Spin-polarized Density Functional Theory on Iron-decorated Planar Aluminene Systems for Hydrogen Storage

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Abstract. The storage of hydrogen gas produced from different processes such as biomass gasification is one of the challenges towards hydrogen economy to achieve a sustainable clean energy. Different 2D materials are being explored for a suitable storage such as aluminene due to its large surface area. In this work, we investigated using spin polarized density functional theory the adsorption of iron on the different sites of planar aluminene: top, bridge and hollow. Results showed that iron can be adsorbed on aluminene on all sites favoring the hollow site with a binding energy of -7.83 eV. The charge density differences show charge transfers from the aluminum atom towards the iron atoms indicating chemical bond. Results showed net magnetization based on the density of states which can be utilize for reversible hydrogen gas induced magnetization switching for hydrogen storage. Hydrogen is physisorped on the Fe atoms located at the top and bridge site of aluminene without energy barrier, while hydrogen is chemisorped on Fe atom located at the hollow site with an energy barrier of 0.063 eV. These results are indicative that Fe-decorated aluminene systems can be a good hydrogen storage material.

1. Introduction
Energy consumption has been accelerating over the years towards the advancement of technology [1]. However, majority of the present methods of energy production results to CO2 emission [2][3]. An alternative source of renewable energy are biomass energy [4–6], and a clean hydrogen energy, wherein hydrogen is used as a commercial fuel [7]. While biomass is commonly being used for nanocomposite materials [8–15], hydrogen gas can also be extracted from it to produce a clean energy with water as its by-product [16][17]. However, finding an ideal storage system is a bottleneck.

Common storage systems for hydrogen are big pressure tanks to hold the compressed hydrogen. Current storage technologies are physical storage (gas or liquid \(H_2\)) and chemical storage (chemical and metal hydrides). Recent studies have focused on using a 2D-material base storage system and found it theoretically possible. Research show that 2D materials such as aluminene [18][19][20], silicene [21], graphene [22], penta-graphene [23], and germanene [24][25], and have promising results to store hydrogen, as they have large surface to volume ratio.
Aluminene can be synthesized on copper substrate [26]. While previous works [19][27] have shown that it can adsorb hydrogen molecule in dissociated form or as a molecule, impurities can be found on synthesized materials. Materials can be designed with certain impurities which can affect the adsorption of hydrogen on the materials' surface. Previous computational works have shown decorated (interstitial) or substituted dopants can improve the adsorption of hydrogen [23][28]. Some studies have shown that decorating iron atom can improve the adsorption of hydrogen [23][29]. No previous studies have been found investigating the adsorption of hydrogen on aluminene with low concentration of iron atoms. Thus, this work theoretically investigated the adsorption of iron at low concentrations on aluminene to identify its stability and hydrogen adsorption ability.

The next section is the methodology section which discusses the optimization of the geometric structure of the pristine aluminene, adsorption of dopants at different sites, and hydrogen adsorption on these doped-aluminene systems using density functional theory. Binding energies, adsorption energies, charge density difference and density of states were calculated as well to describe the interaction between the different species of atom in the system. The methodology section is followed by results and discussion of the energies, charge density difference and density of states. Lastly, significant results are summarized in the conclusion section.

2. Methodology

Vienna Ab initio Simulation Package (VASP) [30] is used to implement density functional theory to solve the many-body Schrodinger equation, and obtain the energies and electronic properties [31]. Projector- augmented-wave (PAW) potentials were used with 600 eV of cutoff energy. The Perdew, Burke, and Ernzerhof (PBE) functional was used for the exchange-correlational energy [32]. The Brillouin zone was sampled using a 5 by 5 by 1 gamma centered grid for geometry optimizations, and 11 by 11 by 1 gamma centered grid for the electronic property calculations. Energy convergence criterion, maximum force per atom were set to $10^{-4}$ eV and 0.02 eV/Å, respectively.

2.1. Aluminene Crystal Structure

The lattice constant $a$ used in this study is 4.486 Å, with alpha and beta at 90°, and gamma at 120° which is in agreement with the previous work [33]. A 3 by 3 supercell unit with a 20-Å vacuum along the z-axis was used to minimize interaction between neighboring Fe atoms as shown in Figure 1.

