioneering work by Goodman and co-workers showed the significance of Pd dimers in the PdAu Highly Dilute Alloy (~0.07% Pd) in catalysis.[9,10] Specifically, dimers consisting of two noncontiguous atoms of Pd were found to be the most active sites for the acetoxylation of ethylene to vinyl acetate. In 2009, Sykes and co-workers proved, using a combination of experiments and theory, that isolated Pd atoms in Cu could activate H_2 to 2H(ads), which could then spill-over to the Cu surface.[11] In 2012, they

successfully used this catalytic property to selectively hydrogenate olefins at low temperatures.[12] These two landmark studies by Sykes and co-workers have, since then, paved the way for the steady development of what is now known as Single-Atom Alloy (SAA) catalysis.[13–15] For instance, SAAs can selectively catalyze coupling reactions (C-C and C-O) as well as oxidation and reduction reactions among others. Our overview of major highlights in this exciting field will revolve around advancements guided by theory, focusing on SAAs that consist of isolated metal atoms doped into the surface of coinage metals (Cu, Ag, Au).

Prior to the early 2010s, a few groups had reported Density Functional Theory (DFT) studies on such systems, which were considered as simple idealized models for dilute alloys (minority metal loadings of ~20%).[16–18] With the increasing power of super-computers and the development of reliable functionals capturing dispersion forces (particularly important to describe the interaction of adsorbates on coinage metals),[19,20] a growing number of theoretical studies have focused on SAAs with dopant loadings similar to those reached experimentally (<10%). In these materials, the dopant site is typically the most active site of the surface, and its well-defined atomic-scale structure makes it amenable to study by periodic DFT calculations on a given facet. DFT-parameterized kinetic simulations have also been crucial in comparing theoretical predictions at the micro-scale with experiments at the macro-scale. The aim of this Account is to highlight representative computational studies related to the development of SAA catalysts and underscore the role of theory in leading the way we understand SAA catalysis by providing insights into their electronic structure, their stability, their interaction with adsorbates, and their reactivity. The success of these four pillars and their synergy are essential for the rational design of future SAA catalysts (Fig. 1).
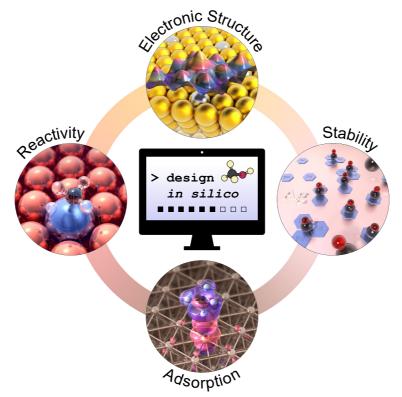

Figure 1. The analysis of the electronic structure of SAAs, their stability, their affinity for different adsorbates, as well as their reactivity using DFT enables the rational design of new catalysts.

Stability of clean SAA surfaces

The stability of SAAs is crucial prior to considering them as potential catalysts. Starting from the SAA phase, two transformations need to be examined to assess stability: the formation of surface clusters, also referred to as *surface aggregation*, and the migration of the single-atom dopants into the bulk of the material, which is the reverse process of *segregation*. The latter is entropically favored, especially for large NPs, as substitution sites in the bulk outnumber those at the surface. It is therefore important to identify compositions that energetically favor segregated systems with the minority metal atoms on the surface. In this context, an early DFT study by Fu and Luo on Cu(111) doped with group VIIIB transition metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt) identified PdCu(111) and PtCu(111) as the only Cu-based SAAs that were resistant to surface-to-bulk migration.[21] Darby *et al.* confirmed this result and further investigated the properties of Ag and Au based SAAs doped with late transition metals (Fig. 2a). However, no other materials were found to stabilize single atoms at the (111) surface.[22] On the more open (211) and (100) surfaces, only PdCu remains stable in the SAA configuration.[23] Clusters of different sizes have also been studied; for instance, Yin *et al.* reported, on the basis of DFT calculations, that the icosahedral $RhCu_{146}$ NP was a segregated SAA but $RhCu_{12}$ and $RhCu_{54}$ were not.[24] A similar trend was found for IrCu NPs. Moreover, in agreement with periodic DFT calculations, only PdCu and PtCu were predicted to be segregated systems for all sizes of NPs considered, while Ag- and Au-based SAAs favored only bulk alloys.

