



Atomic-scale modeling of hydrogen storage in the UiO-66 and UiO-67 metal-organic frameworks



Stefan Andersson*, Per-Erik Larsson

SINTEF Materials and Chemistry, P.O. Box 4760, 7465 Trondheim, Norway

ARTICLE INFO

Article history:

Received 20 October 2015

Received in revised form

30 December 2015

Accepted 31 December 2015

Available online 11 January 2016

Keywords:

Adsorption

Force field

Grand canonical Monte Carlo

Metal organic frameworks

Computational chemistry

ABSTRACT

In this work we predict the key adsorption properties for hydrogen storage applications by investigating a series of recently synthesized zirconium based MOFs. These MOFs consist of an inorganic brick ($Zr_6O_4(OH)_4(CO_2)_{12}$) that binds to organic linkers (1,4-benzene-dicarboxylate and 4,4'-biphenyl-dicarboxylate) to form the two MOFs: UiO-66 and UiO-67. Particular attention has been paid to the performance of different classical force fields to describe the interactions between H_2 and the solid materials. It is found that combinations of several commonly used H_2 potentials in combination with the DREIDING force field give consistently good agreement with experimental adsorption data at 77 K, 95 K, and 110 K. The performance of the different force fields and hydrogen potentials is evaluated and discussed in terms of the physical interactions they describe. All tested force fields clearly underestimate adsorption at 296 K. Possible reasons for this discrepancy with experimental results are discussed and suggestions on how to improve the adsorption simulations are given.

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1. Introduction

The storage of hydrogen in solid materials is currently attracting large interest because of the potential use together with fuel cells in power technologies for the *hydrogen economy*. The use of hydrogen as energy carrier is proposed to solve the adverse pollution and climate effects of the current *hydrocarbon economy*. One key area where new improved hydrogen storage technologies are needed is hydrogen powered automobiles. However, it is technically very challenging to store sufficient amounts of hydrogen on board a vehicle, and to reach a practical range of driving before refilling is a major roadblock for the development of hydrogen fuelled vehicles. To further the research of hydrogen storage materials, the Department of Energy has established targets of 2.5 kWh/kg and 2.3 kWh/L, which becomes 7.0 wt % H_2 stored in the material [1].

A key goal in materials research for hydrogen storage is to construct novel materials that adsorb hydrogen with a higher density than liquid hydrogen. For other gases it is not uncommon to find more gas stored in a solid material than in a gas tank of equal volume, even for relatively high tank pressure. Clearly, the solid material increases the storage density of the gas. For storage of

hydrogen, which interacts relatively weakly, it is more challenging to reach higher storage density in a solid than in a tank. Yet, the storage capacity depends strongly on which type of nanoporous materials that are used. A wide range of experimental observations, of different materials and by several research groups, indicates that the surface area of the porous material governs the maximum adsorption capacity. Thus, it is the surface area of the material that correlates with the amount of hydrogen adsorbed. This is shown to be a good approximation for zeolites, carbon materials, metal-organic frameworks (MOFs), and other similar materials. Thus, in this respect the chemical composition of the material is less important than the total surface area in determining the maximum adsorption capacity [2]. Other adsorption properties do depend strongly on the composition. For instance, chemical interactions decide the pressure at which the maximum adsorption capacity is reached, and the heats of adsorption control the adsorption at low pressures. Thus, at low pressure, the amount of hydrogen adsorbed correlates better with heats of adsorption than with surface area, which controls the adsorption at higher pressures. In addition, the chemical composition also affects the pore size and shape, and it has been shown that curved surfaces in small pores interact stronger with hydrogen than surfaces in larger pores [2]. For practical hydrogen storage at room temperature, it will be important that a large amount of hydrogen is adsorbed at high pressure, but that a significant amount of hydrogen is released at pressures

* Corresponding author.

E-mail address: stefan.andersson@sintef.no (S. Andersson).

close to ambient. To achieve the best balance between adsorption and delivery there have been several estimates of optimum isosteric heats of formation for hydrogen adsorption (see Ref. [3] and references and therein), which fall between 15 and 30 kJ/mol.

At present, MOFs form a promising class of hydrogen storage materials. They consist of nodes, i.e., metal ions or other inorganic clusters, connected to organic ligands with functional groups at the terminal ends, binding to these inorganic nodes. The key is the ability to combine nodes and ligands to control pore size and shape, framework topology and surface area from the synthesis. Thus, in MOFs, by selecting inorganic nodes and organic ligands, it is possible to tune physical and chemical characteristics from these compounds and design nanoporous materials with specific properties, including porosity. Substantial progress has taken place over a very short period of time, and the development of new MOFs has provided many interesting results (see for instance ref. [3] and other papers in the same special issue of Chemical Reviews). Despite the significant progress, the greatest limitation is that many MOFs often are rather unstable, compared to zeolites or carbon materials. Hence, for use in practical applications, novel MOFs that are thermally stable as well as inert towards moisture, air and other impurities are needed.

