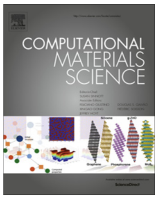
Computational Materials Science 137 (2017) 107–112

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci



A newly designed Sc-decorated covalent organic framework: A potential candidate for room-temperature hydrogen storage

Liang Zhao [b], Bi-Zhi Xu [b], Jianfeng Jia [a,b,*], Hai-Shun Wu [a,b]

[a] Key Laboratory of Magnetic Molecules & Magnetic Information Materials Ministry of Education, Shanxi Normal University, Linfen 041004, China
[b] The School of Chemical and Material Science, Shanxi Normal University, Linfen 041004, China

ARTICLE INFO

Article history:
Received 6 February 2017
Received in revised form 18 April 2017
Accepted 11 May 2017

Keywords:
Hydrogen storage material
Decorated COF
DFT calculation

ABSTRACT

The hydrogen storage properties of newly designed Sc- and Ti-decorated covalent organic frameworks, $(C_6H_3)_2(B_2C_4H_4)_3M_6$ (M=Sc, Ti), were investigated using density functional theory method. We found that each doped Sc atom can effectively adsorb 4 H_2 with the average adsorption energy being in a range from 0.21 to 0.34 eV. On the doped Ti atoms, the first H_2 is dissociated and other H_2 molecules have small, or even negative consecutive adsorption energy. Our calculation results showed that the Sc-decorated $(C_6H_3)_2(B_2C_4H_4)_3Sc_6$ covalent organic frameworks can adsorb 24 hydrogen molecules, which give a hydrogen storage capacity of 7.02 wt% under ambient condition.

1. Introduction

Hydrogen was considered the most potential alternative fuel for fossil fuels because of the high energy density, high abundance and environmentally clean nature [1,2]. The lack of the proper onboard hydrogen storage technology is one of the bottlenecks to limit the usage of hydrogen for vehicular application. In recent years, metal organic frameworks (MOFs) [3–11] and covalent organic frameworks (COFs) [12–16] were reported as promising candidates for hydrogen storage in the molecular form because of their porous structure, large free volume and high accessible surface. However, the interaction between H_2 and the pristine MOFs and COFs is dominated by the van der Waals interaction. The binding energy of H_2 molecules to the MOFs and COFs is in a range of 2.2–5.2 kJ/mol [17–19], which makes them nearly impossible being used in the ambient condition to achieve enough storage capacity.

It is well known from both experimental and theoretical studies that doping with metal atoms can enhance the hydrogen storage capacity of carbon-based structures [20–27]. The hydrogen adsorption capacities of MOFs and COFs also can be improved by doping with metal atoms [28–32]. Typically, doping with alkali metal or alkaline-earth metal atoms can achieve higher hydrogen storage capacities because of their light weight [33]. However, the binding interaction between alkali metal or alkaline-earth metal atoms and H_2 molecules are not strong enough to make them suitable for hydrogen storage at ambient condition. Doping with light transition metal (TM) atoms can significantly enhance the binding interaction between H_2 molecules and the decorated materials, due to the strong Kubas interaction between H_2 and the TM atoms [21,34–36]. The clustering of the TM is a main issue should be considered for designing TM doped hydrogen storage materials [37]. Zou and his coworkers [38] have proposed a two-step doping strategy to make COF promising hydrogen storage materials at ambient conditions. They found that the Sc atoms can well disperse on the boron doped COF-1. And in such designed framework, one Sc atom can adsorb four hydrogen molecules with the binding energy of 0.32 eV. Dixit [39] also have suggested B-substituted Sc-decorated MOF-5 is a potential hydrogen storage material. In many studies, the zero-point energy (ZPE) was not included in the calculated binding energies. Our recent works showed that the ZPE correction is very important to get correct hydrogen adsorption energy [40].

It is a challenging work to fabricate the proposed hydrogen storage candidates. More target candidates will give more chances to obtain a suitable hydrogen storage material. In this work, a new Scandium-decorated two-dimensional (2D) COF has been suggested based on density functional theory calculations. Moreover, ZPE corrections were considered to get more reliable hydrogen binding energy.

2. Computational methods

It was believed that pure local density approximation (LDA) and generalized gradient approximation (GGA) methods of density

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* Corresponding author at: The School of Chemical and Material Science, Shanxi Normal University, Linfen 041004, China.

E-mail address: jiajf@dns.sxnu.edu.cn (J. Jia).

