Oxygen Reduction Reaction Catalyzed by Pt$_3$M (M = 3d Transition Metals) Supported on O-doped Graphene

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Abstract: Pt$_3$M (M = 3d transition metals) supported on oxygen-doped graphene as an electrocatalyst for oxygen reduction was investigated using the periodic density functional theory-based computational method. The results show that oxygen prefers to adsorb on supported Pt$_3$M in a bridging di-oxygen configuration. Upon reduction, the O–O bond breaks spontaneously and the oxygen adatom next to the metal–graphene interface is hydrogenated, resulting in co-adsorbed O* and OH* species. Water formation was found to be the potential-limiting step on all catalysts. The activity for the oxygen reduction reaction was evaluated against the difference of the oxygen adsorption energy on the Pt site and the M site of Pt$_3$M and the results indicate that the oxygen adsorption energy difference offers an improved prediction of the oxygen reduction activity on these catalysts. Based on the analysis, Pt$_3$Ni supported on oxygen-doped graphene exhibits an enhanced catalytic performance for oxygen reduction over Pt$_4$.

Keywords: oxygen reduction reaction; Pt-based catalyst; adsorption energy; transition metals

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) can directly convert the chemical energy stored in hydrogen and oxygen into electricity [1–3], but their adoption for practical application as electrocatalysts is hindered by the high price and limited supply of platinum [4–6]. Efforts have been made to reduce, and even replace, platinum in electrocatalysts. Alloying platinum with inexpensive metals has been shown to maintain or improve the activity for the oxygen reduction reaction (ORR) while significantly reducing the cost [7–12]. Among inexpensive metals, 3d metals, including Ti [13,14], V [13,14], Cr [14], Mn [14], Fe [13–16], Co [13–15,17,18], Ni [13–15,19], and Cu [17,20,21] have been tested as a component of the electrocatalysts for ORR.

Graphitic carbon materials have long been used as electrode materials, with graphene-based materials being natural alternatives due largely to their generally high electrical conductivity, high specific surface areas, and strong chemical strength [22,23]. Therefore, graphene-supported Pt and metal alloy catalysts have been studied for the oxygen reduction process [24–26]. B-, N-, and S-doped graphene have also been investigated for ORR [27–31]. Various functional groups on graphene have been reported to enhance the ORR activity [32]. In particular, graphene oxides and oxygen-containing

graphene materials are widely available. These oxygen-derived defect sites in graphene may form the anchor sites for the active catalyst and/or work synergistically with the active components to promote the reactions. Consequently, the use of graphene oxides either alone or as a support in the electrode has attracted extensive attention [6,33–35]. In the present study, we use O-doped graphene to model the oxygen-containing graphene materials.

Our previous study on the ORR process over Pt_4, Pt_3V, and Pt_3Fe supported on O-doped graphene showed that V and Fe change the ORR mechanism and activity on the Pt-based catalysts differently [36]. Other studies also reported that early and late 3d transition metals could affect the adsorption of O_2 and the ORR activity in a different way [13,37]. Herein, we examined the entire row of 3d transition metals in the form of Pt_3M with M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni on O-doped graphene (OG) as the ORR catalysts. We compared the effect of transition metals on the ORR mechanism and activity. Through a detailed analysis of O_2, OH, and H_2O adsorption energies, as well as the ORR mechanism, we identified Ni as the most effective modifier.

2. Results and Discussion

2.1. Optimized Pt_3M Structures on O-doped Graphene

Our previous study showed that the O-doping site is the anchoring site for the tetrahedral Pt_4 cluster [36]. The OG-supported Pt_3M clusters (OG-Pt_3M) were constructed by replacing one Pt atom of the supported Pt_4 cluster with M at either the interfacial or the top of tetrahedron. Structural optimization showed that the interfacial substituted Pt_3M cluster is more stable, which was used for the ORR study. In this work, we expanded M to include all 3d metals, i.e., M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni. As we showed previously, the doped O atom is 2-C coordinated and 0.72 Å above the plane of the graphene sheet on pure OG [38]. As shown in Table 1, the doped O atom was pushed to the opposite side of the graphene sheet at a distance of 0.17~0.60 Å, depending on M in the supported cluster. The details of the optimized structures are shown in Table S1 of the Supporting Information.

Table 1. Bader charges of the metal atoms, doped oxygen and the carbon atoms bonded with oxygen, and the distance between the doped oxygen atom and the graphene plane ($d_{(O-OG)}$ in Å). The corresponding atoms are labeled in the accompanying structures under the table.

