DFT Studies of $Pt_8V_4Fe_{14}$ Nanoparticles and the O_2 Adsorption

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Abstract

The ability to produce cheap and efficient catalysts for oxygen reduction is essential for cost reduction in fuel cells. This work reports the density functional theory (DFT) results of the investigation of ~1 nm trimetallic nanocatalysts of 26 atoms with a composition of $Pt_8V_4Fe_{14}$. The relative stability of ~50 $Pt_8V_4Fe_{14}$ nanoparticles (NPs) were analyzed to conclude that the most stable NPs had vanadium atoms located at the center of the NP with scattered platinum atoms attached to them from the outside. Adsorption of O_2 on the most stable nanocatalyst was also analyzed at 14 various adsorption sites; it was determined that oxygen preferred to bond to vanadium and iron atoms located at the surface of the NP. Compared to the small sub-nanometer PtVFe clusters of the same composition, the O_2 adsorption strength is slightly decreased on the ~1nm PtVFe NPs. These findings provided important insights into the effectiveness of PtVFe nanocatalysts towards oxygen reduction.

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1. Introduction

Proton Exchange Membrane Fuel Cells (PEMFC) have become increasingly used in industry as well as in commercialized products due to their hydrogen utilization which offers high conversion efficiency, low pollution, light weight, and high power density.[1] One of the crucial limitations for reducing the cost of these fuel cells comes from the high price of platinum based catalysts which account for ~30% of the cost of fuel cell manufacturing.[2] Various bimetallic, trimetallic, and conducting polymers have been tested in order to develop more active, robust, and low-cost catalysts to replace Pt in the cathode for the oxygen reduction reaction (ORR).[3-24] Many nanoparticles, such as Pt,[25-35] Au,[36-39] Pd,[40,41] Cu,[42-54] Ag,[55-57] Ir,[58-60] Ru,[61] and alloys[62-77] including trimetallic nanocatalysts,[5,78-91] have been extensively studied for the catalytic activities on a number of reactions. In addition to ORR, these nanocatalysts play important roles in hydrogen production from steam reforming of nature gas[92-112] or renewable ethanol[113-128] as well as ethanol oxidation[129-137] in ethanol fuel cells.

Trimetallic platinum-vanadium-iron (PtVFe) prepared by nanoengineered synthesis and processing methods were shown to exhibit excellent electrocatalytic activities for ORR in earlier studies[138-142] and recently in PEMFCs.[143,144] Our previous density function theory (DFT) studies focused on the PtVFe clusters of less than 0.5 nm.[145] As PtVFe NPs in ORR experiments[85] were in nanometer scale, it is important to extend the size of computational studies to bigger sizes. Therefore, this work was carried out by studying PtVFe nanoclusters made up of 26 atoms that have the same composition as the 13 atom clusters of $Pt_4V_2Fe_7$ (0.6-nm).[145] In addition, the structures of these NPs were analyzed to determine whether a face-centered cubic (FCC) or a body-centered cubic (BCC) structure was preferred. Oxygen adsorption was also calculated to simulate spontaneous reduction of O_2 and thus determine the efficiency of the composed NPs.

2. Computational Details

In this research, the DFT calculations were carried out using the Vienna Ab-initio Simulation Package (VASP). The electron-ion interaction was described by Projector Augmented Waves (PAW) and the exchange-correlation interaction was described by the Perdew-Burke-Ernzerhof (PBE) functional. Cut-off energies for the plane wave basis set were 300eV in the studies of NPs and 400eV for adsorption calculations. An 18 x 18 x 18 Å unit cell was used in the calculations. The cutoff energies and the size of unit cell were tested for convergence of results. Other convergence criteria were the same as the previous DFT calculations.[145] The binding energies per atom of the $Pt_8V_4Fe_{14}$ NPs were calculated using the following formula:

$$E = - (E_{PtVFe} - 8* E_{Pt} - 4* E_V - 14* E_{Fe}) / 26, \quad (1)$$

where E_{PtVFe}, E_{Pt}, E_V, and E_{Fe} are the energy of PtVFe NP, energy of a single Pt, energy of a single V, and energy of a single Fe, respectively. The O_2 adsorption energies were calculated using:

$$\Delta E = - (E_{adsorption} - E_{O2} - E_{PtVFe}), \quad (2)$$

where $E_{adsorption}$ and E_{O2} are the energy of adsorption complex and energy of isolated O_2, respectively.

We also calculated two NPs of Fe 26-atom and their binding energies per atom were calculated using:

$$E = - (E_{Fe26} - 26* E_{Fe}) / 26. \quad (3)$$

3. Results and Discussion

In order to gain a more accurate picture and understanding of PtVFe nanocatalysts for ORR, this research extended previous DFT studies of sub-nanometer clusters to ~1nm. Specifically, we performed calculations on $Pt_8V_4Fe_{14}$ NPs. The starting structure was made from bulk FCC and BCC and cut down to 26 atoms. These initial structures were chosen due to its relative symmetry and overall spherical shape. All calculations of the various $Pt_8V_4Fe_{14}$ NPs (48 overall) retain the same composition of atoms, starting structures, and methods of calculation to minimize the variables. Each different arrangement of atoms was studied in FCC and BCC initial format. In Table 1, the NPs are presented in decreasing stability together with the initial configuration (fcc or bcc), the binding energy, the number of unpaired electrons, the energy of the HOMO (highest occupied molecular orbital), and HOMO-LUMO (lowest unoccupied molecular orbital) energy gap, and the Fermi energy.

