Shaping Methods of Metal–Organic Frameworks for Natural Gas Storage

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Abstract. The eco-friendly advantages of cleaner fuels such as natural gas have been extensively documented. However, the practical utilization of these fuels is restricted by the limitations of existing gas storage technologies. In this discussion, this paper evaluates the broad spectrum of possibilities that gas fuels present for transforming the energy sector, while also addressing the hindrances posed by current storage technologies that impede this transition. This paper scrutinizes the practical implications of natural gas storage, employing crystalline, porous metal-organic frameworks (MOFs) while referring to the latest benchmark outcomes and ultimate storage objectives in this domain. Specifically, this delve into the industrial constraints posed by the typically powdered form of MOFs and emphasize the recent advancements in MOF shaping. In contrast to their unprocessed powder condition, the features of MOFs as shaped in this study are examined, and a full review of several structuring methods is provided. The industrial usage of MOFs in applications involving gas processing is anticipated to be accelerated by this research.

Keywords: MOFs; natural gas storage; shaping methods.

1. Introduction

Natural gas is a critical component of the worldwide energy scene, functioning as a comparatively cleaner energy source. In comparison to coal, the combustion of natural gas results in nearly 50% less carbon dioxide (CO_2) emissions, along with significantly fewer emissions of sulphur oxides and nitrogen oxides. This translates into lower chances of smog and related health issues. Consequently, it represents a greener choice over other fossil fuels, emphasizing its importance in lessening the collective carbon impact. Given the anticipated surge in global energy consumption in the coming half-century, it is crucial to ensure the broad availability of clean fuels [1].

Liquefied natural gas (LNG) and compressed natural gas (CNG), although being energy-dense, necessitate intricate handling and costly cooling systems due to their low-temperature requirements. Adsorbents present a viable alternative, enabling the storage of natural gas at higher densities under ambient temperatures and moderate pressure conditions [2]. This makes them an attractive choice for gas storage. Actually, for volumetric natural gas storage, the American Department of Energy (DOE) has established an ambitious goal: 263 $cm^3\ cm^{-3}$ at 65 bars [3]. This target equals the storage density of CNG at 250 bars and 298 K.

MOFs have attracted a lot of interest lately because of their distinctive characteristics that make them potentially superior to traditional adsorbents like activated carbon and zeolites. represent a category of porous substances made up of metallic nodes and organic linkers. These metallic nodes within the framework are either individual metal ions (like Mn(II), Co(II), Cu(II), Cu(I), Cr(III), Fe(iii), Al(III), Zn(II), and Zr(IV)) or clusters, commonly referred to as secondary building units (SBUs). It is important to note that carboxylates (or other terminal groups) are frequently shown as components of the nodes in accordance with accepted practice. The organic linkers, which commonly contain imidazolate, pyridyl, carboxylate, and phosphonate or other azolate functional groups, form coordination bonds with the nodes [4].

MOFs possess distinct characteristics like extraordinary porosity, adjustable pore configurations, and easy functionalization. These attributes render MOFs desirable for gas storage and separation purposes (Fig.1). They can offer a high-density energy storage option for methane and hydrogen [5].

They also enable special host-guest interactions and sieving effects that can distinguish between distinct molecules for a separation procedure that uses less energy.

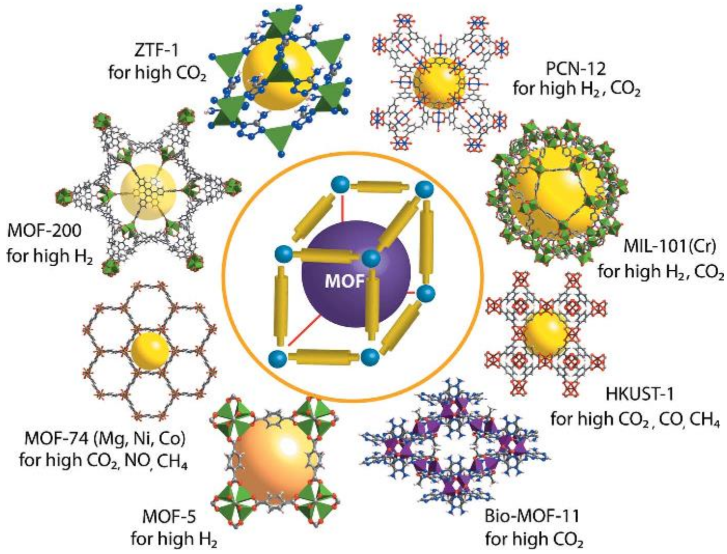

Fig 1. Different applications for MOFs [6].