It is important to note that these observations pertain to pristine catalysts under vacuum conditions, and, in fact, the situation in practice is not as desperate as it may seem. Although PtCu and PdCu were, unsurprisingly, among the first SAAs experimentally identified, other SAAs have also been successfully synthesized and characterized.[14] This suggests that SAAs are kinetically stable; additionally, adsorption of molecules can stabilize SAA structures as will be discussed in the next section.
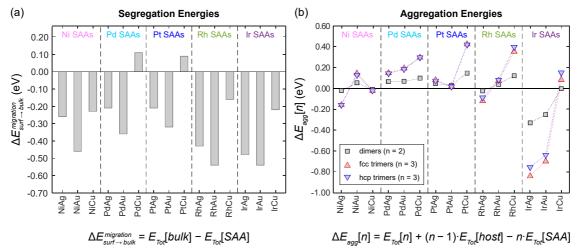

$$\Delta E_{surf \rightarrow bulk}^{migration} = E_{Tot}[bulk] - E_{Tot}[SAA]$$

$$\Delta E_{agg}[n] = E_{Tot}[n] + (n-1)\cdot E_{Tot}[host] - n\cdot E_{Tot}[SAA]$$

Figure 2. Stability of coinage metals doped with late transition metals as SAAs. (a) Segregation energy: positive values correspond to favorable segregation of the dopant atom to the surface; thus, PdCu and PtCu are the only stable SAAs. (b) Aggregation energy investigated looking at the formation of surface clusters of difference sizes and shapes: dimers (gray squares), fcc trimers and hcp trimers (red-up and blue-down triangles). Positive values signify thermodynamic preference for atomically dispersed configurations; thus, several bimetallics form stable SAAs in their surfaces, but some tend to form clusters (*e.g.*, IrAg, IrAu, NiAg, RhAg). Adapted with permission from ref. 22. Copyright 2018 American Chemical Society.

Assuming that dopants can be stabilized in the surface of a NP, their aggregation must be prevented to retain the SAA configuration. Darby *et al.* computed, using DFT, the aggregation energy for SAAs doped with late transition metals (Rh, Ir, Ni, Pd, Pt).[22] Their calculations (Fig. 2b) suggested that most bimetallics were resistant to surface aggregation except Ni-, Ir- and Rh-doped Ag(111) and IrAu(111). Pd-, Pt- and Rh-doped Cu(111) appeared as the most resistant to surface aggregation. Aggregation on NiCu(111) was calculated to be almost thermoneutral. In the latter case, entropy is expected to disperse the dopant as single atoms, and DFT-parameterized Monte-Carlo simulations on this material at 350 K for low surface loading (~1-4%) confirmed this expectation.[2] However, for both NiCu and PdAg, there were nonnegligible amounts of small clusters, especially for loadings close to 4%. No clustering was identified for the materials most resistant to surface aggregation. The trends in the aggregation energies are comparable for more open surfaces: (100) and (211).[23] However, the kinetics of aggregation can alter these thermodynamics-based conclusions. There is experimental and theoretical evidence that dopant diffusion is faster at the (100) facet, making dopant dispersion easier; thus, SAAs could be stable at higher-than-expected loadings.[25]

Electronic properties of SAAs

Analyzing the electronic structure of SAAs can be insightful towards rationalizing their stability. Within this approach, Yin *et al.* computed the segregation energies of group-VIIIB metal clusters doped into coinage metals.[24] By averaging the segregation energies, for a given dopant, over the different host metals, they established a correlation between the averaged segregation energy and the d-band filling of the dopant. Despite this model being able to explain trends in size and geometrical strain effects from the elements' electronic structure, its averaged nature cannot capture the specificities of coinage-based SAAs. There are other approaches aiming at rationalizing the stability of SAAs based on the analysis of Electron Localization Functions (ELF) and Crystal Orbital Hamilton Populations (COHP). Gao *et al.* used these tools to assess the binding energy of a dopant (Pt and Pd) at a vacancy created at the Cu(111) surface.[26] The authors found that the electron density was more localized between Pt and Cu atoms than Pd and Cu atoms. This was further confirmed analyzing the COHP to quantify the bonding and anti-bonding contributions. Both the ELF and COHP analyses confirmed that Pt binds more strongly than Pd at a vacancy at the Cu(111) surface.

