



Ab initio study of hydrogen binding on Ca-inserted porphyrin

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ABSTRACT

To study the binding of hydrogen molecules on Ca-inserted porphyrin, we perform ab initio pseudo-potential calculations within the local density approximation (LDA). One Ca atom is inserted in the central N₄ cavity formed by the removal of two hydrogen atoms of porphyrin. By increasing the number of hydrogen molecules, we investigate hydrogen binding on Ca-inserted porphyrin for hydrogen storage. We find that the binding energy of H₂ molecules to the Ca atom is ~0.25 eV/H₂ up to four hydrogen molecules. When the fifth or sixth H₂ molecule is adsorbed on the Ca atom, the molecule is adsorbed onto Ca-porphyrin with the average binding energy of ~0.2 eV/H₂. Examining the projected density of states, we study orbital hybridization between the Ca atom and hydrogen molecule. Finally, the possibility of Ca-porphyrin as a hydrogen storage material is discussed.

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1. Introduction

Hydrogen is an attractive energy source that is clean fuel without pollution and is able to recycle. The efficient use of hydrogen fuel requires safe, efficient and reversible hydrogen storage materials. Therefore the investigation of hydrogen storage is crucial for finding good storage materials. So far many studies have focused on low-dimensional nanostructures due to their possibility of high storage capacities. Especially, carbon-based nanostructures such as carbon nanotubes and fullerenes have been extensively studied as they were expected to have a large surface area to absorb hydrogen [1–8]. However, pure carbon-based structures do not have good binding energy near room temperature [6,8]. To increase the potential for hydrogen storage of nanostructures, metal-decorated materials such as metal-carbon-based materials [8–14], metal-organic frameworks [15], and metal-decorated polyacetylene [16–18] were suggested.

In a previous study, Lee et al. [16–18] found that *cis*- and *trans*-polyacetylene decorated with Ti atoms bind up to five and four hydrogen molecules per Ti atom, respectively and that optimal binding energy of H₂ molecules for practical applications is 0.2–0.3 eV. However, transition metals such as Ti and V have strong tendency of clustering because of their high cohesive energy

(>4 eV). For alkali-earth metals with lower cohesive energy (1–2 eV), clustering of metal atoms may be prevented. Yoon et al. [14] studied the coating of C₆₀ fullerenes with light alkaline-earth metals to identify Ca as the most desirable coating metal element for high-capacity hydrogen storage media. Up to 5 H₂ molecules a uniform H₂ binding energy of about 0.2 eV/H₂ was found within GGA.

Porphyrin (C₂₀H₁₄N₄), an aromatic and heterocyclic compound, consists of four pyrrole rings joined together by four methine (=CH–) groups. The parent porphyrin is porphyrin and substituted porphyrins are called porphyrins [19]. (Porphyrin is the simplest porphyrin.) Four nitrogen atoms of porphyrin rings can be saturated by a single metallic ion instead of two H atoms. In this paper, we consider the insertion of one Ca atom into the central N₄ cavity of porphyrin and investigate interaction between H₂ and the Ca atom inserted in the center of porphyrin for hydrogen storage.

2. Calculation methods

We have performed first-principles calculations within the local density approximation (LDA) in the Vienna *ab initio* Simulation Package (VASP) [20]. The atoms are represented by ultrasoft pseudopotentials as provided with VASP [21]. The cutoff energy is set to 400 eV and the atomic positions are relaxed with residual forces smaller than 0.01 eV/Å. For the Brillouin-zone integration, we use a 1 × 1 × 1 grid in the Monkhorst–Pack special *k*-point scheme. The vacuum region is about 10 Å between porphyrin molecules.

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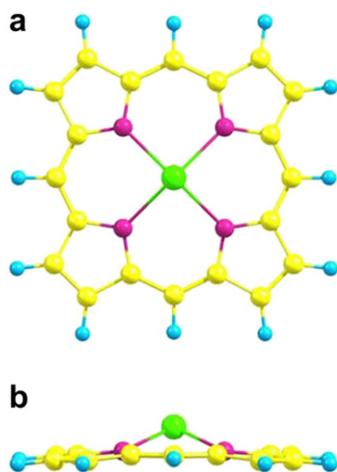


Fig. 1. (a) Top and (b) side views of the optimized structure of Ca-inserted porphyrin.

