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Enhancement of Hydrogen Adsorption in Metal−Organic Frameworks by the Incorporation of the Sulfonate Group and Li Cations. A Multiscale Computational Study

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Abstract: By means of ab initio methods, the effect on the H_2 storage ability of a newly proposed organic linker for IRMOF-14 has been studied. The linker comprises a negatively charged sulfonate ($-SO_3^{-1}$) group in combination with a Li cation. It is found that these two charged groups significantly increase the interaction energy between the hydrogen molecules and the new proposed organic linker of the MOF. The substituted group of the linker may host up to six hydrogen molecules with an average interaction energy of 1.5 kcal/mol per H_2 molecule. This value is three times larger than the binding energy over the bare linker that has been obtained from DFT calculations. GCMC atomistic simulations verified that the proposed material can be qualified among the highest adsorbing materials for volumetric capture of H_2, especially at ambient conditions. This functionalization strategy can be applied in many different MOF structures to enhance their storage abilities.

A great deal of scientific work has been focused on finding alternative energy resources. Widely used fuels, such as diesel and petroleum, are extinguishing very quickly. Molecular hydrogen is considered as the ideal energy carrier, since it has a large power density in contrast to diesel and is environmental friendly. However, the main problem is finding an appropriate storage material for commercial applications. The 2010 U.S. Department Of Energy (DOE)[1] target of 6.0 wt % capacity for the total storage system has not been accomplished yet.

Potential Hydrogen Storage Materials (HSM) must operate under ambient conditions of temperature and pressure. Hydrogen may interact with HSM in two possible ways. The first is dissociative chemisorption. In this case, molecular hydrogen is dissociated and chemically adsorbed as atomic hydrogen. A typical example of such materials are metal hydrides.[2] Although high hydrogen capacities have been achieved, the main disadvantages of such materials have been the slow kinetics for the hydrogen abstraction from the HSM surface and the irreversible hydrogen adsorption/desorption after a few cycles of loading/uploading.

The second way is the physical or the chemical adsorption of hydrogen in HSM where hydrogen retains its molecular form, which has been the case in carbon-based materials,[3,4] Metal−Organic Frameworks (MOFs),[5] and metal doped polymers.[6,7] This would allow fast kinetics in adsorption and desorption to be observed. However the main disadvantage in the case of MOFs and carbon materials has been the low temperatures that are needed, since small amounts of hydrogen can be kept at room temperature. The main reason for the decreased %wt H_2 adsorption can be attributed to the weak[8] interaction energies (0.5 to 1 kcal per mol, for DFT and MP2 level of theory, respectively) between H_2 and HSM. Although transition metal doped polymers have higher interaction energies with the dihydrogen, the experimental synthesis of the proposed structures has been proved to be very difficult. One of the main problems is that the metal atoms prefer to form clusters[9] instead of being separated. This effect causes a loss of active metal sites for hydrogen adsorption.

From our previous work in the field of hydrogen storage in MOFs and carbon nanotubes (CNTs), some useful conclusions have been found for designing promising materials for hydrogen storage applications.[10,11] Among these, it has been found that the decoration of a surface of a porous material with point charges improves the storage capacity since they increase the H_2 binding energy. CNTs doped with alkali metals have shown an increased interaction with H_2. Li doping in MOFs has been theoretically studied by Mavrandonakis et al.,[12] Klontzas et al.,[13] and others,[14,15] leading to increased storage performance. Since

