Reactivity Screening of Single Atoms on Modified Graphene Surface: From Formation and Scaling Relations to Catalytic Activity

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Single atom catalysts (SACs) present the ultimate level of catalyst utilization, which puts them in the focus of current research. Using density functional theory calculations, model SACs consisting of nine metals (Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au) on four different supports (pristine graphene, N- and B-doped graphene and graphene with single vacancy) are analyzed. Only graphene with a single vacancy enables the formation of SACs, which are stable in terms of aggregation and dissolution under electrochemical conditions. Reactivity of models SACs is probed using atomic (hydrogen and A = C, N, O, and S) and molecular adsorbates (AHx, x = 1, 2, 3, or 4, depending on A). Scaling relations between adsorption energies of A and AHx on model SACs are confirmed. However, the scaling is broken for CHx. There is also an evident scaling between adsorption energies of atomic and molecular adsorbates on metals SAs supported by pristine, N-doped and B-doped graphene, which originates from similar electronic structures of SAs on these supports. Using the obtained data, the authors analyze the hydrogen evolution on the model SACs. Only M@graphene vacancy systems (excluding Ag and Au) are stable under hydrogen evolution conditions in highly acidic solutions.

1. Introduction

Battling global challenges related to the energy requirements of our society requires tremendous efforts and innovative approaches. Many processes we use these days for energy conversion or storage require catalysts, and an increasing number of them actually rely on electrocatalysis. It is a fact that electrocatalytic processes most frequently use expensive Pt-group metals (PGM). This makes them less attractive for large-scale use. Strategies to overcome this problem are i) finding new PGM-free electrocatalysts or ii) reducing the content/loading of PGM. Considering the latter point, the first step is reducing size while increasing the number of active sites. However, even at the nanoscale, the interior of a nanoparticle is catalytically inactive and presents a clear loss. For this reason, core-shell or thin-film catalysts have been developed. However, the absolute extremes of the catalyst utilization are single atom catalysts (SACs). In SACs every single atom (SA) has a catalytic function. In this case, the catalyst support is vital. As every SA is in contact with the support, there is a strong interplay between them. For this reason, the same metal atom at two different supports can behave entirely differently. In a way, this is an advantage as the phase space of SACs is enormous. However, it is also a challenge, as we need to understand this interplay to develop new SACs rationally.

The field of SACs developed tremendously in the last decade. Now we have many different SACs for various (electro)catalytic reactions. Only a few examples are the review of heterogeneous SACs, the review of SA alloy catalysts as a class of SACs and others. Different aspects of SACs have been summarized in many timely reviews, like design principles and applications, application of SACs in organic chemistry, heterogenous SACs for CO2 electroreduction, SACs for electrocatalytic hydrogen production, synthetic strategies and electrochemical applications of SACs, SACs for the green synthesis of fine chemicals, SA catalysis on carbon-based materials, and others, addressing some general features of SACs or summarizing SACs for a given (electro)catalytic reaction(s).

Many individual reports on SACs contain theoretical contributions, most frequently within density functional theory (DFT). While nanoparticles cannot be routinely analyzed using DFT, SACs, on the other hand, present perfect study cases. The structure of a SAC can be transferred into the DFT model with much fewer approximations. For example—nanoparticles are most frequently modeled part-by-part, using single-crystal surfaces of a given composition and orientation. In this way, one can obtain an in-depth, electronic structure-level description of a SAC considered for a given reaction. However, we firmly believe that, in the case of SACs, the real power of DFT lies in the possibility...
of investigating a large number of systems and understanding trends. As an example, one can mention the work of Xu et al.\cite{19} who investigated a large number of SAs embedded in graphene with single vacancy, double vacancy with four carbon atoms, vacancy surrounded by four pyridine, and vacancy surrounded by four pyrrole nitrogen atoms. That work not only analyzes adsorption trends of hydrogen and oxygen containing species, but also provides a universal descriptor for the design of novel SACs.

