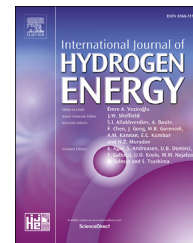




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# Multiscale study of the structure and hydrogen storage capacity of an aluminum metal-organic framework

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## ABSTRACT

First-principles calculations based on density functional theory and Grand Canonical Monte Carlo (GCMC) simulations are carried out to study the structure of a new Aluminum Metal-Organic Framework, MOF-519, and the possibility of storing molecular hydrogen therein. The optimized structure of the inorganic secondary building unit (SBU) of MOF-519 formed by eight octahedrally coordinated aluminum atoms is presented. The different storage sites of H<sub>2</sub> inside the SBU and the BTB ligand are explored. Our results reveal that the SBU exhibits two different favorable physisorption sites with adsorption energies of −12.2 kJ/mol and −1.2 kJ/mol per hydrogen molecule. We have also shown that each phenyl group of BTB has three stable H<sub>2</sub> adsorption sites with adsorption energies between −6.7 kJ/mol and −11.37 kJ/mol. Using GCMC simulations; we calculated the molecular hydrogen (H<sub>2</sub>) gravimetric and volumetric uptake for the SBU and MOF-519. At 77 K and 100 bar pressure, the hydrogen uptake capacity of SBU is considerably enhanced, reaching 16 wt.%. MOF-519 has a high gravimetric uptake, 10 wt.% at 77 K and 4.9 wt.% at 233 K. It has also a high volumetric capacity of 65 g/L at 77 K and 20.3 g/L at 233 K, indicating the potential of this MOF for hydrogen storage applications.

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## Introduction

The depletion of fossil energy resources raises a major worldwide problem, and the future of humanity depends on the transition to renewable and cleaner energy [1]. In recent

decades, research has increasingly focused on the development of new materials for storing gases, such as greenhouse gases, and particularly for the storage of hydrogen as a clean energy source, sustainable and well suited for use in the field of transport [2,3]. However, the storage of hydrogen is the major obstacle for mobile applications [4–6]. Different classes

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of materials have been developed for this purpose: metal hydrides, carbon nanomaterials [7,8] and nanoporous materials exhibiting a wide variety of interesting features, such as metal-organic frameworks (MOFs) and zeolites [9–11].

Despite the variety of classes of proposed materials, none of them fully satisfies the global recommendations for reversible hydrogen storage under ambient conditions. The primary purpose of research in this emerging field is to fulfill the application criteria and to meet the U.S. Department of Energy (DOE) hydrogen storage target capacity: 5.5 wt.% for the system gravimetric capacity and 40 g/L for the system volumetric capacity by the year 2017, at temperatures in the range of 233–333 K and pressures up to 100 bar [12]. Nowadays, some porous materials attain the gravimetric storage requirements, but in all cases at cryogenic temperatures near 77 K, still far from the temperature at which vehicles operate. This is due to the weakness of the interactions between hydrogen molecules and the adsorbent material.

Metal-organic frameworks are a class of nanoporous materials which offer many advantages over traditional nanoporous systems for diverse chemical technologies, such as catalysis, gas separation, biomedical devices, luminescence and gas storage [13–18]. These organic–inorganic hybrid materials consist of metal units connected through organic linkers [19–23]. They exhibit good thermal and mechanical properties [24]. Due to their chemically tunable structures [9], their high porosity and large surface areas, MOFs are particularly appropriate for the storage of gases including hydrogen [25–29].

Usually, gas storage capacity in the bulk material depends on two factors: firstly, the importance of porosity within the nanostructure networks, secondly, the large energy contribution due to interaction between the gas molecule and the various atoms of the material [30]. For optimal hydrogen storage, Bhatia and Myers have shown that the adsorption energy must reach  $-15.1$  kJ/mol [36].

However, the precise determination of adsorption sites in large-pore materials and understanding the interaction of gases with these sites are a challenge, because a single characterization technique is not able to provide adequate information on the structural details of adsorption sites [31]. Therefore, a combination of characterization techniques and theoretical calculations is required to complete the structural picture. This is why there are so many theoretical studies on this topic, especially the adsorption of H<sub>2</sub> gas in MOFs. Density functional theory (DFT) calculations provide information about the adsorption sites by comparing the binding energies of H<sub>2</sub> molecules [32].