Table 1. The properties of $Pt_8V_4Fe_{14}$ nanoparticles obtained from DFT calculations.

NP	Initial configuration	Binding energy (eV/atom)	Unpaired electrons	HOMO (eV)	HOMO-LUMO gap (eV)	Fermi energy (eV)
1	fcc	4.16	36	-3.55	0.18	-3.48
2	fcc	4.14	16	-3.47	0.17	-3.41
3	bcc	4.13	36	-3.45	0.14	-3.42
4	bcc	4.13	28	-3.50	0.19	-3.42
5	bcc	4.12	36	-3.49	0.15	-3.45
6	bcc	4.12	34	-3.52	0.18	-3.47
7	fcc	4.12	32	-3.49	0.23	-3.44
8	fcc	4.12	32	-3.37	0.25	-3.31
9	bcc	4.11	28	-3.47	0.16	-3.41
10	bcc	4.10	32	-3.51	0.09	-3.46
11	bcc	4.10	34	-3.52	0.20	-3.46
12	bcc	4.10	34	-3.43	0.12	-3.40
13	bcc	4.10	32	-3.42	0.11	-3.37
14	bcc	4.10	34	-3.48	0.07	-3.44

15	bcc	4.10	30	-3.43	0.11	-3.37
16	fcc	4.09	34	-3.46	0.23	-3.40
17	fcc	4.09	36	-3.55	0.15	-3.50
18	fcc	4.09	30	-3.40	0.12	-3.35
19	fcc	4.09	30	-3.45	0.11	-3.40
20	fcc	4.09	32	-3.48	0.17	-3.43
21	bcc	4.08	22	-3.47	0.11	-3.42
22	fcc	4.07	24	-3.58	0.18	-3.52
23	fcc	4.07	32	-3.53	0.14	-3.48
24	bcc	4.07	32	-3.40	0.17	-3.35
25	bcc	4.07	33	-3.42	0.25	-3.43
26	bcc	4.06	20	-3.53	0.16	-3.47
27	bcc	4.06	20	-3.39	0.19	-3.36
28	fcc	4.06	30	-3.43	0.17	-3.36
29	bcc	4.06	30	-3.46	0.15	-3.40
30	fcc	4.06	26	-3.52	0.26	-3.49
31	fcc	4.06	34	-3.45	0.05	-3.42
32	fcc	4.05	34	-3.60	0.31	-3.55
33	fcc	4.05	32	-3.53	0.23	-3.47
34	bcc	4.04	27	-3.46	0.31	-3.46
35	bcc	4.04	32	-3.39	0.10	-3.34
36	fcc	4.04	30	-3.38	0.07	-3.35
37	bcc	4.03	10	-3.50	0.25	-3.44
38	fcc	4.03	34	-3.66	0.06	-3.63
39	fcc	4.03	29	-3.38	0.19	-3.39
40	bcc	4.02	24	-3.40	0.04	-3.38
41	fcc	4.02	34	-3.42	0.15	-3.36
42	fcc	4.02	34	-3.58	0.31	-3.52
43	fcc	4.02	28	-3.43	0.10	-3.38
44	fcc	3.99	22	-3.53	0.12	-3.49
45	bcc Fe	3.42	74	-3.19	0.15	-3.13
46	fcc Fe	3.35	50	-3.20	0.13	-3.15

We note that the last two NPs are pure Fe NP. To help the comparison of the different energies of all NPs, we plotted in Fig. 1 the binding energies per atom of the various PtVFe NPs presented in Table 1.