http://dx.doi.org/10.1016/j.commatsci.2017.05.017
0927-0256/

functional theory are not suitable for the calculation of weak interaction. In our previous tests, we find mPW2PLYPD and wB97XD method can give reliable hydrogen adsorption energy for the ScH_2^+:nH_2 [40]. Because of the convergence failure of mPW2PLYPD for some Ti-decorated system, wB97XD method were selected in our present works to calculate the structures and hydrogen adsorption energies of Sc- and Ti-decorated $B_2C_4H_6$ hydrogen storage blocks. wB97XD is a long-range corrected hybrid density functional with empirical atom-atom dispersion corrections, which can yields satisfactory accuracy for non-covalent interactions [41]. The relativistic effects were considered with the Douglas–Kroll–Hess (DKH) method [42–44]. The relativistically recontracted Karlsruhe Valence triple-zeta basis sets DKH-def2-TZVP [45] is employed to describe the orbitals of all atoms involved. Frequency calculations at the same level were performed to confirm that the optimized molecule structures are stationary points on the potential energy surface. The zero-point energies were also obtained by frequency calculations. The basis set superposition error has been corrected using the full counterpoise method [46] to get more reliable hydrogen adsorption energies. For the designed COF, the calculations were carried out under periodic boundary conditions (PBC). The purpose of the PBC calculation is only to confirm that the designed COF can adsorb enough hydrogen molecules and to get the rough hydrogen adsorption energy of the decorated COF. So, the PBE exchange-correlation functional [47] of pure GGA method implemented in the DMol3 program [48] were used. Double numerical basis set plus d-functions (DND) were employed to describe the atomic orbital of all atoms involved. The supercell size were chose large enough to ensure that the vacuum layer thickness between the COF layer is greater than 10 Å. The 2 × 2 × 1 k-point grid generated by Monkhorst Pack scheme [49] were applied in the PBC calculations. No symmetry restriction were imposed for all the cell optimizations. No frequency calculations were carried out under PBC.

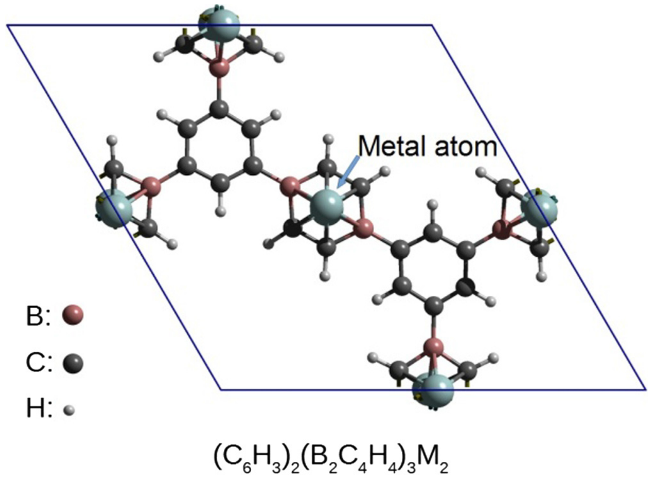

Fig. 1. The potential metal decorated covalent organic framework for hydrogen storage. (M for metal atom.)

3. Results and discussions

To design potential metal decorated hydrogen storage material, some factors must be considered. (1) The metal atoms should strongly bind with the COFs. (2) The metal atoms should disperse well rather than cluster on the COFs. (3) Proper H_2 binding energy were need to achieve fast adsorption/desorption kinetics. Lochan and Head-Gordon [50] suggested that H_2 binding energy of around 0.2–0.4 eV can ensure reversibility and fast adsorption/desorption kinetics. (4) The small mass of the metal atom can give higher gravimetric density of hydrogen storage. Based on these considerations, we designed a new metal decorated covalent organic framework (COF) ($(C_6H_3)_2(B_2C_4H_4)_3M_6$ (M for metal atom)) as shown in Fig. 1 for hydrogen storage. In this decorated COF, the $B_2C_4H_4$ rings are linked by benzene rings. Two metal atoms locates on each $B_2C_4H_4$ ring. The light transition metal Sc and Ti were considered in this work.

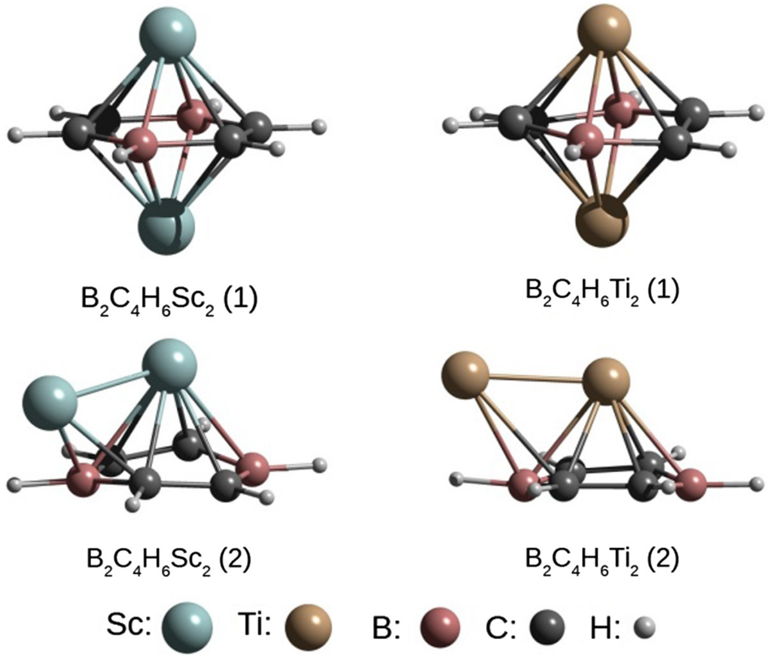

Fig. 2. The optimized structures of $B_2C_4H_6Sc_2$ and $B_2C_4H_6Ti_2$. Their coordinates were listed in the supplementary materials.