

# Improving Hydrogen Storage Capacity of MOF by Functionalization of the Organic Linker with Lithium Atoms

Emmanouel Klontzas,<sup>†</sup> Andreas Mavrandonakis,<sup>†,‡</sup> Emmanuel Tylianakis,<sup>§</sup> and George E. Froudakis<sup>\*,†</sup>

*Department of Chemistry, University of Crete, P.O. Box 2208, 71003 Heraklion, Crete, Greece, and Materials Science and Technology Department, University of Crete, P.O. Box 2208, 71409 Heraklion, Crete, Greece*

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## ABSTRACT

A combination of quantum and classical calculations have been performed in order to investigate hydrogen storage in metal–organic frameworks (MOFs) modified by lithium alkoxide groups. *Ab initio* calculations showed that the interaction energies between the hydrogen molecules and this functional group are up to three times larger compared with unmodified MOF. This trend was verified by grand canonical Monte Carlo (GCMC) simulations in various thermodynamic conditions. The gravimetric capacity of the Li-modified MOFs reached the value of 10 wt % at 77 K and 100 bar, while our results are very promising at room temperature, too, with 4.5 wt %.

A lot of scientific work is concentrated on finding alternative energy resources. The widely used fuels, such as diesel and petroleum, extinguish quickly. Hydrogen is considered as the ideal energy carrier, environmental friendly and the most probable successor of conventional fuels. However, an unsolved problem is finding an appropriate storage material for commercial applications. The 2010 U.S. Department of Energy (DOE) target of 6.0 wt % capacity for the total storage system has not been accomplished yet.<sup>1</sup>

Suitable materials for hydrogen storage application, extensively analyzed in previous studies,<sup>2</sup> must fulfill several requirements. The most important of them are high accessible surface area, high free volume, low adsorbent framework density, and increased energetic interactions with the adsorbed gas. During the past few years, there have been synthesized new porous materials that were close to fulfill the requirements, such as metal–organic frameworks (MOFs) materials (MOF-177 has a BET surface area of 4500 m<sup>2</sup>/gr!).<sup>3–7</sup>

Nevertheless, experimental<sup>7–11</sup> and theoretical<sup>12–21</sup> studies on these materials have shown that the interaction energies between adsorbed molecules and robust hybrid frameworks are low enough to store large amounts of hydrogen at room temperature and relatively low pressure. Optimal

interaction energies should be in a range between physisorption (this is the case in MOFs) and chemisorption (like hydrates). In this case, hydrogen would be sufficiently stored at room temperature and moderate pressures. On top of this, desorption process would be without or with a very small energy barrier.

In general, two main directions for increasing the interaction energy have been proposed. The first is the introduction of point charges in the host material, either by doping with heteroatoms or by incorporating light metal atoms. In this way, the binding energy of the hydrogen molecules will be enhanced due to charge-induced dipole interactions.<sup>22,23</sup> Although doping with heteroatoms yields larger interaction energies, these energies are still quite small, and the complexes are not likely to survive at room temperature.

