Understanding the effect of mechanical strains on the catalytic activity of transition metals

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Abstract

The effect of elastic strains on the catalytic activity for the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR) was analyzed on thirteen late transition metals: eight (111) surfaces of fcc metals (Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir) and five (0001) surfaces of hcp metals (Co, Zn, Cd, Ru, and Os). The corresponding adsorption energies for the different intermediate reactions up to strains dictated by the mechanical stability limits were previously obtained by means of density functional theory calculations. It was found that the elastic strains can be used to tune the catalytic activity of different metals by reducing the energy barrier of the rate limiting step and even to reach the cusp of the volcano plot. The largest changes in catalytic activity with strain for the HER were found in Pt, Au, and Ir while Co and Ni were very insensitive to this strategy. In the case of the ORR, the catalytic activity of Au could be enhanced by the application of tensile strains while that of Cu, Ni, Pt, Pd, Rh, Co, Ru, and Os was improved by the application of compressive strains. However, the catalytic activity of Ir was rather insensitive to mechanical deformations. Elastic strains were able to modify the rate limiting reaction in Au, Pt, Ag, and Os and it was possible to achieve the cusp of the volcano plot in these metals. Final, mechanical instabilities were attained at small strains in Zn and Cd, which did not lead to significant changes in the catalytic activity for HER and ORR. These results

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Preprint submitted to Physical Chemistry Chemical Physics, accepted for publication February 4, 2022
provide a framework to systematically investigate the application of elastic strains in the design of new catalysts.

Keywords: Catalysis, Elastic strain engineering, Materials engineering, DFT, HER, ORR.

1. Introduction

The hydrogen economy, which stands as one of the most promising pillars of the future of clean energy, strongly depends on two key reactions for the production of hydrogen and the generation of green energy: the hydrogen evolution reaction (HER) – whose global process in acidic media is \( H^+ + e^- \rightarrow 0.5H_2 \), and the oxygen reduction reaction (ORR) – whose global process in acidic media is \( O_2 + 4(H^+ + e^-) \rightarrow 2H_2O \) [1, 2]. Without an appropriate catalyst, these processes take place at high temperatures and pressures, which hinders the widespread use of hydrogen in industrial applications. So far, the role model catalyst for the HER and the ORR is platinum, but its high cost and limited availability drives the research to look for more effective and less expensive electrocatalysts [2, 3]. Traditionally, three different strategies have been used to search new materials that fulfill these criteria: the introduction of surface defects [4, 5, 6, 7, 8], the exploration of different facets [9, 10], and alloying [11, 12, 13, 14, 15, 16, 17, 18].

As an alternative, the application of elastic strains to modify the catalytic properties of materials has been comparatively less explored but there is recent evidence of promising results in metals [19, 20, 21, 22, 23, 24, 25, 26, 27] and other materials [28, 29]. Indeed, mechanical strains may have large effects on different physical and chemical properties through the modification of the electronic structure. It has been shown that elastic strains can minimize defect formation in halide perovskites [30, 31], prevent non-radiative recombination [32], and even increase device efficiency [33]. The application of elastic strain can also enhance corrosion [34] and oxidation processes [35]. On transition metals, numerous studies show that mechanical strain can produce important changes in their reactivity [36, 37, 38, 39, 40, 41].

The adsorption energy of the reactants constitutes one of the best descriptors in many catalytic processes and the effect of mechanical strains in the adsorption energy of different metals has been analyzed in various publications [19, 20, 21, 22], including our recent study of the effects of elastic
strain on the adsorption of H, O, and OH onto the surfaces of 11 transition metals [42]. However, the influence of each reaction intermediate should be taken into account to assess the catalytic activity in processes in which many steps are involved, such as the ORR, and this analysis is missing for the catalytic activity of transition metals for the HER and the ORR. For instance, it is known that the application of tensile (compressive) strains can decrease (increase) the adsorption energy of H, O, and OH on transition metal surfaces [42, 43] but the influence of these changes on the catalytic activity has not been explored systematically for the HER and ORR.

Within this context, the present article analyzes the effect of mechanical strains onto the catalytic properties of 8 fcc (Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir) and 5 hcp (Co, Zn, Cd, Ru, Os) transition metals for the HER and the ORR. It was found that elastic strains modify the catalytic activity for all the studied metals: compressive strains were found to favor the catalytic properties of Pt, Pd, Rh, Ni, Ir, Co, Ru, and Os in the HER and Pt, Pd, Cd, Ir, Zn, Rh, Cu, Ni, Co, Ru, and Os in the ORR, while tensile strains improved the catalytic properties of Cu, Au, and Ag in the HER, and Au and Ag in the ORR. Nevertheless, metals presented different sensitivity to the effect of elastic strains on the catalytic activity, which depended on the rate limiting step. It was found that the optimum strain to attain the maximum catalytic activity was determined by either the maximum strain that can be achieved before reaching the mechanical stability limit or when the rate limiting step changes from one reaction to another. Thus, the results on this paper rationalize the mechanisms that determine the influence of mechanical strains on the catalytic activity of transition metals and provide a framework to explore their effect on other materials.