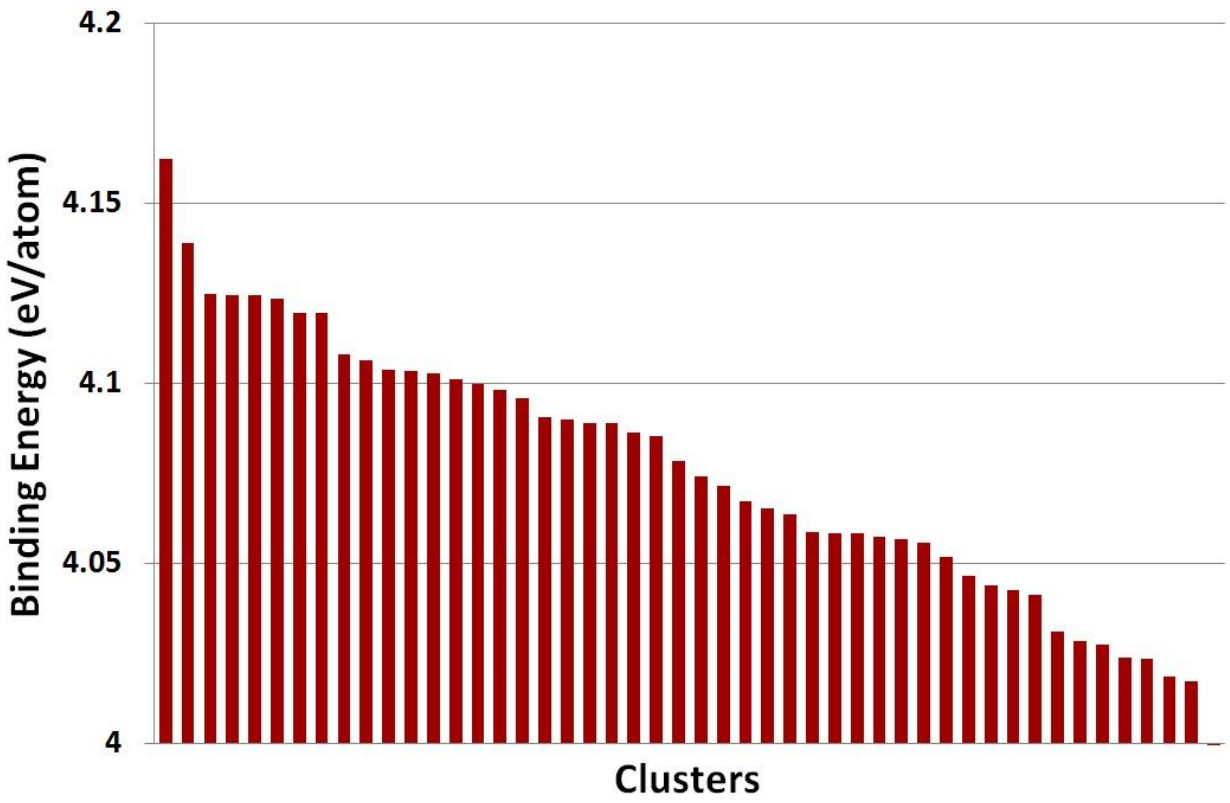

Figure 1. The binding energies of the $Pt_8V_4Fe_{14}$ NPs

Structures of the various PtVFe clusters in Table 1are depicted in Fig. 2 along with their structure number, initial and relaxed structures. The NPs are sorted in descending energies per atom in two columns.

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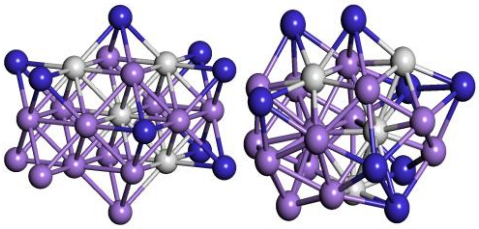

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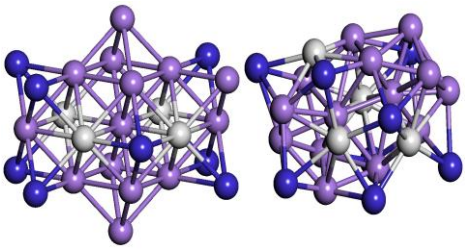

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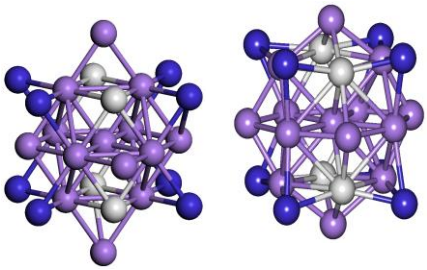

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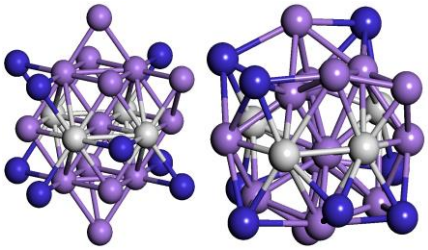

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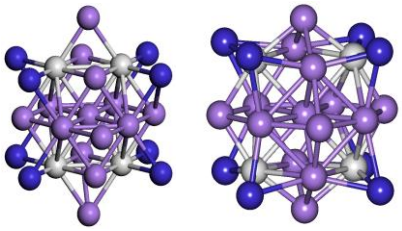

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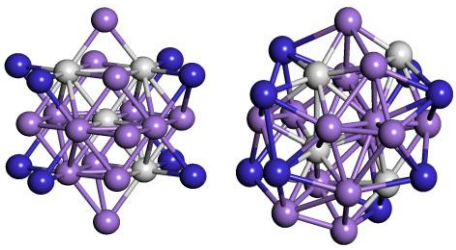

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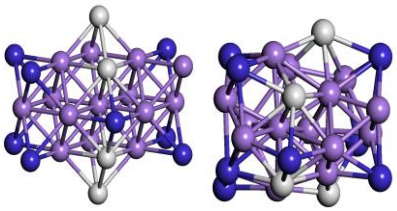