There is growing evidence substantiating the link between the properties of SAAs and their unique electronic structure. Thirumalai and Kitchin reported a detailed analysis of the density of d-states of SAAs,[27] demonstrating that, unlike the host metals, the dopants exhibit very sharp densities of d-states (Fig. 3). This suggests that the d-states of the dopants do not interact strongly with the host metal, a prediction that was further confirmed experimentally.[28] With localized d-states, SAAs are expected to stand out as metal surfaces insofar as their electronic structures are more closely related to free atoms or molecular entities than traditional metal NPs. This is thought to explain the unique properties of SAAs regarding the interaction and reactivity of adsorbates,[29] which we discuss next.
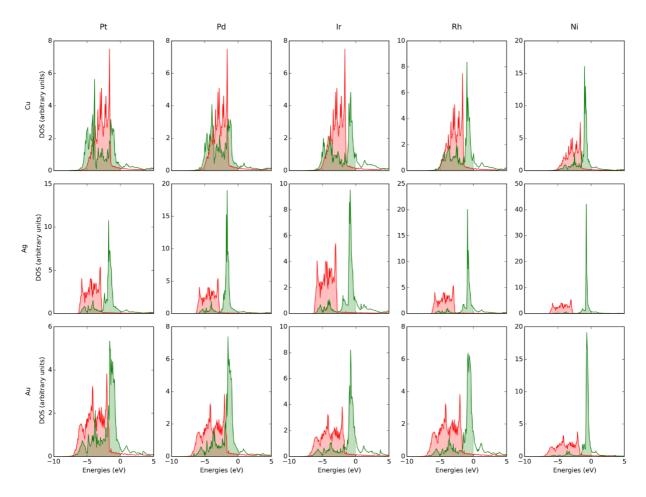
Figure 3. Density of d-states (DOS) for coinage metals (red) doped with late transition metals (green). The DOS of most dopant sites is very sharp close to the Fermi level of the material. Adapted with permission from ref. 27. Copyright 2018 Springer Nature.

Adsorption on Single-Atom Alloys

The early work by Sykes and co-workers focused on the dissociative adsorption of H_2 on PdCu(111) and PdAu(111). In that study, surface science experiments complemented by DFT calculations demonstrated that the dissociative adsorption on the Pd site was exothermic for both host metals.[11] However, the spill-over of atomic hydrogen from the dopant site to host sites was predicted to be less favorable than the associative desorption of H_2 on PdAu(111) SAA. Conversely, PdCu(111) SAA showed a more favorable spill-over to Cu sites, making it possible to load the Cu host surface with hydrogen atoms. Because of their importance in catalysis, hydrogen dissociation and spillover have further been investigated using DFT. By screening Cu-hosted SAAs, Fu and Luo showed that the dissociative adsorption was always more favorable on the dopant than the host.[21] The affinity for H(ads) would increase when going towards the left in the periodic table, making the spill-over to the host more difficult, thereby putting the dopant site at risk of poisoning. Ni, Pd and Pt doped Cu-based SAAs were identified as the best compromise between enhanced dissociative adsorption and spill-over efficiency. Switching to Ag and Au hosts would not facilitate the spill-over process.[1]

To understand these trends, Thirumalai and Kitchin attempted to correlate the adsorption energy of H and the d-band center of the metal, in the spirit of linear scaling

suggested by d-band theory,[30] however, no linear trends were found.[27] Indeed, the model assumes that the d-band of the material is broad; this works well for transition metals, the d-band of which expands over a few eVs. However, as mentioned in the previous section, the d-states of the dopant atoms in SAAs are localized, rendering the d-band model less robust for these materials. Using a machine-learning approach, Han *et al.* developed surrogate models for the adsorption energy of H(ads).[31] Interestingly, each of their models included the d-band center as a parameter. However, more than four other parameters (e.g., ionization potential, electron affinity, d-band center of top and subsurface layers) were needed to reach reasonable non-linear correlations, making these models more complex than the original one-parameter d-band model.

Aside from hydrogen, other intermediates relevant to catalysis, have also been investigated. In this regard, our study of the CH_x, NH_y and OH_z adsorbates ($x = 0\ldots4$, $y = 0\ldots3$ and $z = 0\ldots2$) is insightful.[1] As a general trend, the formation energy of these intermediates increases along with their degree of unsaturation, as observed in pure coinage metal surfaces. This is important for C and CH species, which tend to aggregate and poison the surface of Pt-group catalysts; on the other hand, the high formation energy of these species on SAAs, suggests that these materials could resist poisoning by coking.[4,32] More generally, SAAs are resistant to the formation of highly unsaturated intermediates. Most of these intermediates are consistently more stable on the dopant than the host SAA sites. There are, however, a few exceptions, e.g., OH is more stable on the host sites of the (111) facet on PdCu, PtCu, RhCu and PtAg SAAs than on the dopant site. Alcohols on PtCu(111) also stand out as an exception;[1,33] they bind more strongly, via their oxygen atom, to the Cu sites in the direct vicinity of the dopant, with the proton directly pointing towards the Pt site. This plays a key role in the activation of alcohols into alkoxy intermediates. Interestingly, strong adsorption of methane has also been reported ($E_{ads} < -0.6$ eV).[29] Some SAAs indeed exhibit short dopant-to-hydrogen distances and a reorganization of the electronic structure of methane, suggesting a certain degree of chemical bonding.[4,29]