Cluster		Pt_4	Pt_3Sc	Pt_3Ti	Pt_3V	Pt_3Cr	Pt_3Mn	Pt_3Fe	Pt_3Co	Pt_3Ni
	C_1	+0.72	+0.78	+0.93	+0.70	+0.71	+0.68	+0.73	+0.62	+0.75
	C_2	+0.65	+0.73	+0.32	+0.67	+0.57	+0.58	+0.60	−0.20	−0.22
Bader Charge	O	−1.61	−1.63	−1.42	−1.65	−1.64	−1.64	−1.65	−1.64	−1.61
	Pt_1	−0.16	−0.59	−0.84	−0.61	−0.51	−0.49	−0.44	−0.39	−0.35
	Pt_2	+0.25	−0.1	+0.04	−0.13	−0.02	−0.03	+0.01	+0.06	+0.09
	Pt_3	+0.19	−0.11	−0.52	−0.09	−0.07	−0.04	+0.01	+0.08	+0.11
	M(or Pt_0)	−0.12	+1.56	+2.13	+1.70	+1.28	+1.12	+0.97	+0.71	+0.57
$d_{(O-OG)}$/Å		0.17	0.51	0.60	0.57	0.42	0.38	0.40	0.20	0.18
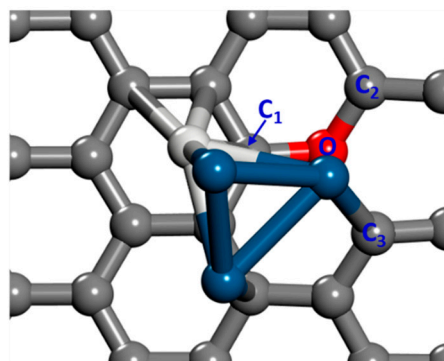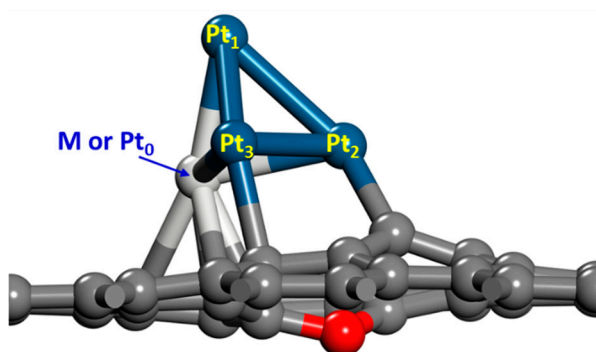
Table 1 lists the Bader charges of C_1, C_2, O, Pt_1, Pt_2, Pt_3, and M (or Pt_0) in the optimized Pt_3M on OG, with numbering of the atoms shown in the figures under Table 1. The charges of the doped O atom and the two linking C atoms were generally maintained at similar values for different Pt_3M clusters. The exception was the C_2 atom in Pt_3Co and Pt_3Ni due to the $O–C_2$ bond breaking and the $O–C_3$ bond formation. In supported Pt_4, two Pt atoms were positively charged, whereas the other two were negatively charged, although the charge differences were not great. When a second metal was introduced to replace one of the Pt atoms to form Pt_3M, charge localization occurred. In particular, the top Pt_1 atom was significantly more negatively charged, whereas the M atom was positively charged and the charge on M decreased from 2.13 $|e|$ on Ti to 0.57 $|e|$ on Ni, due mainly to the change of the electronic structure and atomic radius. We note that the charge on the more active early transition metals (M for M = Sc, Ti, V, and Cr) was much larger than those on the late transition metals (M = Mn, Fe, Co, and Ni). These differences in charge redistribution will in turn affect the oxygen adsorption energies and ORR reactivity.

To characterize the stability of supported Pt_3M on OG, we defined a net binding energy (E_b) as $\Delta E_b = E_b(Pt_4) - E_b(Pt_3M)$, i.e., the binding energy difference of OG–Pt_3M and OG–Pt_4, and plotted the results in Figure 1. According to this definition, a positive value would indicate that the Pt_3M cluster binds OG stronger than Pt_4. As shown in Figure 1, the binding energy of Pt_3Mn and Pt_3Fe was closer to Pt_4, while the binding energy difference was highly negative for Pt_3Ti and Pt_3V, indicating that these two clusters bind OG much weaker than Pt_4. On the other hand, Pt_3M with M = Sc, Cr, Co, and Ni binds OG more strongly than Pt_4, by ~0.1 eV, indicating their higher stabilities. The relative stability of OG-Pt_3M is a reflection of the interaction between Pt_3M and support and will affect the ORR performance.
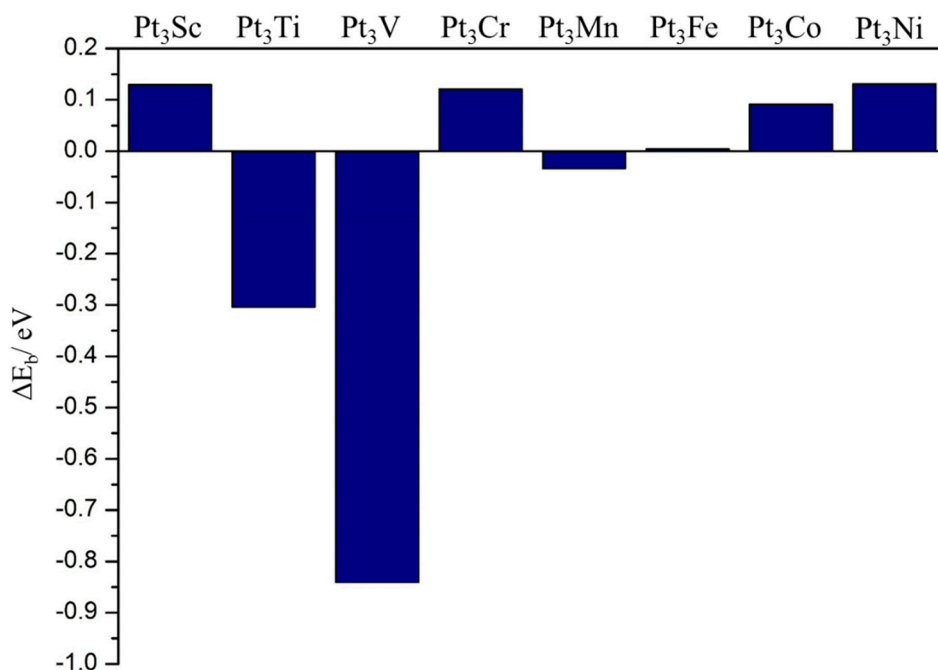