3. Results and discussion

First, we consider a porphyrin molecule ($C_{20}H_{12}N_4$) formed by removal of two hydrogen atoms in the central N_4 cavity of porphyrin and insert a Ca atom into the N_4 cavity. When N atoms are bonded to the Ca atom instead of two H atoms, porphyrin becomes energetically favorable by ~ 4 eV [$=E(\text{porphyrin}) + E(\text{Ca}) - E(\text{Ca-porphyrin}) - E(\text{H}_2)$]. The optimized structure of Ca-inserted porphyrin (Ca-porphyrin) is shown in Fig. 1.

The inserted Ca atom is located in the center of the cavity surrounded by four N atoms with Ca–N bond length of 2.2 Å and about 0.9 Å above the porphyrin plane. When the Ca atom is bonded to the nitrogen atoms of porphyrin, the originally empty d -orbitals of the Ca atom become partially occupied.

To find the most stable configurations for adsorption of a single hydrogen molecule on the Ca-inserted porphyrin, we investigate several adsorption positions of H_2 on the Ca atom. We vary the orientation of H–H bond and distance between Ca and H_2 molecule. Fig. 2 shows several lowest energy minimum configurations, depending on the direction of H–H bond of the single hydrogen molecule adsorbed on or near Ca atom: The orientations of

Table 1

Binding energies (eV/ H_2) and the Ca–H binding distances (Å) for the configurations shown in Fig. 2.

H_2 bond orientation	Parallel		Tilted	
	(a)	(b)	(c)	(d)
Binding energy (eV/ H_2)	0.19	0.24	0.26	0.26
Ca–H distance (Å)	2.49	2.46	2.33	2.36

hydrogen molecules to the porphyrin plane are parallel [Fig. 2(a) and (b)] or tilted [Fig. 2(c) and (d)].

Fig. 2(a) shows the on-top configuration where the center of H–H bond is located just above the Ca atom while Fig. 2(b) is the configuration of H_2 molecule adsorbed on the side of Ca atom. On the other hand, the adsorbed H_2 molecule is tilted along the Ca–N bridge in Fig. 2(c) while the tilted molecule is located in a hollow site in Fig. 2(d). For all configurations in Fig. 2, the bond length of H_2 is slightly elongated from 0.75 Å (free molecule) to about 0.77 Å.

The binding energy E_b per H_2 for n hydrogen molecules adsorbed on Ca-porphyrin is defined by

$$E_b = (1/n) \times [E(\text{Ca-porphyrin}) + nE(\text{H}_2) - E(n\text{H}_2/\text{Ca-porphyrin})]$$

where $E(\text{Ca-porphyrin})$, $E(\text{H}_2)$, and $E(n\text{H}_2/\text{Ca-porphyrin})$ are the total energies of Ca-porphyrin, H_2 , and $nH_2/\text{Ca-porphyrin}$, respectively. Binding energies for configurations ($n = 1$) in Fig. 2 are listed in Table 1 along with the Ca–H binding distances. Tilted configurations are more stable than parallel ones. It is found that the tilted configuration [Fig. 2(d)] is the most stable. In Table 1, the Ca–H binding distance stands for the distance between Ca atom and H atom (nearer to Ca) of the hydrogen molecule.

Fig. 3 shows the projected density of states (PDOS) for the configuration of $H_2/\text{Ca-porphyrin}$ in Fig. 2(d), i.e., the most stable structure for $H_2/\text{Ca-porphyrin}$. As shown in the top panel of Fig. 3, the PDOSs for s and p orbitals of nitrogen are for one nitrogen atom that is closest to hydrogen molecule, while the PDOS for s orbital of H is for a hydrogen atom of H_2 that is closer to Ca. From the PDOS, we find that s , p and d -orbitals of Ca atom around the energy of -4 to -2 eV (below the Fermi level) are well hybridized with s and p orbitals of N while the s orbital of H around -7 eV is hybridized with the d orbital of Ca.

