Catalytic activity of the transition-metal-doped MoS$_2$ basal plane under electrochemical conditions

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Abstract

Transition metal dichalcogenides are cheap and earth-abundant candidates for the replacement of precious metals as catalyst materials. The electrocatalytic activity of MoS$_2$ displays rich behavior depending on several system specifics, and fundamental insight on atomic-scale reaction mechanisms is necessary. Here, we investigate the activation of the otherwise inert basal MoS$_2$ plane with respect to hydrogen evolution by transition-metal doping. We present calculations of reaction and activation energy as a function of the electrode potential under electrochemical conditions, i.e. in the presence of a solvent and accounting for the constant electrode potential. The calculations are based on searches for the relevant saddle points on the energy surface obtained from density functional theory calculations corresponding to a given applied voltage. 3d-metals and Pt-doping are found to enhance hydrogen adsorption onto the basal plane by introducing electronic states within the band gap, and in the most prominent cases (Co, Ni, Cu, Pt) doping is associated with local symmetry breaking through stretching of the Mo-S bonds. The hydrogen evolution reaction occurs via the Volmer and Heyrovsky pathways and the associated reaction barriers display considerable voltage-dependence. The various dopants give rise to a wide range in kinetics of the hydrogen evolution reaction. Nickel appears to be the most promising dopant in terms of catalytic activity under moderate negative applied voltage. However, the predicted catalytic activity of the doped basal plane is still lower than what is indicated by experiment, suggesting that other sites are responsible for the experimental activity, most likely edges or defects on the basal plane.
Introduction

Hydrogen is considered as one of the most promising means of future storage of renewable energy from intermittent sources. Gaseous hydrogen can be produced through electrolysis of water in a potentially cheap and sustainable way of converting electrical energy from renewable sources into chemical energy. The efficiency and cost of this process largely depends on the catalyst material. Currently, the process relies heavily on the high activity of platinum-group metals (PGMs), and particularly platinum itself. The restricted availability of these precious metals in Earth’s crust poses a problem for long-term sustainability, which has motivated a large research interest in identifying and developing new catalyst materials, as well as gaining a better understanding of the fundamental mechanisms of the hydrogen evolution reaction (HER) and electrocatalysis in general.

Among the emerging candidates in the search of sustainable replacements, various metal alloys and transition metal compounds have been found. Transition metal dichalcogenides have been shown to exhibit promising properties for HER, and MoS$_2$ has, in particular, been widely investigated both experimentally and theoretically. An important step in characterizing and designing new electrocatalysts is to identify the atomic sites that exhibit high activity. While the edge sites of pristine 2H-MoS$_2$ have been shown to be catalytically active, the basal plane is inert in its pure form. MoS$_2$ has been synthesized in a wide range of morphologies with a focus on increasing the abundance of edge sites. Further, the basal plane can be activated by introducing defects such as S-vacancies, phase boundaries and impurities. As such, the full picture of MoS$_2$ activity is quite complex and a basic understanding of the features in atomic and electronic structure that enhance HER is needed to optimize performance.

Experiments have indicated that transition metal doping enhances the overall activity, but can also have detrimental effects and conflicting results have been reported illustrating that the result depends strongly on system specifics, notably morphology, the nature and level of doping, and the experimental techniques applied. This indicates that the manifested activity relies on the interplay between several factors and theoretical studies could therefore be helpful to identify the various contributing factors.

In the present study, we investigate the effect of transition metal doping on the electrocatalytic activity of the MoS$_2$ basal plane. Theoretical studies have shown that hydrogen adsorption onto the basal plane is enhanced by transition metal doping, and in the following we will assess whether this corresponds to higher activity (reduced reaction barriers) under electrochemical conditions for the whole sequence of 3d-metals as well as platinum. Calculations of electrochemical reactions are more challenging than calculations of gas/surface reactions in that: i) the reaction occurs in the presence of a liquid and ii) the reaction occurs at a fixed electrode potential. These challenges must be overcome to provide a realistic model for electrochemical reactions, as further discussed in the following section.

Methods

Calculations of Activation Energy

All results were obtained from spin-polarized density-functional theory (DFT) calculations within the generalized gradient approximation (GGA). The revised Perdew-Burke-Ernzerhof (rPBE) exchange-correlation functional by Hammer et al. was used because of its improved results for adsorption energy. In addition, van der Waals interactions were accounted for by the zero-damping D3 parameters as this provides an improved description of the interlayer distance of multilayer MoS$_2$. A cutoff of 400 eV was used for the plane wave kinetic energy in the representation of the valence electrons, and the projector augmented wave (PAW) approach was used to represent the effect of inner electrons. For all transition metals, the outermost s- and d-electrons were treated as valence electrons. For O and S, the
2s²2p⁴ and 3s²3p⁴ electrons were treated as valence, respectively. Test calculations including also 3s- and 3p-electrons for the early 3d-metals did not indicate any discrepancy in adsorption energies nor in the local electronic structure at the adsorption sites. The Vienna Ab Initio Simulation Package (VASP) was used in the calculations.  

The geometry optimization of bulk MoS₂ was performed using the primitive unit cell of 2H-MoS₂, with the Brillouin zone sampled by a Monkhorst-Pack (MP) grid of dimension 9 × 9 × 5. For calculations on doped mono- and bilayers we consider 5 × 5 × 1 supercells (75 atoms), with 3 × 3 × 1 MP grids. For accurate density of states (DOS) calculations, 11 × 11 × 1 MP grids were used. A vacuum layer of ca. 14 Å was introduced to decouple the periodic images of the slab.

The activation energy for the various elementary steps in the electrochemical reaction was calculated by first finding an approximate minimum energy path for the transition using the climbing-image nudged elastic band (CI-NEB) method, followed by calculations with a tighter convergence as the saddle point on the energy surface corresponding to a given applied voltage is found using the minimum mode following (MMF) method. The tolerance for convergence in saddle point searches was set at 0.05 eV/Å while the tolerance in minimization calculations was 0.02 eV/Å.