Table 1. Preferred adsorption sites and adsorption energy of metal atoms on pristine, doped (NDG and BDG), and graphene with a single vacancy (VG).

| M   | Site | PBE | PBE+D2 | Site | PBE | PBE+D2 | Site | PBE | PBE+D2 |
|-----|------|-----|--------|------|-----|--------|------|-----|--------|
| Ni  | H    | −1.44| −1.71  | e    | −2.18| −2.47  | y    | −1.40| −1.68  |
| Cu  | T    | −0.26| −0.53  | a    | −1.38| −1.68  | c    | −0.47| −0.73  |
| Ru  | H    | −1.59| −1.96  | e    | −2.44| −2.83  | y    | −1.92| −2.29  |
| Rh  | H    | −1.43| −1.80  | e    | −2.30| −2.67  | y    | −1.86| −2.22  |
| Pd  | B    | −1.08| −1.49  | b    | −1.58| −1.95  | n    | −1.10| −1.47  |
| Ag  | H    | −0.03| −0.32  | a    | −0.90| −1.26  | y    | −0.04| −0.33  |
| Ir  | B    | −1.34| −1.70  | e    | −2.16| −2.76  | f    | −1.69| −2.26  |
| Pt  | B    | −1.45| −2.01  | b    | −2.12| −2.68  | d    | −1.81| −2.38  |
| Au  | T    | −0.14| −0.70  | a    | −1.12| −1.69  | c    | −0.72| −1.29  |

*Site – preferred adsorption site. Top, bottom, or hollow (t, b, or h) for p-graphene; for modified graphene, refer to Figure 11.*

As the initial step of forming single-atom graphene systems, we consider the deposition of selected atoms on the pristine and modified graphene surfaces. An overview of adsorption parameters is given in Table 1.

The adsorption energies and preferred binding sites on pristine and monovacant graphene are in good agreement with our previous studies of monoatomic adsorption on pristine and monovacant graphene\cite{20,21}, as well as studies of various TM atoms adsorption on pristine graphene\cite{22,23}. On pristine graphene, adsorption is preferential on the bridge and hollow sites, except for Au and Cu. Structural parameters, in accordance with the notation given in Figure 1, are presented in Table S1, Supporting Information.

2. Results and Discussion

2.1. Formation of Single Atom-Graphene Systems and the Viability of Model SACs

As the initial step of forming single-atom graphene systems, we consider the deposition of selected atoms on the pristine and modified graphene surfaces. An overview of adsorption parameters is given in Table 1.
Binding on the monovacant graphene is always on the vacancy site. On average, monovacant graphene shows the strongest bonding of TM atoms, followed by BDG, NDG, and finally pristine graphene. Dispersion interactions give a similar total contribution to adsorption energy in most of the cases. However, the relative contribution is most pronounced in weakly binding systems, such as metal-pristine graphene, which is known to be rather chemically inert. From the density of states (DOS) plots in Figures 2 and 3 (the cases of pristine and VG, for NDG and BDG, see Figures S1–S4, Supporting Information), one can observe that the electronic structure of pristine graphene is weakly affected upon metal SA adsorption, in line with small adsorption energies. SA bands are narrow and relatively close to the Fermi level. An almost identical situation is seen for the cases of NDG and BDG.

In contrast, SA embedding in single vacancy results in strong interactions with the graphene matrix and the SA d-states are wide and buried well below the Fermi level. Bandgap opening was not observed in any of the studied cases, suggesting that conductivity is preserved (see Figures S1–S4, Supporting Information). This is of crucial importance for the electrocatalytic applications.

An aspect of the investigated model SACs related to practical application is maintaining SA on the support to prevent SA

**Figure 2.** DOS plots for single atoms adsorbed on pristine graphene. The energy scale is referred to the Fermi level (vertical dashed line).

**Figure 3.** DOS plots for single atoms adsorbed on graphene with a single vacancy. The energy scale is referred to the Fermi level (vertical dashed line).
aggregation into nanoparticles. This issue has to be considered from the point of the thermodynamic tendency of SA to form a metal nanoparticle and the ability of SA to migrate over the support in order to aggregate. Point (i) can be quickly checked by comparing $E_{ads}(M)$ and cohesive energy of the corresponding metal ($E_{coh}(M)$), like in our previous work.[21] Briefly, if the adsorption energy of SA on a given support is negative and its absolute value is larger than the cohesive energy of the corresponding bulk metal phase, SA should be stable on the support. Such a comparison is presented in Figure 4. As can be seen, among the investigated systems, there are only a few of them from the M@VG family where SA adsorption energy is high enough to overcome cohesive energy and prevent the thermodynamic tendency of metal SA to aggregate. This is because the adsorption energies of metal SAs are relatively small on pristine graphene, NDG, and BDG, so cohesive energy is high enough to cause aggregations. Metals SAs that should be stable on VG have very high cohesive energies, like Ir and Ru, but their interaction with single vacancy is so strong that it stabilizes the SAs. This result agrees with a rule of thumb saying that higher cohesive energy of metal results with higher binding energy to the single vacancy site.[21]

