Hydrogen Storage

DOI: 10.1002/ange.200900960

Lithium-Doped 3D Covalent Organic Frameworks: High-Capacity Hydrogen Storage Materials[**]

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It has become increasingly clear that hydrogen as a viable energy carrier may play an important role in future energy plans. However, development of reasonably safe and reversible hydrogen storage materials for transportation is still a great challenge.[1] Using mesoporous carbon materials, it has to date been difficult to meet the storage capacity target of 6 wt% set by the US Department of Energy for hydrogen fuel-cell vehicles. A pressing task is to seek new materials for efficient hydrogen storage. An important step forward was the introduction of metal–organic frameworks (MOFs).[2] Some MOFs, for example MOF-177 and MOF-5, have high BET specific surface areas (SSAs), and the strong London dispersion between linkers and connectors with hydrogen makes them attractive materials for hydrogen adsorption and storage.[3,4] However, MOFs still behave poorly at room temperature and cannot reach the target for practical use.

Schlapbach and Zuttel[1] pointed out that high SSA is a key factor to store hydrogen efficiently. Recently, a family of three-dimensional (3D) covalent organic frameworks (COFs) was synthesized by Yaghi and co-workers.[5] The crystalline 3D COFs were synthesized by self-condensation and co-condensation reactions of the rigid molecular building blocks tetrahedral tetra(4-dihydroxyborylphenyl)methane (TBPM) or its silane analogue (TBPS) and triangular hexahydroxy triphenylene (HHTP; Figure 1). The B_3O_3 and C_2O_2B rings of these materials are covalently connected to form very stable nanoporous frameworks. These COFs possess not only extremely high surface areas but also extraordinarily low densities. For example, the BET SSAs of COF-102 and COF-103 reach 3472 and 4210 $m^2 g^{-1}$, and the densities are 0.41 and 0.38 $g cm^{-3}$, respectively. COF-105 and COF-108 have even lower densities of 0.18 and 0.17 $g cm^{-3}$, respectively. Important is that the entire material is accessible and an adsorbed molecule "sees" all the atoms of the framework. These impressive numbers make these materials ideal candidates for hydrogen storage. Herein we address the question of whether these materials have excellent hydrogen storage capacity at both cryogenic and room temperatures, and we introduce a multiscale theoretical method,[6] which combines first-principles calculations and grand canonical Monte Carlo (GCMC) simulation, to evaluate the hydrogen-adsorption capacities.

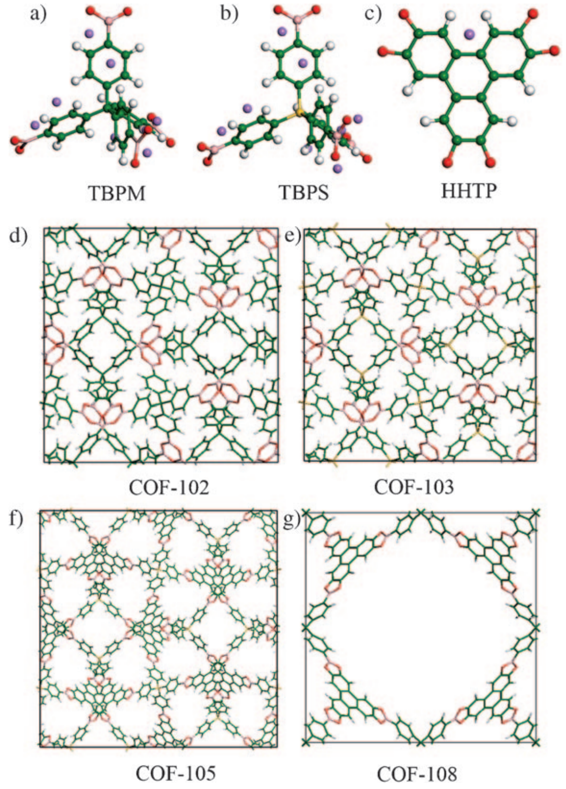

Figure 1. a–c) Li-doped building blocks and d–g) unit cells of 3D covalent organic frameworks. H atoms linked to oxygen in (a–c) are omitted for clarity. The scheme of Li doping on 3D COFs is determined from calculations (see the Supporting Information for details). Li violet, H white, B pink, C green, O red, Si yellow.

