Hydrogen adsorption on calcium-decorated planar aluminene using density functional theory

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Abstract. With the rising demand for clean energy, the concept of hydrogen economy has grown more popular, and with this popularity the need for better hydrogen storage materials increases. Decorated surface materials such as planar hexagonal aluminene are being studied to determine their potential as good hydrogen storage materials. This study theoretically investigates hydrogen adsorption on aluminene decorated with calcium, where calcium is binded on the top, bridge and hollow sites of aluminene using density functional theory. Results on decoration adsorption have shown that calcium can easily bind a distance of 1.80 Å to 2.80 Å on the top, bridge and hollow sites with binding energies of 1.85 eV, 2.01 eV, and 3.32 eV, respectively. The density of states of the calcium-decorated surface show that its electronic property is generally maintained with zero magnetization. Small amount of charges were adsorbed from the aluminium atoms to the calcium atom based on the charge difference. This leads to hydrogen molecule adsorption with low adsorption energies ranging from 34.13 meV to 80.51 meV. In addition, minimal broadening of energy levels were shown by the density of states. With these results, it can be concluded that planar hexagonal aluminene with low concentration of calcium atoms may lower the hydrogen capacity of aluminene.

Keywords: Density Functional Theory, Hydrogen Storage, Aluminene, Calcium, Impurity

1. Introduction

With technology on the rise, the demand for energy has increased [1]. Since some existing methods of energy extraction tend to have high count of CO₂ emission an alternative and cleaner source of energy is left to be desired [2-4]. One promising alternative source of clean energy is the hydrogen fuel cell, in which its by-product is only H₂O [5-8]. A problem with using fuel cells is finding an ideal storage system. Most storage make use of bulky, heavy, pressure tanks to contain the compressed hydrogen [9,10]. Though recent studies have shown that using a material base, in two dimension (2D), is theoretically possible and promising for hydrogen storage due to its large surface to volume ratio. This makes it ideal for more hydrogen molecules to attach to it. [11-19].
The study focused on a new 2D material known as aluminene, which is regarded as a highly hole-doped graphene and has a planar honeycomb structure of aluminum atoms [20]. Computational studies have found that hexagon structured aluminene was stable. Furthermore, its potential to store H$_2$ molecules have been found to be appropriate. These results are promising enough to initiate further exploration of aluminene's capabilities as a material for storage [21, 22].

Though 2D materials are viable for storing hydrogen, computational experiments have found that when decorated/doped with an additional atom, the material’s storage capacity can store more hydrogen molecules [23-25]. A study has been found that when germanene was decorated with Ca, it became more accommodating to hydrogen atoms to adsorb to [26-27]. Therefore, this study investigated calcium (Ca) as the dopant to the aluminene surface using density functional theory [27]. Adsorption energies of hydrogen on Ca-doped aluminene are calculated to determine its potential hydrogen storage material.

2. Methodology

2.1 Structure

Density functional theory (DFT) calculations has been widely used to determine the ground state properties. These are the energy, density of states and charge density [11-19,28]. The calculations were simulated through Vienna Ab initio Simulation Package (VASP) [29]. The approximation for the exchange-correlational energy was calculated using the Perdew, Burke, and Ernzerhof (PBE) functional [30].

The super cell was limited to a 3 by 3 unit of planar aluminene to avoid adatom interactions with its neighboring image. In addition the three adsorption sites were identified as top (T), bridge (B) and hollow (H) as shown in Figure 1a. Visualization for Electronic and Structural Analysis (VESTA) was used to construct the super cell which has 18 aluminum atoms in a hexagonal lattice with a lattice constant of 13.458 Å, with the angles being 90°, 90°, and 120°. Lastly the aluminene sheets were separated by 20 Å, as shown in Figure 1b.

![Figure 1](image)

**Figure 1** (a) adsorption sites of calcium (b) Unit Cell (c) distance of calcium adsorption (d) H$_2$

2.2 Calculations

Static calculations was preformed to determine the potential energies of the decorated systems with adatom at a distance of 0.20 Å to 6.00 Å with an increment of 0.20 Å from the aluminene surface as shown in Figure 1c. Ionic relaxations were performed at the lowest energy position, and the binding energy of the adatom on the aluminene surface was calculated. The binding energy is computed as:

$$E_b = E_{Al} + E_{Ca} - E_{Ca/Al}$$  \hspace{1cm} (1)

The density of states of the decorated aluminene systems were then calculated. In addition, the charge density difference (CDD) was calculated using equation 2. The $\Delta \rho$ represents the change in the charge density, while $\rho_{Ca/Al}$, $\rho_{Ca}$ and $\rho_{Al}$ are the CCD of the overall system, calcium and aluminum, respectively.