![Figure 1. Geometry visualization of aluminene supercell substrate with unit cell in red dashed lines.](image)

2.2. Iron adsorption and $H_2$ adsorption

Three possible interstitial binding sites were identified. The Fe atom was placed on the top (of an aluminum atom), bridge (between two bonded aluminum atoms), and hollow (center of honeycomb)
sites of the aluminene surface as seen in Figure 2. Static potential energy calculations of the decoration’s adsorption were performed from 6.00 Å to 0.20 Å with decrement of 0.20Å above the aluminene surface. This is followed by full relaxation of atoms at the minimum energy position of the Fe. The binding energies of the adatoms on aluminene surface were calculated using Eq. 1.

\[ E_b = E_{Fe/Al} - E_{al} - E_{Fe} \] (1)

where \( E_b \) is the binding energy, \( E_{Fe/Al} \) is the energy of the decorated surface, \( E_{al} \) is the energy of the aluminene, and \( E_{Fe} \) is the energy of the decorative atom (Ca, K, or Mg). The density of states of the doped-aluminene system were also calculated.

The charge density differences (CDD) were also calculated using Eq 2, where \( \Delta \rho \) is the charge density change, \( \rho_{Fe/Al} \) is the CDD of the overall system, \( \rho_{Fe} \) for the adatom and \( \rho_{al} \) for the aluminum.

\[ \Delta \rho = \rho_{Fe/Al} - \rho_{Fe} - \rho_{al} \] (2)

Similarly, static potential energy calculations were performed at distances 0.20Å to 6.00Å between the hydrogen molecule’s center of mass and dopant’s position. The hydrogen molecule was oriented either horizontal or vertical position as shown in Figure 3. Full system relaxation was performed the lowest energy position of the hydrogen molecule. Hydrogen adsorption energy on aluminene was calculated using:

\[ E_{ads} = E_{Fe/Al/H_2} - (E_{H_2} + E_{Fe/Al}) \] (3)

The adsorption energy of the system is represented by \( E_{ads} \). \( E_{H_2} \) is the energy of the \( H_2 \) and \( E_{Fe/Al/H_2} \) is the energy of \( H_2 \) adsorbed on the decorated aluminene. Finally, \( E_{Fe/Al} \) is the energy of the pristine decorated aluminene.

![Figure 2](image-url)

**Figure 2.** (a) Fe adsorption sites: Hollow (H), Top (T) and Bridge (B) with distance \( z \) at about 0.20 angstrom to 6.00 Å. (b) \( H_2 \) horizontal orientation (c) \( H_2 \) vertical orientation a distance \( z' \).

3. Results and Discussion

3.1. Fe adsorption on aluminene

Figure 3 shows the binding energies from the static potential energy calculations of the Fe-aluminene systems. The dotted curved lines (red, green and blue) are the energy readings of the adatoms on aluminene located at the top, bridge and hollow sites, respectively. The negative sign of the binding energies indicate that Fe atom would naturally bind on these sites at the minimum binding energy without additional energy needed. The hollow site is found to be the most favoured binding site on aluminene. The Fe atom appear to sink into the hollow site of the aluminene sheet. The hollow site
allows the Fe to interact more with the surrounding aluminum atoms. On the other hand, Fe atom has smaller binding energies at the top and bridge sites of aluminene. In general, Fe atom located at the hollow site has higher number of neighbouring aluminum atoms leading to higher binding energy, followed by Fe atom at bridge site, and lastly Fe atom at top site.

Figure 3 shows the binding energies of Fe atom at its optimum distance from the aluminene. As seen, Fe atom has the highest binding energy at the hollow site by a large margin. The magnitude of these binding energies indicates a strong binding between Fe atom and aluminum atom. Comparing the adsorption of Fe atom on graphene and silicene, Fe atom binds more strongly on aluminene on all sites as seen in Table 1. Furthermore, its binding energy specifically in the hollow site is large enough compared to the cohesion energy of iron [34]. Iron adsorption at low concentration is preferable compared to high concentration based on the binding energies and cohesion energy [35].