**Reaction Mechanism**

The hydrogen evolution reaction involves the adsorption of H⁺ from solution onto the catalyst surface and subsequent desorption of gaseous H₂. This process can be described in terms of three steps:

1. \( \text{H}^+ + e^- \rightarrow \text{H}^* \)  
2. \( \text{H}^+ + \text{H}^* + e^- \rightarrow \text{H}_2 \)  
3. \( 2\text{H}^* \rightarrow \text{H}_2 \)

where \( \text{H}^* \) indicates hydrogen bound to a surface site. Adsorption occurs through the Volmer (1) mechanism, and desorption through either the Heyrovsky (2) or Tafel (3) mechanisms.

Whether the evolution proceeds through the Tafel or Heyrovsky mechanism (or a combination of both) depends on the kinetics of these in the given system.

The most widely used descriptor for the HER efficiency of a material is the free energy of hydrogen adsorption \( \Delta G_H \) on its surface. In accordance with the Sabatier principle, a value of \( \Delta G_H \approx 0 \) has been shown to correlate with high exchange currents. In the gas phase, we define the \( n \)-th hydrogen adsorption energy as

\[
\Delta E_{n\text{H}} = E_{\text{MoS}_2+n\text{H}} - E_{\text{MoS}_2+(n-1)\text{H}} - \frac{n}{2} E_{\text{H}_2},
\]

Furthermore, the Gibbs free energy is given in terms of this energy as

\[
\Delta G_H = \Delta E_H + \Delta E_{\text{ZPE}} - T \Delta S_H.
\]

We can approximate the entropic term as \( \Delta S_H = S_{\text{H}} - \frac{1}{2} S_{\text{H}_2} \approx -\frac{1}{2} S_{\text{H}_2} \), where we neglect the configurational and vibrational entropy of the adsorbed state. At 298K, the entropy contribution is about 20meV. The zero-point energy \( E_{\text{ZPE}} \) is calculated individually for each system, and compared to the reference value of H₂ (vib. frequency of \( \approx 4400\text{cm}^{-1} \)), so that \( \Delta E_{\text{ZPE}} = E_{\text{H}_2}^{\text{ZPE}} - \frac{1}{2} E_{\text{H}_2}^{\text{ZPE}} \). We assume that the zero-point energy does not vary considerably for different hydrogen coverages.

Under electrochemical conditions, the chemical potential of a H⁺-e⁻ pair in solution is given in terms of the electrode potential \( U(V \text{ vs. SHE}) \) and pH as

\[
\mu_{\text{H}^+} + \mu_{e^-} = \frac{1}{2} \mu_{\text{H}_2} - eU + k_B T \ln a_{\text{H}^+},
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature and \( a_{\text{H}^+} \) is the activity of protons which is related to pH as \( \text{pH} = - \log a_{\text{H}^+} \). Since we consider acidic solutions (pH \( \rightarrow 0 \) corresponding to 1M [H⁺]), the final term is negligible, and the chemical potential is essentially linearly modulated by the electrode potential.
Solvent Model

One of the challenges of modelling electrochemical reactions is to ensure an accurate description of the solvent. Explicit description of the solvent is computationally intensive and the solvent atoms introduce a large number of degrees of freedom which complicates the process of finding energy minima and saddle-point structures. In this work, we employ an implicit solvent model through the implementation in VASPsol, where the solvent (here water) is treated as a polarizable continuum. In this theory, the dielectric permittivity is spatially modulated between the extreme values of 1 (in vacuum) and $\epsilon_b$ (in bulk solvent) by a shape function $\zeta(r)$ as

$$\epsilon_r(r) = 1 + (\epsilon_b - 1)\zeta(r).$$

(7)

The modulation defines regions of solute and solvent, depending on the local electron density $n(r)$ in terms of the complementary error function. The free energy is minimized by equating the variation with respect to both the electron density and the electrostatic potential to zero. The former leads to additional terms in the local potential of the Kohn-Sham equations, as described in detail in Ref. 29. From the latter we obtain the generalized Poisson-Boltzmann equation, which describes the distribution of counter-ions in solution.

The implicit solvent model allows us to largely omit explicit $\text{H}_2\text{O}$ in the calculations, but to model a realistic stability and reactivity of the solvated $\text{H}^+$, some water molecules are still needed. An often used model is the hexagonal ice bilayer. In most systems, however, the periodicity of the system of interest is not commensurate with the typical hexagonal water structure. We therefore employ a cluster model based on the Eigen cation ($\text{H}_9\text{O}_4^+$), where a proton is effectively shared between four water molecules. For such a water model it follows that, since the ion is not externally restricted by hydrogen bonds, we expect to obtain a lower estimate of the activation energy compared to constrained structures such as hexagonal ice.

Test calculations were performed to assess how large the water cluster needs to be. Calculations with Hydronium ($\text{H}_3\text{O}^+$) and Zundel ($\text{H}_5\text{O}_2^+$) ions showed respective discrepancies of at most $\sim 0.24\text{ eV}$ and $\sim 0.04\text{ eV}$ in the (Volmer/Heyrovsky) activation and reaction energies, with respect to the energies obtained with the Eigen cation (see Figure S1). This indicates reasonable convergence with increasing cluster size. We point out that calculations using only a single hydronium ion in the absence of an implicit solvent yield very different results for both the Volmer and Heyrovsky case. The reaction energies were decreased by roughly 1.1eV and 2.7eV, respectively, meaning that a single hydronium ion is far too unstable in the gas phase to provide reliable results. For the Eigen cation, the effect is smaller but still significant; the reaction energies are reduced by roughly 0.3eV and 0.9eV, respectively, in the absence of implicit solvent. Thus the implicit solvent is essential for the description of protonated water in combination with cluster models.

