



## Review

# Adsorption, separation, and catalytic properties of densified metal-organic frameworks



Manjula I. Nandasiri<sup>a</sup>, Sachin R. Jambovane<sup>a</sup>, B. Peter McGrail<sup>b</sup>, Herbert T. Schaef<sup>c</sup>, Satish. K. Nune<sup>b,\*</sup>

<sup>a</sup> Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory (PNNL), Richland, WA 99354, USA

<sup>b</sup> Energy and Environment Directorate, Pacific Northwest National Laboratory (PNNL), Richland, WA 99354, USA

<sup>c</sup> Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory (PNNL), Richland, WA 99354, USA

## Contents

1. Introduction.....	39
2. Properties and applications of densified MOFs.....	39
2.1. Hydrogen storage properties of densified MOF-5.....	41
2.2. Densification of water stable Zr-based MOFs.....	43
2.3. Adsorption and separation properties of densified HKUST-1.....	44
2.4. Densification of flexible MOFs (MIL-53) for CH <sub>4</sub> /CO <sub>2</sub> separation.....	45
2.5. Densified MIL-101(Cr) for adsorption and separation.....	46
2.6. Densification of mechanically robust ZIF-8.....	47
3. Conclusions and future perspectives.....	50
Acknowledgements.....	50
References.....	50

## ARTICLE INFO

### Article history:

Received 6 October 2015

Accepted 5 December 2015

Available online 21 December 2015

### Keywords:

MOF pellets

Densification

Hydrogen storage

Volumetric adsorption

Thermal conductivity

MOF composites

## ABSTRACT

Metal-organic frameworks (MOFs) are one of the widely investigated materials of 21st century due to their unique properties such as structural tailorability, controlled porosity, and crystallinity. These exceptional properties make them promising candidates for various applications including gas adsorption and storage, separation, and catalysis. However, commercial applications of MOFs produced by conventional methods including solvothermal or hydrothermal synthesis are rather limited or restricted because they often produce fine powders. The use of MOF powders for industrial applications often results in pressure drop problems similar to the case with zeolites and limited robustness against water. To realize these materials for practical applications, densification of MOFs (by increasing pellet density) is routinely employed to form pellets, extrudates or beads to improve the overall density, volumetric adsorption, mechanical and thermal properties. However, the improvements come with some drawbacks such as reduction in overall porosity, surface area, and gravimetric adsorption capacity. Thus, optimizing the properties of densified MOF's by tuning the pellet density is very crucial for realizing these materials for industrial applications. Methods that increase the packing density in MOFs (for example by intentional interpenetration, etc.), which is different from pellet density, is not the scope of this review. In this review, the properties and applications of densified MOFs with different metal clusters and organic linkers are discussed.

© 2016 Elsevier B.V. All rights reserved.

**Abbreviations:** MOF, metal organic frameworks; PCP, porous coordination polymers; BASF, Baden Aniline and Soda Factory; DOE, the United States Department of Energy; BDC, 1,4-benzene dicarboxylate; VOC, volatile organic compounds; BET, Brunauer–Emmett–Teller; ENG, expanded natural graphite; XRD, X-ray diffraction; RH, relative humidity; NH<sub>3</sub>, ammonia; CNCl, cyanogen chloride; BSC, broad-spectrum carbon; PVA, polyvinyl alcohol; HPLC, high performance liquid chromatography; IR, infrared; DFT, density functional theory; MIP, mercury intrusion porosimetry; SEM, scanning electron microscopy; BSA, bovine serum albumin; CEC, capillary electrochromatography; nano-LC, nano-liquid chromatography; FTIR, Fourier transform infrared spectroscopy; EDS, energy dispersive spectroscopy; ZIF, zeolitic imidazolate framework.

\* Corresponding author. Tel.: +1 509 371 6632.

E-mail address: [satish.nune@pnnl.gov](mailto:satish.nune@pnnl.gov) (Satish.K. Nune).

## 1. Introduction

Metal-organic frameworks (MOFs); also known as porous coordination polymers (PCP) are one of the most interesting class of porous materials with extremely high porosity (50–90% free volume), very high surface area (1000–8000 m<sup>2</sup>/g), and a high degree of crystallinity [1–5]. In MOFs, inorganic building blocks (metal clusters) are connected by organic linkers with strong bonding; relating two separate disciplines in chemistry; organic and inorganic to create a wide range of porous materials with unique properties including chemical and structural tunability [1,4]. The diverse nature of MOFs due to the variability of metal clusters, judicious choice of structurally tailorable organic linkers, synthesis methods, structure, size, and functionalities resulted in the ever rising number of MOFs, which were highly published and cited in the last decade [1,6,7]. Thus, the various functionalities of MOFs led to a wide range of applications including gas adsorption and storage [8–13], separation [14–16], chemical sensing [17,18], nanofluids [19,20] catalysis [21–24], water adsorption [25], toxic gas removal [26], and energy storage [27]. Colloidal nano-sized MOFs exhibit significantly improved adsorption kinetics compared to bulk crystals due to decrease in diffusion path lengths and potential preference of crystal plane interactions [28].