2. Methodology

The variation of the adsorption energy with strain can be used to modulate the activity of a catalyst following Sabatier’s principle [44]. It states that the adsorption energy should be neither too high nor too low for reactions passing through an adsorbed intermediate. If the energy is too high (endothermic), adsorption is slow and limits the overall rate, whereas the catalyst surface becomes poisoned and desorption is limited if the adsorption energy is too low (exothermic). In terms of hydrogen and oxygen electrocatalysis, this principle leads to the conclusion that the free energy of adsorption
should be close to zero at the equilibrium potential \[45, 46\]. If Sabatier’s principle is the only factor that governs the catalytic process, the plot of the reaction rate versus the energy of adsorption of the intermediate species leads to a volcano-shaped curve \[47, 48\]. Starting from a low, negative (exergonic) free energy of adsorption, \(G_{\text{ads}}\), the catalytic activity initially rises with \(G_{\text{ads}}\), leading to the ascending branch of the volcano. The rate passes through a maximum around \(G_{\text{ads}} = 0\), and then starts to decrease as \(G_{\text{ads}}\) becomes more endergonic in the descending branch of the volcano. The magnitude of \(E_{\text{ads}}\) – obtained from DFT calculations – can be used to determine the overall rate of the reaction according to

\[
G_{\text{ads}} = E_{\text{ads}} + E_{\text{ZPE}} - T\Delta S
\]

where \(G_{\text{ads}}\), \(E_{\text{ads}}\), \(E_{\text{ZPE}}\), and \(\Delta S\) stand for the variation of the free and adsorption energies, the zero point energy and the entropy, respectively, during the adsorption of the intermediate species, and \(T\) is the absolute temperature. This relationship should be evaluated for each intermediate species that appears in the catalytic process (only H in the HER reaction and O and OH in the ORR), taking into account that the process with the highest free energy barrier will limit the rate of the reaction.

The metal surfaces of the thirteen metals were subjected to normal and shear stresses in the surface plane and the adsorption energies were calculated in the most favorable adsorption site (FCC for fcc (111) metals and HCP for hcp (0001) metals). Mixed boundary conditions are imposed to solve the elastic problem in the DFT calculations. They include imposed strains in the slab plane and zero stresses on the free surface. The deformation gradient \(\mathbf{F}\) applied to the supercell was

\[
\mathbf{F} = \begin{pmatrix}
1 + \epsilon_1 & \gamma & 0 \\
0 & 1 + \epsilon_2 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

where \(\epsilon_1\) and \(\epsilon_2\) stands for the normal strains along \(x\) and \(y\) directions while and \(\gamma\) for the shear distortion in the \(xy\) plane. Uniaxial deformation was applied when \(\epsilon = \epsilon_1\) and \(\epsilon_2 = \gamma = 0\), while \(\epsilon = \epsilon_1 = \epsilon_2\) and \(\gamma = 0\) for biaxial deformation.
2.1. Hydrogen Evolution Reaction

The HER is the cathodic reaction in the process of water splitting and plays a key role in the production of hydrogen by dissociation of the water molecule. It is a classic example of a reaction with transfer of two electrons through the Volmer-Heyrovsky or Volmer-Tafel mechanisms [49]. The kinetics of the reaction is limited by the adsorption of hydrogen on the surface for acidic solutions. The adsorption process (Volmer) limits the kinetics if hydrogen binds weakly on the catalyst surface, while desorption (Heyrovsky/Tafel) is the limiting process otherwise. Thus, the adsorption energy of hydrogen can be used to determine the optimum catalyst for the HER reaction. The global process in acidic media can be represented as

\[ \text{H}^+ + e^- \longrightarrow \frac{1}{2} \text{H}_2 \]

but the mechanism involves first the electrochemical hydrogen adsorption (Volmer reaction) followed by the electrochemical (Heyrovsky reaction) and/or chemical (Tafel reaction) hydrogen desorption reactions

\[ \text{H}^+ + \ast + e^- \longrightarrow \text{H}^* \]

\[ \text{H}^* + \text{H}^+ + e^- \longrightarrow \ast + \text{H}_2 \]

\[ 2 \text{H}^* \longrightarrow 2 \ast + \text{H}_2 \]

where \( \ast \) represents a site on the surface of the catalyst and \( \text{H}^* \) the hydrogen atom adsorbed. A more detailed diagram of the different steps is shown in Figure 1(a) of the supporting information. The reaction path for the HER is shown in Figure 1(a) and equation (1) can used to compute the free energy associated with the adsorption process, \( G_{\text{ads}} \), including the differences in zero-point energies between products and reactants, \( \Delta E_{\text{ZPE}} \). These zero-point energies were calculated for the adsorption of \( \text{H} \) on Cu(111) and on Pt(111) and their values were 0.04 eV in both cases, in agreement with the one previously reported in the literature for the adsorption of \( \text{H} \) on Cu(111) [48]. Details about these calculations can be found in section two of the supporting information. The same value of \( \Delta E_{\text{ZPE}} \) was used for all the metals studied below.
Figure 1: (a) Reaction path for the HER. (b) Reaction path for the ORR (dissociative mechanism). The free energies have been calculated for \{111\} Pt adsorbed at FCC positions without applied strain.

The vibrational entropy is determined by the contribution of \(0.5\text{H}_2\)

\[
\Delta S = -\frac{1}{2} S^0_{\text{H}_2}
\]

where \(S^0_{\text{H}_2} = 130.68 \text{ J/mol*K}\) \cite{50} is the entropy of \(\text{H}_2\) in the gas phase at standard conditions (300K and 1 bar).