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(1) See U.S. DOE Web site, http://www.eere.energy.gov.
(2) Fichtner, M. *Adv. Eng. Mater.* **2005**, *7*, 443–455.
(3) Liu, C.; Cheng, H. M. *J. Phys. D: Appl. Phys.* **2005**, *38*, R231.
(4) Lee, H.; Choi, W. I.; Ihm, J. *Phys. Rev. Lett.* **2006**, *97*, 056104−1.
(5) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670.
(6) Durgun, E.; Ciraci, S.; Zhou, W.; Yildirim, T. *Phys. Rev. Lett.* **2006**, *97*, 226102–1.
(7) Zhou, Z.; Gao, X.; Yan, J.; Song, D. *Carbon* **2006**, *44*, 939.
(8) Lochan, R. C.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1357.
(9) Wang, Q.; Jena, P.; Kawazoe, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14582.
(10) Froudakis, G. E. *Nano Lett.* **2001**, *1*, 531.
(11) Mpourmpakis, G.; Froudakis, G. E.; Lithoxoos, G. C.; Samios, J. *Nano Lett.* **2006**, *6*, 1581.

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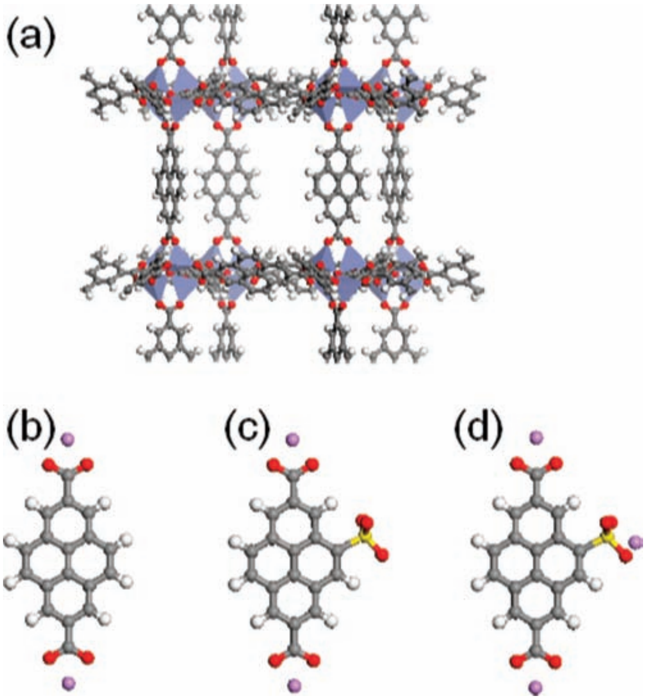

Figure 1. (a) Structure of the IRMOF-14 cell and optimized geometries of the model systems based on the organic linker used in IRMOF-14 that are used in the calculations, (b) unmodified linker, (c) modified with the $-SO_3^{-1}$ group, and (d) modified with $-SO_3^{-1}\cdots Li^{1+}$ (atom colors: Zn, blue polyhedra; C, gray; O, red; H, white; S, yellow; Li, purple).

the importance of Li doping has been proven in many cases, a problem that remains is the synthesis of a Li doped MOF according to an appropriate synthetic procedure.

Lochan et al.[8] has shown that a Li ion could interact with six hydrogen molecules, having binding energies of 6 kcal/mol per molecule. In addition, the sulfate anion could bind multiple hydrogen molecules with energies of 5 kcal/mol each. Based on the above-mentioned results, we propose that doping the linker of MOFs with Li cations will increase the interaction energy with H_2, thus leading to higher storage capacities. In this instance, the Li cations could be combined with a negatively charged sulfonate ($-SO_3^{-1}$) group to obtain a neutral MOF structure. In order to propose an experimentally realistic model, we have chosen the sulfonic acid ($H-SO_3H$) group, since it can be incorporated in organic acids having the formula $R-SO_3^-H^+$. In a recent work, a Zn-sulfonate coordination polymer was synthesized, having a negatively charged framework.[16] The negative charges were compensated by Na cations, which can be potentially exchanged by Li^+.