However, in connection with the point (ii) above, if metal SA is deposited at a very low concentration and its mobility is low enough, the probability of aggregation of the metal phase will be low. Hence, mobility also must be considered. From the values in Table 1 and the heatmaps of adsorption energy (Figure 5; Figures S5 and S6, Supporting Information), we see that in the case of monovacant graphene, the bonding is on the vacancy site, which presents the anchoring site for all the studied SAs. The presence of a single vacancy influences a large portion of the simulation cell, with SAs relaxing to the vacancy even from the very edges of the supercell. In the case of BDG, the B dopant itself and the nearest bridge and hollow site are the most active. With NDG, we observe that the metal SAs bind preferentially on the graphene lattice, either at the top site closest to the N dopant or at the various distant bridge and hollow sites. Considering the overall trends, a single vacancy unambiguously presents a strong anchoring site for SAs. Following the obtained results, we conclude that all studied SAs require at least 1 eV to overcome the barrier and exit the vacancy site. This barrier cannot be overcome at temperatures close to room temperature, suggesting that, in the case of VG, SAs should be stable.

In the case of BDG, the dopant site (or adjacent carbon atoms) also presents the anchoring site for metal SA. The energy surface for SA diffusion is much smoother compared to the VG case, but still, at least 0.5 eV is required for SAs to migrate away from the anchoring site, which is still appreciable activation energy for room temperature conditions. Hence, if the concentration of SAs is low and comparable to the concentration of B atoms embedded in the graphene lattice, it should be possible to make SACs using BDG as SA support, although there is a strong tendency for SA to aggregate (Figure 4). In the case of NDG, the energy landscape for diffusion is smooth, while SAs avoid tertiary nitrogen sites. In combination with the tendency of SAs to aggregate on NDG, it can be concluded that graphene with substitutional nitrogen is not the right candidate for SAs support. SAs would easily migrate over NDG and form larger aggregates. This result might seem contradictory to a number of reports showing enhanced stability of metal nanoparticles over N-doped carbon supports.[25–27] First, we limit our conclusions to the case of tertiary nitrogen sites. Moreover, from Table 1 one can see that studied metals are indeed more stable on NDG than on pristine graphene. However, this stabilization is not high enough to warrant SA dispersion.

So far, the SAC vacuum interface was analyzed. However, these days SACs find their place in electrocatalysis as well. Hence, it is essential to address SA metals’ tendency to dissolve from the support as well, as electrocatalysis typically uses harsh acidic or alkaline solutions. As a great majority of electrocatalytic reactions occur in aqueous solutions, we address the thermodynamic stability of metal SA concerning the theoretical electrochemical window in water, limited by HER on the cathodic side and oxygen evolution reaction (OER) on the anodic side. The reaction considered is $M^{2+} + \text{support} + ze^- \rightarrow M@\text{support}$. For this purpose, we used the approach as in our previous paper.[21] In brief, the standard electrode potential for the above half-reaction (vs. SHE) is obtained by correcting the standard electrode potential for the half-reaction $M^{2+} + ze^- \rightarrow M_{(s)}$ using the difference between metal SA adsorption energy and the cohesive energy of the corresponding bulk metal. Used standard electrode potentials for the $M^{2+}/M$ couples are also provided in ref. [21]. Note that the data for the Ir$^{2+}$/Ir couple are not available. The results for the cases of Ni, Pd, and Pt SA are presented in Figure 6. Calculated standard electrode potentials for all the $E_{M^{2+}/M_{(s)}@$support} couples (except the Ir case) are provided in Table S2, Supporting Information.

The obtained results suggest that, in general, metal SA supported by pristine graphene, NDG, and BDG are more prone to dissolution than the corresponding clean bulk metals. Even noble metals like Ag and Au dissolve at potentials that do not cover the entire electrochemical window at every pH. However, when metal SAs are embedded in graphene at the vacancy site, they become more stable than bulk metals, except Ag and Au, which interact rather weakly with the single vacancy site in graphene (Table S2, Supporting Information). While Ni and Cu are
stable at high pH, Ru, Rh, Pd, and Pt should never dissolve from the vacancy site. Hence, these metal SA embedded in the vacancy should be stable at both SAC|vacuum interface and SAC|aqueous electrolyte interface (in the pH range 0 to 14). In terms of stability, these four model SACs seem to have everything required for the application in practice—they should be easy to make (aggregation is not preferred), while metal corrosion is suppressed.

