Influence of Composition and Size on the Hydrogen Evolution Reaction in 13- and 27-Atom NiPd Clusters

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ABSTRACT – Hydrogen production from water is one of the most promising solutions to the energy and climate crises. However, this process currently requires high-cost rare metal catalysts. To reduce these costs, alloying rare and earth-abundant metals is a potential solution. Ni and Pd 13- and 27-atom alloys and unary clusters showed good stability in previous studies. Since these materials present good catalytic activity in several reactions, we performed theoretical DFT calculations using the PBE functional and PAW wave functions with van der Waals correlations to evaluate the hydrogen evolution reaction (HER). To provide Gibbs free energies, we employed the computational hydrogen electrode model. The results show that hydrogen atoms are bonded only at bridge and hollow sites, which can be explained by the ease of electron transfer from the cluster to H atoms at these sites. Additionally, we found that 13-atom alloys can present better HER activity than their same-size unaries.

Keywords: adsorption, NiPd, HER, hydrogen, catalysis

Introduction

The demand for less polluting fuels makes hydrogen produced by the water-splitting procedure more attractive, since water electrolysis liberates oxygen at the anode and hydrogen at the cathode (1,2). Ni nanoparticles incorporated onto a substrate composed of dispersed nickel nitride (NiN_x) on porous carbon exhibit high activity in the HER, while Pd nanoparticles supported on VS_2 layers have also shown great potential in HER catalysis in acidic media (2,3). According to Ref. 4, Ni-Pd clusters showed significant stability. Therefore, here we evaluate HER in 13- and 27-atom NiPd clusters.

Theoretical Approach

Total energy and ΔG calculations.

We perform DFT (4,5) calculations using the PBE (7) functional and PAW(8,9) wavefunctions with semi-empirical D3 correction proposed by Grimme (10) using the VASP package (11) on nine compositions (0%, 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5%, and 100% Ni) of Ni_mPd_{n-m} (where n = 13 or 27 atoms). This is done in two steps: an initial low-cost exploration, employing a plane wave cutoff energy of 340.939 eV and geometry optimization performed until the force on all atoms fell below 0.100 $eVÅ^{-1}$, and high-cost calculations using a cutoff of 438.351 eV and geometry optimization with forces bellow 0.050 $eVÅ^{-1}$. The adsorption ΔG calculations were carried out at the lowest adsorption energy configuration after the hight-cost calculations employing the computational hydrogen electrode model (12-14).

Generation and selection of adsorbed configurations.

For the generation of adsorbed configurations, we use the same algorithm as Zibordi-Besse (15). This program allows us to generate millions of configurations and remove similar ones, reducing the set to approximately n×1000 configurations, where n represents the number of cluster atoms. We use the *k-means* method to identify representative structures for low-cost calculations. Relative energy (ΔE_{tot}) is then used for selecting configurations to perform the final high-cost calculations and the geometries used to calculate ΔG. ΔE_{tot} is the energetic difference between the total DFT energy calculated from the lowest-energy configuration and other higher-energy configurations. Thus, for high-cost calculations, we apply the root mean square deviation (RMSD) parameter to select non-equivalent structures, and consider only relative energies (ΔE_{tot}) lower than 5 meV/atom, thus reducing computational costs.

Results and discussion

As can be observed in **Figure 1**, there is a reduction in the number of points from low-cost to high-cost calculations. Moreover, the difference between panel c) and d) is due to the selection process

that eliminated many symmetric equivalent and higher-energy configurations in the first step, as well as the fact that some configurations converge to the same local minimum after the high-cost calculations. The most stable structures obtained for 13-atoms clusters are shown in **Figure 2**.

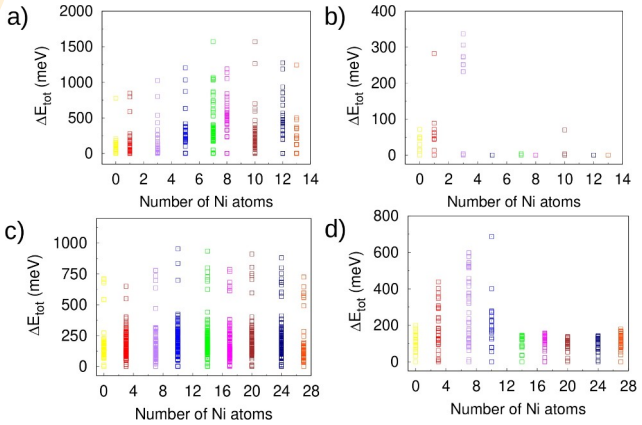

Figure 1. Relative energies for low-cost and high-cost calculations for H/Ni_mPd_{13-m} in panels a) and b); and for H/Ni_mPd_{27-m} in panels c) and d).

In HER catalysis, a ΔG close to 0 is an ideal. This implies that neither significant energy is required to adsorb the H atom onto the cluster (if ΔG>0), nor is substantial energy needed to liberate ½ H_2 (if ΔG is strongly negative). We found that all clusters exhibit ΔG < 0. As the entropic component is very small, this indicates these are exothermic reactions. Furthermore, we note that the ΔG values of Ni-rich alloys tend to be larger than those of Pd-rich alloys. Therefore, the Ni-rich alloys tend to be the better catalysts than the Pd-rich ones, since ΔG is closer to 0.

Table 1 shows the DDEC (16,17) partial charge of the H atom adsorbed in the each cluster. We notice that charge transfer from the cluster to H is more enhanced in the small 13-atom and Pd-rich clusters.

The preference of atomic hydrogen for the hollow site occurs because these sites provide better electron transfer, which might be notice in the DDEC charge analysis, where we can observe that the hydrogen atom assumes a strongly negative partial charge while the cluster atoms lose partial charges.

Table 1. Partial charge on the adsorbed H atom to each of the evaluated clusters, Q in *e*, obtained by DDEC6 charge analysis.

Cluster	Q (*e*)	Cluster	Q (*e*)
Pd_{13}	−0.113	Pd_{27}	−0.116
$NiPd_{12}$	−0.132	Ni_3Pd_{24}	−0.116
Ni_3Pd_{10}	−0.141	Ni_7Pd_{20}	−0.129
Ni_5Pd_8	−0.125	$Ni_{10}Pd_{17}$	−0.140
Ni_7Pd_6	−0.169	$Ni_{14}Pd_{13}$	−0.083
Ni_8Pd_5	−0.143	$Ni_{17}Pd_{10}$	−0.080
$Ni_{10}Pd_3$	−0.106	$Ni_{20}Pd_7$	−0.071
$Ni_{12}Pd$	−0.125	$Ni_{24}Pd_3$	−0.072
Ni_{13}	−0.128	Ni_{27}	−0.079

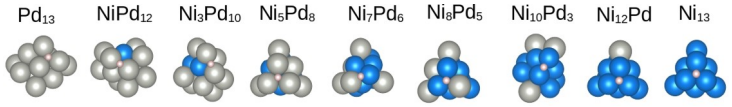

Figure 2. 13-atom NiPd adsorbed clusters. Nickel (Ni) atoms are blue, palladium (Pd) atoms are gray, and hydrogen (H) is represented in pink.

Conclusions

We notice that the Ni-rich nanoalloys have a tendency to be better catalysts than Pd-rich ones. We also observe that hydrogen atom adsorbs on hollow and bridge site, which can be explained by the facility for charge transfer to occur from the cluster to H in these orientations.

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