MOFs carry significant potential for natural gas storage due to their ability to enhance storage capacity and decrease storage pressure for natural gas. These capabilities can cut costs and boost the safety of natural gas vehicles. Moreover, MOFs can be customized to possess specific characteristics, like a heightened selectivity for methane over other gases, or catalytic activity for methane activation or conversion. Importantly, numerous metal-organic frameworks have demonstrated methane capacities that match or even surpass those of the top-performing activated carbons [7].

Despite their potential, the industrial usage of MOFs encounters certain challenges. Typically, samples produced synthetically are powdery, with particle sizes often in the micron range. Although MOFs have shown promising performance for industrial use, their inherent powdered form is not ideal for extensive industrial development and applications. Powder adsorbents have traditionally been less than ideal for industrial use due to issues with scattering. However, using samples with firm shapes could be a better strategy to mitigate problems related to dispersion and pressure drop. Indeed, one of the principal hurdles for the industrial application of MOFs is their densification and pelletization. MOFs created using conventional synthesis techniques are produced as powders with a low packing density, often three times lower than the predicted crystal density [8]. This discrepancy creates a significant obstacle for practical industrial utilization of MOFs.

The current paper presents a summary of the many techniques used to shape MOFs, including using high pressure, chemical binders, sol–gel synthesis of monolithic MOFs and 3D printing. Key parameters like the working capacity for natural gas adsorption, pore size of the samples pre, surface area and post-molding are thoroughly reviewed, as these factors are vital for the performance of MOFs. Additionally, various synthesis methods for MOF monoliths, and their associated benefits and limitations are considered. This analysis aims to guide the formulation of MOFs' shaping strategies for industrial usage.

2. Mechanical Shaping with High Pressure

A common method of MOF granulation is powder compaction by mechanical or hydraulic pressing to manufacture cylindrical granules with a flat end and the required diameter and thickness, usually under 10-100 MPa. This process improves the volumetric working capacity of MOFs by reducing the interparticle space to increase the bulk density of MOFs. A binder can be used during pelletization, although the former procedure may result in decreased MOF adsorption capacity due to the inferior adsorption capabilities of the additional binder. Farrusseng and co-workers, based on the study of densified MOF pellets of Zr- and Cu- MOFs, concluded that the pressure exerted during tablet compression has a positive linear relationship with the mechanical toughness of the finished product [9].

The methods to increase the packing density of MOFs by applying pressure inevitably lead to the collapse of pores, reducing the BET surface area. The reduced BET surface area is related to the mechanical properties of the MOFs themselves, but even UiO-66, which has good mechanical properties in natural gas storage, will lose 80% of its BET surface area under pressures of 63-82 MPa [10]. Under high pressure, the MOF's chemical bonds are destroyed, which results in this.

In a related study, Peng et al. used computational methods to determine that HKUST-1 could potentially surpass the DOE goals for methane storage. They predicted it could hold up to 270 cm^3 cm^{-3} of methane at 65 bar pressure. However, in practical experiments, the density of HKUST-1 in powder form was significantly lower than that of its single crystal form, which resulted in the actual volumetric capacity being less than half of the theoretical value [11]. Furthermore, despite using high pressures to create high-density pelletized disks, the mechanical stability of these pellets was inadequate. As a consequence, there was a significant reduction (59%) in pore volume. This decrease in pore volume meant that the pellets' overall volumetric storage capacity did not increase as expected.

In a different investigation, the scientists employed PCN-250, a material that shows promise for storing methane, as a case study to comprehend the effects of unidirectional pressure on the structure of MOFs – this served as a model for an extrusion technique for MOFs. They found and recorded a series of structural changes, including the bending of Fe–O bonds and the flipping of N=N bonds. They also explored how pressure impacts the methane storage capacity of PCN-250, conducting both experimental and simulation-based investigations. The results showed that when PCN-250 was processed under optimal conditions, it exhibited a 21% increase in volumetric methane absorption, without any noticeable deterioration in its weight-based performance [12].

Mechanical compression is a simple method for forming MOFs that improves the volumetric methane absorption, but high pressure can force particles to pair together and affect the crystal and frame structures of those particles [13].

3. MOFs Shaping with Binders

From the preceding literature review, it is evident that MOFs, when molded without binders, can sustain performance in terms of porosity and surface area. Nevertheless, they typically exhibit insufficient mechanical strength and are easily impacted by pressure. To improve MOFs' mechanical toughness, the introduction of suitable binders is a primary solution to consider. The binder selection is critical as it ensures the original properties of the MOF remain intact. Granulated powders often utilize binders such as inorganic and organic polymer materials, and these can be combined with other shaping methods like 3D printing. Thus, this section will concentrate on the molding process using inorganic binders and organic binders.