The first-principles calculations were performed at the second-order Møller–Plesset (MP2) level of theory using the cc-PVTZ basis set to investigate the interaction between H_2 and COFs. Then, the calculated potential energies were fitted to the force fields (FF), yielding the FF parameters between H_2 and COFs. Using the force fields, GCMC simulations were employed to predict the adsorption isotherm of H_2 in COFs (see the Supporting Information).

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[**] This work is supported by NSF of China (20776005, 20736002), Beijing Novel Program (2006B17), National Basic Research Program of China (2007CB209706), NCET Program (NCET-06-0095) from the MOE, Chemical Grid Program from BUCT. We thank Prof. J. Long at UC Berkeley for his comments.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900960.

To ensure that our method is accurate enough to give correct predictions, the experimental isotherms of Ar in COFs[5] were used as a benchmark to calibrate the accuracy of our method. Figure 2 shows that the calculated adsorption isotherms of Ar in COF-102 and COF-103 at $T = 87$ K are in satisfactory agreement with the experimental data. This result is encouraging, in particular if we compare our approach with the results obtained by Garberoglio,[7] who pointed out that the Dreiding and UFF force fields gave isotherms that deviate 25% from the experimental data. As we used the same multiscale procedure for H_2 adsorption, the agreement of Ar isotherms with experiment gives us some confidence that our method is able to give reasonable predictions for H_2.

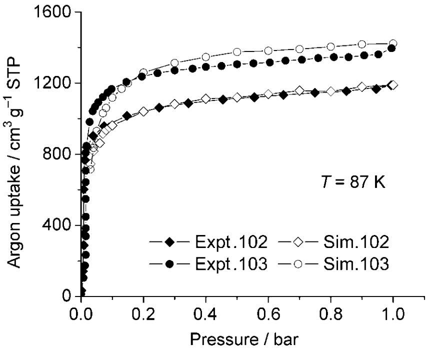

Figure 2. Comparison of the simulated and experimental adsorption isotherms of Ar on COF-102 and COF-103 at $T = 87$ K.

Figure 3 shows the predicted H_2 adsorption isotherms in COFs at $T = 77$ K. Our results show that COF-105 and COF-108 have the highest H_2 gravimetric storage capacities, with uptakes of 18.05 and 17.80 wt%, respectively, at $p = 100$ bar, owing to their high surface areas and free volumes. These values are very exciting compared to the highest reported hydrogen storage capacity of approximate 10 wt% for MOFs at similar conditions (MOF-177,[8] 0.42 g cm^{-3}; MOF-5,[9] 0.59 g cm^{-3}). The storage capacities of COF-102 and COF-103 also reach 10.70 and 11.78 wt% at $p = 100$ bar. Figure 3b shows the excess gravimetric adsorption isotherms of H_2 in COFs. We defined the excess amount as the amount of total adsorption minus the amount of hydrogen in the free volume in the bulk phase. The excess isotherms indicate that at $T = 77$ K, COF-105 and COF-108 display optimal gravimetric adsorption capacities (10.31 and 10.26 wt% at $p = 50$ bar). On the basis of the above analysis, the COFs have exceeded MOFs, owing to their extraordinarily low densities, especially for COF-105 and COF-108. The low densities and the maximized fraction of surface sites[5] make COFs the most promising candidates for hydrogen storage. Most recently, Han et al.[10] and Klontzas et al.[11] reported their predictions on the hydrogen storage capacity of COFs at $T = 77$ K by simulation. Their studies gave results very similar to ours, which shows that our quantum-mechanics-based multiscale method is valid in predicting the hydrogen storage capacity of COFs.

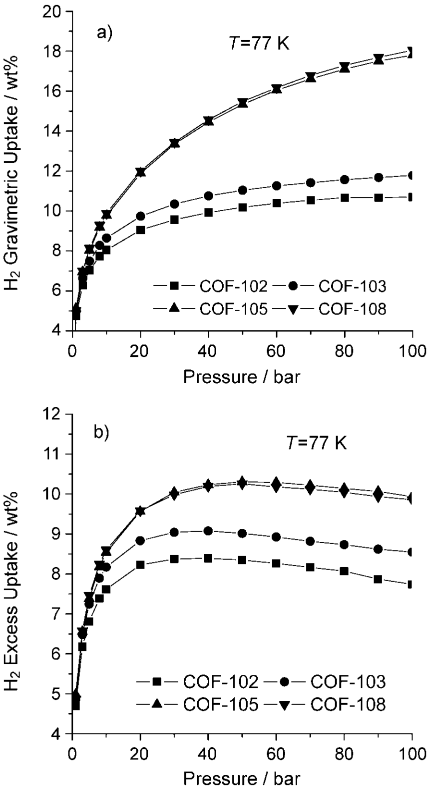

Figure 3. Computed H_2 adsorption isotherms in COFs at $T = 77$ K. a) Total gravimetric isotherms. b) Excess gravimetric isotherms.