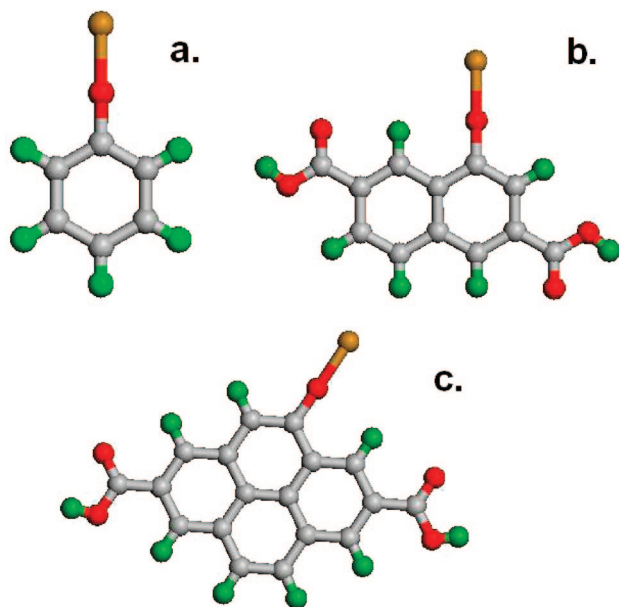
The second direction has to do with orbital interactions. The d orbitals of a transition metal interact with the antibonding orbitals of a hydrogen molecule as has been proposed in the Kubas theory,<sup>24</sup> to provide an energetically very stable scheme. For having Kubas-type interaction, we need accessible and unsaturated metal sites in the structure. Interaction energies are among the highest concerning the case of physisorption, but the introduction of heavy metals increases the weight of the host material drastically, negatively affecting the gravimetric storage. In addition, transition metal atoms prefer to form a cluster<sup>25</sup> instead of being separated. This results in loss of active adsorption sites and as a consequence the dramatic decrease of the storing capacity.

\* Corresponding author. Phone: +30-2810545055. Fax: +30-2810545001. E-mail: frudakis@chemistry.uoc.gr.

<sup>†</sup> Department of Chemistry, University of Crete.

<sup>‡</sup> Present address: Institut für Nanotechnologie, Forschungszentrum Karlsruhe, 76021 Karlsruhe, Germany.

<sup>§</sup> Materials Science and Technology Department, University of Crete.



**Figure 1.** Model systems used in this study: (a) Li-alkoxide-benzene, (b) Li-alkoxide-naphthalene-dicarboxylate (IRMOF-8 linker), and (c) Li-alkoxide-pyrene-dicarboxylate (IRMOF-14 linker).

Following the doping strategy, we have selected MOFs as host materials because of their suitable structural characteristics, functionalized with lithium atoms on the organic groups. In this way, charges are introduced in the structure without a significant increase of the weight. Decoration of carbon nanostructures with Li has been used in the past to increase hydrogen storage on these materials. Recently, Blomqvist et al.<sup>26</sup> and Han et al.<sup>27</sup> have used the same methodology in IRMOF materials. In our case, we thought to follow a similar approach to modify the organic linkers of the robust structure, without changing the material framework (keeping its valuable physical properties). To keep the total system neutral, we have introduced lithium in the form of an alkoxy salt (O–Li group) by substituting a hydrogen atom of the organic linker by an O–Li group (Figure 1a).

In this work, we are studying the effect of the Li-alkoxide linker in various IRMOFs for hydrogen storage. A combined quantum mechanics and grand canonical Monte Carlo (QM/GCMC) theoretical work has been performed in order to find binding sites and interaction strengths of H<sub>2</sub> with the modified linker and to estimate the hydrogen storage under various thermodynamic conditions. For the QM part, the organic frameworks considered are the IRMOF-8 (naphthalene dicarboxylate) and IRMOF-14 (pyrene dicarboxylate), while the larger scale GCMC simulations were performed for IRMOF-8.

Because of the large size of the IRMOFs cells for a QM calculation, the model system must be decreased in size. The reduction of the size can be achieved by separating the organic linker, saturate the carboxylate groups with H ions and treat this as an individual system (Figures 1b and 1c). This approximation is appropriate, since we are mainly interested in the effect of this new modified linker and not

in the metal cluster of the MOFs and also accurate as we have shown in a previous work.<sup>28</sup>

Density functional theory (DFT) in the resolution of identities (RI) approximation<sup>29</sup> is applied to our systems. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional<sup>30</sup> along with the polarized triple- $\zeta$  valence basis set (TZVPP) basis set is applied in the calculations. All structures are optimized without any symmetry constraints and the minima are verified by performing numerical frequency calculations.

