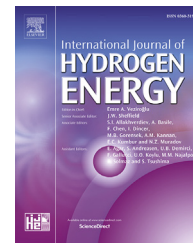


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Transition metal decorated covalent triazine-based frameworks as a capacity hydrogen storage medium

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ABSTRACT

From *ab initio* density functional theory (DFT) calculations, the structural stability and hydrogen adsorption capacity of transition metal (TM, TM = Sc, Ti, V, Cr, Mn) decorated covalent triazine-based framework (CTF) are discussed. It is found that by calculation, these TM atoms can adsorb on the CTF sheet without clusters. The Sc, Ti, V, Cr and Mn decorated CTF are predicated to bind five, four, three, three and two of hydrogen molecules. We found that Sc and Ti decorated CTF are suitable candidates for effective reversible hydrogen storage at near ambient condition, whereas V, Cr and Mn decorated CTF are not promising materials due to too large average bind energies per hydrogen molecule.

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Introduction

Hydrogen is a clean and alternative energy source, and with the development of technology, its feasible application become possible [1,2]. Owing to the fundamental limitations of gas and cryogenic/liquid hydrogen storage, one of the major technical challenges encountered is to find feasible and safe storage materials that can store hydrogen with a high gravimetric and volumetric density. And meanwhile, stored hydrogen can be released easily under ambient thermodynamic conditions [3–5]. In recent years, good progress has been made in the theoretical and experimental studies of

hydrogen storage, and meanwhile a good development has been gained in terms of sorption-based hydrogen storage methods [6–13]. The studies of hydrogen sorbent materials are one of the main directions for the design of such materials. The studies can be classified in terms of two key technical issues [14]: (i) constructing stable framework structures with high porosity, and (ii) increasing the binding affinity of hydrogen molecules to surfaces beyond the usual van der Waals interaction. Many reversible solid-state hydrogen storage nanostructure materials have been discussed, such as fullerenes, nanotubes, graphene, and ethylene.

The suitable H₂ binding energy should be in the range of 0.20–0.40 eV/H₂ for reversible hydrogen storage at ambient

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conditions [15,16]. Most of solid-state pristine materials as suitable candidates have some fatal flaws, such as low gravimetric storage capacity, and very low desorption temperatures or energies for the physisorption materials [17], poor reversibility, and high dehydrogenation temperatures for the chemical hydrides, etc. There are some novel concepts to overcome these obstacles, and one of these technique to increase the storage capacity and the H_2 binding energy is to decorate metal atoms onto porous structures [18–22]. These metal elements are usually alkali metals (Li, Na and K, etc.), alkali earth metals (Be, Mg and Ca, etc.), and transition metals (TM) (Sc, Ti, V, Cr and Mn, etc.). In metal elements, TMs have very unique properties, which are mainly reflected in the following two aspects: (1) the interaction between hydrogen molecules and TMs is belong to well-known Kubas interaction [6,23]; (2) TM atoms have large cohesive energy [24], so they tend to form clusters on the surface of pristine materials. Kubas interaction originates from the hybridization between $H_2 - \sigma^*$ antibonding and TM d orbitals. The Kubas interaction lies between chemi- and physisorption. i.e the interaction between hydrogen molecules and transition metals has a binding energy of about 0.40 eV, which is compatible with ambient temperature desorption/absorption. In addition, owing to large cohesive energy of TM atoms, the hydrogen storage capacity is decreased dramatically, but many methods have been proposed with varying to overcome this obstacle, such as chemically doped graphene, porous graphene, and single carbon vacancies, etc. [25,26]. To avoid clustering, the basic idea of these methods is that TM atoms maybe be chemically bonded onto different hydrogen adsorbent molecules through hybridization of lowest-unoccupied molecular orbital of nano-structure with TM d-orbitals (i.e., Dewar coordination).

Among the reversible solid-state hydrogen storage materials, covalent triazine-based framework (CTFs) [27–29] may become the promising hydrogen adsorbents due to its special qualities [27]. CTFs are newly developed high-performance porous materials, and exhibit remarkably large specific surface areas, a homogeneous porous structures, high quantities of nitrogen functionalities and extremely high thermal/chemical stability. Pristine CTF shows weak hydrogen molecule binding energy, but metal doping and decorating [30–35] have shown to improve its H_2 binding energy and storage capacity.