Owing to the poor hydrogen storage performance of traditional microporous materials at room temperature, we also predicted the isotherms of H_2 in COFs at $T = 298$ K (see the Supporting Information). Our results show that the H_2 storage capacities of COF-105 and COF-108 reach 4.67 and 4.51 wt%, respectively, at $p = 100$ bar, which is significantly higher than the reported capacities of MOFs.[12,13]

To improve storage capacity of hydrogen, Goddard and Han[14] recommended that doping electropositive metals into MOFs might be a good strategy. Mulfort and Hupp[15] used chemical reduction methods to obtain the Li-doped MOF, and they indeed found that the hydrogen adsorption capacity nearly doubled. Mavrandonakis et al.[16] demonstrated that this enhanced adsorption is caused by the strong binding of H_2 at the positively charged Li cations doped on MOFs. In light of these exciting reports, we further studied adsorption of hydrogen in Li-doped COFs at room temperature.

To gain information about the adsorption of Li in COFs, we first systematically performed first-principles calculations to study the doping details of single and multiple Li atoms in COFs. The widely used B3LYP/6-31g(d) method in the first-principles calculation was adopted for geometry optimizations, which is expected to give reliable adsorption sites. In our calculations, we placed eight Li atoms on the TBPM and TBPS building blocks, respectively, and the average binding energy per Li atom is approximately −24.90 kcal mol^{-1}. Moreover, we placed one Li atom on the HHTP building block, and the binding energy is approximately −14.71 kcal mol^{-1} (see Figure 1 a to c). In this scheme, all the Li atoms are positively charged with more than 0.3 |e| per Li atom. Our first-principles calculations indicated that this distribution scheme for Li doping in COFs is reasonable and acceptable, such that it should provide relatively reliable predictions of the hydrogen adsorption capacity of the Li-doped COFs. This scheme is determined based on the fact that only positively charged Li atoms contribute to the enhancement of hydrogen capacity, whereas the neutral Li atoms and anions do not. Furthermore, when the COFs are doped with multiple Li atoms, the adsorbed Li atoms may tend to form clusters, thus inhibiting the charge transfer from Li to COFs to some extent (see the Supporting Information for details).