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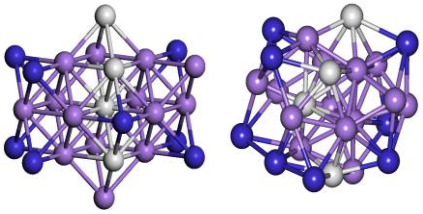

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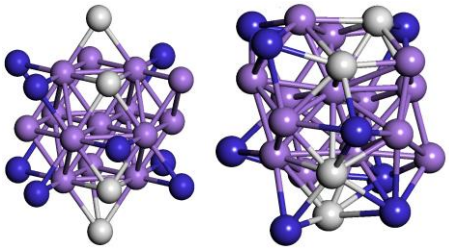

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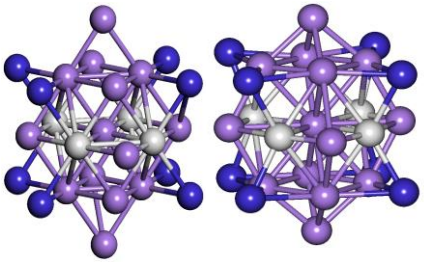

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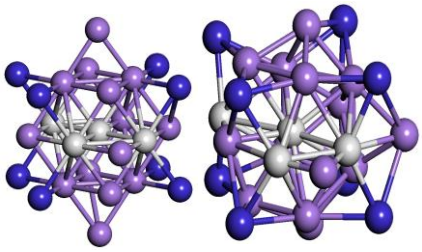

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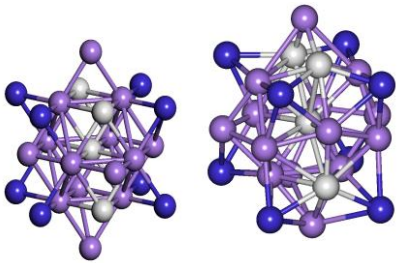
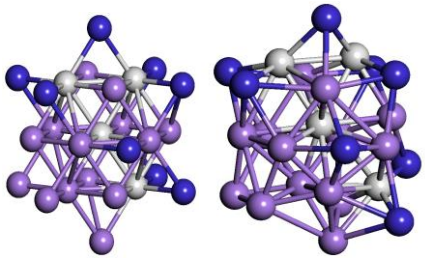
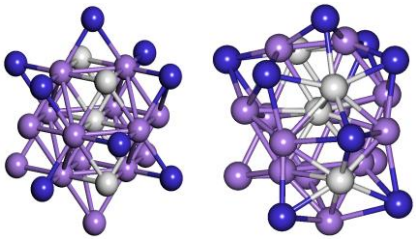
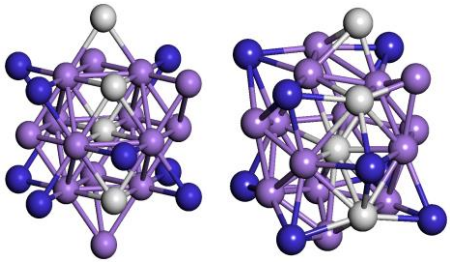
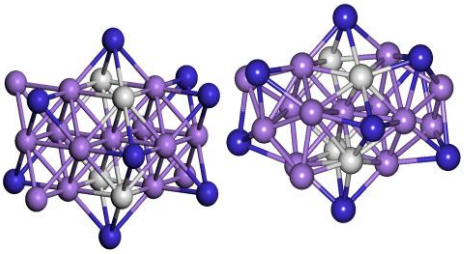
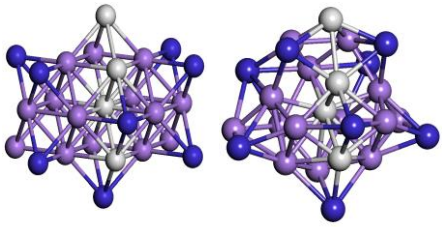