Figure 1. Net binding energy of Pt_3M on O-doped graphene (OG) with respect to Pt_4 on OG.

2.2. Oxygen Adsorption and Reduction Mechanism

The mechanism of ORR on various electrocatalysts was extensively investigated using the density functional theory (DFT) method [4,27,39–42]. Previously, we studied the ORR mechanism over the OG supported Pt_4, Pt_3V, and Pt_3Fe clusters and reported two possible pathways [36]. Herein, we expanded the investigation to include all 3d transition metals.

The first step for oxygen reduction is O_2 adsorption. We calculated the possible adsorption structures of O_2 on OG–Pt_3M and found that O_2 prefers to bind the supported cluster in a di-oxygen form in a bridging configuration, with one oxygen atom on Pt_1 and another on M, as can be seen in Figure 2 and Figure S1. The O–O distance of these adsorbed di-oxygen species was stretched to 1.41~1.47 Å from 1.23 Å of the isolated O_2 molecule. Interestingly, the Pt_3M cluster maintained a tetrahedral structure after being combined with O_2, in contrast to Pt_4, which was transformed into a planar-ring structure by O_2 adsorption, indicating that the transition metal atoms in Pt-based alloys contribute to stabilizing the cluster structure.
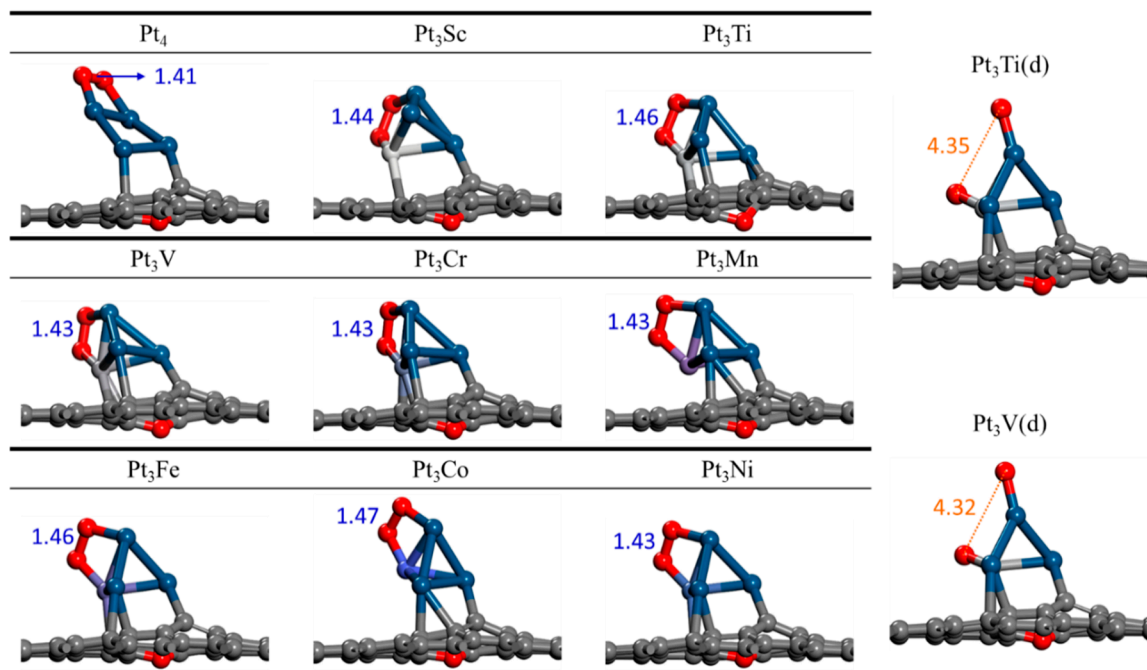

Figure 2. Adsorption configuration and O–O bond distance (shown in Å) of O_2 on OG–Pt_3M. The left three columns show O_2 adsorbed as di-oxygen species, while the two structures on the right are the O adatoms on supported Pt_3Ti and Pt_3V. Red, dark blue, and grey spheres represent O, Pt, and C, respectively. The color of M is different and depends on the element.