Because of the increased affinity of adsorbates for dopant sites and the limited amount of such sites (0.2% to 10% of surface atoms), only a fraction of adsorbates occupies all the dopant sites, leaving any excess on host sites. The situation becomes particularly interesting when the surface is covered by more than one type of adsorbates, which would compete to occupy the dopant sites. This was first evidenced on Cu-based SAAs, on which the thermal dissociative adsorption of H_2 onto Cu(111) is kinetically suppressed. When doping the surface with Pd atoms, a "channel" is created allowing H_2 activation and H spill-over to Cu.[11] Once loaded onto the surface, H(ads) is predicted to associatively desorb at 210 K via the same "channel" under Ultra-High Vacuum conditions (Fig 4a). Adding CO, which has a stronger affinity for Pd than H, blocks the entrance (and exit) "channel" for H_2,[34] preventing the dissociative adsorption of H(ads) until CO starts to desorb (Fig. 4b-c). This phenomenon was termed the "molecular cork" effect. A similar effect has been described on PtCu,[35] but in this case, the temporary spill-over of CO to Cu allows H_2 desorption even prior to CO desorption, giving rise to the "punctured molecular cork" effect.

This preferred affinity of a spectator species for the dopant site, and the ensuing temporary blocking thereof, has also been demonstrated in a system of catalytic relevance.[3,36] In the coupling of CH_3I to ethane on PdAu and NiAu SAAs, iodine atoms, generated upon the

dissociative adsorption of CH_3I, occupy all Pd sites leaving the CH_3 groups on gold sites. To couple, $CH_3(ads)$ needs to overcome the I/CH_3 exchange thermodynamic barrier (Fig. 4d), which penalizes the kinetics of the coupling event, yet prevents $CH_3(ads)$ from being trapped on the active sites, where they could react via undesired pathways (e.g., production of unsaturated species acting as poisons). $I(ads)$ therefore moderate the reactivity of $CH_3(ads)$, similarly to ligands in homogeneous catalysis (Fig. 4d-e). Recently, N-Heterocyclic Carbenes (NHCs), which are important ligands in homogeneous catalysis, have been predicted as potential molecular corks on PtCu and PdCu SAAs. Crucially, NHCs with substituents that have a strong electron-donating character exhibit a stronger "molecular cork" effect,[37] demonstrating the potential to tune this effect via molecular design.
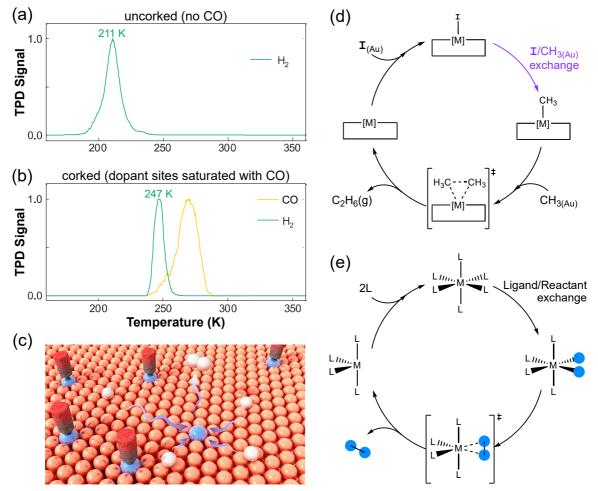

Figure 4. Competitive adsorption of (a-c) CO(ads) and H(ads) on Cu-based SAAs and (d-e) I(ads) and $CH_3(ads)$ on Au-based SAAs. (a-b) In the presence of CO, the desorption of H_2 is suspended until reaching higher temperatures. (c) H_2 can only desorb when dopant sites become available. (d) A similar effect was evidenced for the associative desorption of $CH_3(ads)$ as C_2H_6 in the presence of I(ads) on PdAu and NiAu SAAs. With a larger affinity for the dopant, I(ads) occupies all the dopant sites, pushing $CH_3(ads)$ to the host sites. The reaction only proceeds after the endothermic exchange of I/CH_3. (e) This compares to ligand exchange in homogeneous catalysis. Parts (a), (b) adapted with permission from ref. 34. Copyright 2013 Springer Nature. Part (c) adapted with permission from ref. 35. Copyright 2019 American Chemical Society. Parts (d), (e) adapted with permission from ref. 3. Copyright 2021 AIP Publishing.

