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Short Communication

Optimal isosteric heat of adsorption for hydrogen storage and delivery using metal–organic frameworks

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ABSTRACT

Hydrogen storage and delivery in eight representative metal–organic frameworks (MOFs) was investigated using grand canonical Monte Carlo (GCMC) simulations. The simulations demonstrate that the optimal isosteric heat of adsorption (Q_{st}) for maximum hydrogen delivery using MOFs is approximately 20 kJ/mol. The results also suggest that increasing the Q_{st} for MOFs with large surface areas (>4800 m^2/g) is required to attain current hydrogen storage targets in terms of deliverable capacity.

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1. Introduction

Recently, there has been an intense focus on hydrogen (H_2) energy as a replacement for fossil fuels due to the rapid depletion of petroleum deposits and the air pollution caused by burning fossil fuels [1]. However, the absence of safe and economical techniques for H_2 storage is a major hurdle for transportation applications. Storage methods such as high-pressure containers and liquid hydrogen have been considered, but these methods are energy-intensive and cost-prohibitive. Many researchers are trying to develop metal hydride storage systems, which promise high gravimetric and volumetric storage but suffer from slow kinetics [2]. In addition, the physisorption of H_2 in porous materials is an attractive alternative due to the rapid uptake and release of H_2. Numerous materials have been investigated for physisorption, including zeolites, activated carbons, carbon nanotubes, and metal–organic frameworks (MOFs). Among these, MOFs are the most promising due to their extremely large surface areas (up to 5600 m^2/g) and low crystal densities [2–8]. Several MOFs were reported to meet the H_2 storage targets proposed by US Department of Energy (DOE) but only at cryogenic temperatures [9,10]. Currently, no MOFs can attain the DOE target at ambient temperatures due to the weak H_2–MOF interactions. From a computational study, Frost and Snurr showed that the DOE targets could be attained at ambient temperatures if the isosteric heat of adsorption (Q_{st}) could be increased for MOFs with large free volumes [11]. Thus, a main issue for H_2 storage in MOFs is finding strategies for increasing the Q_{st} without significant losses in free volume [6].

Most studies of H_2 storage in MOFs have focused on the *storage capacity* at high pressures, but for practical applications, the amount adsorbed at the discharge pressure is also an important consideration. The discharge pressure is typically around 1.5 bar. As shown in Fig. 1, the *deliverable capacity* is the amount of hydrogen adsorbed at high pressure (e.g. 120 bar) minus the amount adsorbed at the discharge pressure (e.g. 1.5 bar). Until now, however, only a few studies used the deliverable capacity for judging the H_2 storage capability of MOFs [1,12–15]. A pressure of 120 bar is consistent with the DOE targets.

Frost and Snurr showed that a large increase in the Q_{st} leads to a considerable rise in the storage capacity even at high pressures [11]. However, a large Q_{st} may also increase the H_2 uptake at low pressures and could reduce the deliverable capacity (refer to Fig. 1). As a result, there must be an optimal Q_{st} value for obtaining the maximum deliverable capacity. Bhatia and Myers used simple thermodynamic arguments to calculate that the optimal Q_{st} for ambient temperature storage and delivery of H_2 between 30 and 1.5 bar is 15.1 kJ/mol [15]. Areán and co-workers suggested that a considerably higher value (22–25 kJ/mol) was an optimal Q_{st} for the same delivery conditions based on extrapolation of data for H_2 adsorption in zeolites [16].

In this work, we study H_2 storage and delivery between 120 and 1.5 bar in MOF materials using grand canonical Monte Carlo (GCMC) simulations. First, we compare the deliverable capacity and storage capacity at two different temperatures (77 and 298 K). Second, we test whether an optimal Q_{st} exists for maximum

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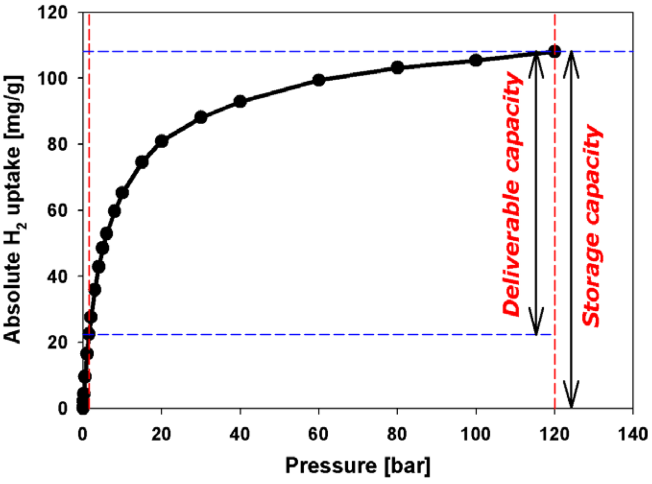

Fig. 1. Storage capacity vs. deliverable capacity (for H_2 adsorption in IRMOF-1 at 77 K as an example). Two dashed vertical lines indicate the storage pressure (120 bar) and the discharge pressure (1.5 bar). Two dashed horizontal lines indicate the absolute H_2 uptake at the storage and discharge pressures.

H_2 delivery at 298 K in MOFs. Finally, we explain the differences between the optimal Q_{st} values from our GCMC simulations and the values from other groups.

