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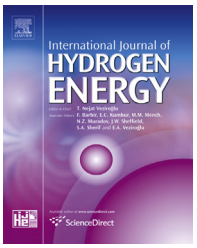

Catenated metal-organic frameworks: Promising hydrogen purification materials and high hydrogen storage medium with further lithium doping

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ABSTRACT

Based on the first-principles derived force fields and grand canonical Monte Carlo simulations, we find that the catenated metal-organic frameworks outperform the non-catenated structures, in terms of H_2 separation from other gases (CH_4, CO and CO_2) and H_2 adsorption by Li doping. A system utilizing IRMOF-11 (or IRMOF-13) for hydrogen separation and Li-doped IRMOF-9 for hydrogen storage is therefore proposed, with hydrogen uptake of 4.91 wt% and 36.6 g/L at 243 K and 100 bar for Li-doped IRMOF-9, which is close to the 2017 DOE target. It is promising to find appropriate microporous materials for hydrogen purification and storage at ambient conditions with structure catenated.

1. Introduction

With the rapid consumption of fossil fuel and the severe environmental problems, new energy source has become a very important issue all over the world. As a new type of clean energy, hydrogen energy has received wide attention from the whole world. Up to date, scientists have been facing a series of challenges, including hydrogen production, separation (purification), storage, and usage. Among these challenges, how to separate and store hydrogen efficiently and safely have been regarded as the critical problems. With the merits of high purity, high crystallization, low cost, large scale productive capability and structure controllable characteristics, metal-organic frameworks (MOFs) [1–4] have been proved to be very promising in the field of gas separation and storage, especially in hydrogen purification and storage.

However, the capacity of hydrogen storage at ambient conditions of pristine MOFs themselves is far away from the target of the U.S. Department of Energy (DOE), which is 5.5 wt % and 40 g/L for the year 2017 [5]. Alternatively, MOFs with much higher adsorption of CH_4 [2,6], CO [7] and CO_2 [6–8] than H_2 [4,7] can be used as hydrogen separation from CH_4/H_2, CO/H_2 and CO_2/H_2 mixtures. In fact, various MOFs for gas separation have been reported both experimentally [9,10] and

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theoretically [11,12]. For better hydrogen storage, plenty of discussions on strategies aiming at improving hydrogen uptake in MOFs have been presented. These strategies include linker modification [13,14], impregnation with other nanostructures [14,15], catenation [16–18], open metal sites [19,20], and substitution with lighter metals [21] for the optimization of pore size and adsorption energy of hydrogen molecule.

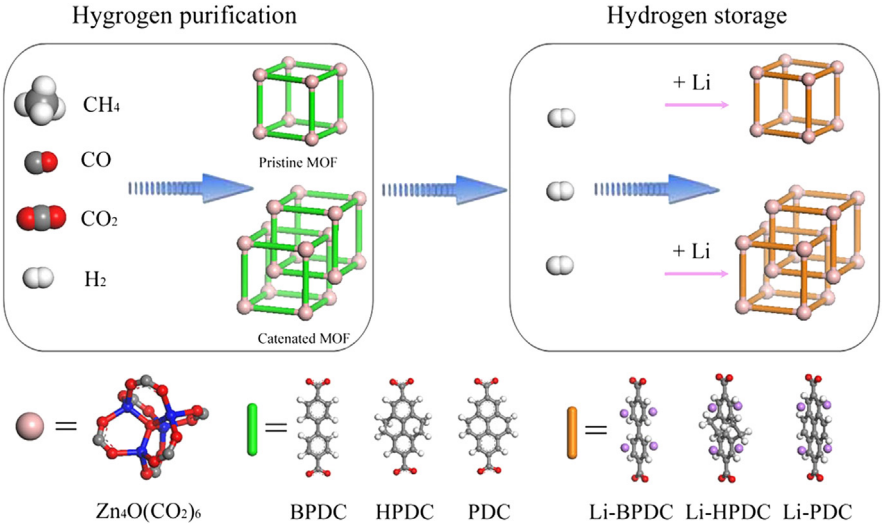
The isoreticular MOFs (IRMOFs) [2] were discovered by Yaghi and co-workers and consist of two parts: metal-corner sites and organic linkers. As seen from Scheme 1, an oxide-centered Zn_4O tetrahedron is connected by six dicarboxylate linkers, reticulating into a three-dimensional cubic porous network. In the series of IRMOFs, different organic linkers correspond to different structures. Herein after, three IRMOFs, IRMOF-10, -12, and -14, which have 4,4′-biphenyldicarboxylate (BPDC), 2,7-tetrahydropyrenedicarboxylate (HPDC), and 2,7-pyrenedicarboxylate (PDC) linkers, respectively, and their catenated structures were chosen to elucidate the effects of catenation on hydrogen separation from CH_4/H_2, CO/H_2 and CO_2/H_2 mixtures, and to find the best structures for hydrogen storage after doping with lithium. Catenation is a kind of structure where two separate frameworks interpenetrate into each other (see the catenated MOF in Scheme 1). IRMOF-9, -11 and -13 are catenated by IRMOF-10, -12 and -14 in proportion. The specific three IRMOFs and their catenated structures employed in this work are derived from experimental data [2].