Another level of complexity in the interaction of adsorbates and SAAs, arises when considering multifunctional molecules, such as crotonaldehyde or styrene. For chemo-selectivity considerations, the important question is: would the C=C bond or the other moiety (carbonyl or phenyl) be reduced under hydrogenating conditions? On transition metal NPs, these molecules adsorb flat onto the surface, exposing all their functional groups to the highly reactive sites of the NP. Reducing the active sites to one isolated atom offers the possibility to only treat one functional group of the substrate. In fact, Kyriakou *et al.* experimentally showed that styrene could be selectively hydrogenated to ethylbenzene on PdCu(111) SAA.[12] DFT calculations showed that flat-lying reactive C_6-aromatic molecules interact with 4 metal atoms on pure transition metal surfaces and require extended clusters and subsurface transition metal atoms in Cu-based alloys.[38,39] However, because of the isolated nature of transition metals, this flat-lying adsorption mode is not possible on SAAs, on which styrene likely prefers to interact with the dopant *via* the vinyl substituent. Many authors have indeed reported a di-σ adsorption geometry for ethylene on SAAs.[17,26,27,40,41] Gao *et al.* were able to rationalize the relative affinity of different SAAs for ethylene based on molecular orbitals (d_{xz} and d_{z^2} of the dopant, π and π* of ethylene).[26] The integral of the COHP (ICOHP) was shown to be a good descriptor of the adsorption energy of ethylene on SAAs (Fig. 5). This ability to selectively interact with the C=C bond could explain the selectivity for ethylbenzene. Following a similar approach, Spivey and Holewinsky studied the adsorption of crotonaldehyde on a large range of SAAs doped with early to late transition metals.[42] They showed that the molecule either adsorbs *via* the C=O or the C=C bond depending on the relative positions of its HOMO (*resp*. HOMO-1) localized on the C=O bond (*resp*. C=C bond) and the sharp d-band of the dopant. The authors suggested that the adsorption mode could be responsible for the selectivity towards C=C versus C=O hydrogenation.
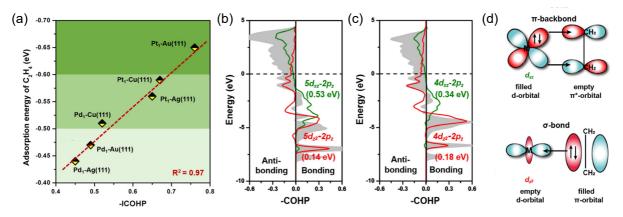

Figure 5. Orbital analysis of the interaction of ethylene on the dopant site of various SAAs. (a) Linear correlation between the adsorption energy and the ICOHP. (a-b) Detailed analysis of the COHP for ethylene on PdCu(111) and and PtCu(111) SAAs. (c-d) Schematics of the interaction based on molecular orbitals. Adapted with permission from ref. 26. Copyright 2021 Elsevier.
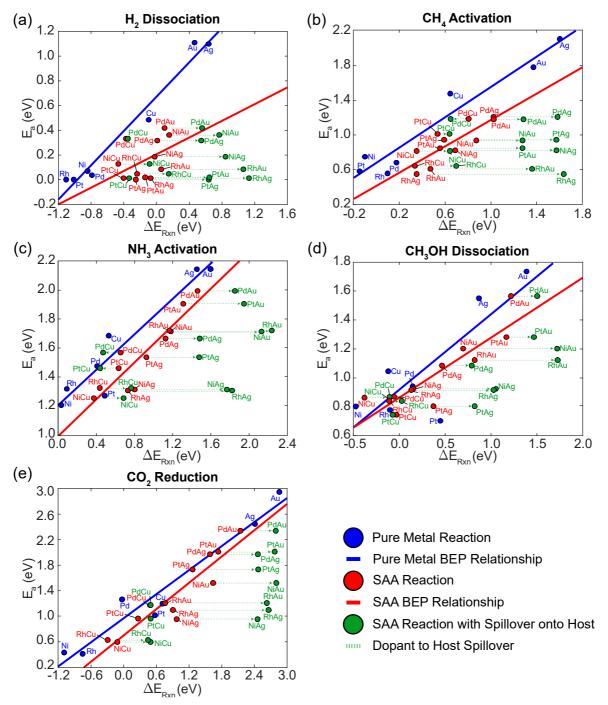
It is important to keep in mind that, especially at high temperatures, NPs are dynamic materials: dopants can migrate within the surface and between the surface and the bulk. During the preparation of the catalyst, or under operating conditions, adsorbates can strongly affect the stability of SAAs.[43] Accounting for the adsorbate spill-over energy is therefore crucial in order to construct a good model of the surface state of the NP under experimental conditions.[4,22,23] The study of such effects is ongoing, but some interesting results have already been demonstrated. For instance, DFT-parameterized Monte-Carlo simulations by Papanikolaou *et al.* showed that the partial pressure of CO could greatly influence the distribution of dopants, going from isolated atoms to dopant clusters, which can in turn affect catalytic performance.[2,44]