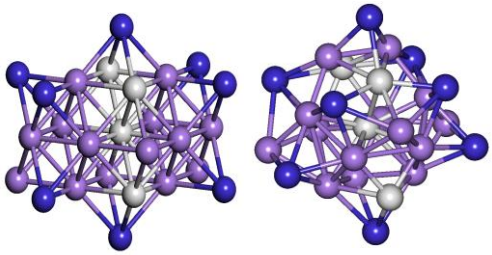
13 

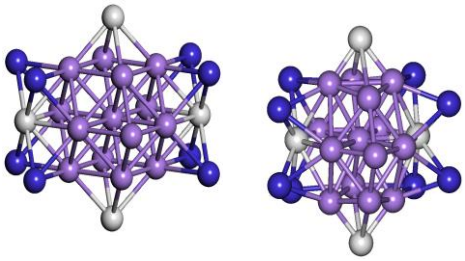
14 

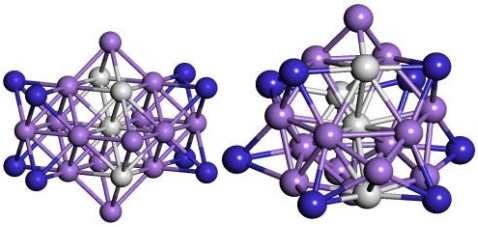
15 

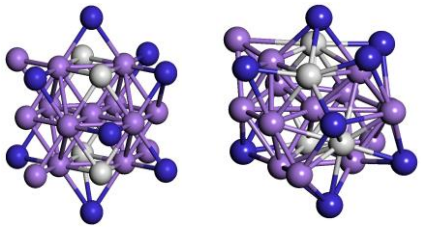
16 

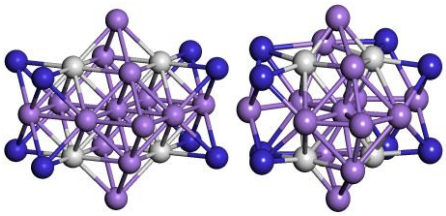
17 

18 

19 

20 

21 

22 

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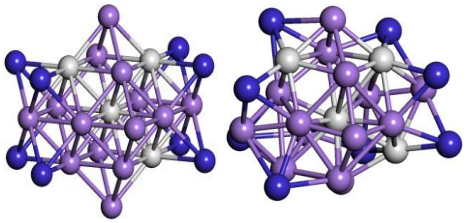

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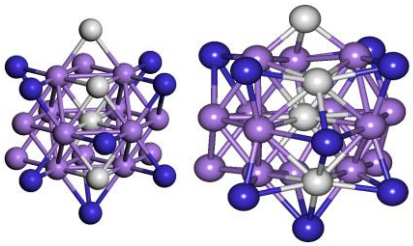

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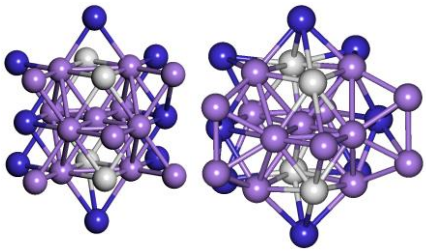

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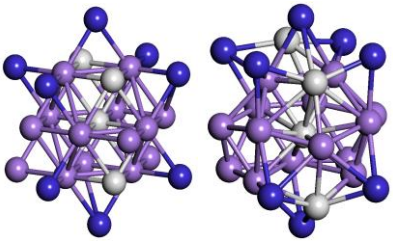

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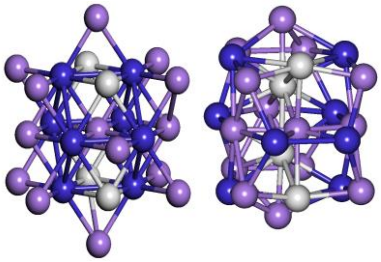

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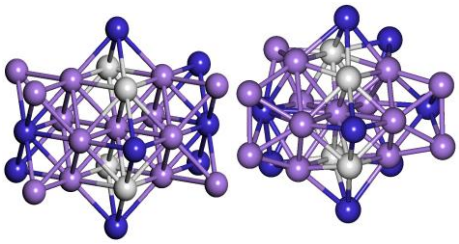

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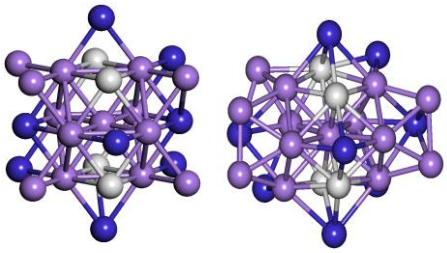

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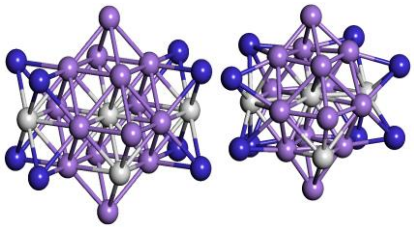

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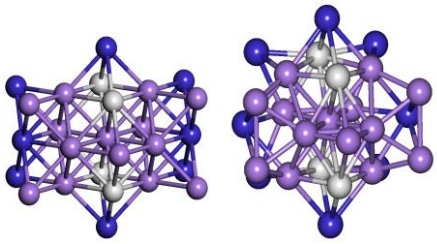

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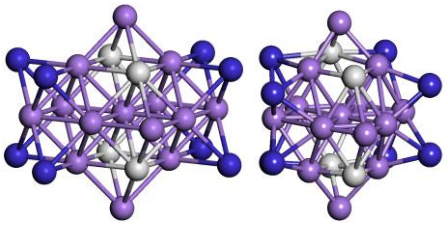

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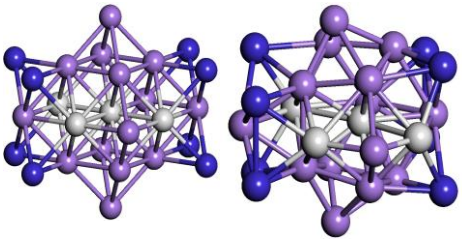