In this work, we examine the single and multiple adsorption of hydrogen molecules at the $LiSO_3$-modified IRMOF-14. The organic linker of this MOF is composed of a pyrene molecule, as presented in Figure 1a. Furthermore, the surface area of this organic linker is larger than the benzene dicarboxylate group in IRMOF-1 (one phenyl ring) allowing up to eight hydrogen molecules to be adsorbed. Nevertheless, this functionalization can be applied to other organic linkers, such as the naphthalene dicarboxylate of IRMOF-8. As a further step, we performed Monte Carlo atomistic simulations at various thermodynamic conditions to explore the effectiveness of the linker modification to increase the gravimetric and volumetric hydrogen storage abilities of the proposed materials.

Computational Details

Due to the large size of the IRMOF-14 cell (Figure 1a), the model system must be decreased in size, to prevent prohibitively large first principles computations. The reduction in size can be achieved by separating the organic linker; saturate the carboxylate groups with Li ions and treat this as an individual system (Figure 1b). This approximation is known to give the correct representation of the effect of the metal unit on the organic linker.[17,18] Our work is divided in two parts. In the first, we study the effect of the $-SO_3^{-1}$ group (Figure 1c), whereas, in the second, we study the presence of the neutral $-SO_3^{-1}\cdots Li^{1+}$ group (Figure 1d) with multiple hydrogen molecules.

Density Functional Theory (DFT) in the Resolution of Identity (RI) approximation is applied to our systems. The PBE exchange-correlation functional along with the TZVPP basis set is used in our calculations. All structures are optimized without any symmetry constraints, and the minima are verified by performing a numerical frequency calculation.

To check the validity of the DFT methodology, high accuracy MP2 calculations were performed. Due to computational restrictions, the organic linker was further reduced to a single benzene molecule modified with the sulfonate group, either in the anionic $R-SO_3^{-1}$ form or in the neutral $R-SO_3^{-1}\cdots Li^{1+}$. Second-order perturbation theory in the Resolution of Identities (RI) approximation is applied again along with the TZVPP basis set. As it is shown in the text, DFT results are in very good agreement with MP2.

All calculations (DFT and MP2) were performed with the TURBOMOLE program.[19] Additionally, all binding energies are corrected for the Basis Set Superposition Error (BSSE) with the counterpoise method. These corrections are essential since the BSSE may become critical for nonbonding interactions.

In an effort to examine the adsorption capability of the modified MOFs for hydrogen storage, Grand Canonical Monte Carlo (GCMC) simulations were carried out at both cryogenic and ambient temperatures for a wide range of pressures. Similar simulations were held for the unmodified MOFs to prove the effectiveness of the proposed modifications to enhance hydrogen storage. The Lennard–Jones potential was used for describing the interactions between sorbate molecules and framework atoms. These classical interatomic potentials were fit to ab initio results that were obtained in this study. The various MOFs used for the simulations were represented in atomistic detail, whereas the guest dihydrogen molecules were modeled as a single spherical atom for the calculation of their interactions. For cryogenic temperatures quantum effects were introduced in the simulation algorithm based on the Feynman–Hibbs formula.

Results and Discussion

First, we examined the hydrogen adsorption on the negatively charged organic linker functionalized with the $-SO_3^{-1}$ group. The structure of the model system is optimized and presented in Figure 1c. As a second step, a single hydrogen molecule was adsorbed over the sulfonate group. The optimized structure is presented in Figure 2a, and the interaction energies are summarized in Table 1. The hydrogen molecule is bound in an "end-on" configuration, similar to that in the SO_4^{-2} case.[8] However

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(12) Mavrandonakis, A.; Tylianakis, E.; Stubos, A. K.; Froudakis, G. E. *J. Phys. Chem. C* **2008**, *112*, 7290.

(13) Klontzas, E.; Mavrandonakis, A.; Tylianakis, E.; Froudakis, G. E. *Nano Lett.* **2008**, *8*, 1572.

(14) Han, S. S.; Goddard, W. A. *J. Am. Chem. Soc.* **2007**, *129*, 8422.