2.2. Adsorption Trends for Atoms and Molecules on M@support Model SACs

Proper interactions of a catalyst with reactants and reaction intermediates are crucial for efficient catalysis. Hence, understanding adsorption and reactivity trends could provide valuable insights into the design of new catalytic materials. When it comes to solid metallic surfaces, adsorption and reactivity (and consequently catalytic activity) trends were efficiently linked to the electronic structure. However, the analysis of DOS (Figures 2 and 3; Figures S1–S4, Supporting Information) suggests that the d-states of metal SAs supported on pristine graphene, NDG, and BDG are highly localized, resembling an atomic or molecular system, while in the case of VG metal d-states are wide and metal-like. If the reactivity is linked to the electronic structure, one would expect quite different reactivity of a given metal atom deposited on VG, on one side, and supports other investigated here, on the other side.

We have analyzed atomic adsorption of H, C, N, O, and S, and AH₄ molecules (A = C, N, O, or S; 11 different species with various levels of A saturation by H) at model SACs for all nine metals and four different supports, resulting in the total of 576 different systems. We note that these atoms and molecules are chosen due to their importance in catalysis. H and OHₓ are relevant for the hydrogen and oxygen electrode reactions, N and NHₓ due to synthesis NH₃ and electrochemical reduction of N₂, CHₓ species are intermediates in numerous catalytic and electrocatalytic reactions, while sulfur species are known as catalytic poisons. Considering the potential importance of M@VG systems, demonstrated in Section 2.1, here we report the data obtained for this family of SACs (Table 2), while the data for other considered supports are provided in Tables S7–S9, Supporting Information. Structural parameters, exemplified by Figure S7, Supporting Information, are provided in Tables S3–S6, Supporting Information.

The results show a strong interaction between metal SA on all of the studied supports and the investigated adsorbates that are not fully saturated by hydrogen. It is important to observe that the Eₐ₅(M) on metal SAs do not correlate to the corresponding adsorption energies of the same adsorbates on the bulk metallic surfaces found in the literature. For example, in the group of M@VG, Au SAs are the most reactive towards atomic adsorbates. However, low-index bulk Au surfaces are rather inert, as justified by Hammer and Nørskov. Another important difference between supported SAs and the corresponding bulk metallic surfaces is that there is no general weakening of the interaction between SAs and adsorbates as they get more saturated by hydrogen, but certain trends are definitely visible. As expected, the interactions of model SAs

Figure 5. Heatmaps of Eₐ₅(M) in units of eV on VG. The values in red represent stronger, while the values blue represent a weaker, bonding. Note that the scale is not the same for different systems.
with fully saturated molecular adsorbates (CH$_4$, NH$_3$, OH$_2$, and SH$_2$) are rather weak.

Figure 7 shows the scaling between $E_{\text{ads}}(A)$ and $E_{\text{ads}}(A\text{H}_x)$ for metal SAs at four different supports (except for C vs. CH$_3$). As can be seen from Figures S8–S11, Supporting Information, where scaling relations are shown separately for different supports, the scaling between $E_{\text{ads}}(A)$, on one side and $E_{\text{ads}}(A\text{H})$ or $E_{\text{ads}}(A\text{H}_2)$, on the other side, is quite good, particularly on M@VG. However, for CH$_4$ and fully saturated AH$_x$, the scaling relations are broken. For all the adsorbates, except the broken scaling cases, the statistics say that the correlation exists (at the 0.05 level). We must note that it is not surprising that scaling does not work for the fully saturated AH$_x$, as the bonding to

| M  | H  | A   | AH | AH$_2$ | AH$_3$ | AH$_4$ |
|----|----|-----|----|--------|--------|--------|
| Ni | −2.01 | −3.34 | −3.56 | −3.62 | −1.89 | −0.10 |
| Cu | −2.20 | −3.29 | −3.83 | −3.65 | −2.00 | −0.13 |
| Ru | −2.44 | −3.58 | −3.84 | −3.72 | −2.34 | −0.24 |
| Rh | −2.65 | −3.30 | −3.68 | −3.85 | −2.52 | −0.15 |
| Pd | −2.03 | −3.04 | −3.27 | −3.35 | −1.64 | −0.10 |
| Ag | −2.26 | −2.51 | −3.11 | −3.26 | −1.57 | −0.15 |
| Ir | −3.26 | −3.87 | −4.44 | −4.57 | −3.15 | −0.11 |
| Pt | −2.44 | −3.72 | −4.13 | −4.19 | −2.26 | −0.11 |
| Au | −3.25 | −4.34 | −4.93 | −4.56 | −2.76 | −0.27 |

Table 2. Adsorption energies in eV of H, A (A = C, N, O, and S) on M@VG model SACs.