Thus, \(G_{\text{ads}}\) at \(T = 300\text{ K}\) can be expressed as
\[ G_{\text{adsH}} = E_{\text{adsH}} + 0.24 \, eV \]  \quad (4)

\( G_{\text{adsH}} \) depends only on the energy of adsorption of hydrogen according to equation (4) and the catalytic activity of the HER can be measured by the exchange current density, \( i_0 \). This parameter describes the electron transfer between the electrode (which in our case would be the catalyst) and the solution and can be calculated following the strategy developed by Norskov et al. \[48\]. If \( G_{\text{adsH}} < 0 \), the proton transfer is an exothermic process and the exchange current density can be expressed as

\[
i_0 = -e k_0 \frac{1}{1 + \exp(-G_{\text{adsH}}/kT)} \quad (5)\]

where \( e \) is the electron charge and \( k_0 = 200 \, s^{-1} \text{ site}^{-1} \) \[47\] is a constant independent of the metal that includes all the effects related to the reorganization of the solvent during the transfer of protons to the surface. \( kT \) stand for the Boltzmann constant and the absolute temperature, respectively. On the contrary, if \( G_{\text{adsH}} > 0 \), the proton transfer is endothermic, and the exchange current density is given by

\[
i_0 = -e k_0 \frac{1}{1 + \exp(-G_{\text{adsH}}/kT)} \exp(-G_{\text{adsH}}/kT) \quad (6)\]

2.2. Oxygen Reduction Reaction

The ORR is the critical reaction for the generation of energy from hydrogen in a fuel cell. Currently, the kinetics of the ORR is limited by the low rate of the reduction reaction of oxygen in acidic media at the cathode

\[ \text{O}_2 + 4 (\text{H}^+ + \text{e}^-) \rightarrow 2 \text{H}_2\text{O} \]

and it has to be enhanced by means of Pt-based catalysts. The high cost and low availability of Pt hinders the widespread application of proton exchange membrane fuel cells (PEMFC) in the transportation sector. The ORR in a
PEMFC is carried out through the transfer of 4e- through either an associative or dissociative pathway [51]. The catalytic activity is limited by the electron-proton transfer to O* or to OH* if oxygen is strongly adsorbed on the surface. Otherwise, the catalytic activity is controlled by the electron-proton transfer to O* or by the fracture of the O-O bond, depending on the applied potential [51]. The energies associated with these processes are controlled by the electronic structure of the catalyst and can be modified by the application of elastic strains [42].

Two different mechanisms, dissociative or associative, can be used to describe the ORR. The molecule of O2 dissociates before it is hydrogenated in the former, whereas hydrogenation happens previously to the dissociation in the latter. A more elaborate diagram of both mechanisms is shown in Figure 1(b) of the supporting information. The steps of both mechanisms are show below

Dissociative mechanism:

\[
\frac{1}{2}O_2 + * \rightarrow O^*
\]

\[
O^* + H^+ + e^- \rightarrow HO^*
\]

\[
HO^* + H^+ + e^- \rightarrow H_2O + *
\]

Associative mechanism:

\[
O_2 + * \rightarrow O_2^*
\]

\[
O_2^* + H^+ + e^- \rightarrow HO_2^*
\]

\[
HO_2^* + H^+ + e^- \rightarrow H_2O + O^*
\]

\[
O^* + H^+ + e^- \rightarrow HO^*
\]

\[
HO^* + H^+ + e^- \rightarrow H_2O + *
\]
Although each mechanism presents different reactions, the reaction rate is independent of the mechanism and this analysis will be based on the dissociative mechanism, which is simpler. Two different adsorbed species have to be considered in this case, O* and HO* (notice the difference with the HER, where the only intermediate adsorbate is H*). The reaction path for the dissociative mechanism in depicted in Figure 1(b). Three different free energies, $G_0$, $G_1$, and $G_2$, that correspond to the three steps of the dissociative mechanism shown above, are involved in the process. As detailed in the supporting information, following eq. (1), they can be expressed as

\[
G_0 = G_{O^*+H_2} - G_{H_2O^{++}} = E_{adsO'} + 0.01 \text{ eV}
\]

(7)

\[
G_1 = G_{HO^*+\frac{1}{2}H_2} - G_{O^*+H_2} = E_{adsOH} - E_{adsO'} - 0.26 \text{ eV}
\]

(8)

\[
G_2 = G_{H_2O^{++}} - G_{HO^*+\frac{1}{2}H_2} = -E_{adsOH} + 0.25 \text{ eV}
\]

(9)

where $E_{adsO'}$ is defined below and it is assumed that $T = 300$ K. $G_0$ and $G_2$ depend only on the adsorption energy of O and OH, respectively, whereas $G_1$ depends on the difference.

