



Insights from theoretical calculations on structure, dynamics, phase behavior and hydrogen sorption in nanoporous metal organic frameworks

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ABSTRACT

Metal organic framework (MOF) materials are gaining lot of interest because of their potential as hydrogen storage materials. Due to their nanosize, understanding hydrogen sorption behavior, structural flexibility, phase behavior, etc. is difficult to study by experimental methods. In this situation, various levels of theoretical calculations have provided us with invaluable insights about these materials. However, applying a general theory may not work for these materials due to their complex chemical environment. Thus, modification to the existing theory, developing new potential, and parameterization of force field has been a focus for theoreticians working in this area. In this review we have summarized these theories and the specific requirements that have been instrumental in studying hydrogen sorption in MOFs and their physicochemical properties and present the current knowledge about these materials. We also provide various physical chemical aspects to achieve high hydrogen sorption capacity in MOF materials.

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1. Introduction

Materials with pore size less than 2 nm are called nano-porous materials, hence providing increased number of sites for interaction with atoms, ions and molecules throughout their bulk and not only on the surface [1]. Thus these materials have application as gas adsorbent in petroleum industry, water treatment, food and beverage industry. Other potential applications are thermal insulation, gas storage, drug delivery, catalysis, photonic crystal, electrode, tissue engineering, etc. In these applications, factors like distribution and uniformity of pores size, shape and volume, atoms present in the pores are all important. The majority application focuses on gas adsorption and separation, and nanoporous materials are studied extensively as potential H₂ storage medium for future hydrogen fuel based economy.

Storage of hydrogen in nanoporous materials is a thriving area of research because H₂ is considered the future energy source. It has the highest gravimetric energy content of all fuels, which is almost three times that of petroleum (142 MJ/kg vs. 47 MJ/kg) [2]. It can be easily produced from various renewable and hydrogen has less environmental impact. However to obtain similar energy output as petroleum, hydrogen has to be liquefied or compressed. This is a major challenge in using hydrogen in the transportation sector. The key problem is the energy consuming compression and liquefaction steps, where 30% of the energy is lost. Thus even if renewable electricity is used for water electrolysis and generate

hydrogen, the overall efficiency will be less in hydrogen powered vehicle compared to electric ones [3]. Thus we need materials that can store large amount of hydrogen without the need for these energy consuming steps.

In order to introduce hydrogen in transport sector, US DOE has set target for efficient hydrogen storage system which is 9 wt.% by year 2015 [4]. Various materials such as metal hydrides, carbon nanotube, graphene, porous metal organic frameworks, zeolites, and coordination polymers are being explored as potential storage materials. Compared to other porous materials, metal organic frameworks (MOFs) cover a wider range of pores, provide flexibility in choosing various combinations of linkers and metal, have different pore size, shape, structure, and functionality [5–9]. MOFs have simple synthesis process and they possess good thermal stability. Thus these are very good materials for hydrogen storage.

In order to build a successful MOF based H₂ storage device, we need to understand hydrogen storage mechanism, related thermodynamics and kinetics. We need information about hydrogen binding energy, preferred binding sites, orientation, effect of the surrounding chemical environment, etc. There are excellent review papers that summarize important findings related to gas adsorption properties, structural flexibility of these MOFs such as Rowsell and Yaghi [5,6], Zhao et al. [7], Thomas [8], and Ferey [9]. Although various experimental study like inelastic neutron scattering (INS), quasi elastic neutron scattering (QINS), spectroscopy, XRD can provide valuable information about hydrogen interaction in these pores, but theoretical studies have played an important role in understanding various aspects of hydrogen storage mechanism and related thermodynamics in these materials Han et al. [10], Duren et al. [11], and Keskin et al. [12].

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In this review paper, we will discuss various theoretical works about structural, mechanical, electronic property and hydrogen sorption behavior in MOFs and summarize the insights gained from them. The review is outlined as follows. In Section 2, we discuss the general MOF structures, mainly different metals and organic linkers used in these materials. Section 3 briefly discusses the mechanism of adsorption to motivate the need for the theories that we are interested in. Section 4 presents various theories that have been used to understand physical properties and adsorption mechanism in MOFs. Section 5 provides insights from various physical properties followed by hydrogen adsorption strategies in MOFs in Section 6. We then conclude with brief outlook and future directions.

2. Structural features of MOF crystals

Metal organic frameworks (MOFs) with stable 3D pores were introduced by Yaghi group in 1999 [13] as promising H_2 storage material. MOFs are porous hybrid crystalline materials made up of metal oxide clusters, also called secondary building unit (SBU), connected by organic linkers [13–15]. In the simplest structure, Iso-Reticular MOF-1 (IRMOF-1), the cubic crystal is formed by positioning ZnO_4 clusters at the vertices and connected by benzene-decarboxylate (BDC) linkers, leaving most of the crystal volume free as empty space (Fig. 1). Due to such structures, they have high porosity and large surface area and very low density (0.21–1.00 g/c [13]).

