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Adsorption of hydrogen in covalent organic frameworks: Comparison of simulations and experiments

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ABSTRACT

In this work, grand canonical Monte Carlo (GCMC) simulations were performed to investigate the adsorption properties of H_2 in 2D and 3D covalent organic frameworks (COFs) with different surface areas and different pore volumes. Good agreements between the simulated and the available experimental data from the literature have been found, indicating the reliability of the theoretical model. We showed also that the buoyancy correction for the adsorbed layer, suggested to correct the adsorbed amount is inadequate. In addition, this work demonstrates that the electrostatic interactions between H_2 molecules and the COF framework play almost no role at 77 and 298 K, while the pore volume and surface area have the dominant effect on the hydrogen storage uptake at high pressure.

1. Introduction

Hydrogen storage is one of the main bottlenecks for the realization of an energy economy based on hydrogen as an energy carrier. Hydrogen storage in metal organic framework materials (MOFs) attracted significant attention because these materials have enormous specific surface area, low density and a crystalline structure that can be tailored to maximize the adsorption uptake. These materials are built up from metal–oxygen carboxylates linked by different organic groups to yield 2D or 3D extended structures with considerable porosity. A large number of MOFs structures have been synthesized and studied in the past few years, some of them show the highest surface areas ever reported for crystalline solids [1,2]. For the current concern hydrogen storage application, some MOFs have remarkable hydrogen storage properties [1]. Nevertheless, currently none of these materials meets yet the demand of the Department of Energy of the USA; 6 wt% under near-ambient conditions. In MOFs the existences of metal atoms add weight to the structure without significantly increasing the heat of adsorption which leads to increase of the storage uptake, unless it is accompanied with exposed metal sites [3,4]. An improvement of hydrogen uptake of MOFs materials can be achieved by substituting the metal in the metal cluster with another lighter element (such as B, N, or O) while keeping all of the important properties such as high surface area, low density and rigidity of the structure. Yaghi and co-workers have successfully synthesized a novel materials called COF-1 and COF-5 [5] (COF = covalent organic framework). These materials are porous and crystalline 2D structures, similar to that of graphite, constructed solely from light elements (C, H, B, and O) that are linked by strong covalent bonds. Later on they synthesized new porous structures COF-6, COF-8 and COF-10 [6]. Jiang et al. [7] have synthesized functional COFs, named TP-COF, with novel properties by utilizing highly ordered π-conjugation systems, which has not been explored for gas storage applications. In all cases, 2D COFs have structures of quasi 1D pores whose size varied between 8 and 32 Å in diameter, comparable to those reported for medium sized carbon nanotubes.

3D COFs materials have been synthesized and characterized by Yaghi et al. [8] from building blocks that contain also light elements, these COFs are the most porous among organic materials, and one of these materials named COF-108 has the lowest density reported for any crystalline material (0.17 g/cm^3). Later on they synthesized a porous covalent organic borosilicate framework designated as COF-202 by linking organic units with the strong covalent bonds found in borosilicate glass [9]. Because of the absence of the heavy metal, COFs have lower densities than MOFs, they also show very high surface area, see Table 1, comparable to the highest reported surface areas of MOFs (MOF-177 (4500 m^2/g) [1] and MIL-101 (4100 m^2/g) [2]). The low density coupled with the high surface area in 3D COFs makes them exceptional hydrogen storage materials.

Currently there are few experimental studies of adsorption of gases in COFs [6,8,10,11], but a large number of theoretical studies have been reported [12–16]. Adsorption isotherms of light gases (Ar, CH_4 and H_2) in 3D COFs have been simulated, in which

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Table 1
Summary of calculated and experimentally estimated properties (surface areas and pore volumes) of different COFs.

Material	Theoretical density (g/cm^3)	Theoretical pore volume (cm^3/g)	Experimental pore volume (cm^3/g)	Theoretical accessible surface area (m^2/g) for H_2	Theoretical accessible surface area (m^2/g) for N_2	Experimental Langmuir surface areas (m^2/g)	Experimental BET surface areas (m^2/g)	Theoretical Q_{st} (kJ/mol)	Experimental Q_{st} (kJ/mol)
COF-1	0.91	0.43	0.36 [10] 0.3 [11]	2011.72	371.39	970 [11]	628 [10] 711 [5] 750 [11]	6.51	6.2 [11]
COF-5	0.58	0.58	1.07 [11]	2112.91	2000.11	1990 [11]	2027 [43] 1590 [5] 1670 [11]	4.677	6.0 [11]
COF-6	1.25	0.33	0.32 [11]	1922.88	1261.07	980 [11]	980 [6] 750 [11]	6.14	7.0 [11]
COF-8	0.71	0.86	0.69 [11]	2159.78	2017.44	1400 [11]	1400 [6] 1350 [11]	5.00	6.3 [11]
COF-10	0.49	1.49	1.44 [11]	2210.15	2093.66	2080 [11]	2080 [6] 1760 [11]	5.33	6.6 [11]
TP-COF	0.52	1.36	0.7907 [7]	2842.48	2192.07		868 [7]	4.64	
COF-102	0.41	1.88	1.345 [8] 1.55 [11]	5458.96	5199.77	4452 [8] 4650 [11]	2926 [43] 3472 [8] 3620 [11]	5.49	3.9 [11]
COF-103	0.38	1.96	1.663 [8] 1.54 [11]	5389.24	5170.67	5207 [8] 4630 [11]	4210 [8] 3530 [11]	4.98	4.4 [11]
COF-105	0.18	5.05		6502.61	6810.02			3.39	
COF-108	0.17	5.26		6277.99	6560.95			4.79	
COF-202	0.52	1.31	1.09 [9]	4660.05	4043.00	3214 [9]	2690 [9]	4.95	