Applied Voltage

A finite simulation cell poses another challenge in determining the energetics of electrochemical reactions, as an electron transfer will lead to a substantial change in the electrostatic surface potential, and therefore to a capacitive contribution to the reaction energy. This contribution is inversely proportional to the lateral cell dimension, and the problem has previously been solved by extrapolating the energies to the limit of infinite lateral cell size. This approach is quite expensive, and when dealing with constant dopant concentrations the cells rapidly become too large. Instead, we use a grand canonical approach where the electron number is allowed to vary to adjust the voltage. Defining the electronic potential as $\mu = \epsilon_F + e\phi_\infty$, where $e$ is the electron charge, $\epsilon_F$ is the Fermi energy and $\phi_\infty$ is the electrostatic potential in the bulk solvent, the potential referred to that of the standard hydrogen electrode (SHE) is $U = \mu/e - \phi_{\text{SHE}}$. For the SHE we use the value $\phi_{\text{SHE}} = 4.43\text{V}$.

Further, we introduce the grand-canonical electronic energy $\Omega$ through the Legendre-transformation of
the free energy $f$ as $\Omega_U = f(n_e) + \delta n_e e U$, where $\delta n_e$ is the number of excess electrons in the cell.

Over a range in applied voltage that is not too large, the number of electrons is varied in increments starting from the neutral value, and the calculated energy of the system is then found to vary in a parabolic way with an extremum corresponding to the potential of zero charge (PZC). The curvature of the parabola represents the negative interfacial capacitance. As illustrated in Figure 1a, reaction and activation energies corresponding to a certain potential can then be obtained from the difference between fitted parabolas. The results shown in Figure 1b coincide well with the alternative (and more computationally expensive, unless only a specific potential value is of interest) approach of converging each reaction geometry to the same potential, though extrapolating the fits outside the potential range of the available data cannot be considered reliable. Most systems display excellent parabolic behavior, but in some cases changing the electron number leads to changes in the geometry or crossing of small electronic gaps. This causes an abrupt change in the Fermi energy, and correspondingly in the potential.

Results

Doped MoS$_2$

The bulk 2H-MoS$_2$ phase consists of alternating layers, bound together by van der Waals forces, as shown in Figure 2. By minimizing the energy with respect to the unit cell volume, we obtain an optimized structure with in-plane lattice parameter $a = 3.18$ Å, interlayer separation $c = 6.20$ Å, and layer height $t = 3.13$ Å. Both the hexagonal lattice parameters are within 1% of the experimental values ($a = 3.15$ Å and $c = 6.15$ Å, respectively). Our calculations show that pristine 2H-MoS$_2$ has band gaps of $\sim 0.9$ eV (indirect) and $\sim 1.6$ eV (direct) in multi- and mono-layer cases, respectively. This qualitatively corresponds to the experimental band structure, though the values are somewhat smaller due to the systematic underes-

Figure 1: Example illustrating the methodology for converging reaction energy to a certain electrode potential, using parabolic fits. a) The neutral (PZC) energy is compared to that at fixed electrode potential $U = U_{\text{PZC}}^{\text{IS}}$. The neutral calculations do not correspond to a specific potential, as it changes over the reaction with a magnitude depending on the size of the simulated system. The reaction is seen to become increasingly exothermic at lower potentials, with corresponding lowering of the required activation energy. For large negative potential, the transition state (TS) converges towards the initial state (IS). b) Comparison of the obtained fits with the data points that are within a certain voltage threshold. The fit accurately reproduces the reaction and activation energy at a given potential. Data from the Heyrovsky reaction on Pt-doped MoS$_2$ with an initial hydrogen coverage of $\theta_0 = 1/3$. 

\[ \Delta \Omega = \begin{array}{c} \text{IS} \\ \text{PZC} \\ \text{TS} \end{array} \]

\[ \Delta U < 15 \text{mV} \]

\[ \Delta U < 60 \text{mV} \]
timation of band gaps in the GGA approach. For comparison, the experimentally measured band gaps of bulk and monolayer 2H-MoS\(_2\) are roughly 1.3 eV and 1.9 eV.\(^{35,36}\)

3d-transition metal atoms are introduced as Mo-substitutional dopants to a 5 × 5 cell of the pristine monolayer, yielding a doping concentration of 4\%. For Co, Cu and Ni, the local symmetry of the pristine geometry is broken, and the dopant atom binds to five surrounding S-atoms. For Sc, Ti, V, Cr, Mn, Fe and Zn, the symmetry is preserved (see Figure 2). In the asymmetric case a sulfur atom has a broken or stretched bond, making it more exposed for adsorption (activated) with respect to the default coordination. We note that for Co, Ni, Cu, Pt, the dopant atom is also shifted down by 0.26 – 0.27\(\AA\) in the direction perpendicular to the plane (not visible in Figure 2). For Zn there is a smaller shift of 0.15\(\AA\). The remaining dopants are within 0.01\(\AA\) of the reference height.

Electronic states within the band gap are introduced as a result of the doping. Figure 3 shows the density of states (DOS) of the various systems near the band gap. Apart from Cr, states are introduced in such a way that the effective band gap is significantly reduced. In the later 3d-transition metals, it appears that higher energy (occupied) S-p states are introduced, consistent with activation. The induced states are mainly localized at the sulfur atoms neighboring the dopant atom, and in the asymmetric cases the dislocated atom contributes the most. DOS and its projections are detailed further for surrounding S in Figure S2.

### Figure 2: Top: Structure of pristine 2H-MoS\(_2\) with optimized lattice parameters. Bottom: Local geometries of MoS\(_2\) doped with 3d-transition metals. Most dopants retain the sixfold symmetry, but notably Co, Ni, and Cu break this symmetry.

### Figure 3: Projected density of states showing gap states emerging in 3d-metal doped MoS\(_2\) monolayers. Gray lines indicate the Fermi level. Pristine MoS\(_2\) in the bottom graph for reference.

### Hydrogen Adsorption

As mentioned above, the hydrogen adsorption free energy is a useful initial descriptor of the hydrogen evolution reaction, and therefore a natural starting point for investigation. We consider first the gas-phase situation, before moving on to solvated systems. Since hydrogen adsorption on the pristine basal plane is highly unfavorable, and due to the localization of the
introduced S-p states, we expect a low surface coverage where only the dopant-induced favorable sites near the dopant atom (and neighboring sulfur atoms) are occupied. Figure 4 shows the adsorption free energy for certain stable sites on Cu-doped MoS$_2$. Only the sites in immediate vicinity of the Cu-atom (A and B) are favorable, and we will focus mainly on these sites in the following.

