

Hydrogen Storage in Metal-Organic Frameworks: A Review



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ARTICLE INFO

Article history:

Received 11 July 2013

Received in revised form 30 October 2013

Accepted 30 October 2013

Available online 11 November 2013

Keywords:

Hydrogen storage

Metal-organic framework

Hybrid hydrogen storage material

ABSTRACT

Metal-organic frameworks (MOFs) for hydrogen storage have continued to receive intense interest over the past decade. MOFs are a class of organic-inorganic hybrid crystalline materials consisting of metallic moieties that are linked by strong coordination bonds to organic ligands. They exhibit a great structural diversity and possess low weight, exceptionally high surface areas, large free volumes, and tunable pore sizes and functionalities, making them extremely attractive for a variety of applications such as hydrogen storage. For these reasons MOFs have been extensively studied. In this paper, a review of recent developments on hydrogen storage in MOFs is presented, with a focus on the effects of various factors including open metal sites, 'guest' metal ions, ligand functionalization, surface area, pore volume, pore size, and Pt or Pd metal nanoparticles, on hydrogen storage. In addition, the review examines the emerging research on MOF hybrid hydrogen storage systems, primarily in the context of employing MOFs for nanoconfinement of high temperature hydrogen storage materials. The review focuses on experimental studies.

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1. Introduction

Hydrogen is an ideal energy carrier for a variety of fuel cell applications including stationary, mobile and portable power applications. The successful implementation of the 'Hydrogen Economy' would alleviate greenhouse gas emissions and reduce dependence on fossil fuels. One of the major challenges to the smooth transition to the 'Hydrogen Economy' is the lack of suitable hydrogen storage systems. Established technologies for hydrogen storage such as compressed gas (in pressurized tanks) and liquefied hydrogen (in cryogenic tanks) exist and are currently being employed in fuel cell vehicles [1]. However, both technologies have major drawbacks for mobile applications. At atmospheric pressure hydrogen gas has a low density ($0.08988 \text{ kg m}^{-3}$) and very high pressures are needed to achieve high storage capacities [2]. This requirement for the storage system results in heavy and bulky storage tanks. Hydrogen also has a low boiling point (20 K) and therefore extensive cooling is required in order to liquefy hydrogen. This leads to a relatively complicated system, boil off losses and also a loss in some of the energy content of hydrogen [2]. Both storage technologies also pose serious safety risks. The search for an effective, safe and affordable hydrogen storage method presents a serious materials challenge [2]. Tremendous efforts have been made to store hydrogen in

solid materials [3–7]. Solid materials-based hydrogen storage is advantageous over compressed and liquid hydrogen storage in that hydrogen is stored in a safer and compact manner. In solid materials the storage of hydrogen may involve molecular hydrogen binding through weak van der Waals forces (physisorption) or predominantly stronger binding of atomic hydrogen (chemisorption) forming a new compound. Consequently, solid hydrogen storage materials are generally classified into four groups: adsorbents (e.g. activated carbon, zeolites, metal-organic frameworks), conventional metal hydrides (e.g. LaNi_5H_6 , Mg_2NiH_4), complex metal hydrides (e.g. NaAlH_4 , LiBH_4) and chemical hydrogen storage (e.g. NH_3BH_3), in order of increasing hydrogen binding strength [6]. Physisorption has several advantages over chemisorption such as fast kinetics of hydrogen adsorption/desorption and complete reversibility of hydrogen uptake. On the other hand, chemisorption leads to relatively high hydrogen storage capacities. However, the kinetics of hydrogen release may be slow and a high temperature is usually required to release hydrogen, with some systems showing irreversibility of hydrogen uptake. Characteristics such as high volumetric and gravimetric storage capacities, fast kinetics, favorable thermodynamics, low desorption temperature, excellent reversibility, long-term cyclic stability and low cost are all desirable for hydrogen storage materials to meet the US Department of Energy (DOE) 2017 targets for on-board hydrogen storage (Table 1) [8]. Current materials available for hydrogen storage are yet to satisfy all the criteria necessary for on-board applications [9].

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Table 1
Summary of US DOE technical system targets for on-board hydrogen storage for light-duty fuel cell vehicles.

Storage parameter	Unit	2017	Ultimate
System gravimetric capacity	wt.%	5.5	7.5
System volumetric capacity	g L^{-1}	40	70
Fuel cost	\$/gge at pump	2–4	2–4
Min/max delivery temperature	$^{\circ}\text{C}$	–40/85	–40/85
Operational cycle life (1/4 tank to full)	Cycles	1500	1500
Min/max delivery pressure from storage system	bar (abs)	5/12	3/12
System fill time (5 kg)	Min	3.3	2.5

Metal-organic frameworks (MOFs) have received tremendous attention as hydrogen storage materials since after the pioneer work of Yaghi and co-workers in 2003 that reported hydrogen adsorption on porous MOFs [10]. The efforts on this subject are collated in many review papers available in the literature [11–21]. Metal-organic frameworks are an extensive class of crystalline materials built from metal ions or clusters linked by organic ligands, which create a network of pores and channels (Figure 1). The co-existence of an organic and inorganic unit results in high tunability of MOFs dependent on the choice of molecular building blocks. MOFs possess extraordinarily high surface areas (experimental value of up to $7140 \text{ m}^2 \text{ g}^{-1}$, theoretical limit of $14600 \text{ m}^2 \text{ g}^{-1}$ [22]), ultrahigh porosity (up to 90% free volume), tunable pore size, and modifiable internal surface. These properties set MOFs apart from other porous materials like zeolites and carbon nanostructures, for a variety of potential applications such as gas storage, separation, heterogeneous catalysis, sensing, optical and electronic applications, biomedical imaging and drug delivery [23,24]. MOFs have been shown to exhibit electrochemical properties [25–28]. Recent investigations on the electrochemical behavior of composites of monovalent polyoxometalates and MOFs [29], and an electrocatalyst comprising Au-SH-SiO₂ nanoparticles immobilized in MOFs [30] have been reported. The electrochemical properties of MOFs make them potentially applicable in fuel cells (as electrolytes and electrode catalysts), lithium-ion rechargeable batteries (as electrode and electrolyte materials) and supercapacitors (as electrode materials) [31].