Reactivity of SAAs

As we have seen in the previous section, understanding the adsorption of molecules on SAAs already provides useful information regarding their reactivity and selectivity. To fully assess the catalytic performance of these materials, calculations of transition state structures and activation energies are necessary. In the context of finding trends, it is known that for several materials, the activation energy of an elementary process scales linearly with its reaction energy via a so-called Brønsted-Evans-Polanyi (BEP) relationship. SAAs may adhere to such trends, *e.g.*, the activation of CO_2 and CH_3OH on SAAs follow respectively the same BEP relationships as those of the pure metals (Fig. 6).[1]

However, SAAs can also deviate from them, *e.g.*, the activation of CH_4 (or NH_3) on SAAs exhibits lower barriers than expected from the "traditional" BEP relationship on pure metals (Fig. 6). This behavior is particularly interesting for escaping the reactivity restrictions of traditional NP catalysts. In certain cases, these deviations appear extreme, *e.g.*, the activation of H_2 into 2H(ads) is a case where no BEP relationship can be established on SAAs.[1] It is interesting to note that the adsorption energy of H(ads) does not correlate with the d-band center as mentioned in the previous section. Thus, the chemistry of hydrogen on SAAs seems to be defying the simple models traditionally used in catalysis.[1,27]

In general, dopants enable low-activation-energy pathways, which can lead to rich behavior. Thus, many SAAs are predicted to activate H_2 and CH_4 with low barriers, although the stability of some of the pertinent SAAs is yet to be assessed. With very low barriers, tunneling effects can become important, as has been demonstrated for hydrogen activation on PdCu SAA.[45] Moreover, the new facile pathways enabled by the dopant may also lead to synergism with the existing pathways on the host, leading to SAAs behaving as bifunctional catalysts. For instance, in the disproportionation of ethyl on PtCu SAA, the oxidation happens on Cu and the reduction on Pt.[40] Although it is difficult to establish clear trends to identify which SAA would catalyze which reaction, it is important to note that detailed case-by-case DFT studies have been able to successfully support and predict many experimental observations relevant to catalysis.[46,47] The comparison between theory and experiments has also been made easier with the help of DFT-parameterized kinetic simulations able to model the catalytic surface at the mesoscale.[32,48] These simulations have been particularly insightful for the identification of the key parameters that control the selectivity of SAAs. For example, PdAu and NiAu SAAs are only active for C-C couplings when the dopant is at an open surface.[3,36] On PtCu SAA, the selectivity of ethyl disproportion can be tuned changing the external pressure of hydrogen.[40] Substrate-to-dopant ratio (usually denoted by σ) has also been proved

to control the transition between regimes (sub- and supra-stoichiometry) with different reactivities. [3,36,40]

Figure 6. BEP relationships for several bond dissociations at the surface of pure transition metals (blue) and SAAs (red). The data represented in green accounts for the spill-over onto host on SAAs. Adapted with permission from ref. 13. Copyright 2018 American Chemical Society.

The aforementioned studies were primarily motivated by challenges in thermal catalysis, however, the theoretical study of SAAs for electrocatalytic applications has also seen growing interest. Darby *et al.* studied the electrochemical oxygen reduction (EOR) reaction on Ag(111) and Au(111) surfaces doped with Ni, Pd, Pt, Co and Rh atoms in the SAA regime.[49]