Additionally, the effect of the potential in the cell has to be taken into account because it is an electron transfer process. The free energy at pH = 0, atmospheric pressure of 1 bar, and 300 K of temperature, with electrode potential corrections, is given by

\[
G(U) = G + neU
\]

(10)

where $U$ is the cell potential, $n$ the number of electrons that flow from the media to the electrode (if the electrons move in the opposite direction, $n$ must be multiplied by -1), and $e$ the elementary charge carried by a single electron, -1. At equilibrium, $U$ would be the equilibrium potential $U_0=1.23$ V [17]. Considering the electrons that flow in each of the three steps, the
corresponding free energies at equilibrium potential, atmospheric pressure
and 300 K are:

\[ G_0(U_0) = E_{\text{adsO'}} + 0.01eV - 2U_0 = E_{\text{adsO'}} - 2.45 \text{ eV} \] (11)

\[ G_1(U_0) = E_{\text{adsOH}} - E_{\text{adsO'}} - 0.26eV + U_0 = E_{\text{adsOH}} - E_{\text{adsO'}} + 0.97 \text{ eV} \] (12)

\[ G_2(U_0) = -E_{\text{adsOH}} + 0.25eV + U_0 = -E_{\text{adsOH}} + 1.48 \text{ eV} \] (13)

The catalytic activity, \( A \), can be expressed [47]

\[ A = kT \log \left[ \exp \left( -G(U_0)/kT \right) \right] \] (14)

where \( G(U_0) = \max\{G_0(U_0), G_1(U_0), G_2(U_0)\} \) and corresponds to the activation energy of the process that limits the catalytic reaction.

2.3. Adsorption energies

The adsorption energies of H \((E_{\text{adsH}})\), O \((E_{\text{adsO}})\), and OH \((E_{\text{adsOH}})\) on thirteen transition metals subjected different elastic strains were calculated using density functional theory by Martínez-Alonso et al. [42]. The adsorption energy, \( E_{\text{adsO'}} \), takes into account that the adsorbed oxygen comes from water in the catalytic process from the reaction:

\[ \text{H}_2\text{O} + * \longrightarrow \text{O}^* + \text{H}_2 \]

and it is expressed as

\[ E_{\text{adsO'}} = E_{\text{O}^*} + E_{\text{H}_2} - E_{\text{H}_2\text{O}} - E_* = E_{\text{adsO}} + E_{\text{H}_2} - E_{\text{H}_2\text{O}} + \frac{1}{2}E_{\text{O}_2} \] (15)
where $E_{\text{H}_2}$, $E_{\text{O}_2}$, and $E_{\text{H}_2\text{O}}$ account for the total energy of the hydrogen, oxygen, and water molecules in the gaseous state, respectively.

The metal surfaces of the thirteen metals were subjected to three different types of strain: biaxial and uniaxial (tension and compression) as well as shear, and the adsorption energies at the most favorable adsorption site (FCC for fcc (111) surfaces and HCP for hcp (0001) surfaces) were determined. The maximum strains were established taken into account the mechanical stability limits for each metal and surface obtained from phonon calculations and varied from -5% compression to 8% tension in Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir, Co, Ru, and Os and from -2% compression to 8% tension in Cd and Zn.

3. Results

3.1. Volcano plots at mechanical equilibrium

Gerischer [52] and Parsons [53] were the first ones to find out that certain models for the activity of the HER resulted in a volcano-like curve. Nonetheless, it was Trasatti [54] who collected experimental data and represented the first volcano plot for the HER. Since then, many authors have represented the exchange current density as a function of the free energy for hydrogen adsorption for the HER and the catalytic activity against the adsorption energy of O for the ORR [48, 55, 56, 57]. These plots provide a very intuitive and visual representation of the catalytic performance of transition metals. The peak of the volcano corresponds to the optimum catalytic properties, the ascending brand corresponds to metals in which the reactions are limited by the desorption of the products, and the descending branch represents the processes that are limited by the adsorption of the reactants. According to Sabatier’s principle [44], an equilibrium between adsorption of the reactants and desorption of the products should be attained to get the maximum activity.

The adsorption energy of hydrogen at equilibrium in the most favorable adsorption site, $E_{\text{adsH}}$, is given in Table 1 [42]. This information can be used to calculate the free energy and the corresponding exchange current density according to eqs. (5) and (6), which are also included in Table 1. Volcano plots at mechanical equilibrium of 23 transition metals for the HER obtained from the DFT calculations are plotted in Figure 2(a). A detailed comparison between the experimental data from the literature and the calculated
exchange current densities as a function of free energy of adsorption of H is shown in section 3 of the supporting information. These results are in good agreement with the ones found in literature [48, 55, 56, 57] with the exceptions of Cu and Ir, whose experimental activity is lower than that computed according to Figure 2(a). In particular, the $G_{\text{adsH}}$ calculated for Cu is around 0.2 eV lower than what has been previously stated, which places Cu on the cusp of the volcano plot.