Immense efforts have been dedicated to the investigation of hydrogen storage in MOFs at low (cryogenic) temperatures as well as room temperature [11,13]. Although MOFs exhibit high hydrogen uptake at cryogenic temperatures (up to 99.5 mg g^{-1} (approximately 9 wt.%) at 56 bar and 77 K [32]) the storage capacities at room temperature are typically less than 1 wt.% due to the weak interaction (usually $4\text{--}12 \text{ kJ mol}^{-1}$ [33,34]) between

H₂ molecules and the MOFs. A plethora of studies have been geared towards enhancing the adsorption interaction (to the recommended $15\text{--}20 \text{ kJ mol}^{-1}$ [35]) between hydrogen and the frameworks so that the MOFs can store and release sufficient amounts of hydrogen at or near ambient conditions. Various strategies, for instance, introduction of coordinatively unsaturated metal sites, functionalization of ligands, increase in surface area and pore volume, inclusion of metal nanoparticles, catenation and manipulation of pore size, have been employed to improve the hydrogen storage capacities of MOFs. It is important to make a distinction between two terminologies i.e. excess hydrogen capacity and total hydrogen capacity, which are often used to report hydrogen storage capacities of physisorption materials such as MOFs. Gross et al. [36] provides elaborate definitions of these terminologies. The excess hydrogen capacity (also referred to as the Gibbs surface excess hydrogen capacity) is the extra amount of hydrogen that is present on the surface of the adsorbent over and above the density of the free hydrogen gas phase. This is the amount which is directly measured during volumetric hydrogen adsorption experiments, and the word “excess” has sometimes been omitted from the terminology when reporting this directly measured value. The total hydrogen capacity is the sum of the capacity arising from hydrogen adsorption on the surface and the capacity resulting from hydrogen compression within the volume of the adsorbent pores. The total hydrogen capacity is more suitable for making comparison between physisorption materials and chemisorption materials as it compares the total amount of hydrogen that is in reality stored within the apparent volume of the materials.

In this article, we review recent developments in hydrogen storage in MOFs at both low and room temperature focusing on the effects of various factors on hydrogen storage, with emphasis on factors that improve hydrogen uptake. The review primarily examines experimental studies. In addition, we report the emerging work on MOF hybrid hydrogen storage systems, particularly in the perspective of using MOFs as ‘scaffolds’ for high temperature (chemisorption) hydrogen storage materials.

2. Low Temperature Hydrogen Storage in MOFs

Metal-organic frameworks can store substantial amounts of hydrogen at cryogenic temperatures. The MOF, NU-100 (NU = Northwestern University), for example, was reported to store 99.5 mg g^{-1} (approximately 9 wt.%) hydrogen at 56 bar and 77 K [32]. Hydrogen adsorption at this low temperature of 77 K occurs by physisorption involving weak van der Waals forces and the adsorption isotherms are typically Type I in nature. Considerable

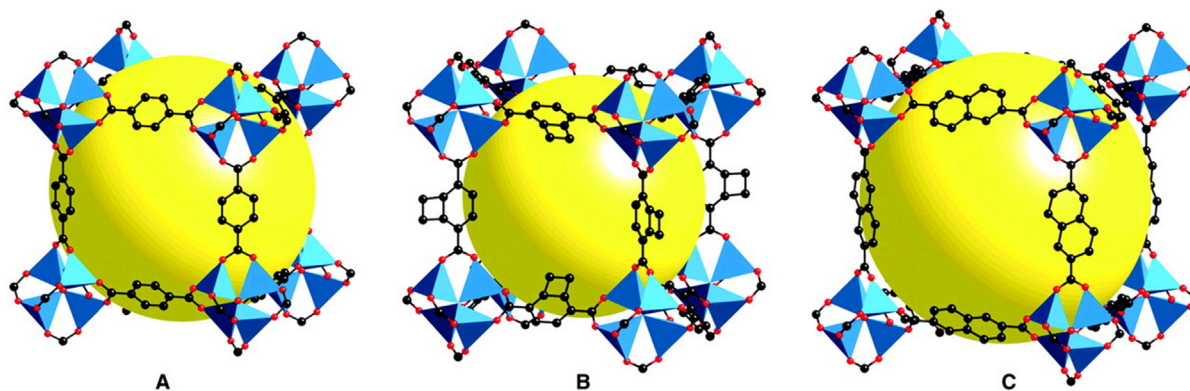


Figure 1. Single crystal x-ray structures of MOF-5 (A), IRMOF-6 (B) and IRMOF-8 (C) illustrated for single cube fragment of their respective cubic three-dimensional extended structure. On each of the corners is a cluster $[\text{OZn}_4(\text{CO}_2)_6]$ of an oxygen-centred Zn₄ tetrahedron bridged by six carboxylates of an organic linker (Zn, blue polyhedron; O, red spheres; C, black spheres). The large yellow sphere represents the largest sphere that would fit in the cavities without touching the van der Waals atoms of the frameworks. Hydrogen atoms have been omitted. Reproduced with permission from [10]. Copyright 2003 American Association for the Advancement of Science.

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