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# Hydrogen storage in 1D nanotube-like channels metal–organic frameworks: Effects of free volume and heat of adsorption on hydrogen uptake

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## ABSTRACT

Metal–organic Frameworks generate significant interest for their potential application as Hydrogen storage materials. Grand Canonical Monte Carlo (GCMC) simulations were performed at two different temperatures 77 and 300 K over a wide range of pressures to describe H<sub>2</sub> adsorption in 7 metal–organic frameworks (MOFs), which all have the same framework topology but different surface chemistry and different pore sizes. DREIDING and UFF force fields were identified to be able to predict adsorption isotherms for H<sub>2</sub> in MOFs in a reasonable agreement with the experimental data from the literature. This work reveals that at 77 K the total amount of H<sub>2</sub> adsorbed correlates mainly with: the heat of adsorption at low pressure and the free volume at high pressure. While at 300 K the amount adsorbed mainly correlates with the available free volume at both low and high pressure. None of the MOFs studied fulfils DOE requirement, this is due to their low heat of adsorption. The required adsorption energy to meet the DOE targets is estimated to be 34 kJ/mol.

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## 1. Introduction

Hydrogen has been recognized as a promising energy carrier for transportation but has not yet been in use. One of the main hurdles in using Hydrogen as a fuel is finding a safe, economical and practical way of storing it with sufficient gravimetric and volumetric densities.

According to the demand of the USA 2 kWh/kg(6 wt%), 1.5 kWh/L, and \$4/kWh in the year of 2010 must be stored practically [1]. Hydrogen is a very light and volatile gas, thus, conventional storage of such amounts of Hydrogen in its molecular form is difficult and expensive because it requires employing either very high pressures as a gas or very low temperatures as a liquid [2]. Therefore the use of low temperatures, high pressures, sorption material, or

a combination of these to store a practical amount of Hydrogen is needed. Currently, no material yet meets the constraint for reversible Hydrogen storage under near-ambient conditions.

Generally, materials for Hydrogen storage vary depending on whether the material operates by a chemisorption or physisorption mechanism. For Hydrogen storage by physisorption four parameter play the main role: first the material must provide a large amount of surface area per gram, since adsorption is mainly due to interactions of Hydrogen molecules with atoms of the adsorbent walls, this can be characterized as the accessible surface area (S<sub>cc</sub>), second the free volume provided by the material to accommodate the Hydrogen molecules, i.e. the pore size should not be smaller than the van der Waals diameter of H<sub>2</sub> which equals  $\approx 3.1 \text{ \AA}$ ,

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third the easy accessibility of the internal surface to the Hydrogen molecules and fourth the interaction strength must be sufficient enough to make the adsorption possible under ambient conditions. The last feature can be characterized by the isosteric heat of adsorption ( $Q_{st}$ ) at low loading.

When designing new materials for the Hydrogen storage purpose, two quantities are of main interest: the Hydrogen capacity and the heat of adsorption ( $Q_{st}$ ). The two quantities can be calculated using the Grand canonical Monte Carlo technique (GCMC).

The activated carbon and carbon nanotubes have BET surface area of 600 and 2000 m<sup>2</sup>/g, respectively. But the adsorption energy of the carbon materials is around 600 K which limits the applicability of pure carbon materials at ambient conditions [3], therefore, functionalizing the surface of the pure carbon materials in order to increase the heat of adsorption is needed.