The HER is a one-step process and the reaction path is controlled by the adsorption energy of hydrogen, whereas the ORR includes three steps with their associated free energies, $G_0(U_0)$, $G_1(U_0)$, and $G_2(U_0)$. The corresponding values of the adsorption energies of O and OH were calculated previously on the most favorable site of the thirteen transition metals [42] and they are given in Table 2. They were used to determine the free energies for each of the steps and to calculate the activity according to eq. (14), which are also included in Table 2. The corresponding volcano plot for the catalytic activity as a function of $E_{\text{adsO}}$ is plotted in Figure 2(b). The highest free energy establishes the rate limiting step for each metal and determines the catalytic activity. The rate limiting step in most transition metals is the desorption of $\text{HO}^*$ ($\text{HO}^* + \text{H}^+ + e^- \longrightarrow \text{H}_2\text{O} + \ast$) and the highest free energy is $G_2(U_0)$. The exceptions to this general situation are Au, where the rate limiting step is the adsorption of $\text{O}^*$ ($\frac{1}{2}\text{O}_2 + \ast \longrightarrow \text{O}^*$) with the associated free energy $G_0(U_0)$, and Ir and Os, in which the rate limiting step is the formation of $\text{HO}^*$ ($\text{O}^* + \text{H}^+ + e^- \longrightarrow \text{HO}^*$) and the highest free energy is $G_1(U_0)$. Pt exhibits the maximum catalytic activity in the volcano plot, followed by Pd, Ag, and Ir, in agreement with experimental data [58]. In addition, these results agree with previous simulations by Norskov et al. [47], with the only discrepancy of Ir, in which they report that the rate limiting step corresponds to the desorption of HO. Additionally, it is interesting to notice that $G_0(U_0)$ is very low for Nb, Mo, W, Re, Fe, Hf, Ta, V, Cr, and Tc. This corresponds to a very favorable oxygen adsorption, which could lead to the formation of oxides.

Finally, it should be noted that metals on the left side of the periodic table (Hf, Cr, Ta, V, Nb, Mo, and W) with less than half-filled d-bands present the worst catalytic properties for the HER and the ORR. These results also agree with previous studies [48, 55, 56, 57].
Table 1: Adsorption energy of hydrogen at equilibrium in the most favorable adsorption site, $E_{\text{adsH}}$, for different transition metals. The free energy of adsorption, $G_{\text{adsH}}$, at 300 K and the logarithm of the exchange current density, $\log i_0$, for the HER according to eqs. 5 and 6 are also included.

| Metal | $E_{\text{adsH}}$ (eV) | $G_{\text{adsH}}$ (eV) | $\log i_0$ (A cm$^{-2}$) |
|-------|------------------------|------------------------|--------------------------|
| Pt    | -0.49                  | -0.25                  | -5.52                    |
| Au    | 0.09                   | 0.33                   | -7.06                    |
| Cu    | -0.25                  | -0.01                  | -1.52                    |
| Ag    | 0.17                   | 0.41                   | -8.27                    |
| Pd    | -0.54                  | -0.30                  | -6.40                    |
| Ni    | -0.52                  | -0.28                  | -6.07                    |
| Ir    | -0.39                  | -0.15                  | -3.83                    |
| Rh    | -0.53                  | -0.29                  | -6.27                    |
| Cd    | 0.81                   | 1.05                   | -19.39                   |
| Zn    | 0.67                   | 0.91                   | -16.92                   |
| Co    | -0.51                  | -0.27                  | -5.97                    |
| Nb    | -0.89                  | -0.65                  | -12.46                   |
| Mo    | -0.74                  | -0.50                  | -9.92                    |
| W     | -0.75                  | -0.51                  | -10.09                   |
| Re    | -0.80                  | -0.56                  | -10.97                   |
| Ru    | -0.64                  | -0.40                  | -8.08                    |
| Fe    | -0.59                  | -0.35                  | -7.26                    |
| Os    | -0.59                  | -0.35                  | -7.29                    |
| Hf    | -1.08                  | -0.84                  | -15.77                   |
| Ta    | -0.99                  | -0.75                  | -14.11                   |
| V     | -0.90                  | -0.66                  | -12.53                   |
| Cr    | -1.06                  | -0.82                  | -15.35                   |
| Tc    | -0.72                  | -0.48                  | -9.58                    |
Table 2: Adsorption energy of O ($E_{adsO}$) and OH ($E_{adsOH}$) at equilibrium at the most favorable adsorption site for different transition metals. The free energies of the three steps of the dissociative mechanism ($G_0(U_0)$, $G_1(U_0)$, and $G_2(U_0)$) at 300 K and the catalytic activity for the ORR according to eq. (14) are also included.