COF-102 was found to show a greater affinity for CH_4 [12]. CO_2 storage in 1D, 2D and 3D COFs have been also simulated [14]. The 3D COFs (COF-105 and COF-108) show an exceptional high storage uptake compared to 1D and 2D COFs, even surpassing the experimentally measured highest uptake in MOF-177.

In this work, we present results of computer simulations (GCMC) for the adsorption of hydrogen on six 2D COF (COF-1, COF-5, COF-6, COF-8, COF-10, TP-COF) and five 3D COF (COF-102, COF-103, COF-105, COF-108, COF-202) materials at two different temperatures of 77 and 298 K. The results of the simulations are compared in detail with the available experimental data from the literature.

2. Computational methodology

The hydrogen adsorption in the COF structures was simulated with GCMC using the multipurpose simulation code Music [17]. Detailed descriptions of GCMC simulations are given in several references (see e.g. Ref. [18]). The sorbent (COF) is described by a periodic super cell, $2 \times 2 \times 3$ for COF-1, $2 \times 2 \times 6$ for COF-5 and COF-10, $3 \times 3 \times 6$ for COF-6 and COF-8, and $2 \times 2 \times 2$ for COF-102, COF-103, COF-105, COF-108 and COF-202 of each unit cell. The COF structure has been treated as a rigid structure at all temperatures, with atom positions obtained by X-ray scattering experiments. The calculations of adsorption isotherms were carried out at two different temperatures ($T = 77$ and 298 K) throughout a wide range of pressure, from low pressure ($P = 1.0\text{E}{-3}$ bar) up to high pressure ($P = 100$ bar) to get a complete picture about the adsorption properties. For each point on the isotherm, the simulations were equilibrated for five million steps, and a further five million steps were used to sample the data. Each Monte Carlo step consisted of insertion attempt of a new molecule, deletion attempt of an existing molecule, translation or rotation of an existing molecule. The probability for each of the previous attempts was equal.

GCMC simulations give the total (absolute) amount of hydrogen adsorbed (n_{ads}), whereas experimentally the excess amount of adsorbed hydrogen is measured. The excess number of molecules (n_{ex}) can be calculated by:

$$n_{ex} = n_{ads} - \rho_p V_g \tag{1}$$

where ρ_p is the molar density of the bulk gas phase calculated with the Peng–Robinson equation of state, and V_g is the pore volume per unit cell of the sorbent.

The isosteric heat of adsorption (Q_{st}) for the structures was performed through the fluctuations over the number of particles in the system and from fluctuations of the internal energy U [19]:

$$Q_{st} = RT - \frac{\langle UN \rangle - \langle U \rangle . \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \tag{2}$$

where R is the gas constant, T is the temperature, U is the internal energy, N is the number of molecules adsorbed and $\langle \; \rangle$ represents a configuration average.

The available pore volume was estimated using a non-adsorbing species (helium) as a probe [14,20]. The accessible surface area was calculated by "rolling" a probe molecule with a diameter equal to the Lennard–Jones parameter for H_2, N_2 (2.72 Å, 3.681 Å) over the framework surface, as described in Ref. [21]. The accessible surface areas for both H_2, N_2 are presented in Table 1.

The H_2/H_2 and H_2/COF framework interactions were described via a repulsion–dispersion 12-6 Lennard–Jones potential to represent van der Waals interactions between the H_2 molecules and the COFs structures (Eq. (3)):

$$V(r_{ij}) = 4\varepsilon^{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{3}$$

where i and j stand for the sites of the adsorbate (hydrogen molecules) and the adsorbent (COF structure); r_{ij}; the distance between them; ε^{ij} and σ_{ij}; the Lennard–Jones parameters.

The H_2 molecule was modelled as a rigid diatomic molecule with a bond length 0.74 Å where each H atom was represented as LJ interaction site. The potential parameters for the hydrogen molecule were taken from Ref. [22] ($\sigma = 2.72$ Å; $\varepsilon = 10.0$ K) by Zhong et al. These parameters show to give good reproduction of the experimental data of hydrogen gas, they were also used to simulate of hydrogen adsorption in MOFs [23,24] and in MIL-102 by Férey et al. [25]. The potential parameters for the framework atoms in COFs were taken from the standard DREIDING force field [26]. The DREIDING force field has been widely used to study the