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SYNTHESIS AND MODIFICATIONS OF POLYMER-BASED CARBON/METAL ORGANIC FRAMEWORK COMPOSITES FOR HYDROGEN STORAGE APPLICATIONS

By

LERATO YVONNE MOLEFE

Student Number: 201602335

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FACULTY OF SCIENCE

of the

UNIVERSITY OF JOHANNESBURG

Supervisor : Prof. Patrick G. Ndungu
Co-supervisor : Dr. Nicholas M. Musyoka

October 2019
DECLARATION

I declare that this thesis “SYNTHESIS AND MODIFICATIONS OF POLYMER-BASED CARBON/METAL ORGANIC FRAMEWORK COMPOSITES FOR HYDROGEN STORAGE APPLICATIONS” is a presentation of my own original research work. It is being submitted for the degree of Doctor of Philosophy (Ph.D.) in Chemistry at the University of the Johannesburg. It has not been submitted for any degree or examination in any other university. All the sources used are accordingly acknowledged by means of complete references.

Some of the work reported in this thesis has been published in journal articles and presented at conferences, as indicated in the academic output section.

The work was done under the supervision and guidance of Prof. Patrick G. Ndungu at the University of Johannesburg and Dr. Nicholas M. Musyoka at the Council for Scientific and Industrial Research, South Africa.

Lerato Y. Molefe……………………… ……………………………………………
STUDENT DATE

Prof. Patrick G. Ndungu ……………….. ……………………………………………
SUPERVISOR DATE

Dr. Nicholas M. Musyoka ……………. ……………………………………………
CO-SUPERVISOR DATE
I dedicate this work to my precious family, especially to my late dad (Mr. Mohapi David Molefe) and my beloved brother (Mr. Sehloho Samuel Molefe).
ACKNOWLEDGEMENTS

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Publications:


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1. School of Chemistry, Inorganic solid state and materials chemistry research group, University of Glasgow, United Kingdom, 1 May-15 June 2018.

2. Department of Chemistry, Microporous polymer chemistry research group, The University of Sheffield, United Kingdom, 15 June-31 July 2018.

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1. Advanced porous materials for Industry: Metal Organic Frameworks, porous Polymers and beyond”. Delft, Netherlands, on 02 November 2017, participant: L.Y Molefe


ABSTRACT

The South African energy landscape is dominated by carbon dioxide (CO$_2$) emitting coal combustion which is currently plentiful and cheap however because of its finite nature, it will soon diminish. With the current growing population and increasing energy need, research scientists all over the world are continuously working towards shifting to cleaner renewable energy sources of which hydrogen (H$_2$) is a promising candidate. Hydrogen has a high gravimetric energy density than any other fuel and its combustion in pure oxygen only produces water vapour and heat. However, since it is very light and as a result has a low volumetric energy density, its storage is very difficult. Generally, adsorbents materials such as metal-organic frameworks (MOFs) such as Materials Institute Lavoisier (MIL-101(Cr)) and Universitetet i Oslo (UiO-66(Zr)) as well as porous carbons such as zeolite templated carbon (ZTC) have been well investigated for H$_2$ storage due to their unique properties such as extremely high surface areas and ultrahigh porosities. However, their great potential in H$_2$ storage applications is limited by their lack of immediate processability, because they are obtained as fine powders in their as-synthesised form. For these materials to gain practical applications in H$_2$ storage they must be shaped into mechanically stable and easy to handle bodies like monoliths. The process of shaping MOFs and carbon powders often includes the use of various non-porous polymers and inorganic materials as binders and that often results in pore-blocking effects and low H$_2$ uptake.