In order to check the validity of the DFT methodology, high accuracy MP2 calculations were performed, too. Because of computation restrictions, the organic linker was further reduced to a single benzene molecule modified with the Li-alkoxide group for the MP2 part of the work only. Second order perturbation theory in the resolution of identities (RI) approximation is applied again along with the def2-TZVPP basis set. As it is explained in the text, the DFT results are in very good agreement with MP2.

All calculations (DFT and MP2) were performed with the Turbomole<sup>31</sup> program package. Binding energies are corrected for the basis set superposition error (BSSE) with the counterpoise method.<sup>32</sup> These corrections are essential since the BSSE may become critical for nonbonding interactions.<sup>28</sup> The charge distributions are computed using the Mulliken and natural orbital population analysis schemes.

Grand canonical Monte Carlo simulations were performed as an effort to calculate the hydrogen uptake for a wide range of thermodynamic states. Lennard–Jones potential was used for describing the interactions between sorbate molecules and framework atoms, where the guest molecules were modeled as a single spherical atom. Quantum effects have been proven to play a significant role in the description of these interactions especially at lower temperatures.<sup>33,34</sup> For that reason, they were taken into account using the Feymann–Hibbs effective potential. For each state, a total amount of  $2 \times 10^6$  runs were accumulated, where the first  $10^6$  were used for reaching equilibrium and the last  $10^6$  were used for calculating the ensemble averages. The parameters of the interatomic potential was either taken from experimental results<sup>35</sup> or obtained by ab initio calculations.<sup>36</sup>

As a first step, the DFT methodology is evaluated with the more accurate second order perturbation theory (MP2). Calculations have been carried out on limited molecular models, as presented in Figure 1a. We have calculated the adsorption energy of four H<sub>2</sub> molecules situated over the Li atom. The total binding energies are  $-9.05$  and  $-8.21$  kcal/mol from RI-PBE/TZVPP and RI-MP2/def2-TZVPP, respectively. Additionally, a single point energy calculation at the RI-MP2/aug-cc-pVQZ was performed, using the triple- $\zeta$  optimized structures. In this case, the total interaction energies is calculated at  $-8.91$  kcal/mol, being in very good agreement with the RI-PBE/TZVPP value of  $-9.05$  kcal/mol.

As a second step, interaction energies between one and five hydrogen molecules with the two organic linkers of IRMOF-8 and IRMOF-14 are studied by performing DFT calculations. The results in both cases are almost identical,

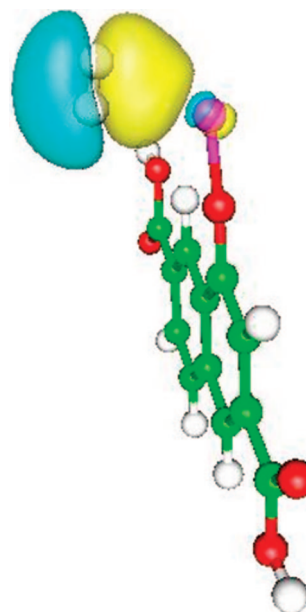
**Table 1.** Binding Energies (B.E.) for One to Five Hydrogen Molecules Absorbed over the Li Atom of the Li-Alkoxide Functionalized IRMOF-8 (naphthalene) and IRMOF-14 (pyrene)<sup>a</sup>

	Naphthalene (IRMOF-8)		Pyrene (IRMOF-14)	
	BE/H <sub>2</sub> (kcal/mol)	Li–H <sub>2</sub> (Å)	BE/H <sub>2</sub> (kcal/mol)	Li–H <sub>2</sub> (Å)
1 H <sub>2</sub>	–3.02	2.03	–2.98	2.04
2 H <sub>2</sub>	–2.87	2.06	–2.87	2.08
3 H <sub>2</sub>	–2.67	2.10	–2.67	2.10
4 H <sub>2</sub>	–2.37	2.19	–2.36	2.20
5 H <sub>2</sub>	–2.15	2.23/2.34	–2.11	2.24/2.34