| Metal | $E_{adsO}$ (eV) | $E_{adsOH}$ (eV) | $G_0(U_0)$ (eV) | $G_1(U_0)$ (eV) | $G_2(U_0)$ (eV) | Activity |
|-------|----------------|-----------------|----------------|----------------|----------------|----------|
| Pt    | 1.66           | 1.19            | -0.79          | 0.29           | 0.49           | -0.23    |
| Au    | 2.43           | 1.52            | 0.06           | -0.02          | -0.04          | -0.69    |
| Cu    | 0.73           | 0.14            | -1.72          | 0.38           | 1.34           | -0.62    |
| Ag    | 2.04           | 0.72            | -0.41          | -0.35          | 0.76           | -0.36    |
| Pd    | 1.25           | 0.85            | -1.20          | 0.57           | 0.63           | -0.29    |
| Ni    | 0.29           | 0.03            | -2.16          | 0.71           | 1.45           | -0.68    |
| Ir    | 0.79           | 0.76            | -1.66          | 0.94           | 0.72           | -0.44    |
| Rh    | 0.45           | 0.27            | -2.00          | 0.78           | 1.21           | -0.56    |
| Cd    | 1.17           | 0.31            | -1.28          | 0.11           | 1.17           | -0.54    |
| Zn    | 0.79           | 0.37            | -1.66          | 0.54           | 1.11           | -0.52    |
| Co    | -0.01          | -0.20           | -2.46          | 0.78           | 1.68           | -0.78    |
| Nb    | -2.17          | -1.80           | -4.62          | 1.34           | 3.28           | -1.53    |
| Mo    | -1.67          | -1.18           | -4.12          | 1.46           | 2.66           | -1.23    |
| W     | -1.65          | -1.01           | -4.10          | 1.61           | 2.49           | -1.16    |
| Re    | -1.19          | -0.64           | -3.64          | 1.52           | 2.12           | -0.98    |
| Ru    | -0.41          | -0.21           | -2.86          | 1.17           | 1.69           | -0.78    |
| Fe    | -0.98          | -1.03           | -3.43          | 0.93           | 2.51           | -1.16    |
| Os    | -0.31          | 0.15            | -2.76          | 1.42           | 1.33           | -0.66    |
| Hf    | -3.67          | -2.54           | -6.12          | 2.10           | 4.02           | -1.87    |
| Ta    | -2.39          | -1.85           | -4.84          | 1.51           | 3.33           | -1.55    |
| V     | -2.99          | -1.54           | -5.44          | 2.41           | 3.02           | -1.41    |
| Cr    | -2.52          | -2.15           | -4.97          | 1.34           | 3.63           | -1.69    |
| Tc    | -1.19          | -0.78           | -3.64          | 1.38           | 2.26           | -1.05    |
Figure 2: Volcano plots at mechanical equilibrium for (a) the HER as a function of $G_{\text{adsH}}$ and (b) the ORR as a function of $E_{\text{adsO}'}$. Cu* in the HER volcano plot corresponds to the free energy obtained from the adsorption energy calculated with the DFT functional SCAN [60].
3.2. Volcano plots under mechanical strain

The effect of elastic strains on the catalytic activity of transition metals for the HER and the ORR is represented by means of volcano plots in Figures 3(a) and (b), respectively. These plots were constructed from the adsorption energies of the biaxially strained slabs of Au, Pt, Pd, Ag, Rh, Co, Ni, Cu, Ir, Ru, and Os from -5% compression to 8% tension, and of Cd and Zn from -2% compression to 8% tension that can be found in Figures 6 and 7 of [42]. These transition metals were chosen due to their position close to the top of the volcanos in Figure 2 and to their widespread use as heterogeneous catalysts. The black dot in each line in Figure 3 stands for the catalytic activity when the applied strain is zero. The lines for Cd and Zn are not included for the HER reaction in Figure 3(a) because they are too far from the top.

The catalytic activity of the transition metals on the left side of the volcanos is limited by the desorption of the products. Compressive strains increase the adsorption energy of the reactants and avoid the poisoning of the catalyst surface, improving the catalytic activity. On the contrary, the catalytic properties of metals on the right side of the volcanos are limited by the adsorption of the reactants, and can be improved with the application of tensile strains, which enhance the adsorption of the reactants by reducing the adsorption energy. In all cases, the effect of elastic strains on the catalytic activity is limited by the mechanical stability limits of the surface of the catalyst.

The effect of elastic strains on the catalytic activity (measured by the log $i_0$) for the HER depends on the metal. The largest variations in the catalytic properties with strain (Figure 3(a)) are observed for Ir and Au, where the activity (measured by the log $i_0$) changes 4.5 and 2.7 units, respectively, when the surface slab is subjected to -5% biaxial compression or to 8% biaxial tension, respectively, with respect to the unstrained slab. On the contrary, Co is very insensitive to the mechanical strains because $E_{\text{ads}}$ does not vary with the elastic strain [42]. There are not well established trends for the effect of mechanical strains on the adsorption energies but our previous investigation showed that the influence of the mechanical strain on the adsorption energy increases with the number of electrons in the valence band for the elements in the 4th period of the periodic table (3d). Nevertheless, the effect of mechanical strains on the adsorption energy is much smaller for the 5th
and 6th periods \[42\]. It should also be noted that the limiting mechanism (either hydrogen adsorption or desorption) does not change with the applied strain (the evolution of the catalytic activity with the applied strain remains to the left or to the right of the volcano cusp) with the exception of Cu in which \( E_{\text{adsH}} \) is very close to 0 in the unstrained slab. In this case, tensile or compressive stresses activate one of either rate limiting steps and reduce the catalytic activity.

The elastic strains also lead to important changes in the catalytic activity of transition metals for the ORR, as shown in Figure 3(b). The largest ones are found in Pt and Au and both metals can be tuned by means of either compressive or tensile strains, respectively, to attain the top of the corresponding volcano plot. This result was already detected for Pt, which is known to improve its catalytic activity through the application of elastic strains \[59, 43\] in agreement with our volcano plot. More interestingly, the application of 2% biaxial tension can improve the catalytic activity of Au (which is known to be a bad catalyst for the ORR) close to that of Pt. In contrast, elastic strains have a minor influence on the catalytic activity of the ORR for Co and Cd. The maximum activity of Ir, Rh, Co, Ni, Cu, Zn, Cd, Pd, Ru, and Os for the ORR is attained when the slab is subjected to the highest compressive strain, while the best catalytic activity of Ag is found in the unstrained condition and the application of tensile or compressive strains always leads to the reduction in activity.