Figure 4: Adsorption free energy of a single H atom coming from the gas phase and binding at various sites on Cu-doped MoS$_2$. Only neighboring sulfur atoms are notably activated. All sites display more favorable adsorption than the pristine basal plane.

The free energy is obtained from the electronic energy as explained in the previous section. The ZPE correction is calculated for a single H-adsorption for each system. Calculated $E_{ZPE}$ for the dopant systems span a range of only 0.015 eV, and it can be approximated as a constant correction. In a similar manner, we assume that the vibrational frequencies do not change considerably as the coverage increases.

The free energy of adsorption for one to three H atoms in the simulation cell is given in Figure 5a. Consistent with the previous arguments of symmetry and electronic DOS, we observe that only the Co, Ni, Cu and Zn systems show energetically favorable adsorption of a single hydrogen atom, and higher coverages are even less favorable. Adsorption configurations that display moderate change in free energy are of interest for hydrogen evolution. This means that for systems Sc through Fe, only single H adsorption is relevant (note that Cr and Mn anyway have high adsorption energies). For systems Co through Zn, we consider an initial coverage of one or two H per dopant atom. For reference, the first adsorption energy was also calculated for the two-layer case of systems Fe through Zn, with only the top layer doped. Compared to the monolayer case, these values differ by less than 0.02 eV, suggesting that the hydrogen binding onto these dopant-activated sites is not sensitive to the presence of underlying layers. Monolayer calculations are thus appropriate for representing the general slab systems.

Figure 5: a) Incremental free energy of adsorption of multiple H-atoms for the doped and pristine MoS$_2$. b) The promotion energy $E_{pd}$ vs. free energy of adsorption for coverages up to the first unfavorable adsorption for each dopant.

A chemical picture of the adsorption mechanism on MoS$_2$ is that excess charge on the sulfur atom upon adsorption is partially distributed
over the surrounding metal atoms. In this regard, the promotion energy is a useful descriptor for the adsorption energy: \( E_{pd} = E_d - E_p \), where \( E_p \) is the p-orbital center of the S-atom in question, and \( E_d \) is the center of the unoccupied metal d-orbitals integrated from the Fermi level up to the point where one electron is added, i.e. the effective LUMO of the local system. Figure 5b shows the correlation between the first adsorption energy and \( E_{pd} \). We note that the local geometry changes upon hydrogen adsorption, which leads to additional energy contributions and deviations from this descriptor. This is especially visible for the Fe-system, where the local six-fold symmetry is broken upon hydrogen adsorption. The other systems maintain their symmetry, but the distance between the dopant atom and the active sulfur changes. The promotion energy captures two important conditions that are necessary for favorable adsorption energy, namely that the sulfur p-orbital states must be high in energy (activated), and that the surrounding d-orbitals must have unoccupied states not far above the Fermi level. It follows that large band gaps are detrimental towards favorable adsorption in these systems.

Neutral Cell Hydrogen Evolution

Next, the presence of the solvent is taken into account and the various steps of the hydrogen evolution are calculated where the systems are kept under neutral conditions, that is at the potential of zero charge. Afterwards the grand-canonical approach will be used to keep the electrode potential fixed during the reaction. We consider first the Volmer step, where a proton from the water cluster adsorbs on the MoS\(_2\) surface. It follows a simple reaction path, depicted in Figure 6 for the Ni-doped system at an initial coverage of \( \theta = 1/3 \). As also demonstrated in Figure 6, the relation between activation and reaction energies for the Volmer reaction on the doped systems follows the Brønsted-Evans-Polanyi principle, where the activation energy \( E^3 \) is linearly proportional to the reaction energy. The Volmer step is highly unfavorable for all the early 3d-metals, even though Sc, Ti, and V have much lower adsorption energies in the gas phase. For Sc, Ti, V, Cr and Mo, there appears to be either no saddle point (transition state, TS) between the initial (IS) and final state (FS), or the TS is very close to the FS, as obtained with both MMF and CI-NEB searches. Thus, the activation energy tends towards the reaction energy as the reaction becomes more endothermic, and the Volmer reaction is effectively only uphill in energy in these systems. Importantly, the adsorption state is not kept (meta)stable by a reverse barrier and its lifetime is insignificant.

![Figure 6: Top: Reaction mechanism for the Volmer reaction step on Ni-doped MoS\(_2\) at an initial coverage of \( \theta = 1/3 \). Bottom: Calculated activation energy vs. reaction energy for the various dopants and coverages studied here at the potential of zero charge, and comparison with the Brønsted-Evans-Polanyi relation (dashed line).](image-url)

The large difference between the gas phase adsorption energy and the Volmer reaction energy in solution obtained for some of the systems (in particular Sc, Ti, V) shows that the solvent plays an important role in the reaction energetics. That is, the water cluster interacts differently with the surface before and after its proton has been transferred. For example, for systems with favorable hydrogen adsorption, the cluster is weakly bonded to the adsorbed hydrogen through a hydrogen bond. Such a con-
figuration is not stable for the systems with unfavorable hydrogen adsorption, as it would lead to the hydrogen atom re-entering the solution. The cluster is thus further from the surface in a metastable final state, not supporting the attractive interaction. The correspondence with gas phase adsorption becomes clear again if one considers the next step of the reaction. After the Volmer step, the water cluster is again supplied with a proton from the bulk acidic solvent. The difference in energy between this state and the initial Volmer state (correcting for the additional H atom), is what corresponds to the adsorption energy. However, what influences the Volmer barrier is the initial Volmer reaction energy, as is clear from Figure 6 and the linear relation. This illustrates one aspect of the significance of the choice of solvent description.

We note that there is a small energy barrier of roughly 0.15 eV associated with the proton transfer step from the bulk solution.