These MOFs have very orderly and well defined pores like that in zeolites, but the pore volume is higher than zeolite [14]. However, the composition of MOFs differs significantly from zeolites which are mainly made up of inorganic materials. In case of MOFs the pore walls are mainly organic surrounded by inorganic clusters that provide rigidity to the framework. Compared to other carbonaceous materials functionalization of pore and localization of H_2 in it is easier [15].

About 11,000 extended MOF structures are available in CSD database [17], of which about 3000 compounds have 3D pores. Their rigidity comes from the metal carboxylate framework. The size of the carboxylate functionality permits chelation of metal cation and produce geometrically defined metal cluster. The most common example is the $Zn_4O(L)_3$, where $Zn_4O(CO_2)_6$ clusters are linked by carboxylate linkers along orthogonal axes giving rise to cubic, hexagonal MOFs. Another common metal carboxylate cluster is formed by bimetallic “paddlewheel” structure as in Cu_2L' , (where L' is tetracarboxylate linker like bptc, tptc, qptc). This is generated by the combination of four carboxylates with two cations such as Cu^{2+} , Zn^{2+} , Fe^{2+} , Mo^{2+} , Ru^{2+} , Ru^{3+} or Rh^{2+} [5,8]. Other series was created by Materials Institute Lavoisier (MIL), for example, MIL 101(Cr) and MIL 101(Al) [18]. MIL 100(Cr) is made up of trimers of Cr octahedral with terminal H_2O or F legand. Their linkage with rigid carboxylate linker creates microporous super tetrahedral

units. The resulting cubic structure has surface area $\sim 380,000$ and $702,000 \text{ \AA}^3$. The third kind of structure is a layered structure where the porous network is formed by hydrogen bonds and thus gives framework flexibility [19].

One variant of MOF called covalent organic frameworks (COFs) are made up of C, H, B, O, and thus have strong C–C, B–O and B–C covalent bonds [20]. These have the lowest density of any crystalline material, (0.17 g/cc for COF-108) and are also promising materials for hydrogen storage. Another nanoporous structure called zeolite imidazole framework (ZIF) which adopt crystalline structure similar to porous silicon and oxygen in zeolite, have shown their potential for hydrogen storage and CO_2 capture [21]. ZIF combines the classical zeolite traits of chemical and thermal stability with rich structural variation of MOF. However in this review we focus only on primary MOF structures. Table 1 presents examples of various MOFs containing different metals, along with their surface, volume and hydrogen uptake capacity.

In the following section we discuss various mechanisms of gas adsorption in these nanoporous materials to lay stress on the physisorption phenomena which is responsible for hydrogen storage in MOF materials.

3. Adsorption mechanism

Hydrogen storage in materials is generally achieved by adsorption process. In this process, when a hydrogen molecule comes in contact with a solid surface it tends to bind to the surface and the adsorption enthalpy (or heat of adsorption) indicates how strongly hydrogen molecule is bound. Higher enthalpy indicates stronger bonding [27]. The strength of this binding depends on the nature of interaction it experiences with the surface molecules. Adsorption is the consequence of the force field or interaction potential present at the material (adsorbent) surface which attracts the gaseous molecules (adsorbate). Depending on this force field, adsorption can be two types, physical-physisorption (by weak van der Waals attraction by weak dipole) or chemical-chemisorption (strong covalent or ionic bonding, transfer of electrons). These are briefly described below.

3.1. Chemisorption

In chemisorption, molecular hydrogen dissociates in two atoms and makes strong bonds with the adsorbent thus making metal hydrides or chemical hydrides. Adsorption enthalpy may exceed 100 kcal/mole [27] and the process may be either endothermic or exothermic. A large number of metals and alloys can store hydrogen at relatively low temperature and pressure by chemisorption, forming metal hydrides. However, chemisorption suffers from problems like high operating temperature, slow kinetics, and low gravimetric contents [4]. Thus it is not a sustainable storage strategy.

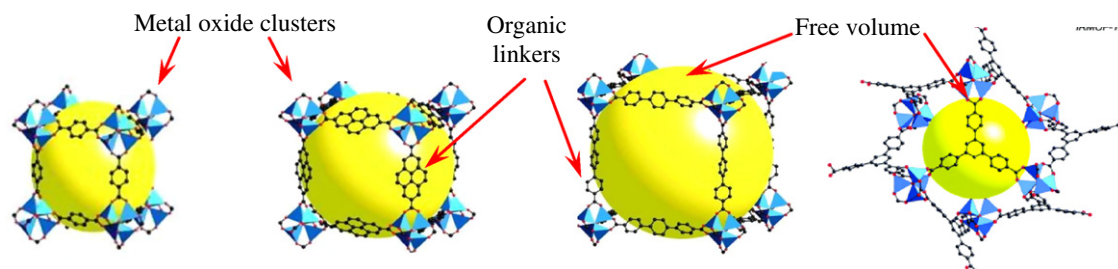


Fig. 1. Various Zn based metal organic frameworks with cubic and hexagonal topologies. Reproduced with permission from Ref. [14] Copyright© 2002 AAAS and Ref. [16] Copyright© 2004 Am. Chem. Soc.

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