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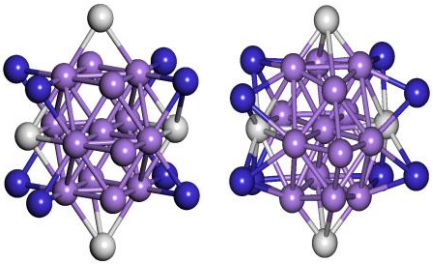

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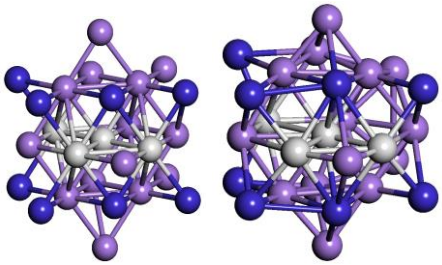

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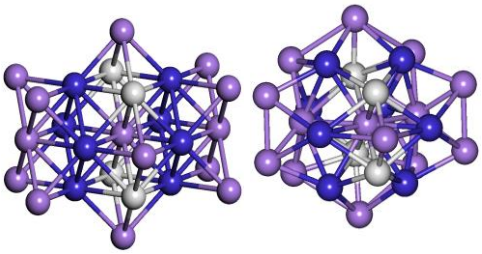

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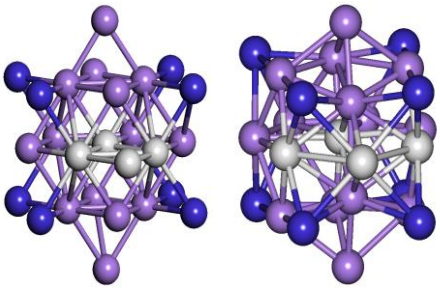

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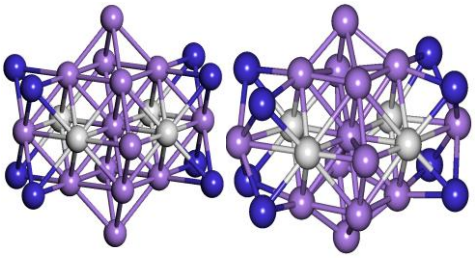

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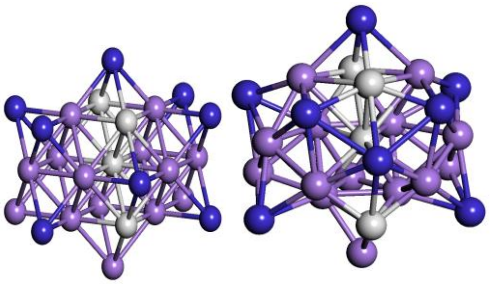

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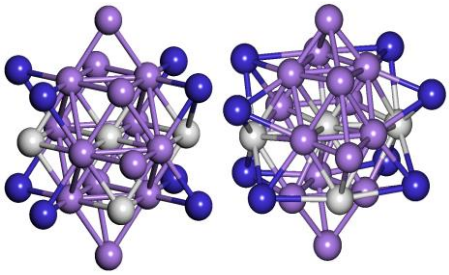

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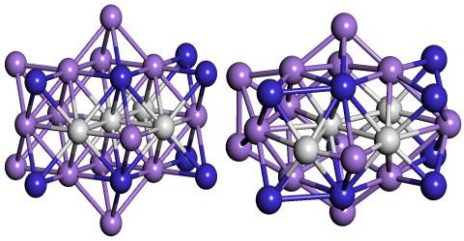

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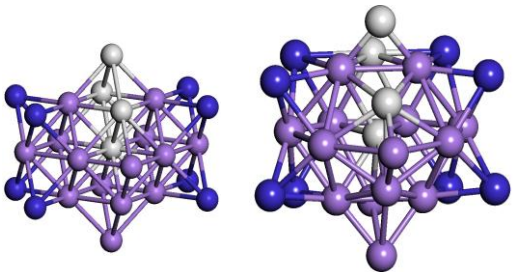


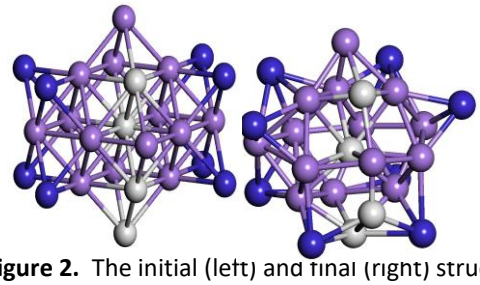
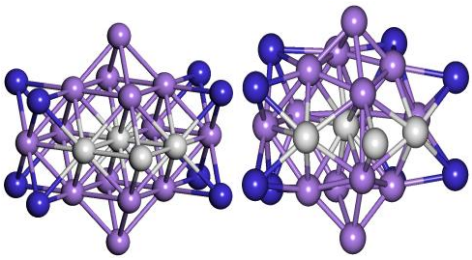
43  44 

Figure 2. The initial (left) and final (right) structures of the $Pt_8V_4Fe_{14}$ NPs. Blue, white, and purple balls denote Pt, V, Fe, respectively.