Table 1. Adatom adsorption on aluminene. This table shows: the binding energy ($E_b$) of the adatom on the considered sites, the cohesive energy ($E_c$), $E_b/E_c$ ratio, the binding energy on graphene ($E_{b\text{ graphene}}$), silicene ($E_{b\text{ silicene}}$) and ($E_{b\text{ aluminene}}$), the Fe atom height $h$ measured from the nearest Al, the nearest distance between the adatom and Al ($D_{M-Al}$).

| Atom | Site     | $E_b$  | $E_c$  | $E_b/E_c$ graphene | $E_b$ silicene | $E_b$ aluminene | $h$  | $D_{M-Al}$ |
|------|----------|--------|--------|------------------|----------------|----------------|------|------------|
| Fe   | Hollow   | 7.83   | 4.28$^1$ | 1.83             | 1.10$^2$       | 7.17$^3$       | 3.25$^5$ | 0.00       | 2.58       |
|      | Bridge   | 3.63   | 0.85   | 0.60$^2$         | 6.58$^3$       | 3.25$^4$       | 1.81  | 2.22       |
|      | Top      | 2.92   | 0.68   | 0.58$^2$         | 6.47$^3$       | 3.70$^4$       | 2.28  | 2.28       |

$^1$Kittle (2010) [34] $^2$Zanella (2008) [36] $^3$Sun (2019) [29] $^4$Pandey (2018) [35]

3.2. Density of states and charge density difference

The density of states (DOS) is illustrated in Figure 4. The alignment of the peaks found in the density of states of Fe atom and aluminene indicate strong interactions. This result is consistent with the magnitude of the binding energies. As shown in the DOS, the 3p orbitals of aluminene interacts with the 3d orbital of Fe atom. The interaction corresponds to chemisorption which also explains the range of the binding energies. With the addition of Fe atom to aluminene, the material has been transformed into a
magnetic material which can be seen in the asymmetry of the density of states. This chemisorption can be explained further by charge transfers which can be seen in the charge density difference.

![Figure 4. Density of States of Fe on the aluminene sheet at different sites (a) Top, (b) Bridge, and (c) Hollow.](image)

The CDD in Figure 5 show the transfer of electrons from the aluminene towards Fe atom. The greenish-blue colour shows the charge loss around the aluminum atoms while the yellow representing the gain of charges. It can also be observed that the Fe atoms have redistributed its charges as well from towards the aluminene sheet as shown by the greenish-blue color in its upper portion. Thus, it can be identified that there is electron accumulation of electrons between the Fe and the aluminene sheet to form the bonds. The large amount of accumulation indicates strongly adsorption to the surface and restricting reversibility [37]. This strong adsorption of Fe atom on aluminene can be an advantage if hydrogen can be adsorbed easily. Thus, almost irreversible bond of chemisorption is ideal for the system itself.

![Figure 5. Top and side views of charge density differences of Fe on aluminene at different sites (a) Top (b) Bridge (c) Hollow (Isosurface level set at 0.001 with greenish-blue (loss) and yellow (gain)).](image)

### 3.3 Hydrogen adsorption on Fe-doped aluminene

Results showed that hydrogen molecules can be adsorbed in horizontal or vertical orientation since energy minima can be found in Figure 6 for all aluminene systems. No adsorption barriers were found for hydrogen adsorption on Fe atom located at the top or bridge site of aluminene based the static potential energy calculations. However, there is a small barrier (0.063 eV) for the adsorption of hydrogen on the Fe atom located at the hollow site. The adsorption energies are -0.1922 eV, (-0.3527, -0.4092) eV, and -0.8455 eV on Fe atoms located at the top, bridge, and hollow sites, respectively. All adsorption energies of H₂ on Fe atoms at the top and bridge sites are physisorption desirable for a hydrogen storage material while chemisorption for the H₂ on Fe atom located at the hollow site.
4. Conclusion

Energetics and electronic properties of low concentrated iron atoms deposited on top, bridge, and hollow site of aluminene were calculated using spin-polarized density functional theory. Results showed iron atoms are chemisorped on the surface based on their binding energies -2.92 eV, -3.63 eV, and -7.83 eV on top, bridge, and hollow sites, respectively. The iron adsorption on aluminene induced a net magnetization as shown by the asymmetry in the density of states due to charge transfer from the aluminene to iron atoms visualized through the charge density difference. The addition of iron on the hollow site can easily be formed based on its energy and ratio with iron’s cohesion energy compared to adding iron atom on the top and bridge site. However, results showed that Fe atoms on top and bridge sites are found to be better hydrogen storage material since hydrogen molecules are physisorped without any energy barriers, while hydrogen atoms are chemisorped on the Fe-aluminene surface. The hydrogen adsorption energies on Fe atoms located at the top, bridge, and hollow sites are -0.1922 eV, (-0.3527, -0.4092) eV, and -0.8455 eV, respectively. Only the first two configurations have hydrogen adsorption energies that lie within the range of desirable adsorption energies for a hydrogen storage material at room temperature. These current results have shown potential of iron-decorated aluminene as a hydrogen storage material.

