Density functional theory study of uni- and bi-metallic small Pt and Ni clusters for fuel conversion applications

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Abstract. In this work, we employed density functional theory calculations to probe the binding characteristics of C and OH on small uni-metallic (Pt3 and Ni3) and bi-metallic (Pt2Re and Ni2Fe) clusters for energy conversion applications. Both uni-metallic and bi-metallic clusters were found to possess relatively good HOMO-LUMO gaps, indicating that the clusters are electronically stable against excitations and high energy environment. It is found that the introduction of foreign atoms on uni-metallic clusters impacts C and OH binding characteristics, which could be useful in the design and fine-tuning of novel nanocatalysts for energy conversion applications such as CO/CO2 methanation and hydrogenation reactions. It is further inferred that Pt3 and Pt2Re clusters bind C and OH moderately, and could be utilized in further studies concerning energy conversion.

1. Introduction

One of the main problems that the world would encounter in the coming years is energy production and usage. It is generally known that the world’s fossil fuel reserves are finite, and thus it will be depleted in the next few decades. Although there is a strong drive in the proliferation of non-conventional and renewable energy sources such as from light and wind, still, the current technology needed for it to fully replace fossil fuel is not matured enough and needed additional tweaking and improvements before it can be realized as a major energy source. It is therefore of importance to find alternative ways of producing conventional fuels that satisfy the following requirements: (1) sustainable and renewable, in a sense that fuel can be produced in a close cycle and that the fuel usage by-products can be converted back, (2) production should be efficient, and can meet current demands, and (3) should be safe and practical for mass production and distribution [1–3]. For such requirements to be met, the reactions accompanying fuel conversion should be at its optimum, which can be attained through proper choice of catalysts. One of the widely used method in producing the so-called “artificial” fossil fuel is steam reforming, in which raw carbon-rich materials such as coke is made to react with steam at high temperature and pressure to produce methane, propane, and other higher-order hydrocarbons [4–9]. Its by-product, called syngas that is composed of H2 and CO gases, can be recycled to produce hydrocarbon fuels. Syngas can also be produced from biomass materials, making syngas conversion one of the most studied reaction in the field of catalysis [10–12].

In this regard, this work focuses on the theoretical study of transition metal atomic clusters as potential catalysts for syngas conversion. Specifically, this work tries to assess the effect of alloying these clusters to create bi-metallic atomic clusters on important parameters such as species binding on certain sites. This is important as the binding of intermediate species on the catalysts could dictate the efficiency of the reaction, and thus proper tuning of this could prove useful in the design of catalysts.
From [13], it was illustrated in the volcano plot that certain transition metal surfaces were found to have good reactivity when it comes to syngas conversion. Syngas conversion proceeds by breaking CO into C and O, and then hydrogenation of C into CH$_4$, O to OH and subsequent conversion to H$_2$O. Thus, C and OH binding on the catalyst surface would determine the efficiency of the reaction, which is the subject of this study.

2. Methodology

The calculations were carried out in the paradigm of density functional theory (DFT) via the Quantum Espresso package suite [14]. Three-atom clusters were considered in this work: the uni-metallic Pt$_3$, Ni$_3$, and the bi-metallic Pt$_2$Re, and Ni$_2$Fe. These clusters were chosen to analyze the effect of alloying those transition metals that were found to either bind strongly or weakly to C and OH, as was presented in [4]. As for calculations details, Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals within the generalized gradient approximation (GGA) were utilized, together with norm-conserving pseudopotentials. Kinetic energy cut-off of 60 Ry is used, and the sampling of the Brillouin zone is done via a 1 x 1 x 1 k-point mesh representing the real-space unit cell with more than 10 Å vacuum in all spatial directions. Electronic convergence is set to 10$^{-5}$ Ry and atoms were allowed to relax until the forces on each is below 10$^{-3}$ Ry/a.u.

Optimized geometries, as well as charge distributions, HOMO-LUMO gap and OH and C binding energies are presented and analyzed. The binding energy of OH and C on the clusters is defined as