4. Discussion

The results presented above show how the systematic application of elastic strains can be tailored to optimize the catalytic response of transition metals for the HER and the ORR. In the former case, the catalytic activity is determined by \( E_{\text{adsH}} \) which determines the free energy of adsorption, \( G_{\text{adsH}} \), at a given temperature. The optimum scenario is achieved when \( G_{\text{adsH}} \rightarrow 0 \) through the application of compressive or tensile strains and the limitations to this strategy are determined by the sensitivity of \( E_{\text{adsH}} \) to the strain and the maximum strains that can be applied before mechanical instability limit is achieved, leading to fracture. The largest changes in catalytic activity with strain for the HER were found in Pt, Au, and Ir while \( E_{\text{adsH}} \) in Co and Ni was very insensitive to elastic strains, which did not modify substantially the catalytic activity.
Figure 3: (a) Effect of mechanical strains on the volcano plot for the HER as a function of $G_{\text{adsH}}$ for thirteen transition metals. The range of activities for Pd, Rh, Ni, Co, Ru, and Os within the rectangle have been plotted to the right, shifted by 0.05 eV along the horizontal axis for the sake of clarity. (b) Idem for the ORR as a function of $E_{\text{adsO}}$. The free energy that limits the reaction rate is indicated at each branch of the volcano plot for each metal. The lines stand for the variation in the catalytic activity of each metal as a function of the applied elastic strain in the range from -5% biaxial compression to 8% biaxial tension in Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir, Co, Ru, and Os, and from -2% biaxial compression to 8% biaxial tension in Cd and Zn. Black circles indicate the activity at the mechanical equilibrium. Cd and Zn are omitted from the HER volcano plot because log $i_0$ is very low.
It should be noted that the catalytic activity of Cu is overestimated in the volcano plot for the HER in Figure 2. This discrepancy may be due to the fact that – according to equation (4) – the exchange current density depends strongly on $G_{adsH}$, which in turn is a linear function of $E_{adsH}$ (Equation (4)). Thus, small errors in the calculation of $E_{adsH}$ may lead to substantial changes in catalytic activity, particularly near the cusp of the volcano plot. In order to test this conjecture, $E_{adsH}$ was calculated again in Pt and Cu using the metaGGA SCAN functional [60] and the methodology presented in [42]. This functional is known to provide more accurate values of the adsorption energy at a much higher computational cost [60]. In the case of Pt, the differences in $E_{adsH}$ between the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional and the metaGGA SCAN functional were only 0.03 eV but they increased to 0.24 eV in the case of Cu. Moreover, these differences remained constant as a function of strain in the case of Pt (supporting information Figure 3). Thus, the predictions of the adsorption energy for Cu seem to be particularly sensitive to the selection of the functional and this explains the overestimation of the Cu activity in the volcano plot of Figure 2. And Cu moves to the appropriate position in the volcano plot for the HER in Figure 2(a) when the more accurate adsorption energy (denoted by Cu*) is used to calculate the free energy. It should be noted that this sensitivity to the functional could be less important in the case of the ORR, because the activity depends on differences in $E_{ads}$ and errors in the calculation of adsorption energies due to selection of the functional tend to cancel each other. This is evidenced by the position of Cu in the volcano plot for the ORR in Figure 2 which is in agreement with the experimental data. However, further investigation of the variations in the adsorption energy with SCAN in the case of Cu is needed.

The effect of mechanical strains on the catalytic activity of the ORR is a little bit more complex because it depends on the free energy of the rate limiting reaction, which is the maximum of $G_0$, $G_1$, and $G_2$. $G_0$ depends on $E_{adsO}$, $G_1$ on $E_{adsOH} - E_{adsO}$, and $G_2$ on $-E_{adsOH}$. The influence of the mechanical strains on the respective adsorption energies is different.

Tensile strains reduce $E_{adsO}$ and $E_{adsOH}$ while compressive strains have the opposite effect. Moreover, $E_{adsO}$ at zero strain is negative for all the analyzed transition metals while $E_{adsOH}$ is positive under the same conditions for all the analyzed transition metals (except Co, with $E_{adsOH} = -0.2$ eV). As a result, the catalytic activity for the ORR of metals in which the rate is controlled by
$G_0$ (adsorption of O$^*$) and $G_2$ (desorption of HO$^*$) are very sensitive to elastic strains and their catalytic activity increases rapidly with the application of tensile strains in the former (Au) or compressive strains in the latter (Cu, Ni, Pt, Pd, Rh, Zn, Cd, Co, Ru, and Os). In some hcp metals, such as Cd and Zn, the range of elastic strains before mechanical instabilities develop is reduced and, thus, the tunability of their catalytic activity with mechanical strains is very limited. Finally, the rate limiting free energy in Ir is $G_1$ (change from O$^*$ to HO$^*$) that depends on the difference between $E_{\text{adsOH}} - E_{\text{adsO}}$. As both energies evolve in the same direction with strain, their difference is not very sensitive to the applied strain (Figure 3) and Ir activity varies slowly (as compared with other metals) with deformation. Thus, the efficiency of elastic strains to modify the catalytic activity not only depends on the catalyst itself but also on the intermediate species that are present in each reaction step. Some reactions are more sensitive to the application of elastic strains than others, which opens the possibility to explore the mechanism to enhance the activity of many other chemical processes with different intermediate species.