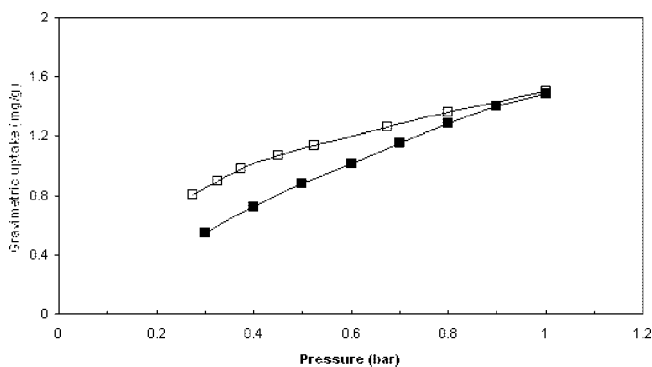
<sup>a</sup> All energies are in kilocalories per mole and are corrected for the BSSE. The distances from the Li atom are measured with respect to the center of mass of the H<sub>2</sub> molecule.

as presented in Table 1. The first two dihydrogens are strongly adsorbed with interaction energies of –3.00 and –2.87 kcal/mol per H<sub>2</sub>, respectively. These values are two to three times higher than the adsorption of the H<sub>2</sub> in the most favorable binding site of any unmodified MOF. According to several works, the adsorption energy of dihydrogen over the metal cluster of MOFs has been estimated between –0.8 and –1.5 kcal/mol.<sup>28,37</sup> The hydrogen molecules interact with a side-on conformation (T-shaped) with the Li atom, forming a triangular structure. This has been reported for the interaction of H<sub>2</sub> with Li cations previously.<sup>38,39</sup> The mean distances of the center of each dihydrogen from the Li are 2.06 Å and 2.08 Å for IRMOF-8 and IRMOF-14, respectively. When the third dihydrogen is placed over the Li atom, binding energy slightly decreases at –2.67 kcal/mol per H<sub>2</sub>. The centers of masses of the three dihydrogens are located at larger distances (2.10 Å) from the Li atom. Finally, when a fourth and a fifth H<sub>2</sub> molecule are adsorbed IRMOF-8, the binding energies per H<sub>2</sub> molecule are –2.37 and –2.15 kcal/mol, respectively. The binding energies per H<sub>2</sub> are calculated to be almost the same, in both of the organic linkers (naphthalene and pyrene). In all cases, the binding energies are attributed to charge-induced dipole, between the positively charged Li atom and the hydrogen molecule. In addition, the bond length of the hydrogen molecule is slightly elongated as a result of the strong interaction with Li. In both models and levels of theory, the Li atom is predicted to be positively charged with 0.8 to 1.0 lel. On the other hand, the adsorbed H<sub>2</sub> molecules are predicted to be slightly polarized, which was also supported by performing a charge redistribution analysis of the modified naphthalene linker upon H<sub>2</sub> adsorption. In Figure 2, we have displayed the charge density difference  $\Delta\rho$ , where the high degree of polarization of the hydrogen molecule can be seen. This can be attributed to the high electric field that is present because of the positive point charge that we have calculated for Li.

Grand canonical Monte Carlo (GCMC) simulations were held for IRMOF-8. Two alkoxide groups were incorporated in every organic linker. These groups are at the different sides of the organic linker. Additionally, storage properties have also been calculated for the unmodified IRMOF-8 for comparison. This was done for presenting the significant enhancement due to the lithium alkoxide group on the