3.1. Inorganic Binders

Inorganic binders are often utilized in the MOF molding process due to their eco-friendly properties and superior thermal stability. Unlike organic polymer-based binders, these rely on metal oxides, such as alumina and silica. Nonetheless, they may also have disadvantages, such as reduced solubility, and increased porosity. Consequently, the selection of inorganic binders hinges on the type of MOF, the shaping method, and the intended application.

In their study, Valekar et al. employed mesoporous alumina (MRA) as a binding agent in the granulation of various MOFs, UiO-66, UiO-66-NH_2, MIL-100, and MIL-101(Fig.2). The selection of MRA was predicated on its high surface area, extensive pore size, excellent solubility in both water and ethanol and cost-effectiveness. The researchers processed the MOF powders with diverse quantities of MRA (5–20 wt%) utilizing a rolling machine, thereby generating spherical granules with a diameter range of 1–2 mm. Subsequent drying of these granules was followed by calcination [14]. This procedure was designed to eliminate the residual solvent and bolster mechanical stability.

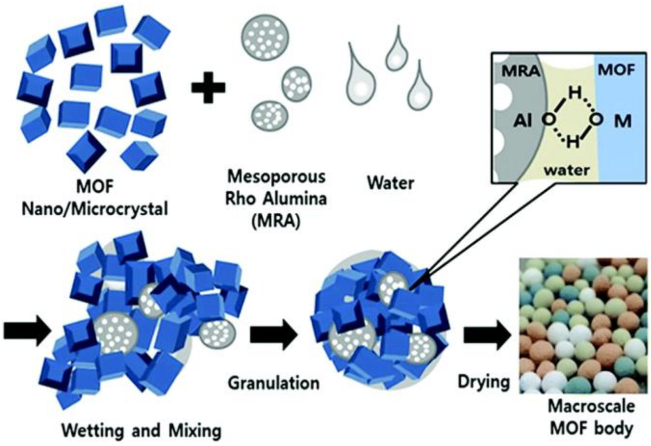

Fig 2. MOFs monolith shaping process using 5 wt % ρ-alumina as a binder [14].

The findings of the research indicated that the inclusion of the MRA binder amplified the mechanical stability of the granules, enabling them to endure pressures of up to 10 MPa without fracturing. Conversely, MOF pellets exhibited breakage at a pressure of just 1 MPa. Kim and colleagues developed MIL-100(Fe) granules by adding silica sol as a binder [15]. The MIL-100(Fe) granule's BET surface area was revealed by the adsorption and desorption isotherms at 77 K to be 1619 m^2/g, or nearly 90% of the value of the powder without any further decrease. The MIL-100(Fe) granules also showed a greater ability to adsorb SF6. Compared to commercial zeolite 13X granules, the breakthrough time was 40 minutes quicker at 1 bar, suggesting increased potential for real-world industrial applications.

3.2. Organic Binders

Organic binders utilized for MOFs are fundamentally constructed from organic polymers, typified by polyvinyl alcohol (PVA) and polyvinyl butyral (PVB). Relative to inorganic binders, organic variants can offer a plethora of benefits, inclusive of enhanced solubility and amplified mechanical strength. Nonetheless, these binders are not without their detriments, which encompass lower thermal stability, elevated cost, and reduced compatibility with certain types of MOFs.

MIL-53 is a prototypical flexible MOF. When subjected to mechanical pressing, MIL-53(Al) pellets tend to fracture when the temperature rises to 110 °C, potentially due to the framework's expansion as it heats up. In a study by Denayer and his team, poly(vinyl alcohol) (PVA), accounting for 13 wt %, was introduced as a binder to enhance mechanical strength [16]. Consequently, the micropore volume dropped by 32% upon activation from pure MIL-53(Al) at 190 °C and by 81 % during activation at 240 °C.

4. Sol-Gel Synthesis of MOFs

The creation of gel monolithic materials typically avoids the need for pressure and binders. Aerogels frequently include changeable porosities and specialized surface areas, and these materials can serve as predecessors for MOF films. In 2017, a research team pioneered a new synthetic method, a sol-gel process, for the fabrication of high-density monolithic HKUST-1 [17]. This process eliminates the need for high-pressure or chemical binders, which are typically responsible for capacity loss. By modifying the final step in the process, the drying condition, traditional powder-like MOFs or condensed, monolithic MOFs can be produced. The shaped HKUST-1 monolith has a BET surface area of 1193 m^2 g^{-1} and a methane capacity of 259 cm^3 cm^{-3} at 65 bar. As a result, it is the first adsorbent to reach the DOE's methane storage volumetric objective of 263 cm^3cm^{-3}. The monolithic MOF showed strong mechanical characteristics in nanoindentation experiments, with a hardness that was at least 130% higher than that of its conventional MOF counterparts. This has considerably improved the usage of mechanically robust, conformed, and densified MOFs for large volumetric energy storage and other industrial applications.