In addition to the di-oxygen form of adsorption, dissociative adsorption of O_2 occurred on OG–Pt_3Ti and OG–Pt_3V, resulting in two O adatoms with O–O distances of 4.35 Å and 4.32 Å, respectively (shown in Figure 2). The dissociative adsorption was more stable than the di-oxygen state, by 1.61 eV for Pt_3Ti and 2.65 eV for Pt_3V. Based on Bader charge analysis, the Ti and V atoms in clusters had the highest positive charges among the 3d transition metals, with values of 2.13 $|e|$ and 1.70 $|e|$, respectively. The oxygen atoms bound to the Ti and V atoms were more negatively charged than the oxygen adatom on Pt_1, indicating that the oxygen atoms in the adsorbed di-oxygen state were strongly polarized by the large difference of electron distribution between Ti/V and Pt_1. As a result, the dissociative adsorption of oxygen was more stable than the di-oxygen state on Pt_3Ti and Pt_3V, which also hindered the following H_2O formation and release. In contrast, the charge difference between the two adsorbed oxygen atoms in the di-oxygen form on other Pt_3M clusters fell in a small range of 0.07~0.17 $|e|$, and consequently, the adsorbed di-oxygen species was more stable. In order to compare the ORR activity on these supported Pt_3M, we chose the di-oxygen species as the reference.

The reduction of adsorbed di-oxygen species occurs by adding a hydrogen atom either on the top O atom on Pt_1 or the interfacial O atom on M. On Pt(111), ORR was believed to proceed via the OOH* intermediate [39,40,43]. However, a stable OOH* intermediate was not isolated on any of the OG–Pt_3M catalysts. Upon hydrogenation, the di-oxygen species dissociates into co-adsorbed O* and OH* species on all Pt_3M. For the early transition metals (M = Ti, V, and Cr), protonation of the top O of

the di-oxygen species leads to more stable $OH_{(t)}*$ and $O*$, while for the late transition metals (M = Mn, Fe, Co, and Ni), the formation of $OH_{(b)}*$ with the interfacial O atom and leaving the top O as $O*$ is more stable (suffix "t" and "b" correspond to the species on the top Pt_1 atom and the interfacial M (or Pt_0) atom, respectively).

Further reduction after either $OH_{(t)}*$ or $OH_{(b)}*$ formation may follow two pathways, as shown in Scheme 1. The calculated reaction free energy for every elementary step indicates that protonating two $O*$s to form two $OH*$s is more preferable than hydrogenating one $O*$ completely to H_2O* before hydrogenating the other $O*$. Further reducing the $OH*$ species will produce H_2O*, which will desorb and liberate the active sites for the continued O_2 adsorption and reduction (see Tables S2 and S3 for details). The step with the most positive reaction free energy is the hydrogenation of the $OH*$ species, which is likely to be the potential-limiting step. Between $OH_{(t)}*$ and $OH_{(b)}*$, the reduction of $OH_{(b)}*$ has a lower reaction free energy and is more favorable than reducing the $OH_{(t)}*$. In Scheme 1, the most favorable pathway is shown in bold black.
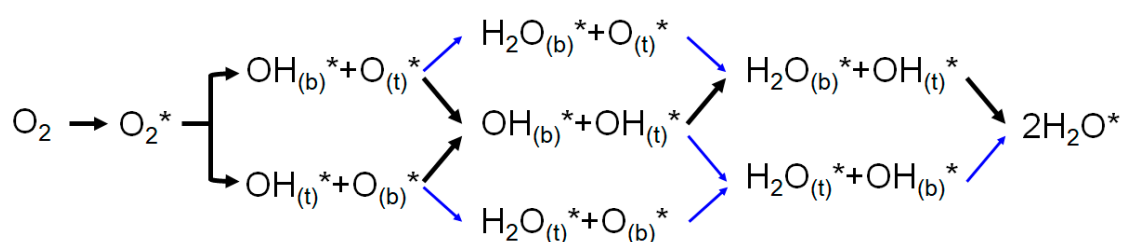
Scheme 1. Reaction pathways of the oxygen reduction reaction (ORR). Labels "b" or "t" correspond to the species on the interfacial M (or Pt_0) atom or the top Pt_1 atom. The pathway following the bold black arrows is the thermodynamically more favorable one.