In this thesis, porous composites containing either MIL-101(Cr) or UiO-66(Zr) or ZTC have been produced by incorporating these powders into polymer of intrinsic microporosity (PIM-1) or acrylonitrile butadiene styrene (ABS) polymers. The PIM-1 based composites were prepared by a simple and yet versatile direct impregnation of PIM-1 with powder fillers by physical mixing in a suitable solvent (tetrachloroethane) forming self-standing monoliths of different shapes possessing easy handling properties. While the ABS based composites were compounded into filaments and 3D printed using a conventional and commercially available thermoplastic 3D printer. Other attempts were made to incorporate the PIM-1/UiO-66 with ZTC and carbon foam (CF) to improve the thermal properties of MOFs. The obtained materials were then characterized using scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), Fourier transform infra-red (FTIR) spectroscopy, thermogravimetric analysis (TGA) and nitrogen gas sorption measurements was used to probe the textural
properties (surface area, pore volume and pore size distribution) at 77 K up to 1 bar. The $\text{H}_2$ uptake measurements were also tested at 77 K and 1 bar.

The resulting PIM-based composites (PIM-1/MIL-101(Cr), PIM-1/UiO-66, PIM-1/ZTC and PIM/UiO-66/ZTC) benefited both from the processability of PIM-1 matrix and the high $\text{H}_2$ uptake capacities of the porous powder fillers. Additionally, the powders in PIM-1 maintained good retention and accessibility of their micropores within the composite as evidenced by an increase in textural properties and $\text{H}_2$ uptake upon increasing their loading ratios. Additional pores were also formed at their interfaces. On the other side, the adsorption performance of 3D printed materials was disappointing, as the surface area and $\text{H}_2$ uptake measurements could not be obtained because the samples did not allow full gas diffusion on the reasonable time scale allowed by the instrument parameters. Nonetheless, using the tensile tester, it was possible to compare the mechanical properties for pristine ABS (47.6 MPa) and ABS/5 wt% UiO-66/5 wt% ZTC (30.9 MPa) proving that 3D printing technique shows a promise for shaping MOFs (reducing dust problems) and increasing their mechanical properties.