(15) Blomqvist, A.; Moyses Araujo, C.; Srepusharawoot, P.; Ahuja, R. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 20173.

(16) Park, H.; Krigsfeld, G.; Parise, J. B. *Cryst. Growth Des.* **2007**, *7*, 736.

(17) Sagara, T.; Ortony, J.; Ganz, E. *J. Chem. Phys.* **2005**, *123*, 214707–1.

(18) Hubner, O.; Gloss, A.; Fichtner, M.; Klopper, W. *J. Phys. Chem. A* **2004**, *108*, 3019.

(19) TURBOMOLE version 5.8 (http://www.turbomole.com).

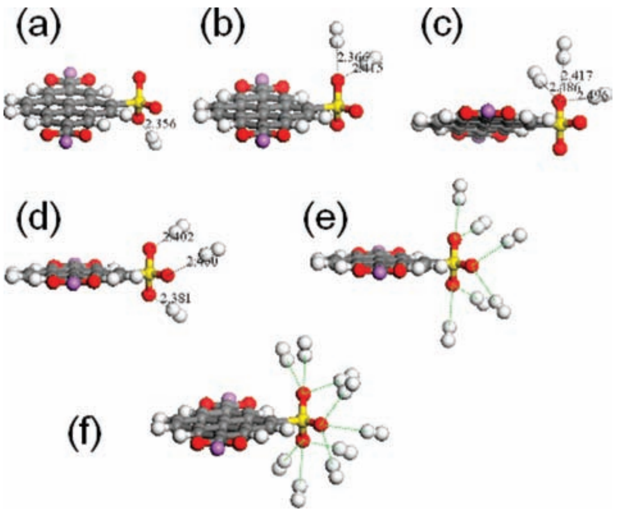

Figure 2. Optimized geometries of hydrogen interacting with the $-SO_3^{-1}$ group, (a) 1 H_2, (b) 2 H_2, (c) 3 H_2 on the same oxygen site, (d) 3 H_2 on different oxygen sites, (e) 6 H_2 and (f) 9 H_2.

Table 1. Binding Energies for Single and Multiple H_2 Molecules Interacting with an Anionic and Neutral Sulfonate Group, Incorporated in the Organic Linker of IRMOF-14 (All Binding Energies Are in kcal/mol)

model systems (Figure 1c and 1d)	no. of H_2's	total binding energy	total binding energy (BSSE corrected values)	average binding energy per H_2 (BSSE corrected values)
anionic group: $R-SO_3^{-1}$ (Figure 2)	1 H_2	2.0	1.7	1.7
	2 H_2	4.0	3.5	1.8
	3 H_2	6.0	5.1	1.7
	6 H_2	11.3	9.2	1.5
	9 H_2	15.3	12.2	1.4
neutral: $R-SO_3^{-1}\cdots Li^{1+}$ (Figure 3)	1 H_2	2.7	2.6	2.6
	2 H_2	5.0	4.8	2.4
	3 H_2	6.9	6.6	2.2
	4 H_2	7.8	7.4	1.9
	5 H_2	8.8	8.1	1.6
	6 H_2	9.7	8.9	1.5

the interaction energy is smaller. It is estimated to be −2 kcal/mol according to DFT.

Application of MP2 in the smaller model system gives a binding energy of −2.2 kcal/mol. We also checked how DFT performs on the same model system, and the results are in very good agreement with the MP2. The binding energy was found to be −2.3 kcal/mol for DFT calculations. The counterpoise correction for the basis set superposition error reduces these binding energies to −1.7 and −1.9 kcal/mol for MP2 and DFT, respectively. For the larger model system, the DFT counterpoise corrected value is −1.7 kcal/mol. Hence, the choice of the DFT functional and the basis set are adequate to describe the electrostatic forces in this molecule, as the counterpoise correction is only 15% of the uncorrected values. The interaction between the $-SO_3^{-1}$ group and the H_2 molecule is larger than typical vdW forces and can be attributed to charge induced-dipole forces. This is also verified by performing natural population analysis, which showed that the hydrogen atoms of the molecule are slightly polarized.