The top five NPs (number **1**-**5**) indicate how vanadium prefers to be placed in the center of the cluster with Pt attached to it on the outside. However, the vanadium is relatively spread out inside the cluster. It does not segregate to any side of the cluster. Nanoparticle **19** and **34** had vanadium placed on the outside of the cluster, but their binding energies were relatively less stable. In another calculation, platinum was placed in the middle (**27** and **36**), and also yielded weaker binding energies. Vanadium did not prefer to stay segregated in the NP as indicated by NPs **35**, **37**, **41**, **42**, and **44**. In fact, NP **44** gave the weakest binding energy overall. Nanoparticle **1** gave the strongest binding energy and thus was used in the oxygen adsorption calculations. We note that the number of unpaired electrons in the NPs shown in Table 1 are substantial, which may contribute to their catalytic activities.

To analyze whether platinum would prefer to stay segregated on one side during synthesis of a PtVFe NP, the relaxed structure (**20**) was re-drawn with platinum on one side and allowed to relax as illustrated in Fig. 3. The binding energy per atom was reduced when the platinum was segregated on one side, indicating that platinum does prefer to be dispersed on the outside of the cluster.

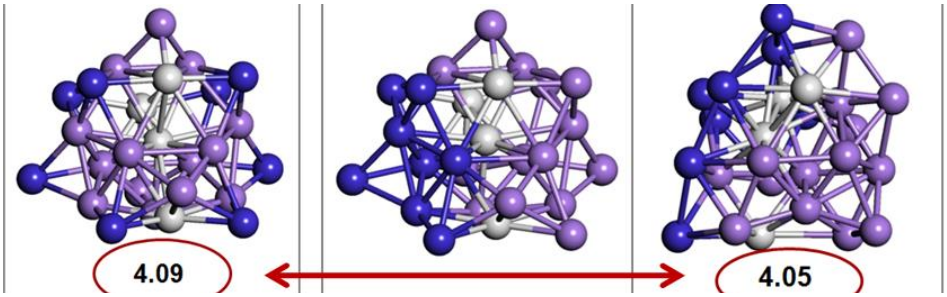


Figure 3. Pt homogeneity on a NP. Blue, white, and purple balls denote Pt, V, Fe, respectively.

Pure NPs of iron were analyzed to determine whether an FCC or BCC structure was favorable. The relaxed structures are shown in Fig. 4. Iron prefers BCC structure in bulk form, but out 26 atom clusters indicated that the shape was actually a hybridization of BCC and FCC. The bond distances were not as clear cut as on a bulk structure. Introduction of other elements has the similar effect as introduction a built-in field[146,147] or of ligands in single atom catalysis[148-153] to facilitate different reactions. Formation of nanoparticles and the reaction dynamics on these nanoparticles including quantum effect[154-156] will be interesting future research.

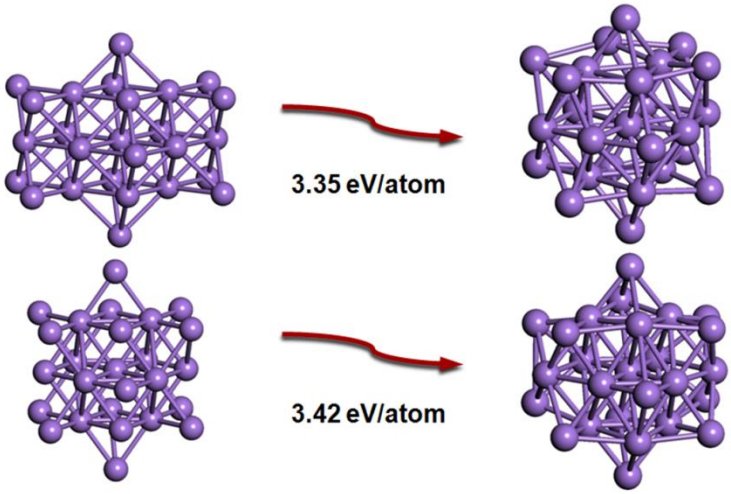
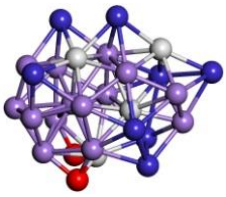
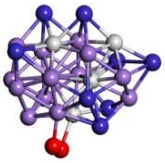
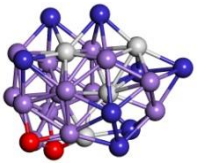
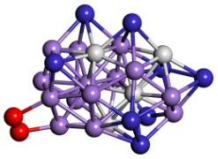
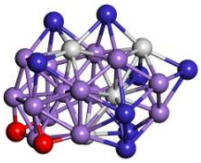
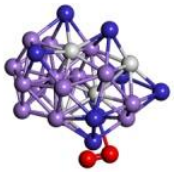
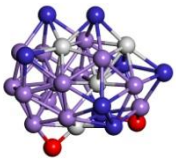
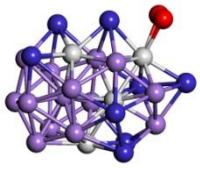
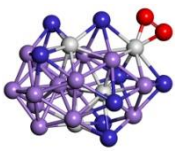


Figure 4. The initial (left) and final structures of pure Fe NPs of 26 atoms.