To compare the reaction on different $OG–Pt_3M$ catalysts, the free energy profiles for ORR through the interfacial site at 0 and 0.85 V (SHE) were constructed on the basis of the DFT results (see details in Figures S2 and S3). Compared with the results on $OG–Pt_4$, the adsorption of O_2 was strengthened on Pt_3M with M = Sc, Ti, V, and Cr. On Pt_3M with M = Mn, Fe, Co, and Ni, the O_2 adsorption energy became 0.1~0.4 eV smaller than that on Pt_4. These results are consistent with previous studies [37,44]. Figure 3 shows a comparison of the free energy profiles of ORR on $OG–Pt_4$, $OG–Pt_3Ti$, and $OG–Pt_3Ni$. Obviously, oxygen bound much stronger on Pt_3Ti than on Pt_4: the binding energy on the supported Pt_3Ti was increased by 0.71 eV, resulting in a highly stable $OH*$ species, which is difficult to hydrogenate to H_2O. In the case of Pt_3Ni, the adsorption energy of oxygen was decreased by 0.4 eV from that of Pt_4. By applying a potential of 0.85 V (SHE), the reduction of $OH*$ to form H_2O* on Pt_3Ni became less endothermic than Pt_4. In addition, the desorption of H_2O* became easier than that on Pt_4, indicating an enhanced ORR activity on Pt_3Ni.
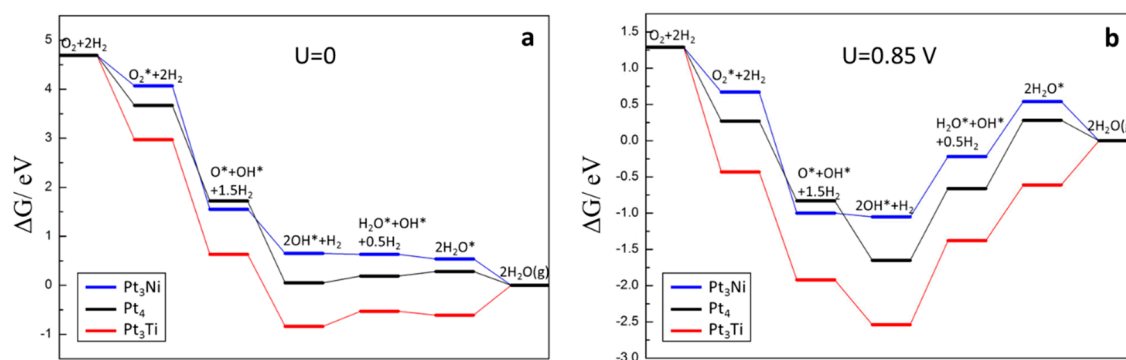

Figure 3. Free energy profiles of ORR on OG-supported Pt_4 (black line), Pt_3Ti (red line), and Pt_3Ni (blue line) clusters at 0 V (**a**) and 0.85 V (**b**) with respect to the standard hydrogen electrode (SHE).

2.3. Correlation of the ORR Activity with the Oxygen Binding Energy Difference

To design an electrocatalyst with improved ORR activity, understanding the relationship between the activity and atomic/electronic structures of the catalyst is important [1,37,45]. On transition metal- and/or metal alloy-based catalysts, the linear relationship between the ORR activity and the d-band center of those electrocatalysts has been established [13,20,37,46,47]. The oxygen binding energy (ΔE_O) has been used as a descriptor for the ORR activity on the transition metal and even on non-metallic surfaces [1,39,48,49]. In fact, the ΔE_O descriptor can be considered an extension and application of the d-band center model in electrocatalysis, as the adsorption/binding energy of oxygen has been shown to correlate with the d states of the surface atoms to which the atom/molecule binds [13,37]. Generally, an upward shift of the d-band center to Fermi level results in a stronger binding [13,17,24]. However, both the d-band center model and the oxygen-binding energy descriptor have limitations [14,50,51]. For example, Lin et al. reported that the ORR activity of the Pt-cored alloy (Pt@M, M = Co, Cu, Pd, and Au) catalysts does not correlate well with the d-band center of surface Pt [17]. Yu et al. showed that the binding energies of O do not always correlate with those of OH [52].

To understand the performance difference of the Pt_3M alloy catalysts in the present study, we plotted the average adsorption energy of di-oxygen species ($1/2 \Delta E_{O2}$) on the $OG–Pt_3M$ as a function of the d-band center (ε_d) of the cluster atoms (as shown in Figure S4) and found a very weak linear correlation. In fact, the present results indicate that a higher d-band center in the clusters involving late transition metals (M = Mn, Fe, Co, and Ni) corresponds to a lower oxygen adsorption energy. Previous reports showed that the adsorption energy of O* had a strong correlation with the adsorption energy of OH* [53–55]. Herein, we evaluated the possible correlation between the adsorption energies of O* and OH* on the interfacial sites of the supported Pt_3M (seen in Figure S5) and also found a rather weak linear correlation, demonstrating that neither ΔE_O nor ε_d is a good descriptor of the ORR activity of the $OG–Pt_3M$.

Charge redistribution is expected to occur upon formation of the O* and OH* species. We analyzed the Bader charge of the interfacial M sites (q(M)) upon forming the O* and OH* adsorbates, as well as the those of the OH* and O* (q(O)) on different alloy clusters. As shown in Figure 4a, there was quite a good linear correlation between q(M) and the charges on OH_b* and O_b*. The slope of the lines is ~1.06, indicating a similar electron transfer from M to OH_b* and O_b*. In the 3d transition metal series, the late transition metals (including Ni, Co, Fe, and Mn) transferred fewer electronic charges to the adsorbates than the early transition metals and resulted in a relatively weaker binding of O*.