The possibility of multiple molecule adsorption over the same oxygen site has also been checked. It was found that after the second and third hydrogen molecule adsorption the total corrected binding energies are −3.3 and −4.5 kcal/mol, respectively. The optimized structures are presented in Figure 2b and 2c, respectively.

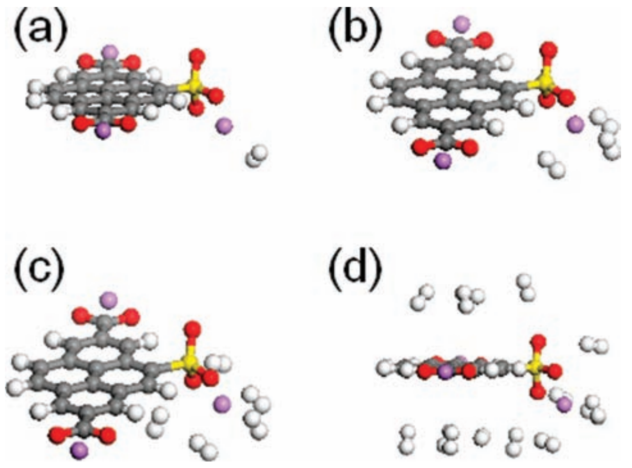

Figure 3. Optimized geometries of dihydrogen interacting with the $-SO_3^{-1}\cdots Li^{1+}$ group, (a) 1 H_2, (b) 3 H_2, (c) 5 H_2 and (d) 14 H_2 on all possible binding sites of the modified neutral linker.

As all oxygen atoms are equivalent, two more binding sites exist in the sulfonate anion. The total corrected binding energies for two and three hydrogen molecules on different oxygen sites are −3.5 and −5.1 kcal/mol, respectively. The optimized structure for three adsorbed hydrogen molecules is presented in Figure 2d. Finally, three and six more hydrogen molecules were allowed to relax, hence two and three molecules per oxygen site, as presented in Figure 2e and 2f, respectively. The total binding energies for four, five, and six dihydrogens are −6.5, −7.9, and −9.2 kcal/mol. The total binding energy scales almost linearly versus the number of H_2 molecules. Finally, when nine hydrogen molecules are allowed to relax over the three oxygen sites, the counterpoise corrected interaction energy is −12.2 kcal/mol.

Afterwards, we examined hydrogen adsorption on the neutral organic linker containing the $-SO_3^{-1}\cdots Li^{1+}$ group. The structure of the neutral molecule is optimized and presented in Figure 1d. Then a hydrogen molecule is allowed to relax either on the anionic or on the cationic side. When the dihydrogen is adsorbed over the Li ion, the binding energy is calculated to be 2.7 kcal/mol. The optimized structure is presented in Figure 3a. The counterpoise corrected value is 2.6 kcal/mol.

For the smaller model system, the MP2 interaction energy is 2.6 and 2.3 kcal/mol after the BSSE correction. In this case too, DFT can sufficiently describe the interactions, since the corresponding uncorrected and corrected values for the small model system are 2.7 and 2.6 kcal/mol, respectively. These values are almost half of the binding energies calculated for the bare metal ion,[8] although the geometries of the $Li-H_2$ cluster are almost identical. This can be attributed to the fact that the full charge of the cation is not available, due to the complexation of the metal with the sulfate anion. The same trend appears also in the $-SO_3^{-1}$ group. When a dihydrogen interacts only with the oxygen atoms of the $-SO_3^{-1}\cdots Li^{1+}$ cluster, the binding energy is significantly lower than that when it interacts with a lone $-SO_3^{-1}$ group. The interaction energy has been calculated at 0.7 kcal/mol.