However, using conventional synthesis strategies, MOFs have been often synthesized in powder form with low density, which are technically not suitable for certain industrial applications. Specifically, hydrogen storage; one of the most important applications of MOFs requires high volumetric hydrogen storage density, high thermal conductivity, and better stability in humid and reactive environments, which are lacking in loose powder materials [29,30]. A similar drawback of low volumetric adsorption capacity was observed when MOF powders were used for carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) storage [31,32]. Moreover, MOFs (for e.g. MOF-5, etc.) in powder form do not exhibit high mechanical strength, or good thermal and chemical stability at high temperatures under reactive conditions, which are required for the industrial applications in catalysis and gas separation [33]. The powder materials are also difficult to handle in commercial applications and can cause possible contamination in gas storage tanks [34]. Thus, there is an ongoing effort for densification of MOFs to improve the overall performance and overcome those engineering drawbacks and make them suitable for commercial applications. Densification of MOFs can be achieved in the forms of pellets, beads, monoliths, or thin film coatings by mechanical pressing, granulation, extrusion, templating, casting, coating, and thin film processing [35–37]. Recent reviews on these shaping and processing techniques can be found elsewhere [29,30,35,37]. However, the effects of densification on the properties and applications of MOFs have not been reviewed up to date, which will be extensively discussed in this review. Researchers in MOF community have briefly focused to maximize the packing density (by intentional interpenetration) for improved hydrogen storage [38]. Strategies that increase the packing density of MOFs for enhanced gas storage and separation applications are out of the scope of this review.

The most common method in densification of MOFs is making cylindrical pellets with flat ends and desired diameter and thickness by mechanical or hydraulic pressing [30]. The pelletization can be done with or without a binder; but in the former method the adsorption capacity of MOFs may be reduced due to the poor adsorption properties of the added binder. Binders typically improve mechanical strength and thermal conductivity of MOFs [39]. Methods such as chemical activation and hot pressing have been employed to limit the use of binders or in some cases avoid binders completely that resulted in densified MOFs without any loss in adsorption capacities [30]. Therefore, binder-less pellets or monoliths of MOFs are highly recommended as shaped structures

in large applications. In extrusion, a MOF-binder composite is pushed through a die with the shape of the structure under the heating and the cooled structure can be cut into desired lengths for suitable applications [30]. The extrusion produces higher volumes of the sample in contrast to mechanical compaction. Templating can also be utilized to obtain MOFs with desired shapes using solid or emulsions templates [30]. Solid templating is the most common method which uses silica monoliths, resorcinol, or zeolite membranes as templates to synthesize MOFs with certain shapes and ordered morphology [30]. The emulsion template techniques utilize a continuous structured phase obtained by sol-gel or polymerization methods and an internal phase emulsion, which is subsequently removed to obtain a porous replica of the emulsion [40]. Spherical beads of MOF with a reasonable micro-porosity have been prepared by emulsion-template technique [41]. Thin film coatings of MOFs are also considered as a densified form of MOFs, which have been reviewed by Fischer et al. [37,42,43]. Betard and Fischer discussed the fundamentals and applications of MOF thin films [42]. Fisher's group has also critically reviewed the status and future applications of thin film coatings of MOFs [37,43]. Thus, MOF thin films will not be a subject of this review. We will mainly focus on the densified MOFs in the forms of pellets of various materials for specific applications.

## 2. Properties and applications of densified MOFs

The crystal structures and specific applications of various densified MOFs (in the forms of pellets or monoliths) are illustrated in Table 1. MOF-5 has emerged as one of the next generation hydrogen (H<sub>2</sub>) storage materials due to its extremely high gravimetric H<sub>2</sub> adsorption capacity [11]. However, low volumetric H<sub>2</sub> adsorption capacity, structural decomposition in humid and reactive environments, low density, and poor thermal conductivity of MOF-5 powder materials seriously limit its industrial applications including hydrogen storage [44]. Thus, a collaborative effort has been made by Ford, Baden Aniline and Soda Factory (BASF), and University of Michigan in densifying MOF-5 to improve the adsorption capacities, thermal conductivity, and kinetic stability [45–50]. As a result of their efforts on densification of MOF-5, over 350% increase in volumetric H<sub>2</sub> storage has been achieved for MOF-5 pellets with a density of 0.5 g/cm<sup>3</sup> compared with powder (estimated density of 0.13 g/cm<sup>3</sup>) [49]. They also recognized several other MOFs such as MOF-177, IRMOF-8, ZIF-8, and Cu<sub>3</sub>(BTC)<sub>2</sub> as promising candidates for H<sub>2</sub> storage [51]. The major goal of their effort was to identify the densifying and processing conditions for MOFs to improve their adaptability in commercial H<sub>2</sub> storage and enhance the driving range of a hydrogen powered automobile above 300 miles [51]. In addition to MOF-5, densified MOF-177 and MIL-101(Cr) have shown increased volumetric H<sub>2</sub> storage capacities in another effort to achieve the United States Department of Energy's (DOE) targets for hydrogen storage [34,52–55]. Densified MOFs including Cu<sub>3</sub>(BTC)<sub>2</sub>, MIL-101(Cr), and UiO-66 have also showed improved volumetric CO<sub>2</sub> adsorption capacities compared with powder materials [32,56,57]. Densified MIL-53 with flexible organic linkers has mostly utilized for CO<sub>2</sub>/CH<sub>4</sub> separation, which showed higher CH<sub>4</sub>/CO<sub>2</sub> separation factors [39,58–60] compared with MOF powders. To this end, ZIF-8 pellets and monoliths have also been tested for various applications in catalysis, H<sub>2</sub>S and N<sub>2</sub> adsorptions, iodine storage, and separation of hexane isomers and bioalcohols [33,61–65]. In all the above discussed cases, densified MOFs exhibited improved volumetric adsorption capacities or separation properties.

Despite the volumetric adsorption capacity enhancement in densified MOFs, in some cases densification resulted in considerable reduction in the surface area and porosity due to the collapsing

Download English Version:

<https://daneshyari.com/en/article/1299270>

Download Persian Version:

<https://daneshyari.com/article/1299270>

[Daneshyari.com](https://daneshyari.com)