In the Heyrovsky step, a proton in the water cluster binds to an adsorbed hydrogen atom, and an electron is transferred from the electrode to form an H₂ molecule that is released from the surface. The reaction path is shown in Figure 7. As in the Volmer reaction, the activation energy follows a linear trend with respect to the reaction energy. In this case, the four last 3d-metals, as well as Sc and Ti, are seen to have highly unfavorable Heyrovsky reaction energies at low coverage. For the late 3d-metals this is expected from the Volmer energies, but Sc and Ti appear to have highly unfavorable energies for both reactions. This is related to the previous discussion on the distinction between the initial Volmer reaction and the following proton resupplying step. Once resupplied, Sc and Ti return to lower energies, while V does not. This is consistent with the obtained Heyrovsky energetics.

The Tafel step involves the desorption of two adsorbed H-atoms on the surface. The kinetics of this step therefore depend heavily on the geometries and relative energies of the adsorption sites, as well as the surface H-coverage. This step depends less on the presence of the solvent than the Volmer and Heyrovsky steps. Adsorption of several H atoms will naturally involve occupying the less favorable sites, as well as introducing H-H interactions. From the single-H adsorption energies, we expect that subsequent adsorption will still be confined around the dopant atom, although energetically less favorable due to H-H repulsion. As shown in Figure S3, it is evident that the dopant-induced sites are still preferred despite repulsive H-H interaction. Referring to the labeling of the sites in Figure 7, the optimal reaction path proceeds from a neighboring A-A configuration through the A-B and B-B intermediates. For details on the reaction path and resulting activation energies and scaling relation, we refer to Figures S4 and S5.

Comparison of the activation energies of the Tafel step and the Heyrovsky step at the same hydrogen coverage (θ = 2/3) shows that HER is more likely to occur by a Volmer-Heyrovsky mechanism rather than a Volmer-Tafel mechanism, for all dopants except Zn. In these systems the barrier of the Tafel mechanism is significantly larger than for the Heyrovsky mech-
anism at the same initial coverage, but for Zn, the Heyrovsky and Tafel barriers are comparable, at 1.70 and 1.67 eV, respectively.

**Constant Electrode Potential**

So far, neutral systems at the PZC have been considered. We investigate next the energetics when the reaction occurs at a certain constant potential by varying the number of electrons as explained earlier. Fixation of the electrode potential will lead to a certain correction to the PZC energies as demonstrated in Figure 1a. The preferred reaction mechanism is not expected to change for most systems, but in general it will be a function of the applied potential. The Volmer-Heyrovsky process is expected to become more favorable the more negative the applied potential is, while the Tafel step is only weakly affected. Calculations for Fe through Zn confirm that the Tafel barrier potential dependence in general is weaker for Fe through Zn than that of the electron-transfer processes. For Zn, the applied potential will thus be (slightly) preferred in a range within this voltage window, but otherwise the Volmer-Heyrovsky path is preferred. For all other systems, the Volmer-Heyrovsky path remains more favorable at all potentials. With this in mind, we consider for simplicity the Volmer-Heyrovsky path of all systems in the following comparison.

Around 0 V vs. SHE, the adsorption energies are quite similar to those in the gas phase, and the configurations we noted earlier are still of interest. We therefore consider the initial hydrogen coverages of 0 (Sc, Ti, V, Cr, Mn, Fe, Mo), 1 (Co, Ni, Zn, Pt), and 2 (Cu) per dopant atom in equilibrium. For reference, the initial zero-coverage is also considered for all dopants.

Figure 8a shows the potential dependence of the Volmer and Heyrovsky barriers for each investigated system in the range between 0V and −1V, evaluated at the equilibrium coverage at 0V. Both barriers are lowered by the negative applied potential. Most notably, we observe that the Co- and Ni-doped systems with an initial hydrogen atom display significantly smaller Heyrovsky barriers than the rest of the systems with small Volmer barriers, especially around $U = −0.5V$. Since balanced moderate barriers in general will lead to faster reaction kinetics than one small and one large barrier, these systems seem to have the most active basal planes for HER. Note again that higher hydrogen coverage is favored as the potential decreases, which here would lead to qualitative increase (decrease) in the calculated Volmer (Heyrovsky) barrier. The pristine MoS$_2$ shows a particularly strong dependence on the applied voltage and surprisingly exhibits low barriers at large negative potential ($U = −1V$).

A detailed evaluation of reaction kinetics would require calculations of several other parameters, such as pre-exponential factors. However, using the fact that all the systems studied are comparable, we can estimate the relative kinetics with a simple kinetic model. We characterize the turnover frequency (TOF) $f$ by $f_i \propto p_i e^{-\Omega_{h}^{i}/k_B T}$ where $p_i = Z^{-1} e^{-\Delta\Omega_i/k_B T}$ is the probability of being in the state with $i$ adsorbed hydrogen and $\Omega_{h}^{i}$ is the Heyrovsky barrier. $Z$ is the partition function. At temperature $T = 298 K$, the resulting TOF assumes the characteristic volcanic shape with respect to $\Delta\Omega_i$, as seen in Figure 8b. Points are calculated directly from the energetics for each system, while the solid lines represent the theoretical activity obtained by using the scaling relation between $\Delta\Omega_{h}$ and $\Omega_{h}^{i}$ at the corresponding potential. This correlation is shown in Figure S6, where the same outliers as in Figure 8b are visible, notably Sc, Ti, Cr, Ni at $U = 0V$ and Sc, Ti, Ni at $U = −0.5V$. These outliers lead to the different shapes between the two volcanoes.

We further note that the transition state geometries change slightly as a function of potential. For the Heyrovsky reaction, the distances $r_{H-H}$ (between the two reacting hydrogen atoms), $r_{O-H}$ (between oxygen atom and proton), and $r_{S-H}$ (between sulfur atom and adsorbed hydrogen atom) largely define the reaction coordinate. As the potential is lowered, the magnitude of these values at the transition state tends to respectively increase, de-
Figure 8: a) Activation barriers for the Volmer and Heyrovsky steps at $U = 0V$, $U = -0.5V$ and $U = -1.0V$ for the various dopants. The initial H-adatom coverage is taken to be the equilibrium coverage at $U = 0V$. Dashed bars indicate the values for the case of $\theta = 0$ for systems Co, Ni, Cu, Zn and Pt. Since the first adsorption is favorable in those systems, it is seen to be associated with a small Volmer barrier, and a correspondingly large Heyrovsky barrier. b) Relation between the activity obtained from a simple kinetic model and $\Delta\Omega_H$ for each studied dopant and coverage at $U = 0V$ and $-0.5V$. Dashed lines show fits of the calculated points, while solid lines show the theoretical activity calculated from the relation between the Heyrovsky barrier $\Omega^\prime_H$ and hydrogen adsorption energy $\Delta\Omega_H$. The slope of this relation determines the resulting volcano shape.