2. Simulations

Eight MOFs with a wide range of free volumes and surface areas were selected: UMCM-1 [17], MOF-177 [18], Cu-BTC [19] and five isoreticular MOFs (IRMOFs-1, -9, -10, -15, -16) [20]. H_2 adsorption isotherms and Q_{st} in the eight MOFs were predicted up to 120 bar at 77 and 298 K from GCMC simulations. The same model reported in our previous studies was used for these simulations [11,21,22], and this model was already shown to reasonably predict the low-pressure H_2 isotherms and Q_{st} in IRMOFs-1 and 8 at 77 K [11,22]. Moreover, simulated H_2 isotherms from this model agreed well with experimental data for IRMOF-1 up to 120 bar at both 77 and 298 K [21]. The free volume and surface area were calculated by using simple geometrical techniques [11]. The detailed simulation methods are provided in the Supporting Information. Table 1 shows the calculated free volumes and surface areas of the eight MOFs.

Several strategies, such as introduction of open metal coordination sites have been suggested as means of increasing the H_2 adsorption enthalpy in MOFs. Open metal sites have been introduced at the metal nodes of the framework [6] or as extraframework cations, especially Li^+ [23]. In this study, to model the increase in Q_{st} in a general way the Lennard–Jones (L–J) epsilon parameters (ε) for H_2/MOF interactions were systematically increased in eight MOFs. The ε parameters were multiplied by 2, 3, 4, 5, 6, 7, 8, 9, and 10 times their original values. Using these 10 different parameter sets (the original and nine systematically augmented interaction models), H_2 isotherms and Q_{st} were predicted up to 120 bar at 298 K. H_2/H_2 interactions were not scaled.

Table 1
The free volumes and surface areas of eight selected MOFs.

	Free volume (cm^3/g)	Surface area (m^2/g)
IRMOF-16	4.32	6167
IRMOF-10	2.53	4992
UMCM-1	2.06	4316
IRMOF-15	1.87	6176
MOF-177	1.80	4823
IRMOF-1	1.25	3579
IRMOF-9	1.02	3276
Cu-BTC	0.74	2115

3. Results and discussion

Fig. 2 shows a comparison between the storage capacities (at 120 bar) and the deliverable capacities (from 120 to 1.5 bar) for H_2 adsorption in the eight MOFs. At 77 K, the deliverable capacity is lower than the storage capacity due to the considerable adsorption at low pressures. An important observation is that some MOFs cannot attain the DOE targets in view point of the deliverable capacity although their storage capacities exceed the targets (Fig. 2a). At 298 K, however, the deliverable capacities nearly coincide with the storage capacities due to minor adsorption at low pressures. At ambient temperature, the DOE targets cannot be achieved in these materials due to the weak H_2–MOF interactions.

Fig. 3a charts the storage capacities at 120 bar and 298 K vs. the isosteric heat of adsorption at low loading, Q_{st}^{o}. The graph contains data from all eight MOFs and all 10 parameters sets where the H_2/MOF interactions were artificially increased. As Q_{st}^{o} increases, the storage capacity of each MOF increases linearly. This indicates that it is possible for all MOF structures to attain the DOE targets if Q_{st}^{o} is increased enough without loss in free volume. For example, IRMOF-16 can attain the DOE 2015 target if Q_{st}^{o} is increased up to around 10 kJ/mol. However, this observation is true only for the case of storage capacity. If we consider the deliverable capacity, different behavior is observed (Fig. 3b). For each MOF structure, an optimal Q_{st}^{o} giving the maximum deliverable capacity exists. Interestingly, all the optimal Q_{st}^{o} values for the different MOF structures are in the range of 23–28 kJ/mol. Remarkably, MOFs with small free volumes (IRMOF-9 and Cu-BTC) cannot achieve the 2010 target in view point of the deliverable capacity even if Q_{st}^{o}

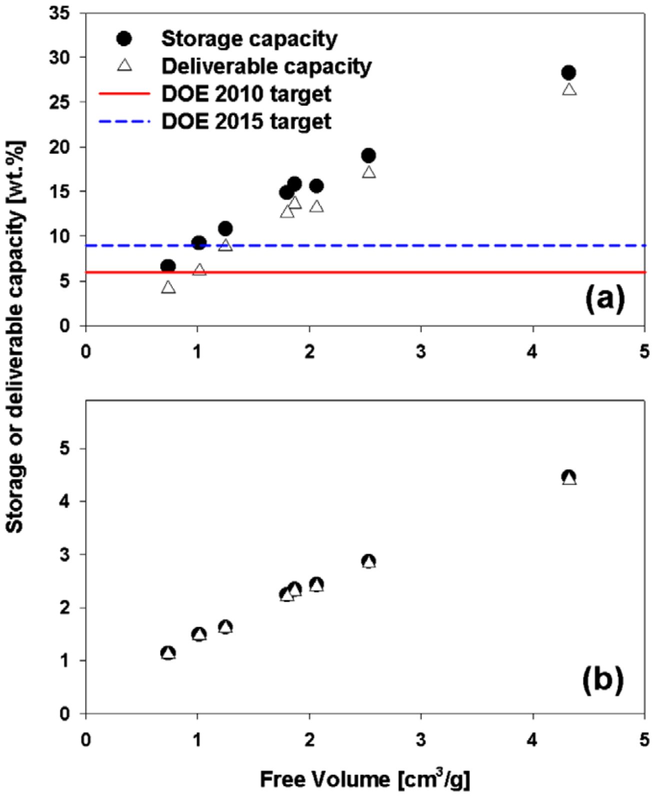

Fig. 2. Comparison between the storage capacity at 120 bar and the deliverable capacity from 120 to 1.5 bar for eight MOFs with varied free volumes at (a) 77 K and (b) 298 K.

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