From Figure 4b, the positive charges on the interfacial M site generally increased by following the order of the 3d elements in the periodic table from right to left, with the exception of Sc upon O* formation. In $OG–Pt_3Sc$, the positive charge on Sc with adsorbed O_b* was even smaller than that on Cr in Pt_3Cr. We also plotted the adsorption energy of O_b* ($\Delta E(O_b)$) against q(M) of O_b* (seen in Figure S6) and found no strong correlation between the two.

Since the O_2 molecule prefers to form a di-oxygen species on the bridge sites of the top Pt_1 and interfacial M (or Pt_0) atoms, both sites were expected to contribute to the ORR activity. Therefore, we needed a descriptor that takes into the contribution of both sites to account for the observed ORR activity. Herein, we used the adsorption energy difference between the interfacial oxygen adatom O_b* and the top oxygen adatom O_t* species (ΔE_{Ob-Ot}) to characterize the clusters and plotted the adsorption energy difference on each $OG–Pt_3M$ as a function of q(M) of O_b* in Figure 4c. As shown in the figure, there was a reasonable correlation between the two ($R^2 = 0.64$). The correlations shown in Figure 4 are useful to understand the observed ORR activity, although they cannot be used as a descriptor to predict superior ORR catalysts.
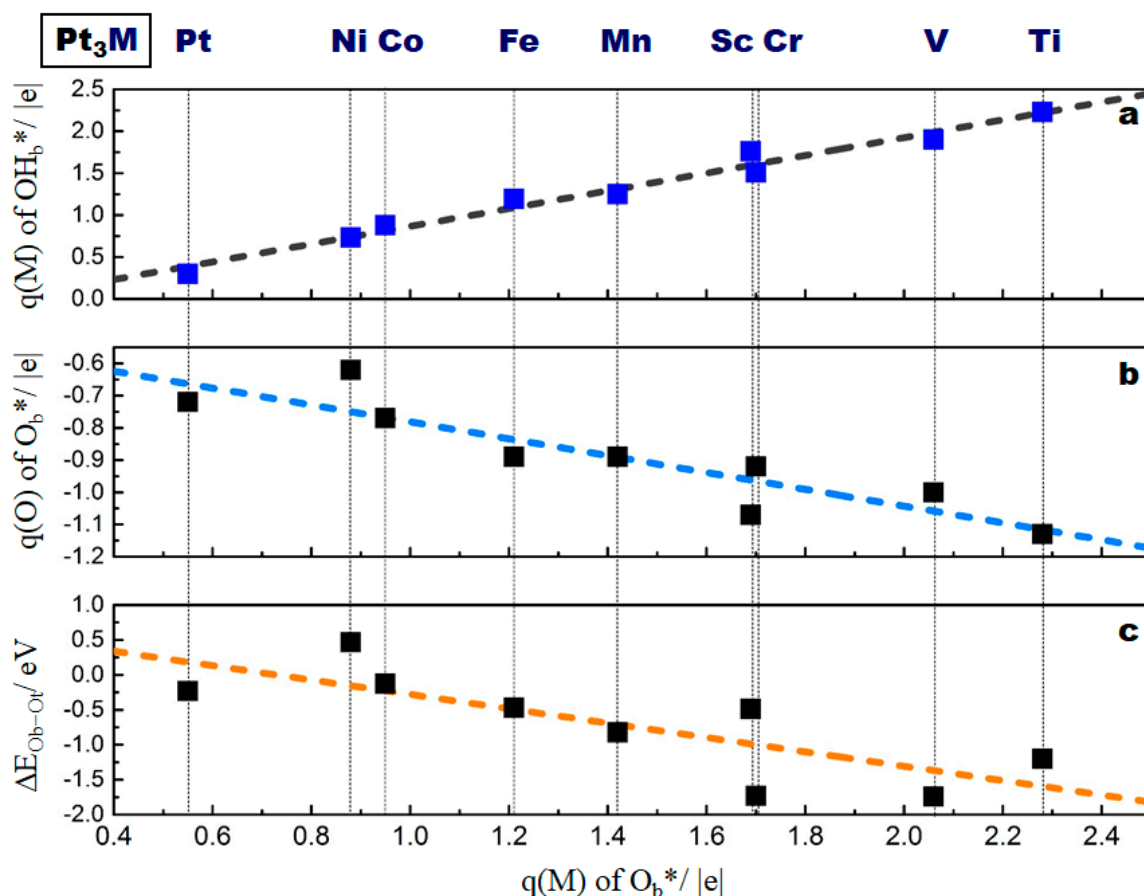
Figure 4. The Bader charges on the (**a**) OH* intermediate, (**b**) O_b* adatoms, and (**c**) the adsorption energy difference between O_b* and O_t* as a function of the charge changes of interfacial M sites. The vertical dash line indicates the location of the Bader charge values of the corresponding element.