Hydrogen storage in metal–organic framework materials (MOFs) attracts 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 containing divalent (Zn<sup>+2</sup>, Cu<sup>+2</sup>...) or trivalent (Al<sup>+3</sup>, Cr<sup>+3</sup>hellip;) cations, where the metal is locked into a position to produce rigid entities of the porous geometry, and interconnected by different organic groups. It is usually referred to the inorganic part as secondary building unit (SBU). A large number of MOFs structures have been synthesized and studied. Some of them have been shown to have remarkable methane and Hydrogen storage adsorption properties [4–6]. Some MOFs have very high surface areas. For example, Cu-BTC, MIL-101 and MOF-177 has a surface area of 1800 m<sup>2</sup>/g, 4100 m<sup>2</sup>/g and 4500 m<sup>2</sup>/g respectively, estimated from nitrogen adsorption. These are some examples of the largest surface areas reported for any material to date, which are much higher than in zeolite. For example, the zeolite Y has a surface area of 904 m<sup>2</sup>/g. Amongst MOF materials, a novel MOF of infinite rod-shaped metal-carboxylate secondary building units (SBU) have been synthesized [7–9]. Because of the intrinsic packing arrangement of the rods in the crystal structure, the rod-shaped metal-carboxylate SBUs provide a new class of MOFs that do not interpenetrate. Férey and co-workers have synthesized MIL-47 [7] and MIL-53[10,11] materials. These structures are made up of chains of corner-sharing transition metal octahedra interconnected by benzene dicarboxylate (BDC) groups. Later on, they synthesized large one-dimensional tunnels and a high surface area MOF, based on lanthanide (MIL-103) [12]. Yaghi and co-workers have systematically studied such rod-shaped MOFs. They presented strategies for the design and construction of porous structures from rod-shaped building blocks, and successfully synthesized 14 new materials with 12 different structures [9]. Recently Shi-Lun Qiu and co-workers have synthesized a novel metal–organic framework (JUC-48). Of particular interest is that the SBUs are interconnected through the biphenyl groups, generating to the best of our knowledge the largest 1D nanotube-like channels reported to date [13]. Several groups reported a linear relationship between surface area and the amount of adsorbed Hydrogen for different types of porous materials [14,15]. Frost et al. [16] showed that the

Hydrogen uptake at 77 K correlates with the heat of adsorption at low pressure, surface area at medium pressure and with the free volume at high pressures. They obtained this result by performing GCMC simulations on a set of materials, which all have the same framework topology and surface chemistry but different pore sizes.

In this work, Grand canonical Monte Carlo (GCMC) simulations were performed over a wide range of pressure to predict adsorption isotherms at 77 K and room temperature for Hydrogen in seven metal–organic framework materials, which all have the same framework topology but different metal ion in the metal cluster and different pore size. This enables us to get an insight into molecular level details of the adsorption mechanisms, to test if the previously mentioned correlations also hold for MOFs with different chemistry at both 77 K and room temperature and to study which parameters affect mostly the adsorption at room temperature. We have chosen MOFs that contains 1-D nanotube-like channels. We have selected seven rod-shaped structures as representative examples of rod-shaped MOFs. Most of these materials showed interesting properties in terms of Hydrogen storage [17,18].

The MOF structures were constructed from their corresponding single-crystal X-ray diffraction data. They have the same topology and mainly differ by the metal in the SBU and the pore size. The super cells of these materials are shown in Fig. 1:

MIL-53(Al) (MIL = Material Institut Lavoisier) [11]

MIL-53 (Cr) [10]

MOF-74 [17]

MMOM (MMOM = Microporous Metal–Organic Material) [19]

Fe(OH)(BDC) [20]

MIL-103 [12],

and JUC-48(JUC = Jilin University China) [13].

## 2. Simulation method

The Hydrogen adsorption in the MOF structures was simulated with GCMC using the multipurpose simulation code Music [21]. Detailed descriptions of GCMC simulations are given in several references (see e.g. Ref. [22]). The gas-phase fugacities for Hydrogen at different pressures and temperatures were calculated with the Peng–Robinson equation of state. Atomistic models were employed for both the Hydrogen molecules and MOF structures. The non-bonding interactions between the framework of the MOF structure and Hydrogen molecules are described via a pair-wise additive potential. The corresponding site–site interactions are described by a Lennard–Jones type potential:

$$V(r_{ij}) = 4\epsilon^{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where  $i$  and  $j$  stand for the sites of the adsorbate (Hydrogen molecules) and the MOF structure;  $r_{ij}$ ; the distance between them;  $\epsilon^{ij}$  and  $\sigma_{ij}$ ; the Lennard–Jones parameters.

Lorentz–Berthelot mixing rules ( $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ ,  $\epsilon^{ij} = \sqrt{(\epsilon^i \times \epsilon^j)}$ ) were employed to calculate H<sub>2</sub>-MOF Lennard–Jones (LJ) potential parameters. For MOFs atoms, We have tested

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