| M  | H  | O   | S  |
|----|----|-----|----|
| Ni | −2.50 | −3.00 | −2.70 | −0.36 |
| Cu | −2.42 | −2.79 | −2.68 | −0.96 |
| Ru | −2.36 | −2.71 | −2.85 | −1.34 |
| Rh | −2.24 | −2.63 | −3.00 | −0.76 |
| Pd | −1.94 | −2.51 | −2.35 | −0.66 |
| Ag | −1.26 | −1.88 | −2.49 | −0.92 |
| Ir | −2.99 | −3.37 | −3.64 | −0.72 |
| Pt | −2.73 | −3.36 | −2.79 | −0.46 |
| Au | −3.72 | −3.70 | −3.52 | −1.52 |

Figure 6. Stability of Ni, Pd, and Pt in terms of dissolution from the support in the form of Mz$^+$ ions. In all three cases z = 2.
the M sites is essentially different than in the case of atoms and molecular fragment (see Section 2.4). However, considering the importance of scaling relations and the possibility of breaking them,[30] the case of CH$_3$ should be considered further in details. While we look at the overall trends and cannot address it here in detail, we emphasize that the understanding of broken scaling can provide useful strategies for the design of new materials. The theory of Abild-Pedersen et al.[28] obviously cannot be applied here directly, which we consider a consequence of a partial atom- or molecule-like character of metal SAs on studied supports, which can be concluded from presented DOS plots (Figures 2 and 3). However, it is important to mention that, previously, scaling relations for O-containing species relevant for oxygen reduction reaction have not been found on metal SAs embedded in graphene lattice.[31] Nevertheless, new insights on the reactivity of graphene with heteroatoms show that such relations exist and that scaling is actually very good over a wide range of SAs embedded in different graphene-based surfaces.[19,32] The parameters of scaling relations presented in Figure 7 are given in Table S10, Supporting Information. Obviously, the slopes of the scaling relations group are around 0.4 and 0.7. This observation needs further theoretical treatment to provide justification.

Another type of scaling can be checked to confirm a general connection between the electronic structure and the reactivity of metal SAs on different supports. Namely, metal SAs interact relatively weakly with pristine graphene, as well as NDG and BDG (Table 1). As a result, DOSes of SAs on these supports are very similar (Figure 3; Figures S1–S3, Supporting Information). Hence, the similarity of the electronic structure should result in similar reactivity. This is indeed confirmed when adsorption energies on M@pristine graphene are correlated with the adsorption energies on M@NDG and M@BDG (Figure 8, top and middle left). Much stronger interactions of metal SAs with the vacancy site (Table 1) results in a more disrupted electronic structure of SAs, and the correlation between adsorption energies of atomic and molecular adsorbates on M@VG scales is much poorer with the corresponding adsorption energies on M@pristine graphene (Figure 8, bottom left). First, one should look at the integrated local density of states (ILDOS) of Pt and Au SAs at different supports (Figure 8, right; see also Figure S12, Supporting Information, that shows that the integration is done in the energy window where SAs d-states are located). It becomes clear that Au and Pt (and other SAs) on pristine graphene, NDG, and BDG are atom-like as the interaction with the supports relatively weakly disrupts the electronic structure of SAs. However, the d-states of SAs on VG are strongly hybridized with the graphene π system and metal-like, as indicated by Figure 3. Hence, as a rule of thumb, one can say that M@NDG and M@BDG bind studied adsorbates like M@pristine graphene. The dopant in graphene lattice gently modifies metal anchoring on the support.
2.3. Catalysis on Model SACs—The Case of Hydrogen Evolution Reaction (HER)

Provided datasets of adsorption energies of investigated simple adsorbates can be used to analyze different chemical and electrochemical processes on the model SACs. Here we look into more details a relatively simple case of electrocatalytic HER on studied model SACs. Current views suggest that, in a simple model, it is possible to relate the catalytic activity to the energetics of hydrogen adsorption on the catalytically active site, and we follow that approach.\cite{33} Considering that the thermodynamic stability of model SACs was already investigated (Section 2.1) and that only M@VG systems are not prone to the dissolution in highly acidic solutions (except Ag@VG and Au@VG), we focus on this family of SACs. We converted $E_{\text{ads}}(\text{H})$ to the free energy of the formation of adsorbed H ($\Delta G_{\text{ads}}(\text{H})$), which is the intermediate for HER, in order to obtain HER reaction energy profiles on M@VG (Figure 9, left). The reactivity of SAS is altered in comparison to the parental extended metal surfaces. Hence, the trends in HER activity, depicted via the volcano curve (Figure 9, right), are also rather different. For example, Pt, Ir, and Pd take their place close to the apex of HER volcano in the case of the extended metal surfaces. However, in the case of M@VG SACs, only Pt shows high activity. Ir is found at the