While the monoHKUST-1 demonstrated impressive volumetric methane adsorption at high pressures, its intense physical interaction with methane and heightened microporosity at lower pressures diminish its effective working capacity for CH_4 storage. Furthermore, HKUST-1's adsorption ability and crystallinity deteriorate in humid ambient conditions. As such, in 2019, the same research team developed an advanced synthetic method to design UiO-66 [18]. This innovative approach provides several advantages compared to conventional powder MOF designs. Initial steps included making 10 nm primary MOF particles for a UiO-66 gel. The initial MOF particles were then further processed using four different techniques, leading to the production of macroscopic monolith samples of UiO-66(Fig.3). The researchers highlighted that these seemingly minor variances in the synthesis led to noteworthy changes in the physical attributes of the resultant UiO-66 monolith samples. Changes were observed in factors such as adsorption properties, density, and fluorescence. Notably, all the resultant monoliths featured both mesopores and micropores.

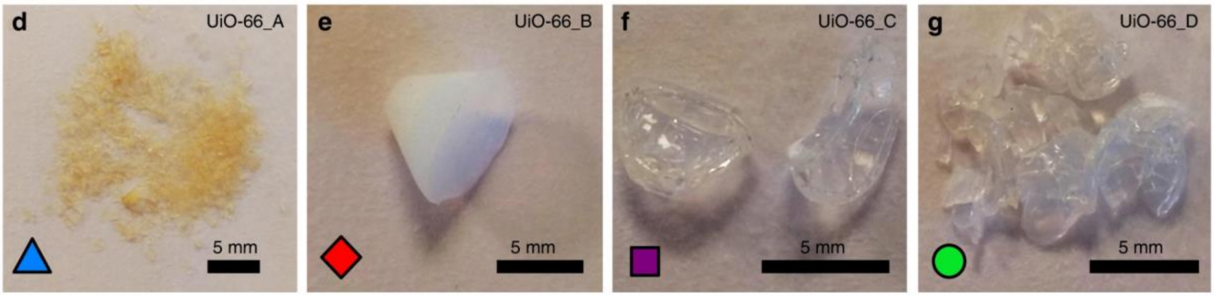

Fig 3. The optical photos of (d) monoUiO-66_A, (e) monoUiO-66_B, (f) monoUiO-66_C, and (g) monoUiO-66_D [18].

5. 3D Printing

Over recent years, the construction of intricate products based on MOFs through the utilization of 3D-printing systems has been attracting considerable interest. The process of 3D printing, a method that facilitates the creation of multifaceted shapes and structures through the layer-by-layer application of material, provides an array of benefits when applied to MOFs. These advantages encompass digital design, precision in control, elevated porosity and surface area, along with facile integration with diverse materials. However, the major hurdle in the 3D printing of MOFs lies in preserving the porosity, functionality, and surface area of the MOF crystals after the shaping process. This necessitates a meticulous choice and refinement of the printing method, the formulation of the MOF ink, the steps involved in post-processing, and the MOF-composite materials

Direct Ink Writing (DIW) has emerged as the most prevalent technique for 3D printing of MOFs, a process that entails the extrusion of a highly viscous MOF ink through a nozzle, subsequently deposited layer-by-layer on a substrate. This method can result in self-supporting, densely populated, and pure MOF monoliths that possess a high porosity and surface area. In a study conducted by Jun Ding et al. in 2019, it was shown that pure, tightly packed, and self-supporting MOF monoliths may be directly printed using colloidal gels containing just ethanol and $Cu_3(BTC)_2$ nanoparticles [19]. Fig. 4 shows the printability of the gel. The MOF gel has the ideal rheological characteristics for 3D extrusion-based printing, indicating the possibility of using this method with additional gel-forming MOF families. Notably, after shaping, the MOF's porosity and surface area are virtually maintained. The HKUST-1 monolith, which was 3D printed, has a sizable mesopore volume and an incredibly high BET surface area of 1134 m^2/g. The performance of the 3D printed monolith when used for methane storage, which is a conventional application of HKUST-1, is on par with or even better than monoliths made using other shaping methods.

