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Improved design of metal-organic frameworks for efficient hydrogen storage at ambient temperature: A multiscale theoretical investigation

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ABSTRACT

A multiscale theoretical technique is used to examine the combination of different approaches for hydrogen storage enhancement in metal-organic frameworks at room temperature and high pressure by implementation lithium atoms in linkers. Accurate MP2 calculations are performed to obtain the hydrogen binding sites and parameters for the following grand canonical Monte Carlo (GCMC) simulations. GCMC calculations are employed to obtain the hydrogen uptake at different thermodynamic conditions. The results obtained demonstrate that the combination of different approaches can improve the hydrogen uptake significantly. The hydrogen content reaches 6.6 wt% at 300 K and 100 bar satisfying DOE storage targets (5.5 wt%).

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Introduction

Hydrogen is considered as an ideal fuel, environmental friendly, however, application as an energy carrier in mobile applications is limited by the key problems with efficient hydrogen storage. The US Department of Energy's (DOE) H₂ storage targets is 5.5 wt% by 2017. Nowadays, it is believed that metal-organic frameworks (MOFs) are promising materials for meeting hydrogen storage demands [1–8]. MOFs are crystalline porous materials consist of metal or metal oxide nodes connected by organic molecules – linkers [9,10]. The most advanced MOFs show very high surface area and pore volume, which are necessary for successful gas storage [11–18]. Experimental and theoretical studies on MOFs have

shown that the interaction energies between hydrogen and the framework are not large enough to meet industrial requirements for hydrogen storage at moderate thermodynamic conditions [3,7,8]. Interaction energies have to be larger than physisorption. A variety of strategies have been employed to improve capacity at room temperature, for example, framework catenation and linker functionalization. The most promising strategy is incorporating metal atoms into linkers [5]. Metal sites on linkers are sterically more accessible than open sites of nodes of MOFs. Light metal atoms are used for this purpose: Li, Na and K. Decoration of carbon nanostructures with Li atoms shows the significant increase of hydrogen uptake. Modification of MOFs by lithium atoms was studied by groups of George Froudakis [4–8] and William Goddard III [1–3]. They employed different strategies for

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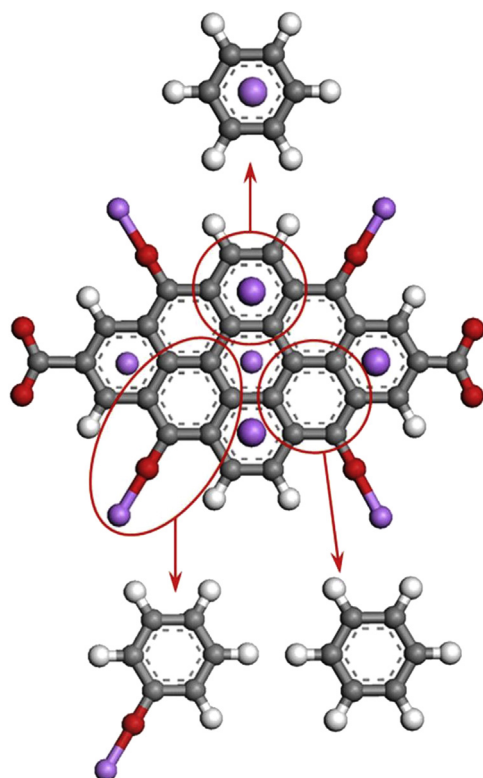


Fig. 1 – The linker of MOF is modified by lithium atoms in different ways. The linker is divided into several clusters for hydrogen binding calculations using MP2 level of theory. Lithium atoms are shown in violet colour. The large violet spheres means Li atoms are situated above the linker and small spheres means Li atoms are below the linker. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lithium incorporation in MOFs. In this work, we study the effect of the Li-doped linker for hydrogen storage enhancement. Two ways of Li-atoms dopation have been used for linker modification. The first one is replacing hydrogen atoms in linker by O–Li group. The lithium atoms have been presented

Table 1 – The parameters for grand canonical Monte-Carlo simulations developed through MP2 simulations in this work. H_H2 means hydrogen atom in hydrogen molecule. Other atoms are from the framework.

		Sig (Å)	Eps (K)
H_H2	H_H2	3.18	7.62
H_H2	Carbon	2.78	42.34
H_H2	Hydrogen	2.89	0.37
H_H2	Oxygen	2.96	10.56
H_H2	Magnesium	2.95	71.35
H_H2	Lithium	1.80	906.16
H_H2	Zinc	2.46	52.28

The parameters obtained have been checked by performing grand canonical Monte-Carlo simulation of hydrogen sorption in MOF-C6 at 77 K and at pressure up to 100 kPa. The comparison of simulated and experimental isotherms is shown in Fig. 3 and data obtained via simulation are in a good agreement with available experimental work [20].

in the form of an alkoxy salt (O–Li group) [6]. The second one is decorating linkers by placing lithium atom on planes of the linker [3] as it is shown on Fig. 1. Accurate *ab initio* calculations were employed for obtaining the preferable sorption sites and energies. Then grand canonical Monte Carlo simulations are based on interaction parameters obtained from accurate MP2 simulation and are carried out to obtain hydrogen sorption properties of MOFs modified by lithium atoms.

Computational details

MOF-C30 [3] is chosen as a starting point and the secondary building unit is modified in two ways: lithium atoms are presented as an alkoxy salt (O–Li group) by replacing hydrogen atoms in linker by O–Li group and linkers are decorated by placing lithium atom on each side of the linker as shown on Fig. 1. The modified linker is divided into several parts for the hydrogen binding energy calculations because of the huge size of the linker. Li-alkoxidebenzene is optimized using the second-order Møller-Plesset (MP2) level of theory with the approximate resolution of the identity (RI-MP2). Geometry optimization of clusters with Li atoms is performed with

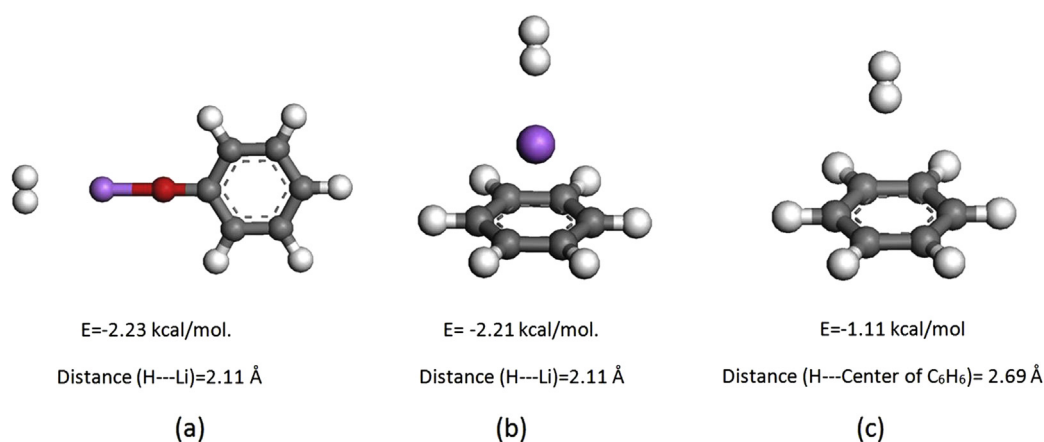


Fig. 2 – Models of parts of the linker: modified by lithium atom (a,b) and unmodified (c).

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