![Figure 8. Correlation of atomic and molecular adsorption energies on M@pristine graphene ad M@NDG (top left), M@BDG (middle left), and M@VG (bottom left). On the right, isosurfaces of integrated local densities of states (ILDOS) are presented for selected supported metals SASs. Integration was performed in the energy windows that cover the metal the d-states (see Figures 2 and 3; Figure S11, Supporting Information).]
ascending branch due to the very strong bonding of H_{ads}, while Pd is at the descending branch as it binds H_{ads} weakly. Hence, in the case of Pd (and other metals on the descending branch), the Volmer reaction, that is, the formation of H_{ads}:

\[ M@VG + H^+ + e^- \rightarrow H_{ads} - M@VG \] (1)

is the potential determining step for HER. For the metals at the ascending branch, H_{ads} removal controls HER. In the case of extended metal surfaces, H_{ads} can be removed by either Tafel reaction:

\[ H_{ads} + e^- \rightarrow H_2 \] (2)

or Heyrovsky reaction:

\[ H_{ads} + H^+ + e^- \rightarrow H_2 \] (3)

As the Equation (2) requires two H_{ads} adjacent to each other to recombine, H_{2} formation should go through the Equation (3), irrespective of the position of SAC on the HER volcano. This conclusion holds if a metal SA site binds only one H during HER, which is likely for the metals at the descending branch.

The results indicate that Pt@VG and Ru@VG have the highest HER activities. This result is not exciting as both Pt and Ru are scarce and expensive, but using SACs could still be beneficial due to the lowering of the metal loading in the catalyst. In this sense, M@BDG is more attractive as Cu@BDG should show even better HER activity than Pt@VG and Ru@VG (Figure 9, right), but all the M@BDG dissolve at pH = 0.

One must not forget that practically each metal SA is at the interface with the support. Hence, additional interfacial effects can boost H_{2} production. This particularly relates to H_{ads} spillover, which is beneficial when strong interactions with active metal sites exist. We have previously shown that defects in graphene lattice (and metals’ SAs are, in this sense, defects) usually increase the reactivity of the graphene basal plane in the vicinity of a defect. Hence, H_{ads} could spill to the graphene plane around the defect (C_x):

\[ H_{ads} - M@VG + C_x \rightarrow M@VG + H_{ads} - C_x \] (4)

and H_{2} could form via recombination from the support around the defect:

\[ H_{ads} - C_x + H_{ads} - C_x \rightarrow H_2 \uparrow + C_x + C_x \] (5)

While we do not address this possibility here in details, it is important to note that the H_{ads} spillover could be greatly beneficial for HER as it provided cleaning action for metal SACs. Nevertheless, it should be generally considered as in SACs all the catalytic sites are interfacial ones. Altered reactivity of the support in the vicinity of metal SA changes the energetics of H_{ads} formation. This modulation could render the activity of the support so that Equations (1)–(3) could proceed directly on the support. Here we briefly investigated a few systems of the M@VG family, which are at the apex of the Volcano curve in Figure 9 (right). For the cases of Pt@VG and Ru@VG, the H adsorption energies at the C sites next to the metal SAC are −1.57 eV and −1.63 eV, respectively. Hence, the formation of H_{ads} is energetically unfavorable, and H_{ads} spillover from metal SAC to the support is unlikely to occur. However, in the case of Cu@VG, E_{ads}(H) at the C atom of the vacancy site amounts to −2.52 eV. This value is almost perfect E_{ads}(H) regarding maximizing HER activity. Hence, if HER is also considered at the C atoms of the vacancy, Cu@VG would be the most active catalyst among considered ones. Moreover, H_{ads} formation at the Cu site is followed by −2.20 eV (Table 2), so H_{ads} can transfer from the support to Cu atom in the reverse spillover process analogous to Equations (4) and (5). The thermodynamic barrier for this process is roughly 0.32 eV, which can be overcome at room temperature. As we observed that in the case of Cu@VG, H binds stronger to the C site in the vacancy, we checked the same for all considered metals. Such behavior was also seen for Ag@VG and Au@VG (Table S11, Supporting Information).
Information). Without any doubts, this is ascribed to the weak bonding of Cu, Ag, and Au at the vacancy site (Table 1), so the C atoms are not as saturated as in other cases. In other cases, H$_{ads}$ forms at the metal sites. Finally, in the case of Rh@VG, the H adsorption energy at the C site of the vacancy is $-2.04$ eV. Hence, H$_{ads}$ might migrate from Rh SA to the C sites in the vicinity with a thermodynamic barrier of 0.61 eV. This barrier is relatively large, but it can be overcome at room temperature or higher temperatures. With the results above, the apex of the volcano curve (Figure 9) can be redrawn, as presented in Figure 10. Different possibilities where HER take place in parallel are indicated, like in Ref. [41].