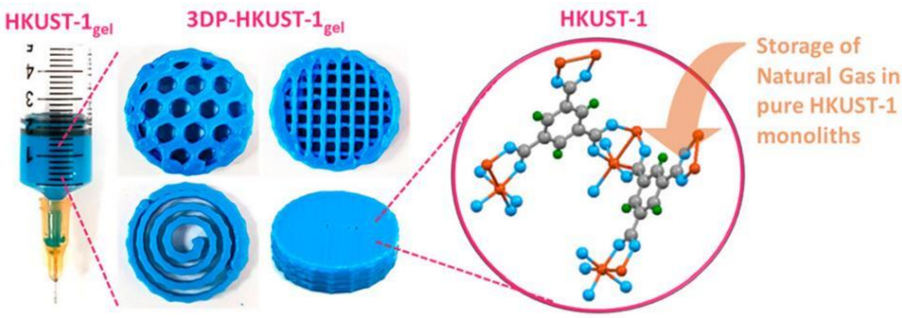

Fig 4. Different 3D printed structures of HKUST-1.
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An additional promising method for fabricating MOFs via 3D printing is the 'gel-print-grow' technique. This process entails the printing of a colloidal gel composed of MOF nanoparticles, followed by the growth of MOF crystals by submerging the printed structure in a solvent. Like Direct Ink Writing, the 'gel-print-grow' technique can generate pure, densely aggregated, and self-supporting MOF monoliths characterized by high surface area and porosity. Lawson and his team conducted a study utilizing this method, where they created HKUST-1 MOF monoliths using ethanol as a solvent and triethylamine (TEA) as a binder, subsequently employing these structures for methane storage [20]. Fig.5 presents the overall printing process. The results exhibited comparable performance, if not superior, to other shaped HKUST-1 materials. This study represents a significant improvement in additive manufacturing and a promising development in the field of 3D printing of MOFs.

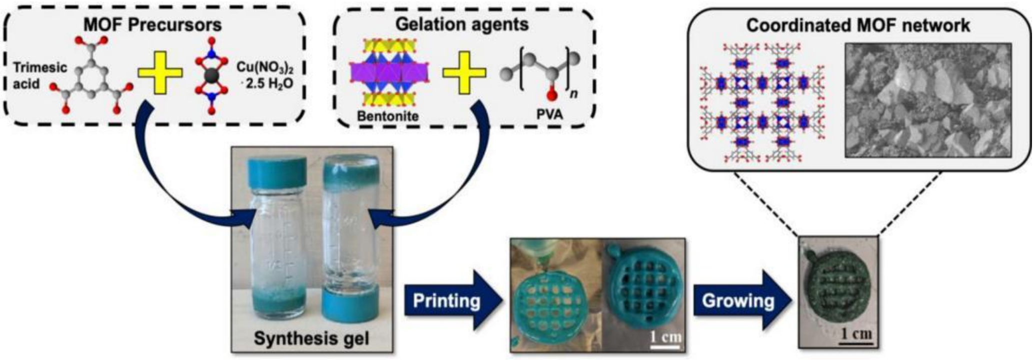

Fig 5. HKUST-1 monolith formulation using a new GPG
method. Reprinted with permission [20]. Copyright 2020 ACS.

6. Conclusion

This review delves into various methodologies for structuring MOFs into monoliths, an endeavor of significant relevance for future industrial applications. The BET surface area, mechanical strength, and porosity are evaluated in this study in order to determine the effect of binders on the adsorption performance of the shaped MOFs. Notably, the structural frameworks of the tablets or extrudates obtained through pressurization tend to collapse to varying extents, generally exhibiting a reduction in the BET surface area proportionate to the magnitude of pressure applied. The addition of a binder in the process of shaping MOF monoliths results in varying levels of pore obstruction compared to MOF powder, resulting in a minimum 10% and maximum 50% reduction in the BET surface area and porosity from theoretical values. The synthesis of porous monolithic MOFs via a sol-gel process emerges as a successful strategy. Upon successful packing and densification. However, the recent emergence of advanced 3D printing methods has significantly expanded the range of MOF monolith shaping. 3D printing has unveiled novel avenues for constructing adsorbent monoliths of unique geometries. This technique, capable of printing a variety of shapes as per computer-aided designs, expands the scope of potential MOF applications. However, 3D printing MOFs is not a perfect process and it may face some challenges, such as limited materials and quality issues. The forthcoming hurdles in MOF shaping encompass (1) circumventing the egress of minuscule MOF particles from shaped products during prolonged usage, (2) mitigating the adverse impact of shaping on MOFs' adsorption kinetics, and (3) pinpointing the most suitable shaping techniques for specified applications. These challenges have been predominantly neglected in existing literature, indicating the areas where future research needs to focus.

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