In terms of electronic structure, the previously discussed promotion energy $E_{pd}$ captures the overall picture well. $E_{pd}$ is positively correlated with adsorption energy, and relates to the Heyrovsky barrier as seen in Figure 9b. Interestingly, the relation within each individual system does not necessarily follow the overall trend. This illustrates the different contributions to the activation mechanism (chemical adsorption energy as described by $E_{pd}$, and the electrode potential), and is especially visible for the Mn and Fe systems. These systems are hexagonally symmetric at PZC, but the ground state symmetry is spontaneously broken once a certain amount of excess negative charge is introduced. Additional charge further increases the distance between the dopant atom and the activated S, but during this transition the Fermi level (and hence potential) remains nearly constant, as the energies of unoccupied S-$p$ states are lowered simultaneously with introduction of more electrons. In Figure 9b this manifests as a local horizontal trend. For Fe and Mn, the changes in $r_{M-S}$ are roughly $0.20\text{Å}$ and $0.25\text{Å}$, respectively. Comparing with vertical trend systems such as Cu and Pt$_{\theta=1/3}$, we find changes of roughly $0.015\text{Å}$. Within each system, $E_{pd}$ is thus closely related to the distance $r_{M-S}$ and does not seem to otherwise depend strongly on the amount of excess charge, unless it leads to the crossing of small gaps. Large change in $E_{pd}$ due to gap crossing without significant geometrical change can be seen in Figure 9b for systems Sc and Ti. In systems with small change in the promotion energy, the potential is the main contribution to barrier decrease.
Discussion

In all cases, single-atom doping results in a lowering of the PZC hydrogen adsorption energy. For the later 3d-metals, the doping results in breaking the local hexagonal symmetry, which leads to relatively larger affinity of the sulfur atom to hydrogen adsorption. This further leads to a wide range of HER-behavior for the different dopants, from Volmer-limited to Heyrovsky-limited and even Tafel-limited in the case of Zn at moderate applied potential. Within the setting of the basal plane, particularly Co and Ni stand out with a good balance of the two barriers at moderate applied potential, though according to the kinetic model Ni is clearly more active at $-0.5$ V. At that point the Ni-doped system exhibits barriers of 0.47 and 0.76 eV. In comparison, the Volmer and Tafel barriers on Pt$_{111}$ have with similar methodology been found to be 0.66 and 0.55 eV, respectively, at 0 V and a full monolayer H-coverage.$^{31}$ Therefore, the performance of the doped basal plane will be (at best) comparable to monocrystalline Pt$_{111}$ at a 0.5 eV more negative applied potential. However, experiments often display comparable exchange currents at significantly lower potential offsets, see e.g. Ref. 12. This coincides with the consensus that the pristine basal plane is not the main origin of MoS$_2$ activity, and edges and defects must be considered. When sites on certain facets are more active than others, the experimentally observed activity will depend largely on the morphology of prepared samples. Also the orientation of MoS$_2$ crystals with respect to the electrode substrate is important, as there is considerable resistance associated with electron transport between layers.$^{38}$

In the work by Humphrey et al.$^{17}$ planar support is thought to have produced relatively low edge-content MoS$_2$ for the pristine case and with low levels of Co-doping. As noted there, the larger overpotential compared to other studies suggests that this activity is more representative of the basal plane. This inherent activity of the basal plane cannot be explained without introducing defects, as the pristine adsorption sites are much too unfavor-

Figure 9: a) Correlation of the distances $r_{O-H}$ and $r_{H-H}$ at the transition state, and the Heyrovsky activation energy $\Omega^\dagger_\text{h}$ for all dopants at various values of potential and hydrogen coverage. b) Correlation of the promotion energy $E_{pd}$ before hydrogen adsorption and $\Omega^\dagger_\text{h}$ at the corresponding potential and hydrogen coverage. The promotion energy captures the main trend of $\Omega^\dagger$. Some particular features are exemplified by the Fe-system (horizontal), Pt-system (vertical), and Ti-system (gap crossing).
able for evolution to occur. Most synthesized MoS$_2$ does however contain a significant number of sulfur vacancies, with certain deposition methods yielding stoichiometries of MoS$_{1.6}^{39}$ and MoS$_{1.8}^{15}$, although this total deficiency will also depend in part on the stoichiometry and prevalence of the edge terminations. These vacancies create local sites with adsorption energies of roughly 0.1 eV. However, neighboring sites are not significantly activated and (assuming evenly dispersed S-vacancies) the reaction would still be limited to a Volmer-Heyrovsky mechanism. More complex defect configurations could possibly facilitate the Tafel mechanism.

For reference, the Tafel slope of the basal plane of pristine MoS$_2$ under acidic conditions has been measured to be around 120mV dec$^{-1}$, indicative (but not conclusive) of a mechanism rate-determined by the Volmer step, from which neither the Tafel nor Heyrovsky path can be disregarded. Importantly, the aforementioned study finds that low levels of Co-doping is detrimental to the inherent activity, in contradiction to the results of the present study in which only stoichiometric MoS$_2$ is considered. This indicates that the combination of atomic doping and intrinsic defects can lead to overall deactivation of the basal plane. In Ref. 17 this is supported by the calculated adsorption energies and equilibrium defect configurations, and it would be interesting to study this problem in terms of activation barriers and possible reaction paths of the Co- and Ni-doped defect systems.