Generally, the monolithic bodies of polymer-based MOF/carbon composites materials that possess improved surface and physical requisite properties resulting from the synergistic effects of compositing their individual counterparts were successfully obtained in this thesis and tested for $\text{H}_2$ storage applications. The maximum surface areas and $\text{H}_2$ uptake capacities were obtained as follows 1045 m²g⁻¹ and 1.22 wt.% for PIM-1/UiO-66(Zr), 1767 m²g⁻¹ and 1.65 wt.% for PIM-1/UiO-66(Zr)/ZTC, 2433 m²g⁻¹ and 1.87 wt.% for PIM-1/ZTC and 2347 m²g⁻¹ and 1.73 wt.% for PIM-1/MIL-101(Cr) composites. Having achieved attractive powder shaping option that did not adversely alter their gas adsorption properties, the properties and shapes of the monoliths can be further optimised for transitioning MOFs and porous carbons from laboratory scale to various large scale applications.
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<td>N,N-Dimethylformamide</td>
<td></td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
<td></td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra-Red</td>
<td></td>
</tr>
<tr>
<td>HCP</td>
<td>Hyper Crosslinked Polymer</td>
<td></td>
</tr>
<tr>
<td>HATN</td>
<td>Hexaazatrinaphthylene</td>
<td></td>
</tr>
<tr>
<td>HIPE (s)</td>
<td>Polymer High Internal Phase Emulsion (s)</td>
<td></td>
</tr>
<tr>
<td>HK</td>
<td>Horvarth-Kawazoe</td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric</td>
<td></td>
</tr>
<tr>
<td>ICE</td>
<td>Internal Combustion Engine</td>
<td></td>
</tr>
<tr>
<td>IRMOF</td>
<td>Isoreticular Metal Organic Framework</td>
<td></td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
<td></td>
</tr>
<tr>
<td>LH₂</td>
<td>Liquid Hydrogen</td>
<td></td>
</tr>
<tr>
<td>MIL</td>
<td>Material d'Institute Lavoisier</td>
<td></td>
</tr>
<tr>
<td>MIL-101(Cr)</td>
<td>Chromium (III) terephthalate MIL-101</td>
<td></td>
</tr>
<tr>
<td>MMM (s)</td>
<td>Mixed Matrix Membrane (s)</td>
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<tr>
<td>MOF (s)</td>
<td>Metal Organic Framework (s)</td>
<td></td>
</tr>
<tr>
<td>MOP (s)</td>
<td>Microporous Organic Polymer (s)</td>
<td></td>
</tr>
<tr>
<td>MWCNT (s)</td>
<td>Multi Wall Carbon Nanotube (s)</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
<td></td>
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</tr>
<tr>
<td>Nm</td>
<td>Nanometer</td>
<td></td>
</tr>
<tr>
<td>PAM</td>
<td>Macroporous Polyacrylamide</td>
<td></td>
</tr>
<tr>
<td>PIM</td>
<td>Polymer of Intrinsic Microporosity</td>
<td></td>
</tr>
<tr>
<td>PAF</td>
<td>Porous Aromatic Framework</td>
<td></td>
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<tr>
<td>PAni</td>
<td>Polyaniline</td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
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<td>Polyacrylonitrile</td>
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</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
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<tr>
<td>PPN</td>
<td>Porous Polymer Network</td>
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</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene Terephthalate)</td>
<td></td>
</tr>
<tr>
<td>PUF</td>
<td>Polyurethane Foam</td>
<td></td>
</tr>
<tr>
<td>PSD</td>
<td>Pore Size Distribution</td>
<td></td>
</tr>
<tr>
<td>(P) XRD</td>
<td>(Powder) X-Ray Diffraction</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
<td></td>
</tr>
<tr>
<td>U.S</td>
<td>United States</td>
<td></td>
</tr>
<tr>
<td>UiO</td>
<td>Universitetet I Oslo</td>
<td></td>
</tr>
<tr>
<td>UiO-66(Zr)</td>
<td>Zirconium terephthalate UiO-66</td>
<td></td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage</td>
<td></td>
</tr>
<tr>
<td>ZIF</td>
<td>Zeolitic Imidazolate Framework</td>
<td></td>
</tr>
<tr>
<td>ZTC</td>
<td>Zeolite Templated Carbon</td>
<td></td>
</tr>
<tr>
<td>SYMBOL</td>
<td>UNIT</td>
<td>DESIGNATION</td>
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</tr>
<tr>
<td>(a)</td>
<td>m(^2)s(^{-1})</td>
<td>Thermal diffusivity</td>
</tr>
<tr>
<td>(c_v)</td>
<td>Jm(^3)K(^{-1})</td>
<td>Volumetric heat capacity</td>
</tr>
<tr>
<td>(c_m)</td>
<td>Jg(^{-1})K(^{-1})</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>(P)</td>
<td>kgm(^{-3}) or gm(^{-3})</td>
<td>Density</td>
</tr>
<tr>
<td>(q)</td>
<td>Wm(^{-2})K(^{-1})</td>
<td>Heat flux</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wm(^{-1})K(^{-1})</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>(dT)</td>
<td>dx</td>
<td>Temperature gradient</td>
</tr>
<tr>
<td>(T)</td>
<td>K or °C</td>
<td>Temperature</td>
</tr>
<tr>
<td>(x)</td>
<td>m</td>
<td>Distance</td>
</tr>
<tr>
<td>(Q)</td>
<td>J</td>
<td>Heat transferred</td>
</tr>
<tr>
<td>(V)</td>
<td>m(^3)</td>
<td>Volume</td>
</tr>
<tr>
<td>(\Delta T)</td>
<td>K or °C</td>
<td>Temperature change</td>
</tr>
<tr>
<td>(\Delta H_{ad})</td>
<td>kJ/mol</td>
<td>Heat of adsorption</td>
</tr>
<tr>
<td>(\Delta H_{opt})</td>
<td>kJ/mol</td>
<td>Optimal heat of adsorption</td>
</tr>
</tbody>
</table>
CHAPTER 1: INTRODUCTION

Summary Statement

This chapter presents the background information of the study with some emphasis on the hydrogen storage methods. It further outlines the research motivation, aims and objectives and concludes with a presentation of the research framework and thesis structure.