In most metals, mechanical strains change the catalytic activity but not the rate limiting mechanism. This is not the case, however, for Au, Pt, Ag, and Os. The influence of biaxial strains (in the range -5% to 8%) on the free energies in the ORR reaction path for Au, Pt, and Ag is plotted in Figures 4(a), (b), and (c), respectively. At zero strain, the adsorption of O is the limiting step in Au (Figure 4(a)) and this energy barrier increases with compressive strains while $G_1$ fluctuates due to the competition between the adsorption energies of O and HO. As a result, compressive strains reduce the catalytic activity for the ORR of Au. However, the application of tensile strains switches the rate limiting step to the desorption of HO$^*$ because $G_2$ becomes positive and increases rapidly with the tensile strains while $G_0$ becomes negative and $G_1$ fluctuates between negative and positive values. The optimum catalytic activity is obtained at small tensile strains around 2% biaxial tension.

In the case of Pt (Figure 4(b)), the desorption of HO$^*$ is the limiting step at zero strain, while the adsorption of O is strongly exothermic and the reaction from O$^*$ to HO$^*$ is slightly endothermic. The application of compressive strains reduces rapidly the energy barrier for HO$^*$ desorption and the rate limiting step changes to the reaction from O$^*$ to HO$^*$, which becomes endothermic. The application of tensile strains increases the energy barrier for HO$^*$ desorption, leading to a constant reduction in the catalytic activ-
ity. Thus, the maximum catalytic activity is achieved for small compressive strains (-1.57% biaxial compression). The rate limiting step also changes from $G_2$ to $G_1$ with the application of compressive strains in the case of Os.

Additionally, unstrained Ag is at the cusp of the volcano plot and the application of either tensile or compressive strains reduces the activity as one limiting reaction becomes dominant. In this case, the rate limiting step is found to be the desorption of HO$^*$ under tensile strains and the O adsorption under compressive strains (Figure 4(c)). Finally, the application of strain in Ir does not change the rate limiting step of the ORR, which is the change from O$^*$ to HO$^*$ in all cases (Figure 4(d)). $G_1$ decreases slightly with compressive strains and increases slightly with tensile strains and the optimum catalytic activity is found at the maximum compressive strains allowed by the mechanical stability limits.

**Conclusions**

The effect of elastic strains on the catalytic activity for the HER and the ORR was analyzed at (111) surfaces of eight fcc transition metals (Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir) and (0001) surfaces of five hcp transition metals (Co, Zn, Cd, Ru, Os). The catalytic activity for both reactions was determined from the adsorption energies for H, O, and OH calculated by density functional theory under strain. Tensile, compressive, and shear stresses were applied to slabs until the mechanical stability limit (given by phonon calculations) was achieved. The volcano plots of the catalytic activity for the HER and the ORR in the absence of strain were in good agreement with the experimental data in the literature, validating the theoretical model. It was found that elastic strains led to significant changes in the catalytic activity of most transition metals, which could be rationalized as a function of changes in the free energy of the rate limiting step.

In the case of the HER, it was found that compressive strains increased the catalytic activity of metals on the ascending branch of the volcanos (Pt, Pd, Rh, Ni, Ir, Ru, and Os) because they decreased the energy barrier for H$^*$ desorption, which is the limiting step. On the contrary, tensile strains improved the activity of metals in the descending branch of the volcano, as they decreased the energy barrier for H adsorption (Au and Ag). The largest improvements in activity were found in Au, Ir, and Ag which combined a
large sensitivity of the H adsorption energy to strain while large mechanical strains could be applied without leading to failure.

The catalytic activity of the ORR was controlled by the maximum free energy for the reactions in the dissociative mechanism: adsorption of O, reaction from from O* to HO*, and desorption of HO*. In particular, the free energies associated with the adsorption of O and the desorption of HO* were very sensitive to mechanical strains. Thus, the catalytic activity of Au (controlled by the former) could be enhanced by the application of tensile strains while that of Cu, Ni, Pt, Pd, Rh, Zn, Cd, Co, Ru, and Os (controlled
by the latter) was improved by the application of compressive strains. The optimum catalytic activity of Ag was found in the unstrained condition and mechanical deformation always reduced the catalytic activity in this metal. Moreover, only small elastic strains could be applied to Cd and Zn before the mechanical instability was reached and elastic strain engineering is not a suitable strategy to modify the catalytic activity of these metals. Finally, it was also found that the application of elastic strains could change the rate limiting step for the ORR in Au, Pt, Ag, and Os because of the different effect of mechanical deformation of the free energy of the different intermediate reactions.

Acknowledgments

This investigation was supported by the MAT4.0-CM project funded by the Madrid region under program S2018/NMT-4381 and by the HexaGB project (reference RTI2018-098245) funded by MCIN/AEI/10.13039/501100011033. Computer resources and technical assistance provided by the Centro de Supercomputación y Visualización de Madrid (CeSViMa) are gratefully acknowledged. Additionally, the authors thankfully acknowledge the computer resources at CTE-Power and Minotauro in the Barcelona Supercomputing Center (project QS-2021-1-0013 and QHS2021-3-0019). Finally, use of the computational resources of the Center for Nanoscale Materials, an Office of Science user facility, supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Project No. 73377, is gratefully acknowledged. CMA also acknowledges the support from the Spanish Ministry of Education through the Fellowship FPU19/02031.

Conflicts of interest

There are no conflicts of interest to declare.

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