References

[1] Jones G A and Warner K J 2016 The 21st century population-energy-climate nexus Energy Policy 93 206–12
[2] Samset B H, Fuglestvedt J S and Lund M T 2020 Delayed emergence of a global temperature response after emission mitigation Nat. Commun. 11 1–10
[3] Gui E M and MacGill I 2018 Typology of future clean energy communities: An exploratory structure, opportunities, and challenges Energy Res. Soc. Sci. 35 94–107
[4] Itliong J N, Villagracia A R C, Moreno J L V., Rojas K I M, Bernardo G P O, David M Y, Manrique R B, Ubando A T, Culaba A B, Padama A A B, Ong H L, Chang J S, Chen W H, Kasai H and Arboleda N B 2019 Investigation of reverse ionic diffusion in forward-osmosis-aided dewatering of microalgae: A molecular dynamics study Bioresour. Technol. 279 181–8
[5] Villagracia A R C, Mayol A P, Ubando A T, Biona J B M M, Arboleda N B, David M Y, Tumlos R B, Lee H, Lin O H, Espiritu R A, Culaba A B and Kasai H 2016 Microwave drying characteristics of microalgae (Chlorella vulgaris) for biofuel production Clean Technology. Environment Policy 18 2441–51
[6] Mayol A P, Villagracia A R, Ubando A, Biona J B, Ong H L, Espiritu R, Lee H, Tumlos R, Arboleda N and Culaba A B 2016 Investigation of the drying characteristics of microalgae using microwave irradiation 8th IEEE Int. Conf. Humanoid, Nanotechnology, Information Technology, Communications Control Environment Management. HNICEM 2015 1–6
[7] Nehrir M H and Wang C 2016 Fuel cells *Fuel Cells* (Boston: Academic Press) pp 92–113
[8] Owi W T, Lin O H, Sam S T, Mern C K, Villagracia A R, Santos G N C and Akil H M 2017 A comparative study of green composites based on tapioca starch and celluloses *American Institute of Physics Conf. Proc.* vol 1865 (AIP Publishing LLC) p 040019
[9] Mohaiyiddin M S, Ong H L, Othman M B H, Julkapli N M, Villagracia A R C, Md. Akil H and Akil H M 2018 Swelling behavior and chemical stability of chitosan/nanocellulose biocomposites *Polym. Compos.* 39 E561–E572
[10] Ong H L, Villagracia A R, Owi W T, Sam S T and Akil H M 2020 Revealing the Water Resistance, Thermal and Biodegradation Properties of Citrus aurantifolia Crosslinked Tapioca Starch/Nanocellulose Bionanocomposites *J. Polym. Environ.* 28 3256-69
[11] Owi W T, Ong H L, Sam S T, Villagracia A R and Akil H M 2019 Unveiling the physicochemical properties of natural Citrus aurantifolia crosslinked tapioca starch/nanocellulose bionanocomposites *Ind. Crops Prod.* 139 111548
[12] Owi W T, Lin O H, Sam S T, Villagracia A R and Santos G N C 2017 Tapioca starch based green nanocomposites with environmental friendly cross-linker *Chem. Eng. Trans.* 56 463–8
[13] Anis Sofiiah M K, Lin O H, Akil H M and Villagracia A R 2014 Effect of compatibiliser on the accelerated weathering performance of polypropylene-silica nanocomposites *Mater. Res. Innov.* 18 S6-438
[14] Ong H L, Toh G Y, Villagracia A R, Tsai C kuo and Akil H M 2019 Unveiling the physicochemical properties of natural Citrus aurantifolia crosslinked tapioca starch/nanocellulose bionanocomposites *Ind. Crops Prod.* 139 111548
[15] Mohaiyiddin M S, Lin O H, Akil H M, Yee T G, Adik N N A N and Villagracia A R 2016 Effects of polypropylene methyl polyhedral oligomeric silsesquioxanes and polypropylene-grafted maleic anhydride compatibilizers on the properties of palm kernel shell reinforced polypropylene biocomposites *Polímeros* 26 228–35
[16] Lamb J J and Austbø B 2020 *Hydrogen, Biomass and Bioenergy* (Elsevier) pp 9–20