1.1. Overview of the Hydrogen Economy

A transition from exploitation of fossil fuels to a clean and sustainable energy supply is a crucial issue in the 21st century and in the coming decades. As illustrated in Scheme 1.1a, the use of non-renewables such as coal, of which South Africa heavily depends on for energy production, releases toxic emissions into the atmosphere and are not sustainable. Therefore, the rapidly growing world population and energy demands require the use of more sustainable and clean renewable energy sources (Scheme 1.1b). Now, with the fourth industrial revolution fast approaching, the advancement of current energy generation technologies and introduction of new ones is a priority. The technological challenges involved in speeding up this transition will require chemists and material scientists to develop novel materials with enhanced properties for energy related applications. Owing to its excellent properties such as light weight, high energy density by weight, abundancy and zero carbon dioxide emissions, hydrogen (H\textsubscript{2}) has been designated as the best promising energy carrier [1]. Hydrogen is a tasteless, colourless and non-toxic abundant element which is found bound to other elements in nature [1]. However, it is worth noting that H\textsubscript{2} is considered an energy carrier and not an energy source meaning that it has to be produced from the source. The reason why hydrogen is considered as a green energy is because it can be produced from renewable sources and is environmentally friendly. The use of hydrogen as a sustainable fuel also offers security of supply for the drastically increasing world-wide energy demand and would thus play a critical role in reducing dependence on fossil fuels which will soon run out. South Africa views the adoption of hydrogen and fuel cell technology as a strategy to secure the country’s future energy demands and advance its scientific and economic interests. Currently, the country is focusing more on developing knowledge that will reduce the technology cost, addressing safety issues and creating a new energy paradigm in the world [2]. There is no doubt that hydrogen is at the forefront when it comes to development of
novel energy carriers for mobile applications but its safety issues and storage targets as set out by Department of Energy (DOE) are key concerns [3].

**Scheme 1.1.** Schematic representation of the unsustainable non-renewable energy system (a) and sustainable renewable energy system (b). Reprinted from ref. [4], Copyright (2008), with permission from Elsevier.

### 1.1.1. Hydrogen Energy System

Hydrogen as an energy carrier has a very high gravimetric energy density of 120 MJ kg\(^{-1}\), about three times the energy density of petrol (44 MJ kg\(^{-1}\)) [5] and almost seven times the energy density of conventional fossil fuels [6]. Conversely, on a volume basis, liquid hydrogen (LH\(_2\)) has a density of 8 MJ L\(^{-1}\) whereas petrol has a density of 32 MJ L\(^{-1}\), on lower heating values. Nonetheless, there are still significant challenges hindering the large scale
applications of hydrogen fuel especially in mobile transportation owing to the lack of safe and reliable H₂ storage options. Based on the existing H₂ compression storage technology to move a hydrogen-powered fuel cell vehicle (FCV) requires a far larger, heavier and complicated fuel tank than a typical petrol-fuelled internal combustion engine (ICE) vehicle for an equivalent distance. In this case, the strategy for the development of efficient and safe storage of hydrogen is very essential for promoting a sustainable “hydrogen economy”. The problem of hydrogen storage remains so far unsolved and it continues to represent a significant hindrance to the advancement of the hydrogen technologies [1].

1.1.2. Hydrogen Production
Although hydrogen is one of the most abundant elements on the earth’s crust, it is always found bound with other elements. Therefore, to obtain it in its free natural state, it must be produced by separating it from hydrogen containing sources/feedstocks using chemical, thermal or electrical energy. The hydrogen sources include water, waste, solar sources, coal, biomass, natural gas and hydrocarbons [7]. Currently, the primary methods used for H₂ production are chemical (electrolysis) and thermal (gasification, reforming). However, the steam reforming of hydrocarbons like methane yields carbon dioxide (CO₂) as a by-product which contributes to the global warming crisis. Another method is through the pyrolysis of biomass, hydrocarbons and municipal solid waste which yields hydrogen and carbon black. However, this process is more expensive than steam reforming of natural gas. Whereas water electrolysis is a well-established technology, the large scale electrolysis using fossil or nuclear generated electricity is only 35-40% efficient. The production of H₂ using energy derived from renewable sources such as wind and solar should be highly encouraged to guarantee ‘green’ hydrogen. Technological developments in this direction would later result in cost-competitive production which would replace the conventional methods.