Both the O* and OH* species are important intermediates for ORR, and their stability will have a strong influence on the overall reaction activity. However, the adsorption energy of individual OH* and O* only shows a weak linear relationship on the single interfacial site. As the adsorption energy difference of $\Delta E_{Ob\text{-}Ot}$ presents a good correlation with the charge changes of cluster, we investigated the adsorption energy difference of OH* species adsorbed on the interfacial and top sites ($\Delta E_{OHb\text{-}OHt}$). The correlation between $\Delta E_{OHb\text{-}OHt}$ and $\Delta E_{Ob\text{-}Ot}$ is shown in Figure 5a. Following the increased energy difference of O*, O* adsorbed on the interfacial site became less stable, resulting in a similar trend to that of the OH* species. Compared to pure Pt_4, Pt_3Ni and Pt_3Co showed weaker binding toward the O* and OH* at the interfacial site. All the other Pt_3Ms exhibited stronger binding toward O* at the interfacial M site. Therefore, the adsorption energy difference between the top Pt site and the interfacial M site provides a good indicator of the alloying effect on the ORR reactivity.

In Figure 5b, the reaction free energy of the potential limiting step was plotted as a function of the adsorption energy difference of O* on top and interfacial sites. Again, a good correlation ($R^2 = 0.81$) was obtained. In general, a higher positive adsorption energy difference corresponds to a lower reaction-free energy, and therefore, a higher activity. If the OG–Pt_4 is chosen as a reference, both Pt_3Fe and Pt_3Ni have smaller reaction free energies, indicating a better ORR performance than Pt_4. Among all the OG–Pt_3Ms, Ni exhibited the largest decrease in the reaction free energy, and thereby, the limiting potential. Consequently, OG–Pt_3Ni is the best catalyst among all OG–Pt_3Ms. This conclusion is supported by the free energy profiles (Figures S2 and S3). The limiting potential for ORR on OG–Pt_3Ni was reduced to 0.83 V from 1.00 V on OG–Pt_4.
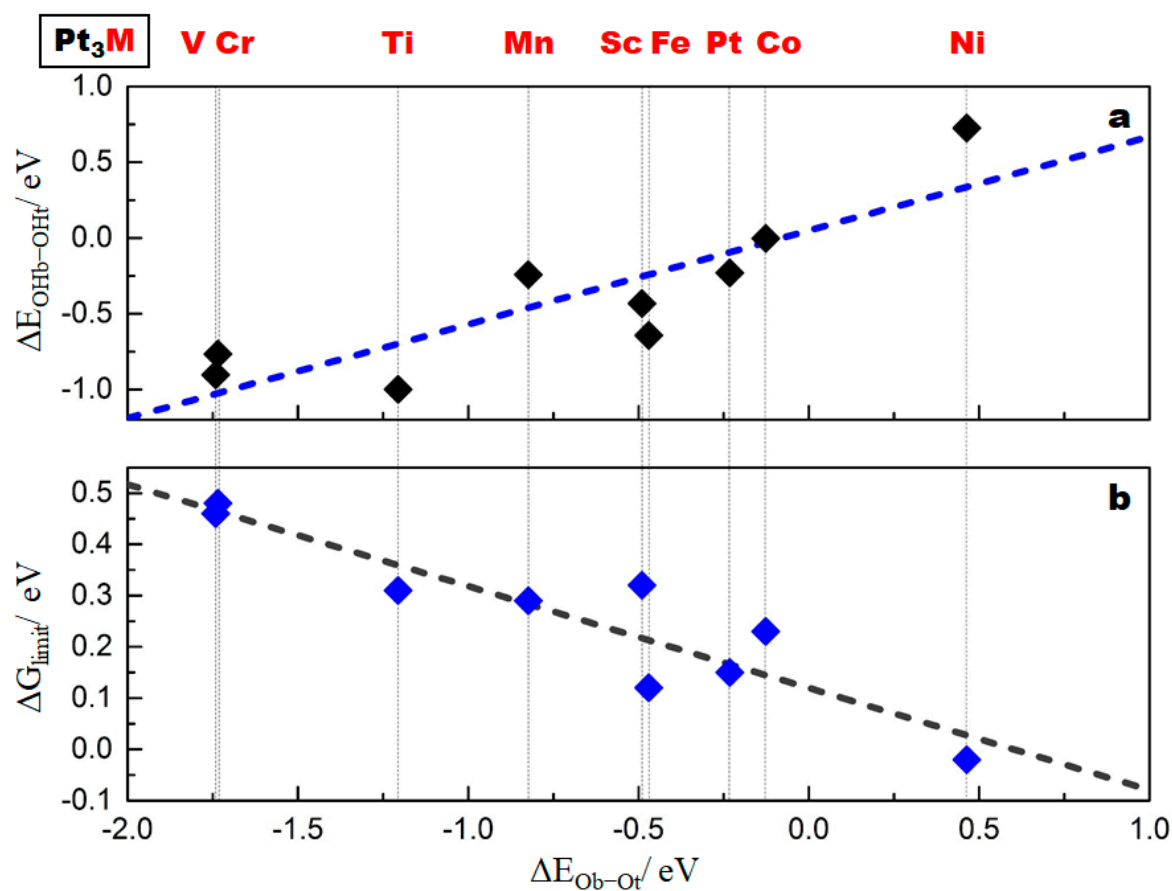
Figure 5. The correlations of (**a**) the adsorption energy difference between OH* species adsorbed on the interfacial and top sites ($\Delta E_{OHb\text{-}OHt}$), and (**b**) the free energy change for the rate limiting step (ΔG_{limit}) of ORR to the oxygen adsorption energy difference of both sites ($\Delta E_{Ob\text{-}Ot}$).