Although the full charge of the ions is not available, multiple hydrogen molecules can be absorbed on the ionic part of the linker. The binding energy per H_2 atoms falls versus the number of the H_2 molecules. We have calculated the adsorption of up

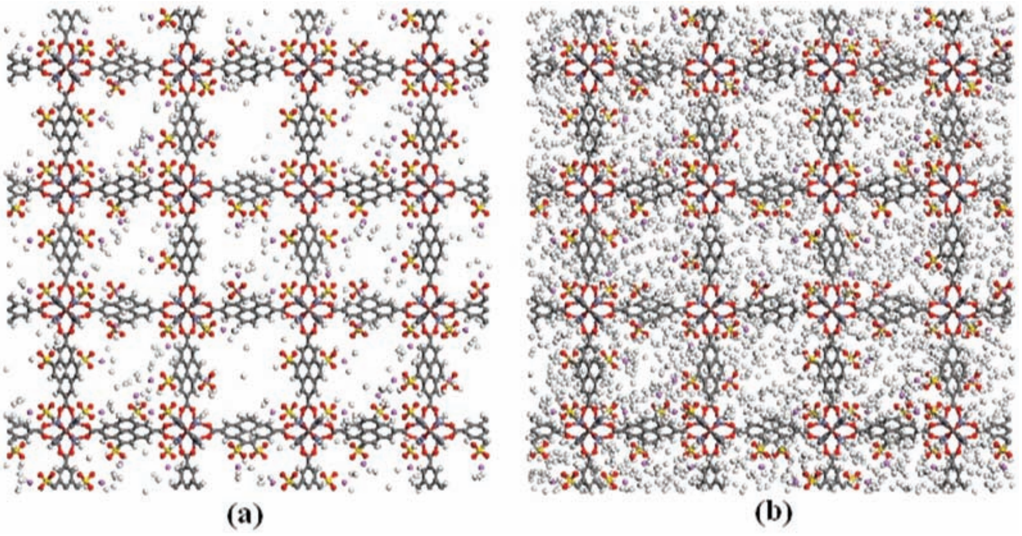

Figure 4. Snapshots from GCMC simulation of SO_3Li group modified IRMOF-14 for (a) the low loading region of 300 K and 10 bar and (b) the high loading region of 77 K and 30 bar.

to 6 H_2, and the total binding energies are 4.8, 6.6, 7.4, 8.1, and 8.9 kcal/mol for two, three (Figure 3b), four, five (Figure 3c), and six adsorbed molecules, respectively. Due to stereochemical repulsions, only the first three H_2 molecules may interact directly with the Li cation. The other H_2 are located over the oxygen atoms of the $-SO_3^{-1}$ group.

The next step of our investigation involved some GCMC simulations to calculate the adsorption isotherms of the various MOFs that were examined in this study. Figure 4 presents two snapshots from the simulation of the $-SO_3Li$ group modified MOF, for low loading at 300 K and 10 bar [Figure 4a] and for high sorbate loading at 77 K and 30 bar [Figure 4b]. The hydrogen storage capacity of the material was calculated in terms of gravimetric and volumetric uptake for various thermodynamic conditions. Figures 5 and 6 show the predicted gravimetric and volumetric isotherms respectively at 77 and 300 K. An inspection of volumetric uptake isotherms indicates that the volumetric capacity is enhanced constantly for the $-SO_3Li$ modified IRMOF-14, in comparison with the other three frameworks simulated in this study. The only exception to this trend is the uptake at high pressures at cryogenic temperature, and the reason for this will be explained afterward. As it was expected and has already been proved from first principles calculations, the Li presence improves the interaction energy between the framework and the dihydrogen molecules, since the frameworks containing Li adsorb a larger amount of H_2. Uptake enhancement can be attributed mainly to Li atoms of the $-SO_3Li$ group. The adsorption improvement is more pronounced at low loadings, where almost all sorbates tend to accumulate close to Li sites. This can also be seen in the snapshot of the simulation in Figure 4, where the density of adsorbed molecules is higher close to Li atoms. The density enhancement of H_2 close to Li atoms tends to diminish at high loadings where the number of sorbate molecules increase due to high bulk density. Thus, all the accessible volume of the material possesses almost the same sorbate density, as can be seen from the high loading snapshot in Figure 4b.