The overpotential needed to overcome the thermodynamic barrier associated with the EOR was predicted to be consistently lower on Au based SAAs. Among them, PtAu and PdAu SAAs showed the lowest overpotentials, similar to Pt(111) with a better resistance to CO poisoning. Cheng *et al.* investigated the CO_2 reduction reaction (CO_2RR) on Ag(100) and Au(100) surfaces doped with Cu, Ni, Pd, Pt, Co, Rh and Ir.[50] They identified Rh-doped surfaces as the most promising bifunctional catalysts, with the initial electroreduction of CO_2 to CO happening on the host and the hydrogenation of CO catalyzed on the dopant site. Zhi *et al.* also investigated the CO_2RR on Cu-based SAAs doped with Co, Ni, Ru, Rh, Ir, Pt, Pd, Au, Ag, Zn, In and Sn,[51] focusing on different pathways yielding C_2 species, moderately reduced C_1 species (CO and HCOOH) and highly reduced C_1 species (CH_4 and CH_3OH). Interestingly, the binding energies of O and H to the dopant were identified as good descriptors for predicting the preferred pathway. A similar approach was followed by Zheng *et al.* for the Nitrogen Reduction Reaction (NRR) on Au(111) surfaces doped with Ti, V, Nb, Ru, Ta, Os, W, and Mo.[52] They identified a new descriptor, referred to as φ, based on the number of valence d electrons and the electronegativity of the dopant. The Gibbs free energy for the first hydrogenation step of the NRR was found to be minimized for intermediate values of φ obtained for three dopants: Ta, W and Mo. Although all these electrocatalytic studies are purely based on DFT calculations, they provide insightful information on the elementary steps of interest. In each study, various linear relationships were established to correlate the stability of different intermediates. These relationships simplify the catalysis design problem, by decreasing the high dimensionality arising from the large number of intermediates, which are, however, chemically related.

As a final note, we highlight plasmonic photocatalysis of SAAs, which was being investigated using *ab initio* calculations. Zhou *et al.* showed that the light-driven dry reforming of methane was more than 5 times more efficient than thermal catalysis and highly selective.[53] Using DFT calculations, further refined with embedded multiconfigurational *n*-electron valence second-order perturbation theory, the authors showed that the activation energy of CH→C+H could be reduced from 1.10 to 0.40 eV when considering light-induced excited states. This is an excellent example where the physical properties of the host, a plasmonically active metal, have been used to enhance the reactivity of the active site.

Perspective and Outlook

Over the last decade, the knowledge in the growing field of SAA catalysis has significantly expanded. The tight synergy between computational and experimental studies has not only delivered realistic models for the understanding of SAAs, but also enabled the benchmarking of simulation methods, the accuracy of which seems to be reasonable enough to support and explain experimental observations. In recent years, this validation has given credit to purely computational studies, the predictions of some of which are yet to be confirmed experimentally. Thus, the *in silico* design of SAA catalysts appears certainly within reach.

One such example of *in silico* catalyst design, is the recent development of a RhCu SAA for propane dehydrogenation to propene (Fig. 7).[4] Using DFT calculations, the authors first identified the RhCu SAA as a promising candidate that minimized the barrier for alkane activation and maximized the resistance to dopant's migration to the bulk. Even though RhCu was not predicted to be a segregated system *in vacuo*, further calculations showed that the interaction with surface alkyl groups, likely to be formed under catalytic conditions, would

stabilize surface dopant atoms. Surface science and reactor experiments confirmed the predictions related to the stability and the activity of RhCu SAA, making it the first computationally designed SAA catalyst.
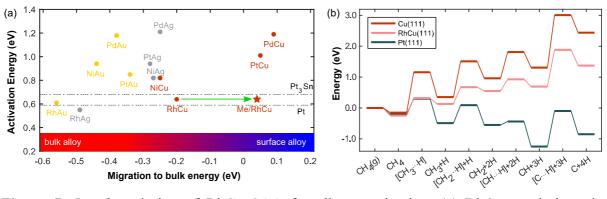

Figure 7. *In silico* design of RhCu SAA for alkane activation. (a) RhCu maximizes the resistance to bulk segregation and minimizes the activation energy for methane activation. (b) The full energy diagram of methane activation to atomic carbon shows that RhCu(111) SAA performs as well as Pt(111) regarding the first C-H activation but prevents further unsaturated fragments from being stabilized, similarly to Cu(111). Adapted with permission from ref. 4. Copyright 2021 American Association for the Advancement of Science.
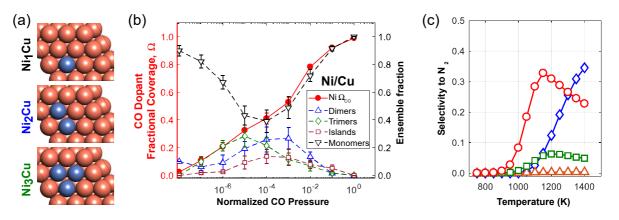