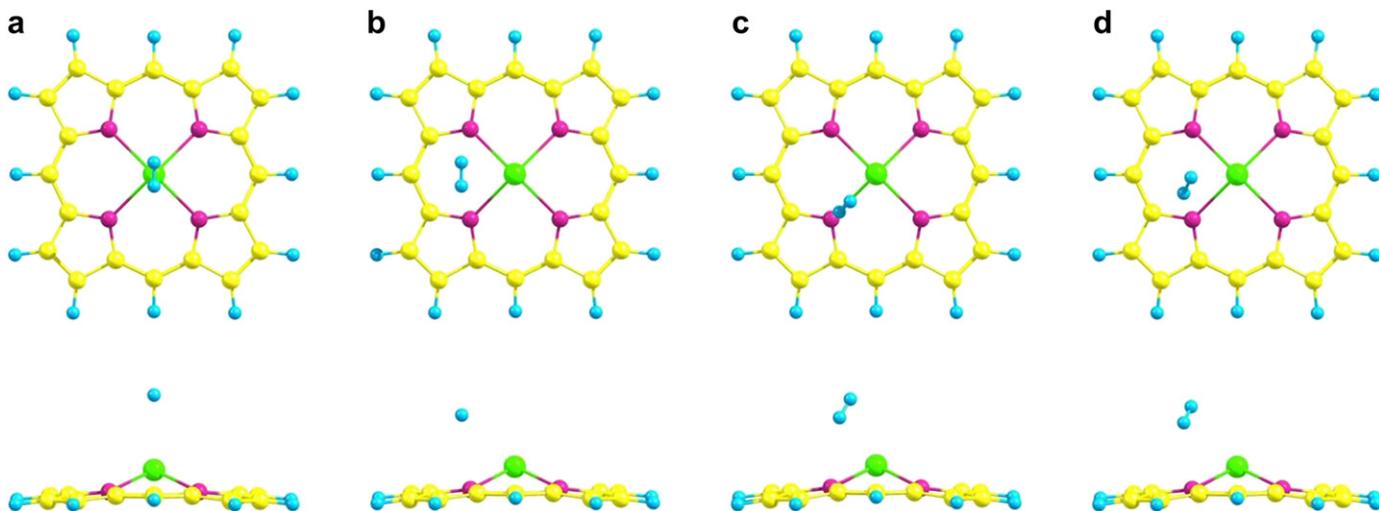


Fig. 2. Top views (upper panel) and side views (lower panel) of structures of four local minimum energy configurations of single hydrogen molecule adsorbed on or near the Ca atom.

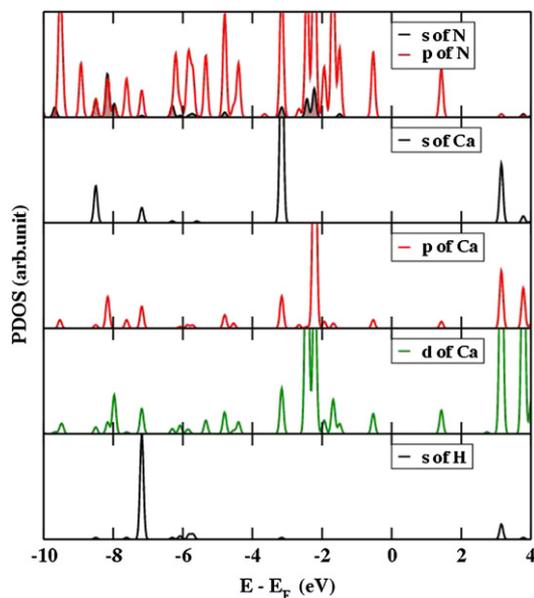


Fig. 3. Projected density of state (PDOS) for the configuration of H_2 /Ca-porphyrin shown in Fig. 2(d).

Next, we increase the number of hydrogen molecules to investigate dihydrogen binding on Ca-porphyrin for hydrogen storage. Up to four hydrogen molecules are attached on Ca-porphyrin with a uniform binding energy value of about 0.25 eV/ H_2 for LDA. After finding the optimized structures for up to $4H_2$ molecules on Ca-porphyrin, we add the two more molecules to the sites just above and below Ca atom. For the fifth and sixth molecules located above and below Ca atom, the average H_2 binding energy decreases down to 0.2 eV/ H_2 . Since the distances between Ca and the fifth (or sixth) H_2 molecule are longer than those of the other four H_2 molecule, these two more hydrogen molecules are weakly bonded to the Ca atom. Finally, by calculating the hydrogen storage capacity the possibility of Ca-porphyrin as hydrogen storage materials is discussed. The storage capacity is estimated to about 2.3 wt% for $4H_2$ /Ca-porphyrin, and about 3.4 wt% for $6H_2$ /Ca-porphyrin.

4. Conclusion

We have investigated hydrogen binding on Ca-inserted porphyrin for hydrogen storage. By successively increasing the

number of adsorbed hydrogen molecules on a Ca-porphyrin molecule, we obtained the optimized structures and the H_2 binding energies. Up to four adsorbed hydrogen molecules, tilted configurations of H_2 molecules are the most stable for LDA calculations. Their binding energy of H_2 is about 0.25 eV/ H_2 . From the PDOS, we investigate orbital hybridization between the Ca atom and hydrogen molecule. The fifth and sixth molecules are weakly adsorbed on Ca-porphyrin. Thus, the maximum number of H_2 molecules (directly) adsorbed on the Ca atom is six.

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