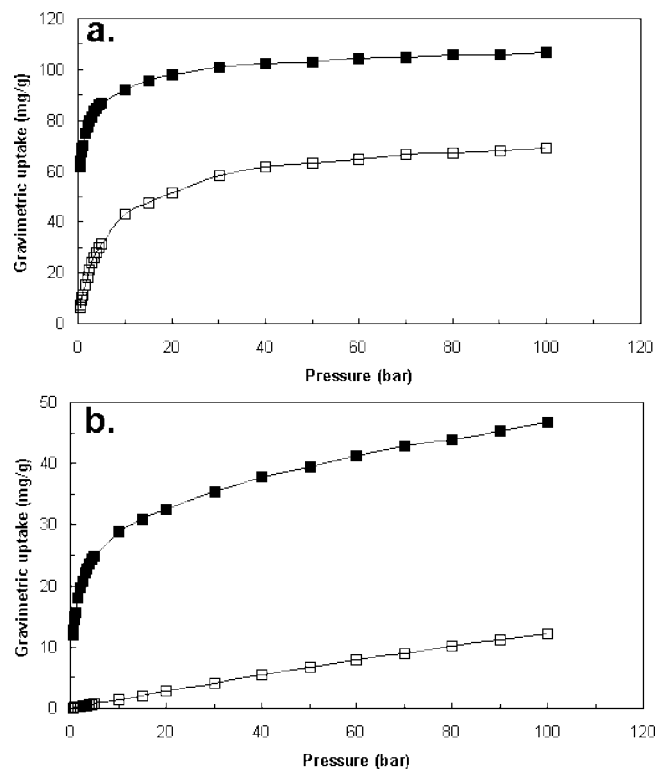
**Figure 2.** Charge density redistribution plot for the interaction of the modified organic linker with H<sub>2</sub>.  $\Delta\rho = \rho[\text{modified linker} + \text{H}_2] - \rho[\text{modified linker}] - \rho[\text{H}_2]$ . Yellow and blue represent charge gain and charge loss distributions, respectively.



**Figure 3.** Simulated and experimental adsorption isotherms of unmodified IRMOF-8 for low pressures at 77 K. Open squares, experimental results taken from ref 40; filled squares, simulated results from this study.

hydrogen storage ability. In addition, the GCMC calculations on unmodified IRMOF-8 were also used to compare our results with the corresponding experimental data of IRMOF-8,<sup>40</sup> as a validation of the GCMC methodology. This can be done mainly at 77 K, since at ambient temperatures the literature lacks of experimental results. Figure 3 shows the comparison of the results of our simulations with the experimental results, taken from ref 40 by Roswell et al. From Figure 3 can be concluded that there is a reasonable agreement between theory and experiment. In this reference, there are no results for elevated pressures. However, in a similar experimental work of the same research group,<sup>41</sup> there are results for other types of metal–organic frameworks at elevated pressures. From an effort to reproduce these results at higher pressures by applying the same methodology, it was revealed that the saturation adsorption was overestimated, although at lower pressures there is also a good agreement with other types of MOFs. This discrepancy at