We summarize that a direct comparison of our results with experiment is not possible without also considering MoS$_2$ edge sites and defects in the basal plane, as well as other possible doping configurations and interplay with inherent sulfur vacancies. A systematic investigation of activation barriers and coverage dependence across these systems is needed for drawing solid conclusions.

The overall trend of relative activity is clear in Figure 8b, the optimum lies in the vicinity of $\Delta \Omega_H \approx 0$ eV, though we note that the peaks of the directly fitted volcanoes are in this case centered at 0.3eV. The discrepancy between the solid line and the points illustrates the expected inaccuracies associated with $\Delta G_H$ as a descriptor, as the relation to the activation energy is only implicit. Overall the description works well, but comparing individual systems in terms of only $\Delta G_H$ will be prone to errors. On a larger scale, it is important to note that the condition $\Delta G_H \approx 0$ eV is not sufficient to guarantee high absolute HER activity, but is merely a necessary condition to be near the optimum for a given class of systems. By itself, it should not be trusted without reservations to assume that a system is comparable with other classes of systems without considering possible evolution mechanisms and their activation energies. As an example, we see from this study that the Heyrovsky mechanism on local impurity-induced S-sites in MoS$_2$ behaves markedly differently from e.g. the Tafel mechanism on uniformly covered Pt$_{111}$, even if the H adsorption energy is near zero in both cases.

**Conclusions**

Methodology for computing reaction and activation energies under electrochemical conditions corresponding to a specified applied voltage was used to investigate the HER mechanism on the basal plane of 2H-MoS$_2$ with single-atom 3d-metal doping. The effect of the aqueous solvent is included by using a cluster of a few H$_2$O molecules in the neighborhood of the active site and then a polarizable continuum solvent for the rest of the solvent phase. The effect of the various transition-metal dopants spans a wide range and within this scope Ni stands out with the best overall activity at moderate negative applied potential. The reaction barriers can be correlated with the potential-dependent promotion energy $E_{pd}$, and the modelled kinetics has the characteristic volcano-shape with respect to the hydrogen adsorption energy. The results were compared with the commonly used $\Delta G_H \approx 0$ eV model.

The calculations used a single monolayer of 2H-MoS$_2$, but the results are expected to be representative for multi-layer slabs as the adsorption energies are found to be similar. The
reaction was found to proceed predominantly through a Volmer-Heyrovsky path, where the dopant-activated sulfur sites provided a large reduction in the adsorption energy, and therefore also in the activation energy of the Volmer step, which on pristine MoS$_2$ is so unfavorable that it essentially does not occur. The inherent activity of MoS$_2$ observed in experiments must therefore come from defect sites (e.g. sulfur vacancies on the basal plane) or from edge sites. These sites are expected to be more active than the pristine basal plane, and a full picture of the various possible sites is necessary for more in-depth comparison with experimental data. Such an investigation is planned for future work.

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Supporting Information Available

The supporting information contains further details on reaction and activation energy dependence on water cluster size in the Volmer and Heyrovsky reactions, the local nature of induced gap states, the Tafel mechanism and scaling relation between the grand-canonical adsorption energy and Heyrovsky barrier.

References

(1) Dawood, F.; Anda, M.; Shafiullah, G. Hydrogen production for energy: An overview. *International Journal of Hydrogen Energy* 2020, 45, 3847–3869.

(2) Holladay, J.; Hu, J.; King, D.; Wang, Y. An overview of hydrogen production technolo-gies. *Catalysis Today* 2009, 139, 244–260, Hydrogen Production - Selected papers from the Hydrogen Production Symposium at the American Chemical Society 234th National Meeting & Exposition, August 19-23, 2007, Boston, MA, USA.

(3) Faber, M. S.; Jin, S. Earth-abundant inorganic electrocatalysts and their nanostructures for energy conversion applications. *Energy Environ. Sci.* 2014, 7, 3519–3542.

(4) Hinnemann, B.; Moses, P. G.; Bonde, J.; Jørgensen, K. P.; Nielsen, J. H.; Horch, S.; Chorkendorff, I.; Nørskov, J. K. Biomimetic Hydrogen Evolution: MoS2 Nanoparticles as Catalyst for Hydrogen Evolution. *Journal of the American Chemical Society* 2005, 127, 5308–5309, PMID: 15826154.

(5) Bonde, J.; Moses, P. G.; Jaramillo, T. F.; Nørskov, J. K.; Chorkendorff, I. Hydrogen evolution on nano-particulate transition metal sulfides. *Faraday Discuss.* 2009, 140, 219–231.

(6) Benck, J. D.; Chen, Z.; Kuritzky, L. Y.; Forman, A. J.; Jaramillo, T. F. Amorphous Molybdenum Sulfide Catalysts for Electrochemical Hydrogen Production: Insights into the Origin of their Catalytic Activity. *ACS Catalysis* 2012, 2, 1916–1923.

(7) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. Engineering the surface structure of MoS2 to preferentially expose active edge sites for electrocatalysis. *Nature Materials* 2012, 11, 963–969.

(8) Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. Identification of Active Edge Sites for Electrochemical H2 Evolution from MoS2 Nanocatalysts. *Science* 2007, 317, 100–102.

(9) Kong, D.; Wang, H.; Cha, J. J.; Pasta, M.; Koski, K. J.; Yao, J.; Cui, Y. Synthesis of MoS2 and MoSe2 Films with Vertically
Aligned Layers. *Nano Letters* **2013**, *13*, 1341–1347, PMID: 23387444.

(10) Li, H.; Tsai, C.; Koh, A. L.; Cai, L.; Contryman, A. W.; Fragapane, A. H.; Zhao, J.; Han, H. S.; Manoharan, H. C.; Abild-Pedersen, F. et al. Activating and optimizing MoS2 basal planes for hydrogen evolution through the formation of strained sulphur vacancies. *Nature Materials* **2016**, *15*, 48–53.

(11) Zhang, T.; Zhu, H.; Guo, C.; Cao, S.; Wu, C.-M. L.; Wang, Z.; Lu, X. Theoretical investigation on the hydrogen evolution reaction mechanism at MoS2 heterostructures: the essential role of the 1T/2H phase interface. *Catal. Sci. Technol.* **2020**, *10*, 458–465.

