

REGULAR ARTICLE

First-Principles Investigation of Li⁺-doped Conjugated Microporous Polymer as a Potential Hydrogen Storage Medium

Rui-Feng Lu^{1,2}, An Li³ and Wei-Qiao Deng^{1,*}

¹ State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.

² Department of Applied Physics, Nanjing University of Science and Technology, Nanjing, 210094, China.

³ College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, China.

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Abstract: We used first-principles calculations to investigate the adsorptive binding of hydrogen molecule with lithium doped triethynylbenzene. The prior binding site of Li⁺ is above the C≡C triple bond rather than the aromatic ring at the computational level of UM06-L/6-311G(d,p), which could provide an accurate description of cation- π interaction. For single, double, and multiple dihydrogen interaction with a formula unit of Li⁺-doped triethynylbenzene, the average binding energies per H₂ are found to be in the range of $-5.08 \sim -4.58$ kcal/mol. The strong binding affinity is promising for hydrogen storage, since it will play a crucial role in physisorption at ambient condition. Further, with a saturated 4-5-5 adsorption, a reversible hydrogen storage capacity of 14.0 wt% is attained. Based on the calculated results, we designed Li cation doped conjugated microporous polymer as hydrogen storage medium and obtained excellent hydrogen uptake performance.

AMS subject classifications: 65D18, 68U05, 68U07

Key words: Density functional theory, conjugated microporous polymer, Li doping, hydrogen storage, physisorption

*Corresponding author. *Email addresses:* rflu@njust.edu.cn (R.-F. Lu), lian2010@lut.cn (A. Li), dengwq@dicp.ac.cn (W.-Q. Deng)

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1 Introduction

The non-renewable fossil fuel resources are fast diminishing and the combustion of them always leads to not only environmental pollution but also global warming, nowadays it is imperative to exploit new sources of energy. Molecular hydrogen is thought to be an ideal replacement, because it is clean and renewable, and also abundant on earth. While considerable challenges exist in hydrogen economy, enormous efforts have been focused on developing viable hydrogen storage materials [1]. Previous studies have been devoted to complex light metal hydrides [2] as well as carbon [3–8] or BN [9, 10] based nanostructures, metal-organic frameworks (MOF) [11–16], covalent organic frameworks (COF) [17–21], zeolites [22–24], and even organic chemical hydrides [25–28]. Although many of them exhibit interesting characteristics, the problems still remain due to that they all have poor thermodynamics or kinetics, and actually none in experiment yet meet the new 2017 US Department of Energy target of 5.5 wt% reversible hydrogen storage at ambient condition. The current stage prompts us to expedite the hydrogen energy research that demands safe, efficient, and economic hydrogen storage materials.

Of the existing materials, porous polymer would be a kind of appropriate candidate for hydrogen storage as relatively simple and economic synthesis, for example, Ti-coated polymers, particularly polyacetylene [29] and ethylene [30] complexes have been suggested to possess good gravimetric densities, but Ti atoms tend to cluster and severely undermine the hydrogen storage capacity [31]. Through numerous studies of porous solid structures, such as MOF and COF, porosity and accessible surface area are prerequisite factors for gas uptake. So far, there are lack of pertinent investigations on polymer systems, partially because of their amorphism in nature and low thermal stability. Very interestingly, a new family of rigid conjugated microporous polymer (CMP) using triethynylbenzene as building block were synthesized by Cooper et al. [32, 33], who claimed that the CMP has very good chemical and thermal stability and retention of microporosity under a variety of conditions, moreover, the physical properties like micropore size and surface area can be fine tuned by varying the monomer strut.

Various *ab initio* calculations, grand canonical Monte Carlo and molecular dynamics simulations have recently shown that doping with alkali metals can enhance the fundamental interaction of H₂ with the host structures in a desired range of magnitude [5, 34–42]. The mechanism can be generally attributed to electrostatic charge–quadrupole and charge induced dipole interactions, which is further related to the localization and