Metallic atoms constitute the backbone of the MOF and their choice is important for the development of applications. For this, their availability, their cost and their chemical properties are the most important criteria. In this context, Uzun and Keskin reported a computational study on the mechanism of hydrogen adsorption in Cu-based MOFs [33]. They used DFT calculations and Grand Canonical Monte Carlo (GCMC) simulations for H<sub>2</sub> adsorption in MOF-505 and showed that metal (Cu)-oxygen clusters are the preferred adsorption sites for H<sub>2</sub>, and the strongest adsorption of H<sub>2</sub> was found at coordinately unsaturated metal sites. Also, Dixit et al. reported an ab initio study on hydrogen storage in light-metal-

decorated zinc-based MOF-5 [34]. In another computational study, Forrest et al. reported the mechanism of hydrogen adsorption in PCN-61 [35] having open metal sites. These simulations also revealed that there are three distinct favorable sites in PCN-61: cub octahedron, the corner of the truncated tetrahedron, and the corner of the truncated octahedron. Other transition metals have been used to develop efficient and large-scale production of nanoporous MOFs [36–38]. Recently, it was shown that a chromium-based MOF synthesized by green chemistry has significant hydrogen storage capacity [39]. MOFs based on heavier atoms, such as zirconium [40], palladium [41], platinum [42] or silver [43], with significant storage properties have been reported.

Among these porous materials, MOF-200, MOF-210, MOF-74 and MOF-177 are known to show a high potential for gas separation and the highest H<sub>2</sub> uptake [37,44–46]. Unfortunately a cryogenic temperature near 77 K is required for storage systems, far from the operating temperature range required in vehicles, between 233 and 333 K, where these materials cannot store significant amounts of hydrogen [47]. This is due to the weak interaction between hydrogen molecules and the MOFs [48]. Thus, we need to find new MOF-based porous materials with strong interactions with H<sub>2</sub>, to increase the efficiency of MOFs for hydrogen storage at higher temperatures. To enhance the hydrogen storage capacity, several strategies for improving hydrogen storage capacity based on MOF materials are developed. These strategies include the inclusion of open metal sites and lighter metals [49–51]. Indeed, Both experiments and molecular simulations based on first-principles show that MOFs with accessible metal sites can highly improve hydrogen uptake in microporous materials. For example, it is reported that Li-doped MOFs significantly improve H<sub>2</sub> uptake capacity near ambient conditions [52,53]. At 233 K and 100 bar the Li-MOF-C30 have gravimetric H<sub>2</sub> uptake of 6.0 wt %, reaching the 2017 DOE target. Another approach for improving hydrogen volumetric density optimization is to insert additional adsorbate surface within large-pore MOFs [54,55]. This can be achieved by either impregnation with a nonvolatile guest or catenation by another identical framework. Impregnation with reactive species could provide the more attractive sites that are ultimately necessary to improve hydrogen uptake at room temperature [56,57]. For example Aaron W. Thornton et al. reported that the impregnation of MOF pores with magnesium-decorated Mg<sub>10</sub>C<sub>60</sub> fullerenes denoted as Mg-C60@MOF, delivers remarkable the gas uptake [58]. Also Framework catenation is a topic of interest in MOF research [59]. For example, Rowsell and Yaghi suggested that it can improve hydrogen uptake due to the smaller pores that would increase the strength of hydrogen binding [60]. Also, Ma et al. reported substantial increases in hydrogen uptake at 77 K and 1 bar in a catenated MOF [61].

From a practical perspective, Yaghi et al. recently synthesized two new aluminum-based MOFs, termed MOF-519 and MOF-520 [62]. This new class of materials has a permanent porosity and exhibits high capacity for methane storage at both ambient and cryogenic temperatures. In particular, MOF-519 shows an exceptional storage capacity and significant enhancement of delivery of large amounts of methane up to 80 bar [62].

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