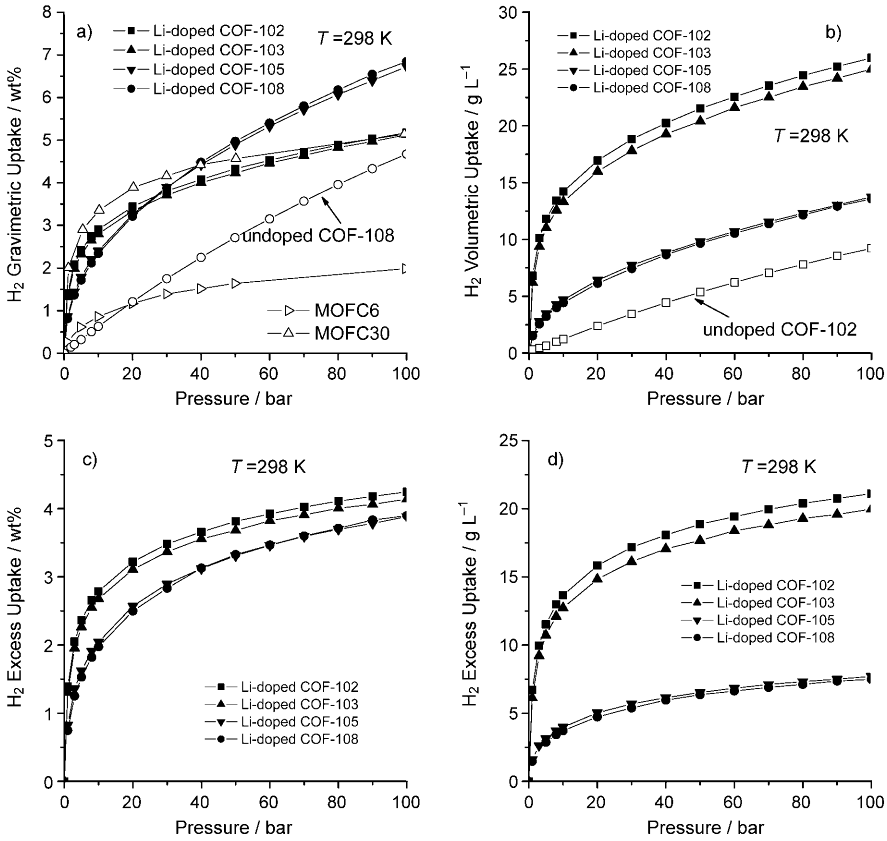

Figure 4. Computed H_2 adsorption isotherms in Li-doped COFs at $T = 298$ K. a) Total gravimetric isotherms. The H_2 isotherms for MOFC6 and MOFC30 are also presented for comparison.[14] b) Total volumetric isotherms. c) Excess gravimetric isotherms. d) Excess volumetric isotherms.

It is essential to define the interactions between Li and H_2 after the determination of the doping of Li atoms. The Mulliken and natural population analysis reveal that the quantity of charge transferred from Li atoms to COFs is mainly determined by two factors: the ratio and distribution of Li dopants. In the distribution scheme presented in Figure 1, the charges transferred from the doped Li atoms to the COFs are in the range from 0.3 to 0.5|e| per Li atom. Previous studies[16,17] found that the strong affinity of the positively charged Li atom for H_2 is due to the formation of a dative bond between the electrons of the H_2 σ bond and the empty Li 2s orbital. When a H_2 molecule is adsorbed near a Li atom doped on the HHTP building block as shown in Figure 1c, the total charge transfer from H_2 is about 0.06|e|. The interaction between Li and H_2 was obtained from high-quality first-principles calculations (PW91/6-311g(d,p)). The FF parameters of the Li–H_2 interaction derived from our first-principles calculations are presented in the Supporting Information.

Figure 4a presents the simulated adsorption isotherms of H_2 in Li-doped COFs at $T = 298$ K. We observed that the gravimetric storage capacities of H_2 in Li-doped COF-105 and COF-108 are significantly higher than all the Li-doped MOFs. Among the four frameworks, COF-105 and COF-108 show more than double increase and reach 6.84 and 6.73 wt%, respectively, at $T = 298$ K and $p = 100$ bar. A comparison of the volumetric capacities of the doped and undoped COFs shown in Figure 4b indicates that all four Li-doped COFs achieve an approximately doubled enhancement in volumetric adsorption capacity of H_2 at $T = 298$ K and $p = 100$ bar (25.98, 25.00, 13.75, and 13.57 g L^{-1} for Li-doped COFs 102, 103, 105, and 108, respectively) compared to corresponding undoped COFs. The excess isotherms of H_2 in Li-doped COFs (Figure 4c and d) indicate that Li-doped COF-102 and COF-103 exceed COF-105 and COF-108 not only in the gravimetric but also in the volumetric adsorption capacities at room temperature. At $T = 298$ K the excess gravimetric and volumetric adsorption capacities of H_2 in Li-doped COF-102 reach 4.25 wt% and 21.11 g L^{-1}, respectively. At present, this performance is excellent for a microporous material at room temperatures. This above observation is in agreement with the predictions from the first-principles calculations.[18]

The capacity for reversible storage of hydrogen is of practical importance. Although a small portion of the hydrogen cannot be released at the discharge pressure, the gravimetric delivery capacity of hydrogen in the Li-doped COF-108 still reaches 6.03 wt% at $T = 298$ K and $p = 100$ bar (see the Supporting Information).

Our calculations show that COF materials are superior to MOF materials in hydrogen storage. To meet the requirements for practical use in hydrogen storage, we suggest doping these materials with Li atoms; the gravimetric adsorption capacities for hydrogen in Li-doped COF-105 and COF-108 reach 6.84 and 6.73 wt% at $T = 298$ K and $p = 100$ bar. To our knowledge, these are the most promising candidates for hydrogen storage to date. Our results will need further experimental validation and will help guide the development of new porous materials for hydrogen storage.

Received: February 18, 2009
Revised: April 16, 2009

Keywords: adsorption · computer chemistry · covalent organic frameworks · first principles · hydrogen

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