Both experiments [22–25] and molecular simulations [13,14,26–30] based on first-principles show that lithium doping can highly improve hydrogen uptake in microporous materials. When doping MOFs with Li, the charge of Li atom is separated by the electron affinity of the aromatic sp^2 carbon framework so that the positively-charged Li could provide strong stabilization of hydrogen molecule. Therefore, in order to improve hydrogen uptake as much as possible, we theoretically study hydrogen adsorption in these catenated IRMOFs with Li doping at ambient temperature and pressure up to 100 bar. For the interaction between Li atom and organic linkers, one Li atom is adsorbed on each side of the aromatic rings which are connected to the carboxyl at both ends of the linkers. The positions of the Li atoms adsorbed on the aromatic rings were determined based on our density functional theory (DFT) calculations at the X3LYP/6-311G(d,p) level [31] (see the supporting information).

In this paper, we establish a system in which both functions of hydrogen purification and storage are combined. As we can see in Scheme 1, the mixtures of H_2 and other gases (CH_4, CO and CO_2) extracted from industrial hydrogen production enter into the separation chamber (pristine MOFs or their catenated structures) where most of the impurity gases are adsorbed. The gases out of the separation chamber will be sampled for testing purity of hydrogen till the requirements set beforehand are achieved. After the purification of hydrogen, the qualified hydrogen will be conveyed into the adsorption chamber. With proper materials (Li-doped MOFs) for reversible hydrogen storage, hydrogen energy could be put into service.

2. Simulation method

Force field (FF) plays a decisive role in molecular simulation. In this work, methane was modeled as a single Lennard-Jones (LJ) interaction site, with the potential parameters quoted from the TraPPE FF [32]. During the simulations on the adsorption of the CH_4/H_2, CO/H_2 and CO_2/H_2 mixtures, the hydrogen molecule was treated as a single LJ sphere with the empirically derived parameters [33]. Electrostatic interactions were ignored among the interactions of CH_4/H_2/MOFs system as previous simulations have demonstrated that these interactions barely affect the adsorption of hydrogen in MOFs at room temperature [34]. The three-site model of Straub and Karplus (SK model) was used for carbon monoxide [35]. The SK model combines three LJ pair potentials with partial point charges located at the LJ centers and the center-of-mass site. Carbon dioxide was modeled as a rigid linear triatomic



Scheme 1 – A strategy for hydrogen purification and storage as well as components of studied IRMOFs. Color spheres stand for different atoms: C, gray spheres; H, white spheres; O, red spheres; Zn, blue spheres; and Li, purple spheres.

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