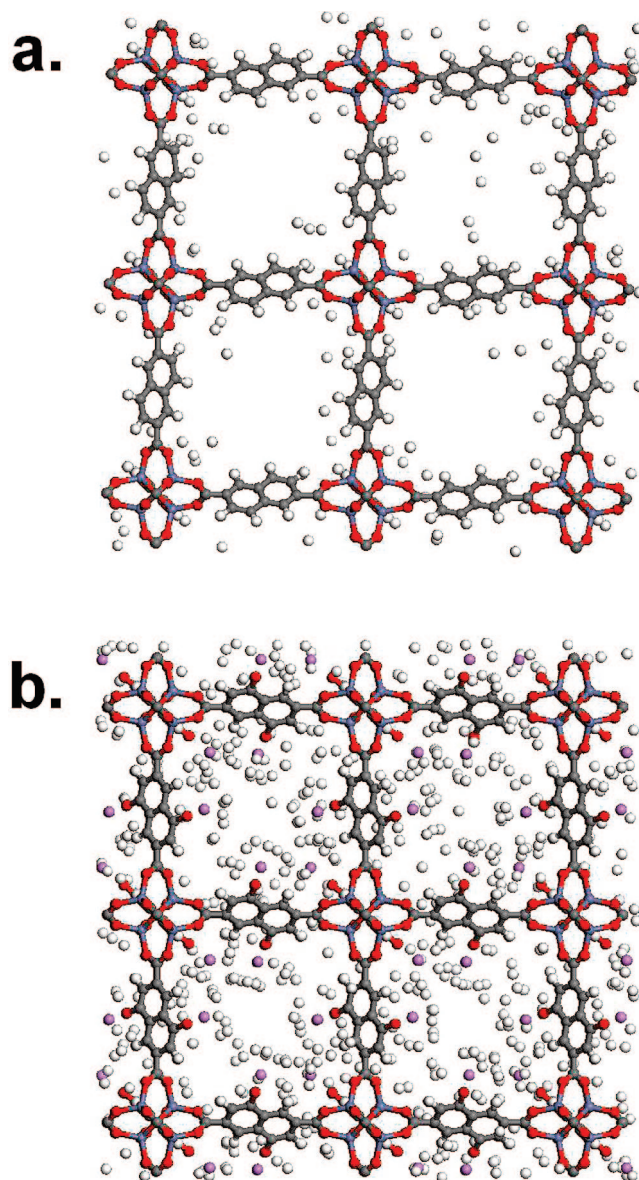


**Figure 4.** Simulated adsorption isotherms of unmodified and modified IRMOF-8 at (a) 77 K and (b) 300 K. Filled squares, results for modified IRMOF-8; open squares, results for unmodified IRMOF-8.

higher pressures between simulations and experimental results has been reported from several research groups using different force fields.<sup>12,14,42,43</sup>

Figure 4 shows the hydrogen adsorption isotherms of unmodified and modified IRMOF-8 at 77 and 300 K. The enhancement of the uptake in both cases because of Li-alkoxide modification can clearly be seen. This enhancement becomes more pronounced at ambient temperature and pressure conditions, leading to an increase by a factor of 75 and reaching 1.57 wt % for modified IRMOF-8. This result is a consequence of the stronger binding (up to 3 times stronger) of H<sub>2</sub> in Li-modified organic linker compared with the unmodified. At high temperatures and low pressures, the binding strength is the factor that makes the difference. Similar enhancement has been observed in other cases where Li has been used as a dopant for improving the adsorption capacity.<sup>27,36,44</sup> This can be seen also from Figure 5, which presents a snapshot of GCMC calculation for each system we studied, that is, the modified and unmodified IRMOF-8. Both snapshots are under the same thermodynamic state (77 K and 1 bar). The enhancement of hydrogen adsorption capacity is obvious. In addition, the preference of hydrogen molecules to accumulate sites close to lithium atoms, as a consequence of the strong interaction between lithium and hydrogen, is visible.

As a conclusion, a multi-scale theoretical investigation has been performed in order to present the effect of the lithium alkoxide modification on the hydrogen storage ability of MOFs. The ab initio calculations showed that the interaction



**Figure 5.** Snapshots of the IRMOF-8 cage with adsorbed H<sub>2</sub> at 77 K and 1 bar; (a) unmodified IRMOF-8, (b) Li-alkoxide modified IRMOF-8.

energies between the hydrogen molecules and the functionalized organic linker are significantly enhanced. This trend was verified by performing GCMC simulations at various thermodynamic conditions. The results are very promising showing a gravimetric uptake of 4.5 wt % at room temperature that reached the value of 10 wt % at 77 K, both at 100 bar. The corresponding volumetric uptake is 22.0 gr/lit at 300 K and 59.5 gr/lit at 77 K. The main novelty in this work is that Li atoms are part of the material framework and not just dopants.<sup>26,27,37</sup> The main difference from previous works<sup>27,36</sup> is that the Li atom is not adsorbed over the aromatic ring. As a consequence, the aromatic binding sites remain free and active and dihydrogen could be absorbed also over them.

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