Figure 8. NiCu SAAs and Highly Dilute Alloys. (a) Structure of monomers, dimers and trimers of Ni on the surface of NiCu. (b) Distribution of clusters of different sizes at the surface of NiAu as a function of the normalized partial pressure of CO from DFT-parameterized Monte Carlo simulations. (c) Selectivity to N_2 for the reduction of NO by CO on four different catalysts (the other product being N_2O) from DFT-parameterized microkinetic modeling. Adapted with permission from refs 2,48. Copyright 2020 American Chemical Society. Copyright 2021 the authors, published by Royal Society of Chemistry under a Creative Commons Attribution 3.0 Unported License. https://creativecommons.org/licenses/by/3.0/

Further, the work by Papanikolaou *et al.* provides insight on the design of active sites for specific reactions (Fig. 8). Using DFT-parameterized Monte-Carlo simulations, they showed that by exposing a SAA to CO(gas) one can modify the structure of the surface. In the case of NiCu, low or high pressures of CO stabilize dopants as monomers at the surface, but moderate pressures lead to the formation of clusters and islands.[2] Crucially, Ni dimers were predicted to outperform Ni single atoms in NiCu for the reduction of NO to N_2 in the presence

of CO. Using DFT-parameterized microkinetic modeling, $Ni_2Cu(111)$ was shown capable of reaching a similar selectivity as Rh(111) at lower temperatures.[48]

Although the field would gain from the development of a unified, descriptor-based model explaining the interaction and reactivity of adsorbates on SAAs, the growing high-throughput computational literature has already opened the possibility for the design of SAA catalysts *in silico*. The development of a simple and qualitative, as opposed to accurate, model that could give trends in reactivity (e.g., early versus late transition metal dopants), would be particularly useful to narrow down the potentially active catalysts for a targeted reaction. Additionally, since several SAAs are known to be resilient against poisoning by coke or CO, as well as resistant to sintering, it would be important to further elucidate the mechanisms that give rise to these beneficial properties, and incorporate the pertinent "lessons learnt" into screening studies. As the experimental conditions are particularly important regarding the stability of SAAs, the study of explicit solid/liquid interfaces could be of particular interest, especially for electrochemical applications. Effort should also be made to investigate the metal/support interaction for SAA nanoparticles deposited on supports, which could significantly affect the availability of dopant atoms at the surface of these nanoparticles. Such restructuring effects should be investigated more broadly and under realistic reaction conditions, to include surface reconstruction but also topological changes to the site-ensemble of the minority metal.

Conclusions

A multitude of pioneering experimental-theoretical studies within the last decade, have enabled the synergistic development of SAA catalysts at the crossroads of theory, surface science and practical catalysis (reactor studies). The modelling of these highly promising materials has been greatly facilitated by the well-defined nature of the active sites under various conditions and has provided key insights into their unique properties. Their electronic structure, akin to molecular entities, has offered the possibility to reach chemistries that could not be explored with traditional metal catalysts. Moreover, the use of spectator adsorbates to modulate the reactivity of the active site and control the distribution of the species on the surface of SAAs offers additional flexibility in an analogous way to homogeneous catalysis. The rationalization of such effects has been possible thanks to detailed modelling studies combining first-principles approaches at the electronic and atomistic levels with kinetic modelling at the mesoscale. After a decade of close comparisons between theoretical predictions and experimental observations, the design *in silico* of SAAs for specific reactions is now within reach.

Biographies

Romain Réocreux received his M.Sc. in Science of Matter at the École Normale Supérieure de Lyon in 2014 and completed his Ph.D. in Chemistry under the guidance of Prof. Philippe Sautet and Dr Carine Michel in 2017. Thereafter, he joined the department of Chemical Engineering at University College London as a Post-Doctoral Research Associate in the lab of Dr Michail Stamatakis. His research focuses on the multi-scale modeling of reactive heterogenous systems beyond the mean-field approximations.

Michail Stamatakis holds a Diploma in Chemical Engineering from the National Technical University of Athens, Greece, and a Ph.D. from Rice University, USA, which he

obtained under the supervision of Dr Nikos V. Mantzaris and Prof. Kyriacos Zygourakis. Prior to joining the faculty of University College London (UCL) he performed post-doctoral research at the University of Delaware, USA, in the lab of Prof. Dionisios G. Vlachos. He is currently Associate Professor of Chemical Engineering at UCL. His research interests revolve around the development and use of stochastic multiscale methods for modelling complex systems in chemistry and materials science.

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