1.1.3. Hydrogen Transportation, Distribution and Utilisation
Today, limited H₂ distribution pipeline networks and tanker trucks are used in certain parts of the world to supply and transport H₂ from gas production plants to industries. Therefore, there is still a need for a reliable and low-cost H₂ distribution network. On the other hand, fuel cell (FC) is by far the most studied conversion and utilisation technology that can be fuelled with hydrogen to convert the chemical energy in H₂ into electrical energy. Fuel cells are quiet, pollution-free and their efficiencies are 2-3 times > than an ICE [7]. Moreover, their
scalability makes them suitable for a variety of applications ranging from portable devices like laptops (50–100 W) to central power generation (1–200 MW). However, FCs are currently relatively expensive compared to the conventional ICEs. Thus, further developments to reduce their costs and improve durability are still under way to make them economically viable [8]. In general, the applications of FCs include generating electricity for micro and utility grids, in transport to power vehicles and in portable devices such as toys, cell phones and laptops. The general H₂ value chain is presented in Scheme 1.2.

![Scheme 1.2](image)

**Scheme 1.2.** The H₂ energy chain showing a pathway to H₂ economy from production to end-use application.

### 1.1.4. Hydrogen Storage

Hydrogen storage is a challenging endeavour all over the world. As a reference; imagine driving a FCV for 400 km, it would need 4-5 kg of H₂ which at ambient temperature will need to be compressed at 700 bar in a 70 L size tank [9]. Figure 1.1 presents an overview of existing hydrogen storage technologies. These technologies are classified as either physical or materials-based storage options. The limitations of a compressed storage system are due to the large amount of energy needed for compression of the gas, safety concerns of high pressure and embrittlement of cylinder material during the numerous charging/discharging cycles [5]. The cryo-compressed tanks are used for increasing the gravimetric and volumetric storage capacities of compressed gas tanks because at fixed pressure and volume, the volumetric capacity increases as the tank temperature decreases [10]. Therefore, strategies for developing low cost alternative methods for storing H₂ at safer low pressures remain a
challenge. On the other side, storing hydrogen in the liquid state, the LH₂ tank must be maintained at -253 °C, thus a large amount of energy is required to achieve liquefaction [11]. Moreover, the limitations of LH₂ tanks include; the hydrogen “boil-off” issue, high energy consumption and the very high cost of the tank. Another problem is safety when handling liquid hydrogen, when storing, pressurizing and cooling it to such extreme temperatures [12]. The next sub-section briefly discusses the advantages and challenges of materials-based H₂ storage.

**Figure 1.1.** Overview of existing hydrogen storage technologies. Reproduced from ref. [13].

### 1.1.5. Material-based hydrogen storage

It is clear that safety concerns for high pressure containment and boil-off loss issues for hydrogen liquefaction really puts a major limitation on their use as far as the practical application is concerned. However, these issues can be resolved by materials-based hydrogen storage options which either involves physisorption of hydrogen on the surface of porous materials or chemisorption in hydrides. These methods are attractive because the volumetric and cryogenic constraints are abandoned. However, these storage options also possess inherent drawbacks that are related to their eventual applications [14]. Hydrogen physisorption is described as a process where hydrogen gas molecules bind weakly onto the adsorbent’s surface through van der Waals forces without forming any chemical bonds. This
process has low binding energies that are less than 10 kJ.mol⁻¹. In this case, the H₂ adsorption and desorption process is reversible and has fast kinetics. However, the weak interactions between H₂ and the adsorbent result in low H₂ uptake at ambient conditions. In contrast, chemisorption is based on strong interactions (binding energies that are higher than 50-kJ.mol⁻¹) and results in the formation of chemical bonds between H₂ and the adsorbent. Therefore, to desorb the hydrogen higher temperatures are often required [11, 15].