$$\Delta \rho = \rho_{Ca/Al} - \rho_{Ca} - \rho_{Al}$$  \hspace{1cm} (2)

For the hydrogen adsorption, static calculations of H$_2$ calcium-decorated aluminene systems were made to estimate the adsorption distance of H$_2$ on top of the calcium atom. Two initial orientations of the
hydrogen molecule were used: parallel and perpendicular to the x-axis as shown in Figure 1d. Ionic relaxations were then performed at the lowest energy level positions. The hydrogen adsorption energy was calculated using

\[ E_{ads} = E_{H_2} + E_{Ca/Al} - E_{Ca/Al/H_2} \]

(3)

\[ E_{ads} \] is the total adsorption energy, \[ E_{H_2} \] and \[ E_{Ca/Al} \] are the H\textsubscript{2} energy adsorbed on the H\textsubscript{2} molecule and the Ca-decorated aluminene and lastly \[ E_{Ca/Al} \] is the energy of pristine Ca-decorated aluminene.

### 3. Results and discussion

#### 3.1 Calcium Decoration

![Figure 2 Total Energy of Calcium on Aluminene](image)

Figure 2 shows the total energy of calcium on the aluminene sheet. The blue dashed lines indicate the sum of the individual energies of the calcium and aluminene surface. The hollow site was found to have the shortest adsorption distance of 1.75 Å. In contrast, the top site resulted in having the farthest distance at 2.74 Å. The top, bridge and hollow sites’ binding energies are then found to be 1.85 eV, 2.01 eV, and 3.32 eV, respectively.

#### 3.2 Density of States

![Figure 3 Density of States at (a) top (b) hollow and (c) bridge](image)

Figure 3 shows the partial density of states for Ca-decorated systems. The peaks in the density of states of the calcium atom aligns with the peaks of the aluminium atoms near the calcium atom. This is an indication of chemical bonding in agreement as well with the range of the calculated binding energies. In addition, the same number of states shows that it is non-magnetic. The charge density difference in addition shows electron transfer from the aluminum atoms to the calcium atoms as shown in Figure 4.
3.3 Hydrogen adsorption

Figure 5 shows the total energies calculated for the H$_2$ molecule’s static system when it reaches either parallel or perpendicular to the doped-aluminene surface. The blue dashed lines indicate the sum of the individual energies of the hydrogen and calcium-decorated aluminene. For both parallel and perpendicular orientation of H$_2$ on the calcium, the hollow site was found to obtain the lowest total energy of about -56 eV. In contrast, the top site had the largest energy readings showing that the H$_2$ preferred the hollow site.

Figure 5 Total Energy of Hydrogen on Ca-decorated aluminene systems
Table 1 shows the summary of calculated adsorption energies of the relaxed systems. For both parallel and perpendicular, the distances of the H₂ to the calcium atom are the same, this is true for all sites. Furthermore, results showed that hydrogen molecule can be adsorbed on any site. Though the hollow energy was found to be the most stable site through physisorption based on the energy values.

4. Conclusion

The adsorption of hydrogen on a Ca-doped aluminene sheet was examined using first principle calculations. Results have shown that calcium easily binds at a distance of 1.80 Å to 2.80 Å with binding energies of 1.85 eV, 2.01 eV, and 3.32 eV on the top, bridge and hollow sites respectively. The density of states of the calcium-decorated aluminene non-magnetic, and calcium is bonded through chemisorption. Additionally, the adsorption energies of H₂ directly on calcium decorated systems ranges from 34.13 meV to 80.51 meV without van der Waals correction. Other binding sites near the decoration can be further investigated. In conclusion planar hexagonal aluminene decorated with calcium can be a hydrogen storage material below the room temperature. With calcium as an impurity to aluminene, it can lower the storage capacity of aluminene. However, further investigation can be performed by monte-carlo simulations to determine its hydrogen gravimetric capacity.