Oxygen adsorption was performed on NP **1** since it is the most stable NP. Diatomic oxygen was placed in proximity to the NP at various places and initial formations to determine

the effectiveness of $Pt_8V_4Fe_{14}$ as a catalyst. Resulting clusters where oxygen bonded too strongly with the PtVFe structure present a problem since the oxygen has to separate from the cluster eventually to undergo reduction in the fuel cell. However, when attached to platinum, the oxygen was relatively loose (farther away) from the structure indicating efficient ORR. Overall, fourteen oxygen adsorptions were calculated. Figure 5 includes the adsorption energy in eV, initial structure, and final structure.

NP	Adsorption energy (eV)	Initial Structure	Final structure
1	7.11		
2	7.10		
3	6.84		
4	5.58		
5	2.82		

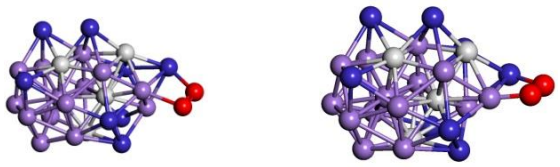
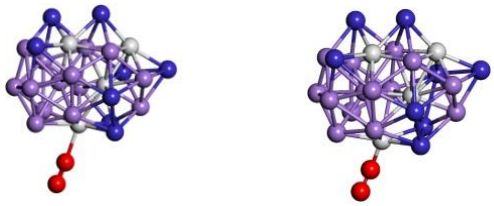
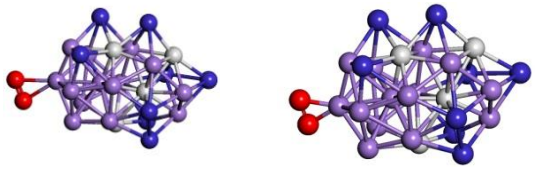
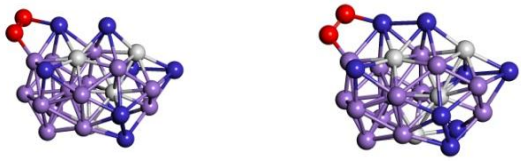
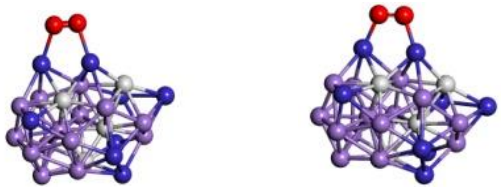
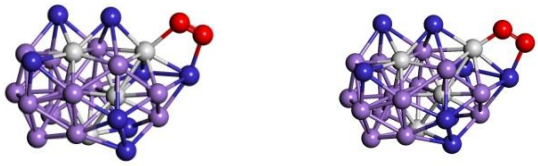
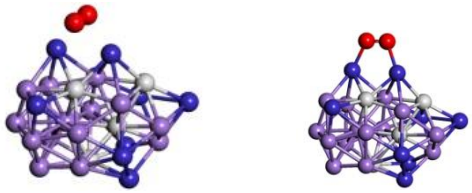
6	2.05	
7	1.99	
8	1.89	
9	1.67	
10	1.51	
11	1.35	
12	1.16	
13	1.14	
14	0.87	

Figure 5. The adsorption of O_2 on the PtVFe NP **1**. Blue, white, purple, and red balls denote Pt, V, Fe, and O respectively**.**

We note that the O_2 adsorption strength is slightly decreased on the ~1nm PtVFe NPs when comparing to the small subnanometer PtVFe clusters of the same composition. As catalytic activities are size dependence,[157] which may be dictated by the oxidizability,[158] it would also be interesting to further investigate the size dependence of the adsorption properties of O_2.

4. Conclusion

The results obtained in this work are critical to the previous studies[10] in order to fully analyze the efficiency of PtVFe nanocatalysts in fuel cells. $Pt_8V_4Fe_{14}$ NPs with platinum dispersed on the surface and vanadium kept homogenous in the center of the cluster showed strongest binding energies. From the current DFT study, clusters of 26 atoms preferred a hybrid of FCC and BCC structures. While the central atoms were not equidistant from other atoms (FCC), the structures showed less of a discrepancy between distances to the center atom then would be expected in a BCC structure. The 26 iron cluster favored more BCC as expected, but also showed this hybrid phenomenon.

Oxygen adsorption was most stable when oxygen attached to vanadium and iron atoms, however, other adsorption sites illustrate that PtVFe could be used as an effective catalysts for oxygen reduction. When oxygen bonded to platinum, the bond distances were greater, indicating easily transferrable oxygen atoms to the oxidation-reduction reaction in PEM fuel cells.

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