2.4. Additional Computational Aspects

As graphene is generally chemically inert, taking dispersion interactions into account when theoretically treated is very important.$^{[20,42]}$ In this contribution, we used the PBE-D2 approach consistently, which is not of the highest importance when strong chemical bonds are present (M-A and M-AH$_x$ interaction), but it is taken into account because of the graphene-metal interaction (particular cases of pristine graphene, NDG, and BDG). In this sense, the importance of dispersion interactions is visible in Table 1, where $E_{ads}(M)$ are reported. The contributions are up to 0.6 eV, which in some cases presents a large portion of $E_{ads}(M)$. When adsorption of different atomic and molecular species at the active sites of SACs is considered, the effects are also visible and amount up to 0.3 eV (Figure S13, Supporting Information). This value is somewhat smaller than the absolute impact on the $E_{ads}(M)$, but relative contributions of dispersion interactions are extremely high in the case of fully saturated adsorbates (CH$_4$, NH$_3$, OH$_2$, and SH$_2$), which is not surprising. The largest contribution is in the case of CH$_4$ as dispersion interactions are practically the only ones that govern the adsorption this case. NH$_3$, OH$_2$, and SH$_2$ have lone electron pairs and are polar molecules so that the interactions can be electrostatic, or the lone electron pairs can interact directly with the d-states of metal SAs. Considering the results above, we conclude that dispersion should always be considered when graphene or modified graphene surfaces are an integral part of the system under the investigation.

3. Conclusion

We considered nine metals frequently used in catalysis and electrocatalysis (Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au) and their employment in SACs with graphene-based supports. Substitutional doping of pristine graphene with B and N modified slightly modifies metal SAs anchoring to chemically inert graphene basal plane. On the other side, a single vacancy presents the site of very strong bonding. As a result, stable SACs (except in the case of Ag and Au), which are not expected to aggregate or dissolve under harsh electrochemical conditions, can be obtained. Using atomic (hydrogen and A = C, N, O, and S) and molecular adsorbates (AH$_x$, $x = 1, 2, 3, or 4$, depending on A), we screened the reactivity of model SACs, resulting in scaling relations (except in the case of CH$_4$). Moreover, the similarity of the electronic structures of metals SAs on pristine, NDG and BDG results in clear scaling between adsorption energies of atomic and molecular adsorbates on metals SAs supported by these surfaces. These conclusions can be used to rapidly screen considered SACs for different catalytic processes that involve studied atomic and molecular species. Using the obtained data for hydrogen adsorption energetics on metal SAs considered model SACs were analyzed in terms of HER activity. The only promising systems, in this case, are M@VG, and Pt@VG and Ru@VG stand out as the most active SACs for HER. However, if the contribution of the support is also considered, the most active catalyst is Cu@VG.

Figure 10. The apex of the HER volcano, where different reaction pathways are presented. In the case of Rh@VG, HER takes place at the metal site, while Hads spillover on the support is possible. In the case of Cu@VG, active sites for HER are the C sites around the vacancy, while Hads can spill onto the Cu site. For Pt@VG and Ru@VG HER, the active sites for HER are only metal sites. The positions of the SACs are determined based on the $E_{ads}(H)$ at the most stable site.
In real life, nanosized particles are very difficult for theoretical treatment as even very small nanoparticles have a relatively large number of atoms compared to electronic structure calculations’ capabilities. Hence, some simplifications must be taken into account. In this sense, relative simplicity and the sizes of model SACs make them a dream comes true for theoretical analysis. However, additional effects must be considered when analyzing SACs, which are less critical for nanosized catalysts. These are primarily interfacial effects, as every SA is the interfacial atom. Both contributions of the support and altered reactivity of the support are essential to completely understand and explain or predict the catalytic performance of SACs. Moreover, with (modified) graphene as the SA support and molecular adsorbates which lack dangling bonds of lone electron couples that allow strong chemical bonding to SAs, dispersion interactions should be considered when analyzing (re)activity of model systems using DFT.

4. Experimental Section

The adsorption of nine transition metal atoms (Au, Ag, Cu, Ir, Ni, Pd, Pt, Rh, and Ru) was investigated on the (modified) graphene surfaces in a 4 × 4 supercell (32 atoms). Pristine, graphene with a single vacancy (VG), BDG, and NDG were considered (Figure 11a). Doping was performed substitutionally, so the doped structure had the formula of C31X, X being B or N.