(12) Deng, J.; Li, H.; Xiao, J.; Tu, Y.; Deng, D.; Yang, H.; Tian, H.; Li, J.; Ren, P.; Bao, X. Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS2 surface via single-atom metal doping. *Energy Environ. Sci.* **2015**, *8*, 1594–1601.

(13) Wang, H.; Tsai, C.; Kong, D.; Chan, K.; Abild-Pedersen, F.; Nørskov, J. K.; Cui, Y. Transition-metal doped edge sites in vertically aligned MoS2 catalysts for enhanced hydrogen evolution. *Nano Research* **2015**, *8*, 566–575.

(14) Merki, D.; Vrubel, H.; Rovelli, L.; Fierro, S.; Hu, X. Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution. *Chem. Sci.* **2012**, *3*, 2515–2525.

(15) Escalera-López, D.; Niu, Y.; Yin, J.; Cooke, K.; Rees, N. V.; Palmer, R. E. Enhancement of the Hydrogen Evolution Reaction from Ni-MoS2 Hybrid Nanoclusters. *ACS Catalysis* **2016**, *6*, 6008–6017, PMID: 27818842.

(16) Lau, T. H. M.; Lu, X.; Kulhavý, J.; Wu, S.; Lu, L.; Wu, T.-S.; Kato, R.; Foord, J. S.; Soo, Y.-L.; Suenaga, K.; et al. Transition metal atom doping of the basal plane of MoS2 monolayer nanosheets for electrochemical hydrogen evolution. *Chem. Sci.* **2018**, *9*, 4769–4776.

(17) Humphrey, J. J. L.; Kronberg, R.; Cai, R.; Laasonen, K.; Palmer, R. E.; Wain, A. J. Active site manipulation in MoS2 cluster electrocatalysts by transition metal doping. *Nanoscale* **2020**, *12*, 4459–4472.

(18) Hakala, M.; Kronberg, R.; Laasonen, K. Hydrogen adsorption on doped MoS2 nanostructures. *Scientific Reports* **2017**, *7*, 15243.

(19) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* **1999**, *59*, 7413–7421.

(20) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* **2010**, *132*, 154104.

(21) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(22) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(23) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **2000**, *113*, 9901–9904.

(24) Henkelman, G.; Jónsson, H. A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. *The Journal of Chemical Physics* **1999**, *111*, 7010–7022.
(25) Trasatti, S. Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 1972, 39, 163–184.

(26) Nørskov, J. K.; Bligaard, T.; Logadottir, A.; Kitchin, J. R.; Chen, J. G.; Pandelov, S.; Stimming, U. Trends in the Exchange Current for Hydrogen Evolution. *Journal of The Electrochemical Society* 2005, 152, J23.

(27) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *The Journal of Physical Chemistry B* 2004, 108, 17886–17892.

(28) Mathew, K.; Sundararaman, R.; Letchworth-Weaver, K.; Arias, T. A.; Hennig, R. G. Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. *The Journal of Chemical Physics* 2014, 140, 084106.

(29) Mathew, K.; Kolluru, V. S. C.; Mula, S.; Steinmann, S. N.; Hennig, R. G. Implicit self-consistent electrolyte model in plane-wave density-functional theory. *The Journal of Chemical Physics* 2019, 151, 234101.

(30) Rossmeisl, J.; Skúlason, E.; Björketun, M. E.; Tripkovic, V.; Nørskov, J. K. Modeling the electrified solid–liquid interface. *Chemical Physics Letters* 2008, 466, 68–71.

(31) Van den Bossche, M.; Skúlason, E.; Rose-Petruck, C.; Jónsson, H. Assessment of Constant-Potential Implicit Solvation Calculations of Electrochemical Energy Barriers for H2 Evolution on Pt. *The Journal of Physical Chemistry C* 2019, 123, 4116–4124.

(32) The absolute electrode potential: an explanatory note (Recommendations 1986). *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 1986, 209, 417–428.

(33) Santos, E.; Schmickler, W. Changes in the surface energy during the reconstruction of Au(100) and Au(111) electrodes. *Chemical Physics Letters* 2004, 400, 26–29.

(34) Wakabayashi, N.; Smith, H. G.; Nicklow, R. M. Lattice dynamics of hexagonal MoS2 studied by neutron scattering. *Phys. Rev. B* 1975, 12, 659–663.

(35) Böker, T.; Severin, R.; Müller, A.; Janowitz, C.; Manzke, R.; Voß, D.; Krüger, P.; Mazur, A.; Pollmann, J. Band structure of MoS2, MoSe2, and α–MoTe2: Angle-resolved photoelectron spectroscopy and ab initio calculations. *Phys. Rev. B* 2001, 64, 235305.

(36) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS2: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* 2010, 105, 136805.

(37) Liu, M.; Hybertsen, M. S.; Wu, Q. A Physical Model for Understanding the Activation of MoS2 Basal-Plane Sulfur Atoms for the Hydrogen Evolution Reaction. *Angewandte Chemie International Edition* 2020, 59, 14835–14841.

(38) Yu, Y.; Huang, S.-Y.; Li, Y.; Steinmann, S. N.; Yang, W.; Cao, L. Layer-Dependent Electrocatalysis of MoS2 for Hydrogen Evolution. *Nano Letters* 2014, 14, 553–558, PMID: 24397410.

(39) Cuddy, M. J.; Arkill, K. P.; Wang, Z. W.; Komsa, H.-P.; Krasheninnikov, A. V.; Palmer, R. E. Fabrication and atomic structure of size-selected, layered MoS2 clusters for catalysis. *Nanoscale* 2014, 6, 12463–12469.

(40) Bentley, C. L.; Kang, M.; Maddar, F. M.; Li, F.; Walker, M.; Zhang, J.; Unwin, P. R. Electrochemical maps and movies of the hydrogen evolution reaction on natural crystals of molybdenite (MoS2): basal vs.
edge plane activity. *Chem. Sci.* **2017**, *8*, 6583–6593.