References

[1] Jones G and Warner K 2016 The 21st century population-energy-climate nexus. *Energy Policy*, 93, 206-212.
[2] C Popp D 2001 The effect of new technology on energy consumption. *Resource and Energy Economics*, 215-239.
[3] Ritchie H and Roser M 2017 CO₂ and other Greenhouse Gas Emissions.
[4] Gui E and MacGill I 2018 Typology of future clean energy communities: an exploratory structure, opportunities, and challenges. *Energy research & social science*, 35, 94-107.
[5] Romm J 2005 The Hype About Hydrogen: Fact and Fiction in the Race to Save the Climate.
[6] Schlapbach L and Züttel A 2001 Hydrogen-storage materials for mobile applications. *Nature*, 414, 353.
[7] Steele B C H and Heinzel A 2001 Materials for fuel-cell technologies. *Nature*, 414, 345.
[8] Hydrogen Europe. 2017 *Hydrogen storage*. From Hydrogen Europe: https://hydrogeneurope.eu/hydrogen-storage
[9] Eftekhari A and Fang B 2017 Electrochemical hydrogen storage: opportunities for fuel storage, batteries, fuel cells, and supercapacitors. *International Journal of Hydrogen Energy*, 42(40), 25143-25165.
[10] Eberle U, Müller B, & Von Helmolt R 2012 Fuel cell electric vehicles and hydrogen infrastructure: status 2012. *Energy & Environmental Science*, 5(10), 8780-8798.
[11] Zaluska A, Zaluski L, & Ström–Olsen J O 1999 Nanocrystalline magnesium for hydrogen storage. *Journal of Alloys and Compounds*, 288(1-2), 217-225.  
[12] Züttel A 2003 Materials for hydrogen storage. *Materials today*, 6(9), 24-33.  
[13] Liu C, Fan Y Y, Liu M, Cong H T, Cheng H M & Dresselhaus M S 1999 Hydrogen storage in single-walled carbon nanotubes at room temperature. *Science*, 286, 1127  
[14] Ding F and Yakobson B I 2011 Challenges in hydrogen adsorptions: from physisorption to chemisorption. *Front. Phys.*, 6, 142  
[15] Rojas K, Villagracia A R, Arboleda N B 2016 H2 adsorption on K decorated germanene surface: an ab-initio investigation. *Materials Research Express*, 3(11), 115015  
[16] Hong-Zhe P, Yong-Long W, Kai-Hua H, Ming-Zhen W, Yu O, & Li C 2013 First-principles study of hydrogen adsorption on titanium-decorated single-layer and bilayer graphenes. *Chinese Physics B*, 22(6), 067101.  
[17] Wang Y, Zheng R, Gao H, Zhang J, Xu B, Sun Q and Jia Y 2014 Metal adatoms-decorated silicene as hydrogen storage media. *International Journal of Hydrogen Energy*, 39 14027  
[18] Yu Z Y, Wan N, Lei S Y & Yu H 2016 Enhanced hydrogen storage by using lithium decoration on phosphorene. *J. Appl. Phys.* 120 024305  
[19] Rojas K, Villagracia A R, Narido S, Moreno, J and Arboleda N, 2019 First principles study of H2 adsorption on Ni-decorated silicene. *Materials Research Express*, 6(5) 055509.  
[20] Kamal C, Chakrabarti A, & Ezawa M 2015 Aluminene as highly hole-doped graphene. *New Journal of Physics*, 17(8), 083014.  
[21] Lukačević I, Pajtler M V, Mužević M, & Gupta S K 2019 Prospects for experimental realization of two-dimensional aluminium allotropes. *Journal of Materials Chemistry C*, 7(9), 2666-2675.  
[22] Villagracia A R, Ong H L, David M, & Arboleda Jr N 2019 First Principles Investigation on H2 Adsorption on the Pristine 2-Dimensional Hexagonal Aluminum. In IOP Conference Series: *Earth and Environmental Science*, 268, 012135  
[23] Enriquez J I G and Villagracia A R C 2016 Hydrogen adsorption on pristine, defected, and 3d-block transition metal-doped penta-graphene. *International Journal of Hydrogen Energy*, 41(28), 12157-12166.  
[24] Gueriba J S, Padama A A B, David M, Arboleda Jr N, & Kasai H 2017 Ab initio study on hydrogen interaction with calcium decorated silicon carbide nanotube. *International Journal of Hydrogen Energy*, 42(16), 11452-11460  
[25] Abanador P, Villagracia A R, Arboleda N and David M 2013 First principle investigation of atomic hydrogen adsorption on Pd-doped MgB2. *Philippine Science Letters* (6)(2) 176-181  
[26] Rojas K, Villagracia A R, Moreno J, David M and Arboleda N B 2018 Ca and K decorated germanene as hydrogen storage: An ab initio study. *International Journal of Hydrogen Energy*, 43(9), 4393-4400  
[27] Yang W and Ayers P 2003 Density-functional theory. In *Computational Medicinal Chemistry for Drug Discovery* (103-132). *CRC Press*.  
[28] Enriquez J, Moreno J, David M, Arboleda N, Ong, H L and Villagracia A R 2018. DFT Investigation on the Electronic and Water Adsorption Properties of Pristine and N-Doped TiO2 Nanotubes for Photocatalytic Water Splitting Applications. *Journal of Electronic Materials*, 46(6), 3592-3602  
[29] Kresse G and Furthmüle J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter*, 54, 11169  
[30] Perdew J P, Burke K & Ernzerhof M 1996. *Generalized Gradient Approximation Made Simple*, 77, 1865