Our previous report [27] suggests that light metal such as alkali metals and alkali earth metals decorated CTFs are promising materials for hydrogen storage. As is known to all that transition metals have unique properties, we would plan to investigate whether TM atoms can be strongly localized on the CTF sheet, and transition metals is suitable candidates. The CTFs sheets have the structure with the C–N ring and the N atomic vacancy of open sites which are formed by three nitrogen atoms, and these structure may have strong transition metal adsorption energy, thereby avoiding transition metal reunion, and improve the hydrogen storage capacity. Therefore, the adsorption of transition metals (TM = Sc, Ti, V, Cr, Mn) on the CTFs surface and the hydrogen storage properties are studied in this paper. Our studies indicated that, the atoms of Sc, Ti, V, Cr, Mn can be bound strongly to the CTF. Due to the interaction between hydrogen molecules and transition metals, the hydrogen molecules are very well

adsorpted on the complexes decorated the atoms of Sc, Ti, V, Cr, and Mn.

Computational methods

The calculation were performed based on density functional theory (DFT) [36] as implemented in the Vienna *ab initio* simulation package (VASP) [37]. The electron-ion interactions and exchange-correlation potential with the generalized gradient approximation of Perdew-Bruke-Ernzerhof [38,39] integrated with the projector-augmented wave method [40]. Dispersion correction is adopted at DFT-D2 level of Grimme approach [41], and van der Waals is taken into account. The energy cutoff for the plane wave expansion was set to 450 eV to ensure a sufficient convergence. The Brillouin zones were programmed by Monkhorst-Pack [42] ($3 \times 3 \times 1$) k-point meshes for all compounds with meshes chosen to give a roughly constant density of k-points (30 \AA^3) for all compounds. Test showed that the choice of k-points get energies that are converged to within $0.01 \text{ eV (f.u.)}^{-1}$. The geometry optimization was performed in fixed lattice constants while the atomic positions in the cell were allowed to be fully relaxed until the residual forces were less than 0.02 eV \AA^{-1} .

The binding energy of the transition metal atoms on CTF is defined as $E_B = E_{TM} + E_{CTF} - E_{CTF-TM}$, where E_{CTF-TM} , E_{CTF} , and E_{TM} are the total energy of the transition metal decorated CTF, pristine CTF and the isolated transition metal atoms, respectively. Similarly, the binding energy per H_2 molecule on the transition metal decorated CTF is defined as $E_B = (E_{CTF-TM} + nE_{H_2} - E_{CTF-TM-nH_2})/n$, where n indicates the number of H_2 molecular, E_{CTF-TM} , E_{H_2} and $E_{CTF-TM-nH_2}$ are the total energies of the transition metal decorated CTF, hydrogen molecules and CTF-M- nH_2 complexes, respectively.

Results and discussion

Adsorption of TM on CTF

We studied the bonding of a single TM-atom (TM = Sc, Ti, V, Cr, Mn) to a CTF molecular. For the absorption of TM-atom on CTFs, four possible sites, including the top site of the carbon atom, the top site of the nitrogen atom, the bridge site over CN bond and the hollow site of the hexagon CN ring were tested. After full structural optimization, the TM atoms were found to locate the hollow site of the hexagon CN ring, regardless of the initial location of the TM atom. Because the absorption structures are very similar, so for simplicity only Sc absorption structure is showed [see Fig. 1]. The length of chemical bond Sc–C and Sc–N is the range of 2.17–2.25 and 2.13–2.20 Å respectively, it is evident that the length of chemical bond Sc–C and Sc–N is very close, besides the length of Sc–C and Sc–N is slightly larger [see Table 1]. At the same time, the results have shown that the length of TM–C and TM–N (TM = Sc, Ti, V, Cr, Mn) is getting smaller and smaller. The results suggested that the bond length of M – C (M = Li, Na, K, Ca, Mg and so on) in the previous report [27] are bigger than the ones of TM–C in this paper. The decrease of bond length can be attributed to the difference of the metal atomic radius. Except the metal Li,

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