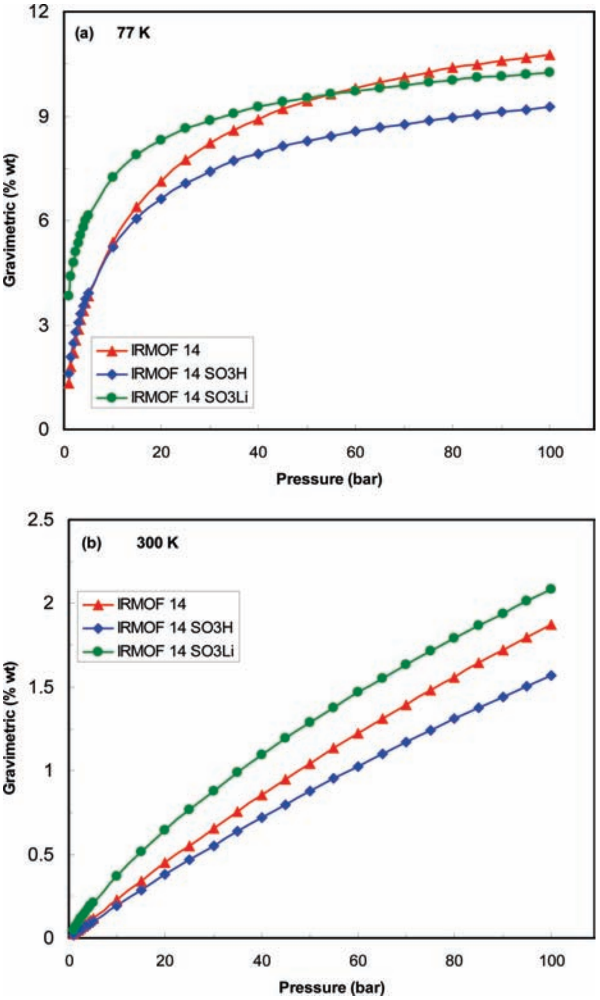

Figure 5. Total gravimetric hydrogen adsorption isotherms for pristine and structure modified IRMOF-14 at (a) 77 K and (b) 300 K.

The interaction energy between adsorbent and sorbate molecules is larger, compared even with the case for the Li doped material. This can be explained by the fact that the $-SO_3Li$ group offers four more interaction sites, i.e., due to the three oxygen and the single sulfur atom sites. These additional sites enhance the interaction between sorbate and adsorbent. In fact, the $-SO_3^{-1}$ group increases significantly this interaction energy, an effect similar to the one that has been referred to in the