The present analysis demonstrated that oxygen adsorption energy alone is not effective in predicting ORR reactivity. For the alloy catalysts, the adsorption of the ORR intermediates on different metal sites should be taken into account when both metals participate in the reaction. On the OG–Pt_3M catalysts, $\Delta E_{Ob\text{-}Ot}$ provides a more effective indicator of the ORR activity. In reactions involving sites of different metals, the adsorption energy difference between the alloying metals would provide a more complete description of the ORR activity.

3. Model and Computational Details

Spin unrestricted DFT calculations were performed using the Vienna ab initio simulations program (VASP), with the projector augmented wave method [56–58]. In short, the Perdew–Burke–Ernzerhof functional [59] and a cutoff energy of 400 eV for the plane wave basis set were used in the calculations. The same oxygen-doped graphene supercell of 12.30 × 17.04 Å with a vacuum of 20 Å as that used in our previous work was employed in the present study [36], and the same 3 × 2 × 1 k-point grid and convergence criteria were used in the present study.

The binding energy (E_b) of metal clusters (Pt_3M) on the OG support was calculated as $E_b = E_{OG\text{-}Pt3M} - (E_{OG} + E_{Pt3M})$, with $E_{OG\text{-}Pt3M}$, E_{OG}, and E_{Pt3M} being the total energies of the OG with supported metal cluster, isolated OG sheet, and metal cluster, respectively. The adsorption energies of O_2 on the supported metal clusters were calculated with respect to the gas-phase O_2 molecules. The Gibbs free energy change (ΔG) of the elementary reactions was used to identify the most favorable oxygen reduction reaction pathway. The free energies of every intermediate along the reaction pathways were calculated based on the computational hydrogen electrode (CHE) model proposed by Nørskov

et al. [53,60,61]. The reference potential was set to the standard hydrogen electrode (SHE), i.e., the free energy of ($H^+ + e^-$) equaled half of the chemical potential of a gas-phase H_2 at 0 V under the standard conditions of pH = 0 and the pressure of H_2 was 1 bar. The free energy change for each elementary step was determined as $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U$, where ΔE corresponds to the reaction energy calculated using DFT. ΔZPE and $-T\Delta S$ are the corrections due to zero-point energy (ZPE) and entropy (S) at 300 K. Both ZPE and S were calculated based on the harmonic vibrational frequencies. Adding $\Delta G_U = -eU$, where e is the unit positive charge and U is the electrode potential with respect to SHE, will allow the external potential to modulate the chemical potential change of an elementary step. The entropic contribution of gas-phase molecules was taken from the National Institute of Standards and Technology database [62].

Bader charge analysis was conducted for every OG-supported Pt_3M (OG–Pt_3M) catalyst [63,64]. The d-band centers (ε_d) of Pt atoms in the cluster were calculated based on the follow equation:

$$\varepsilon_d = \frac{\int_{-\infty}^{\epsilon_F} \rho \cdot E \, d\epsilon}{\int_{-\infty}^{\epsilon_F} \rho \, d\epsilon}$$

in which ρ, *E,* and ϵ_F represent the density of electronic states, the energy of electron, and Fermi energy, respectively [50,65]. The reaction free energy of an elementary step refers to the Gibbs free energy difference of reactant and product. The kinetic barrier originating from the non-electrochemical activation of the reactant was not considered in the present study. The barriers associated with the electron and proton transfer were believed to be small and were also not considered in the present study [66].

4. Conclusions

We performed a DFT computational study on the mechanism and activity of O-doped graphene-supported Pt_4 and Pt_3M (M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) catalysts toward oxygen reduction reactions. Co-adsorbed H_2O^* and O^* species are highly unlikely and water formation is the potential limiting step on the supported Pt_3M catalysts.

The late transition metal alloyed clusters (M = Mn, Fe, Co, and Ni), especially Pt_3Co and Pt_3Ni, bound the oxygen intermediates weaker than Pt_4 and would have a better ORR activity. On the other hand, alloying with an early transition metal atom (M = Sc, Ti, V, and Cr) increased the binding energy of the oxygen intermediates, thereby hindering the oxygen reduction process. Among the systems examined, OG–Pt_3Ni lowered the adsorption energies of O and OH the most and was the best catalyst for ORR. The present study demonstrated that the oxygen adsorption energy alone may not be a good predictor of the ORR activity. Instead, the oxygen adsorption energy difference on the ensemble of the active sites (ΔE_{Ob-Ot}) is an effective indicator of the ORR activity.

Author Contributions: C.C. and M.S. performed the calculations and drafted the manuscript; X.Z. and J.H. helped to collect and analyze the data; H.W. and Q.G. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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