Nevertheless, at present there exist several examples of stable MOFs. One group with a high degree of stability are the UiO-66, UiO-67 and UiO-68 MOFs developed at the University of Oslo [4], which are built from an inorganic node ($Zr_6O_4(OH)_4(CO_2)_{12}$) and the ligands 1,4-benzene-dicarboxylate for UiO-66, 4,4'-biphenyl-dicarboxylate for UiO-67, and terphenyl dicarboxylate for UiO-68. The inorganic node and the respective ligands then form the Zr-MOF structures shown in Fig. 1 for UiO-66 and UiO-67, which are the structures investigated in this work. In addition, the $Zr_6O_4(OH)_4(CO_2)_{12}$ inorganic node forms an $Zr_6O_4(OH)_4$ inner core for the hydroxylated structure, while if the MOF is heated up to 300 °C, the cluster dehydroxylates and forms an inner core of Zr_6O_6 , which is the inner core for the dehydroxylated structure. The UiOs are of particular interest because they are thermally stable to above 500 °C [4]. This high thermal stability has therefore caused substantial interest in the hydrogen storage properties of the UiOs, or novel Zr-MOFs.

Atomic-scale modeling for hydrogen storage in MOFs is a highly active research area [5–18]. Computational techniques, such as grand canonical Monte Carlo (GCMC), are able to predict adsorption properties but are also used to gain insight into the molecular scale phenomena taking place inside the MOFs. The simulations are typically carried out to predict the hydrogen adsorption isotherms, or to investigate the details of how hydrogen molecules interact

with the MOFs. The overall aim is to develop criteria of how to optimise the design of hydrogen storage materials. Current knowledge gained from atomic-scale modeling of hydrogen storage was reviewed recently by Getman et al. [8]. For example, the simulations of the IRMOF-1, -8, and -18 materials showed that metal-oxide clusters are the preferential adsorption sites for hydrogen at low pressure, while the organic ligands only becomes active adsorption sites at higher pressure when the inorganic sites are already occupied [18]. Quantum chemistry corroborates this conclusion, in that hydrogen binds stronger to metal oxide sites than to organic ligands, for instance shown for MOF-5 [17]. In addition, the simulations suggest criteria for designing improved MOFs [8]. The two most important criteria were found to be the need to increase the strength of the hydrogen–solid interaction and to further increase the surface area of the nanoporous material.

Traditionally hydrogen adsorption simulations in MOFs with GCMC use transferable classical force fields together with hydrogen potentials. For the solid material, force fields such as DREIDING [19] or UFF [20] are used, while hydrogen is either treated as spherical Lennard–Jones potentials [21,22] or with a partial charge representation of the quadrupole moment of H_2 added to the Lennard–Jones potential [23]. These simulations are in many cases successful, but may also fail in some cases. For a recent overview of the results from GCMC simulations of hydrogen adsorption in MOFs using a variety of force fields and hydrogen potentials, see the review by Getman et al. [8].

Sometimes the use of more complex force fields may be necessary. The transferable force fields are developed to be applied to a wide range of materials, but because of their generality there exist special cases where all the interactions needed to properly predict hydrogen adsorption are not included in the force field. Recent examples in MOF simulations are open metal sites and metal-cation doped or functionalized MOFs. To improve predictions of adsorption properties in such cases, quantum chemical techniques and more advanced interaction potentials are used to improve the treatment of hydrogen–solid interactions [6,8–10,13].

In view of the current interest in simulating hydrogen adsorption with the ultimate aim to aid development of new hydrogen storage materials, we saw the need to systematically assess the predictive power of classical force fields for such materials. Initially we investigate how the force fields treat different interactions, and how this correlates with the performance for simulating hydrogen adsorption. By identifying interactions that are not well described by these force fields, it will be possible to devise schemes of how to improve force fields in a systematic way. With such improvements, the hydrogen storage capacities of previously untested materials can be predicted with higher confidence in the results, and be an aid in the design of new and improved hydrogen storage materials. In recent experiments, three independent research groups have reported that the UiO-66 [24–26] and UiO-67 [25] MOFs have a comparatively high hydrogen storage capacity. Through these experimental results, we can evaluate the quality of currently used force fields on a set of chemically closely related materials, as well as their performance over a range of temperatures and pressures. There are some discrepancies between the experimental results that should be mentioned. The measurements by Chavan et al. [25] and Zlotea et al. [26] both agree on a maximum hydrogen storage capacity in UiO-66 of 2.3–2.4 wt% excess adsorption at 77 K around 30–40 bar, whereas the study by Abid et al. [24] suggested that excess adsorption could be at least 4.2 wt% at 77 K and 60 bar (and over 3 wt% at 30–40 bar). However, the material in the latter study was reported to have a significantly larger BET surface area and total pore volume than for instance the material studied by Chavan et al. (1434 vs. 969 $m^2 g^{-1}$ and 0.65 vs. 0.52 $cm^3 g^{-1}$, respectively). This could potentially be attributed to the reported significant

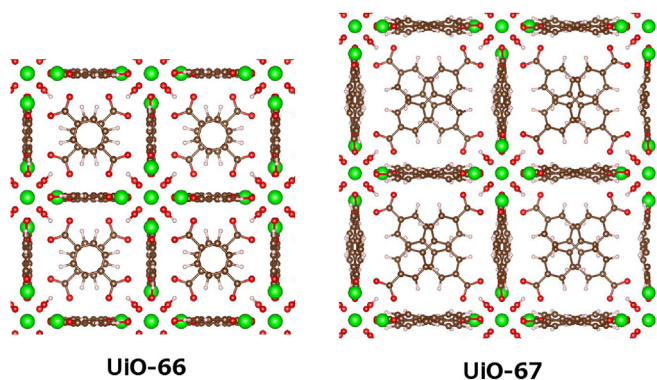


Fig. 1. Structures of UiO-66 and UiO-67. Depicted atoms are Zr (green), O (red), C (brown), and H (white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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