Calculations were based on DFT using the generalized gradient approximation in PBE parametrization. The calculations were performed with Quantum ESPRESSO ab initio package (QE), using ultrasoft pseudopotentials. Periodic graphene sheets were separated from each other by 15 Å of vacuum. The kinetic energy cutoff of the plane-wave basis set was 490 eV, and the charge density cutoff was 16 times higher. Spin polarization was included for all the investigated systems. The contribution of the long-range dispersion interactions was investigated using the DFT+D2 scheme by Grimme, as implemented in QE. For certain systems, calculations were also done without the D2 correction. A Monkhorst-Pack Γ-centered 4 × 4 × 1 k-point mesh was used for structural optimization. DOS calculations were done using denser 20 × 20 × 1 k-point mesh.

Three adsorption sites were considered on pristine graphene: T, B, and H (Figure 11b). Upon introducing the vacancy or dopants, the symmetry of the supercell is lowered, resulting in 25 nonequivalent adsorption sites (Figure 10c). These sites were later assigned to every top, bridge, and hollow site within the supercell using simple symmetry operations. Boron and nitrogen were selected for doping since they induced minimal structural change upon substitutional doping, remaining in the graphene basal plane.

The graphene lattice was fully optimized with the given calculation parameters. The C–C bond length and the value of cohesive energy were calculated to be 1.42 Å and −7.84 eV, respectively, similar to previously reported values. Vacancy formation energy was calculated as

$$E_{Vf} = E_{0}^{vac} - \frac{n-1}{n} E_{0}^{G}$$

where $E_{0}^{vac}$ and $E_{0}^{G}$ are the ground state energies of the monovacant and pristine graphene systems, and $n$ is the total number of atoms in the supercell ($n = 32$). The calculated value of 7.76 eV is in good agreement with previous reports.

Doping with B and N was performed substitutionally on the vacancy site, and the dopant binding energy was calculated as:

$$E_{dop} = E_{0}^{y} - E_{0}^{y,x} - E_{0}^{X}$$

where $E_{0}^{y}$ and $E_{0}^{X}$ are the ground state energies of doped graphene and the isolated dopant atom, respectively, with X denoting B or N. Dopant binding energies were calculated to be −13.15 eV for BDG, and −11.74 eV for NDG, in close agreement with previous reports.

Magnetic behavior is observed only in the case of monovacant graphene, the vacancy giving rise to a total magnetic moment of 1.74 μB, somewhat higher than previously observed and close to the value calculated by Rodrigo et al. for a 30 × 30 cell.
Metal ad-atom adsorption was probed at each of the sites mentioned above. During structural optimization, the relaxation of all atoms in the simulation cell was allowed. The adsorption energy of single metal atoms \( E_{\text{ads}(M)} \) was evaluated as:

\[
E_{\text{ads}(M)} = E_{\text{M@G}} - E_{\text{C}} - E_{M}
\]

(8)

where \( E_{\text{M@G}} \), \( E_{C} \) and \( E_{M} \) stand for the total energy of (modified) graphene surface with adsorbed metal \( M \), the total energy of the corresponding clean surface and the total energy of the isolated metal atom, respectively. The adsorption energy of the adatom at the site it finally relaxed at was ascribed to the initial site in which it was placed (e.g., in Figure 12: c, d, f, and y sites all relaxed into the b site; thus, the adsorption energy of the b site was taken for all four initial sites. Based on this approach, heatmaps (Figure 12, right), which show reactivity of the entire \( 4 \times 4 \) supercell, were constructed for each surface and each metal under the study.

Once the preferential adsorption/tethering sites for SAs were determined, we investigated the atomic and molecular adsorption on these model SACs, considering the adsorption on the metal site, which is of primary interest here. The adsorption of \( H, C, N, O, \) and \( S \) was analyzed. Adsorption was quantified using the adsorption energy \( (E_{\text{ads}}(A) \) or \( E_{\text{ads}}(AH_{x}) \)), defined as

\[
E_{\text{ads}}(A) = E_{\text{M@G@A}} - E_{\text{M@G}} - E_{A}
\]

(9)

where \( E_{A} \) stands for the total energy of isolated adsorbate. Following definitions of \( E_{\text{ads}}(M) \) and \( E_{\text{ads}}(A) \), stronger adsorption gives more negative values of adsorption energy.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

catalyst stability, computational screening, graphene-embedded single atoms, scaling relations, single atom catalysts

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