$$E_{binding} = E_{system} - E_{cluster} - E_{OH/C}$$

3. Results and Discussions

Figure 1 shows the optimized geometries of the metal clusters, together with the corresponding bond lengths. All structures possess the isosceles triangle geometry, except for Ni$_3$ which possess an equilateral triangle geometry. Using Bader charge analysis, it was found that for uni-metallic clusters such as Pt$_3$ and Ni$_3$, the electron distribution among the atoms is relatively uniform. On the other hand, for the bi-metallic ones which include Pt$_2$Re and Ni$_2$Fe, the foreign atoms Re and Fe act as electron donor. The Re atom in Pt$_2$Re donates around 0.56 e to the Pt atoms, while Fe in Ni$_2$Fe donates around 0.41 e to Ni atoms. To analyse the electronic structure of the metal clusters, their HOMO-LUMO gaps were calculated, as presented in Table 1. The HOMO-LUMO gap can be used to draw conclusions on the stability and reactivity of the clusters [15,16]. As can be observed from the given values, all metallic clusters have relatively fine HOMO-LUMO gaps, with Ni$_3$ having the largest gap among the clusters. Clusters with large HOMO-LUMO gaps are said to be stable under excitations or high energy environment. In catalysis perspective, this is quite a good indication that the catalyst will still function close to ideal operations, as the chance of it being used up in the reaction, and exhibit the so-called “site-poisoning” is lower.

![Figure 1](image)

**Figure 1.** Optimized geometries of the three-atom uni-metallic and bi-metallic clusters. Bond lengths are reported in units of Å.

For the calculation of the binding energies of OH and C, the optimized geometries and bond lengths for C and OH adsorption are shown in Figures 2 and 3 respectively. It can be inferred that both C and
OH binds with shorter bond lengths to Ni$_3$ and Ni$_2$Fe. To analyse charge distribution, charge difference isosurfaces were plotted for C and OH adsorption (Figure 4). Here, red regions denote electron rich regions, while blue ones denote electron deficient regions. The isosurfaces indicate that the binding between the clusters and C and OH has an ionic nature. To substantiate on these, we calculated the charge transfer to C and OH to the clusters via Bader charge analysis (Table 1). It is found that C and OH gains substantial amounts of electrons from the clusters (except for the case of Ni$_3$, in which C loses a minimal 0.15e of charge to Ni). These charge transfers become more pronounced for bimetallic clusters. The calculated binding energies is also listed in Table 1, and a plot of the C binding energy ($E^C$) against that of OH ($E^{OH}$), and the plot of C binding energy ($E^C$) against that of OH ($E^{OH}$) is shown in Figure 5.

![Figure 2](image1.png)

**Figure 2.** Optimized geometries of adsorbed C on uni-metallic and bi-metallic clusters. Bond lengths are reported in units of Å.

![Figure 3](image2.png)

**Figure 3.** Optimized geometries of adsorbed OH on uni-metallic and bi-metallic clusters. Bond lengths are reported in units of Å.
Figure 4. Charge difference isosurfaces for (a) C adsorption and (b) OH adsorption on uni-metallic and bi-metallic clusters. The isosurface level is set to $0.02e\text{Å}^3$.

Figure 5. Plot of the C binding energy against that of OH for each small metallic cluster.
For proper reactions to proceed, for instance in the case of methanation or CO/CO₂ hydrogenation reactions, the binding of intermediate species on the catalyst must be at the optimum level [13,17,18]. Analyzing each C and OH adsorption pair, it can be observed that Ni₃ binds C and OH quite too strong, and thus it can be inferred that the cluster would not be a good catalyst for syngas conversion. For the bimetallic case, Ni₂Fe, it appears that C adsorption energy is reduced, although OH binding is further enhanced. On the other hand, Pt₃ and Pt₃Re clusters seem to have good binding characteristics with respect to C and OH. In the uni-metallic case, there is moderate OH binding, although C binding is still quite high. Replacing one Pt with Re significantly lowered C binding energy, with a modest increase in OH binding. In general, Ni₃ and Ni₂Fe clusters adsorb C and OH quite strongly as compared to that of Pt₃ and Pt₃Re. This work has demonstrated that small bi-metallic clusters could be employed to fine tune C and OH binding energies, which could be utilized in the design of useful catalysts for energy conversion applications.

4. Summary and Conclusion
The work carried out theoretical calculations in the paradigm of DFT to assess the catalytic potential of select small metal clusters: uni-metallic Pt₃ and Ni₃ clusters, and the bi-metallic clusters Pt₃Re and Ni₂Fe clusters. Results showed that the clusters are structurally and electronically stable. C and OH binding were found to be too strong on Ni₃ and Ni₂Fe, while these are quite reduced in the case of Pt₃ and Pt₃Re especially in the case of C adsorption. Due to the moderate adsorption characteristics of C and OH on Pt₃ and Pt₃Re clusters, it is inferred that these could be employed in the fine tuning of reaction intermediates’ binding properties for syngas conversion and energy conversion applications as a whole. Moreover, this work has demonstrated the effectiveness of introducing foreign atoms to form bimetallic clusters in improving binding characteristics of C and OH.

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