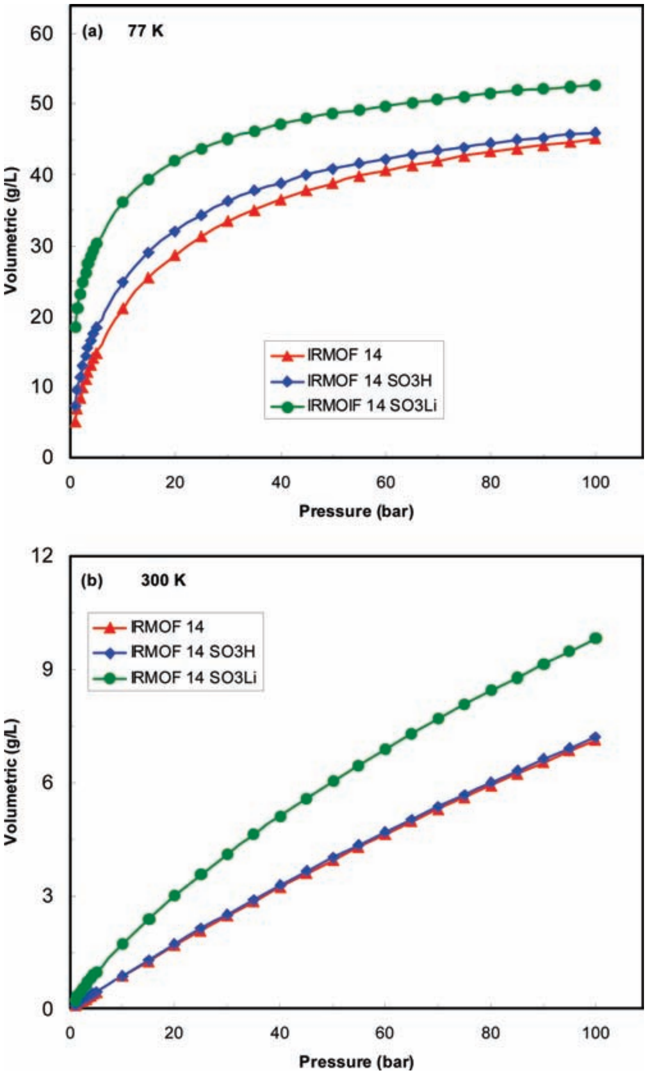

Figure 6. Total volumetric hydrogen adsorption isotherms for pristine and structure modified IRMOF-14 at (a) 77 K and (b) 300 K.

literature by Lochan[8] for the case of SO_4^{-2}. This enhanced binding energy leads to the increase of adsorbed molecules and to a proportional increase of volumetric uptake, since it solely depends on the number of molecules adsorbed and the dimensions of the material which are exactly the same for all of the systems studied here. Nevertheless, this uptake enhancement is not reflected in the gravimetric uptake at 77 K and high pressures. The reason for this inconsistent behavior of the gravimetric versus the volumetric uptake is that the increase of the interaction energy is not high enough to overcome the additional weight due to the modified structure. Indeed, IRMOF-14 was modified by replacing a hydrogen atom of 1 amu mass with the $-SO_3Li$ group of 87 amu mass. Thus, weight is added in the structure without a proportional increase of the binding energy. At low loadings however, the gravimetric uptake is larger compared to the other two MOF structures. This is due to the fact that, at low loadings, the interactions between H_2 and the MOF structure have a dominant role.

At high loadings the surface area and pore sizes are the most important properties of the hydrogen storage materials. In this case, the bulky $-SO_3Li$ group occupies a considerable part of the MOF volume. This causes a decrease in the available volume, where hydrogen molecules could be adsorbed. Furthermore, the functionalization of the MOF material leads to a decrease in the surface area with respect to the unmodified material. As a consequence, hydrogen sorption characteristics at elevated pressures are not improved significantly with respect to the IRMOF-14.

Conclusions

We propose the chemical modification of the organic linker of IRMOF-14 with the $-SO_3^{-1}\cdots Li^{1+}$ group. A similar MOF has already been synthesized.[16] By applying ab initio methods, it is found that the interaction energies of this charged group with H_2 molecules are significant higher than that with a single aromatic molecule due to the polarization of the H_2. The nature of these interactions is attributed to charge-induced dipole forces, which are stronger than typical vdW dispersion forces. This new proposed linker may adsorb up to 14 H_2 molecules, whereas the unmodified ligand may absorb only up to 8. GCMC simulations showed a constant increase of volumetric uptake due to the modification, since it offered more and stronger binding sites compared to the unmodified material. The gravimetric uptake has been enhanced at low and moderate pressures also, which correspond to the desired thermodynamic states for automobile applications. The present work suggests a new direction which can be taken into account to synthesize new MOFs that fulfill the DOE hydrogen storage targets.

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