[17] Züttel A 2003 Materials for hydrogen storage *Mater. Today* 6 24–33
[18] Pedrosa G R, Villagracia A R, Bayasen D S, Lin H, Ong H L, David M and Arboleda N 2020 First principles investigation on the nitrogen-doped planar aluminene for hydrogen storage application *Institute of Physics Conf. Series Earth Environ. Sci.* 463 012103
[19] Villagracia A R and Ong H L 2020 Density functional theory investigation on hydrogen adsorption on buckled aluminene *IOP Conf. Ser. Earth Environ. Sci.* 463 012105
[20] Bayasen D S, Villagracia A R, Pedrosa G R, Lin H, Ong H L, David M and Arboleda N 2020 Hydrogen adsorption on calcium-decorated planar aluminene using density functional theory *Institute of Physics Conf. Series Earth Environ. Science.* 463 012104
[21] Rojas K I M, Villagracia A R C, Narido S C, Moreno J L V and Arboleda N B 2019 First principles study of H2 adsorption on Ni-decorated silicene *Mater. Res. Express* 6 055509
[22] Pan H, Wang Y-L, Kai-Hua H, Ming-Zhen W, Yu O and Li C 2013 First-principles study of hydrogen adsorption on titanium-decorated single-layer and bilayer graphenes *Chinese Phys. B* 22 67101
[23] Enriquez J I G and Villagracia A R C 2016 Hydrogen adsorption on pristine, defected, and 3d-block transition metal-doped penta-graphene *Int. J. Hydrogen Energy* 41 12157–66
[24] Rojas K I, Villagracia A R, Arboleda N B and Arboleda Jr N 2016 H2 adsorption on K decorated germanene surface: An ab-initio investigation *Mater. Res. Express* 3 115015
[25] Rojas K I M, Villagracia A R C, Moreno J L, David M and Arboleda N B 2018 Ca and K decorated germanene as hydrogen storage: An ab initio study *Int. J. Hydrogen Energy* 43 4393–400
[26] Lukačević I, Varga Pajtler M, Mužević M and Gupta S K 2019 Prospects for experimental realization of two-dimensional aluminium allotropes *J. Mater. Chem. C* 7 2666–75
[27] Villagracia A R, Ong H L, David M and Arboleda N 2019 First Principles Investigation on H₂ Adsorption on the Pristine 2-Dimensional Hexagonal Aluminum Institute of Physics Conf. Series: Earth and Environmental Science vol 268 (IOP Publishing) p 012135
[28] Gueriba J S, Padama A A B, Villagracia A R, David M, Arboleda N and Kasai H 2017 Ab initio study on hydrogen interaction with calcium decorated silicon carbide nanotube Int. J. Hydrogen Energy 42 11452–60
[29] Sun Y, Huang A and Wang Z 2019 Transition metal atom (Ti, V, Mn, Fe, and Co) anchored silicene for hydrogen evolution reaction RSC Adv. 9 26321–6
[30] Sun G, Kürti J, Rajczy P, Kertesz M, Hafner J and Kresse G 2003 Performance of the Vienna ab initio simulation package (VASP) in chemical applications J. Mol. Struct. THEOCHEM 624 37–45
[31] Nazmul Islam S K 2018 Conceptual Density Functional Theory and Its Application in the Chemical Domain (Taylor & Francis: CRC Press) p 5
[32] Perdew J P, Burke K and Ernzerhof M 1996 Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77 3865–8
[33] Chinnathambi K, Chakrabarti A and Ezawa M 2015 Aluminene as Highly Hole Doped Graphene New J. Phys. 17 8-083014
[34] Kittel C 2010 Introduction to Solid State Physics vol 8 (New York: Wiley)
[35] Pandey D, Kamal C and Chakrabarti A 2018 First-principles study of adsorption of 3d and 4d transition metal atoms on aluminene Comput. Condens. Matter 16 e00319
[36] Zanella I, Fagan S B, Mota R and Fazzio A 2008 Electronic and magnetic properties of Ti and Fe on graphene J. Phys. Chem. C 112 9163–7
[37] Kolasinski K W 2012 Surface Science (John Wiley & Sons, Ltd) pp 115-183