The physisorption method is considered to have more advantages for hydrogen storage when compared to the chemisorption route such as low operating pressure, low weight, and the relatively low cost of the materials involved. The amount of H₂ that an adsorbent material can store at a specific temperature and pressure condition is influenced by the material’s surface area and the strength of surface interactions. The tremendous research progress made in nanoporous materials for hydrogen storage applications shows great promise, as high gravimetric H₂ capacities greater than 5 wt. % can be achieved at 77 K and low pressures. For example, at 77 K activated carbons such as CA-4700 exhibit H₂ capacities of up to 3.9 wt. % and 8.9 wt. % at 1 bar and 30 bar respectively [16]. However, volumetric capacities remain low at the same conditions. Therefore, the properties of these adsorbents must be improved to achieve high gravimetric and volumetric capacities at both low and ambient temperatures. Furthermore, nanoporous materials need modifications for enhancing their physical properties such as thermal conductivity for fast dissipation of heat generated during H₂ adsorption and mechanical strength for better handling [17].

1.1.6. Technical Targets for Hydrogen Storage Materials

Despite the progress made so far, among the currently available candidate storage materials, none is capable of meeting the DOE’s criteria for light-duty vehicles at moderate temperatures and pressures. The United States (U.S.) DOE’s 2020 hydrogen storage targets for on-board light-duty vehicle, material handling equipment, and portable power applications for the gravimetric and volumetric densities are 1.8 kWh/kg system (5.5 wt.% hydrogen) and 1.3 kWh/L system (0.040 kg hydrogen/L), respectively. Likewise, the ultimate DOE targets beyond 2020 for the gravimetric and volumetric densities of the system are 2.5 kWh/kg (7.5 wt.% hydrogen) and 2.3 kWh/L (70 kg hydrogen/L), respectively [18]. These targets are set for the entire system, which is the adsorbent, storage container and other apparatus, thus the adsorbents alone should have higher capacities than the targets. The U.S. DOE targets are the main driving force for fabrication of advanced, novel hydrogen storage
materials. Therefore, specific materials with moderate H$_2$-adsorbent interactions (binding energy of ~15 kJ.mol$^{-1}$) and other mentioned suitable properties will be a breakthrough for achieving high hydrogen storage capacity since the objective is to store a large amount of hydrogen at near room temperature and at safe pressures. The next sub-section further discusses the importance of considering the specific adsorbent’s properties which play an important role for their inclusion in a hydrogen storage unit.

![Scheme 1.3](image)

**Scheme 1.3.** Illustrating how hydrogen adsorption on nanoporous materials at relatively low costs can reduce the pollution.

**1.1.7. Important Characteristics of Materials for Practical H$_2$ Storage**

Basically, both the temperature of adsorption and the specific surface area influence the maximum H$_2$ adsorption capacity [19]. However, in order for the nanoporous materials to be considered for their practical use in a hydrogen storage unit, there are other additional key requirements that they must possess. In this case, they must have good thermal stability, thermal conductivity and be in macroscopic form. The good thermal stability allows regeneration and activation at relatively higher temperatures without destroying the adsorbent’s structure. Zeolites and porous carbon are usually stable at high temperatures and vacuum conditions without degradation. On the other hand, concerns about many metal organic frameworks (MOFs) stability towards air, moisture and lack of thermal stability remain a challenge. However, certain MOFs such as UiO-66, UiO-67 and ZIF-8 have been reported to be quite robust [20-21]. MOPs, on the other hand, were also reported to suffer from lack of chemical and thermal stability, except for PPN-4 [22] and PAF-1 [23]. For instance, the thermal decomposition temperature of PAF-1 is 520°C in air and it was also found to be stable after boiling in water for seven days [23]. PPN-4 showed to be stable in air for one month and thermally stable above 400°C in nitrogen without structural degradation.
Thus, in general the stability (thermal, chemical, hydro, mechanical etc.) and thermal conductivity should be taken into consideration when comparing different materials and choosing the best ones because it is very possible for a high performing material to have insufficient strength for practical applications. Nonetheless, real \(\text{H}_2\) tank simulations are essential to understand the processes involved during charging and discharging for a realistic assessment of a materials potential in \(\text{H}_2\) storage while still chasing improvements of materials performance.

The thermal conductivity of the storage bed is very crucial and it has effect on the charge and discharge characteristics during hydrogen storage. The adsorbent bed must be thermally conductive to dissipate the heat generated during the exothermic process of adsorption and thermal effects from compression and rapid \(\text{H}_2\) charging which reduces the storage capacity. During the discharging of the storage tank, decompression and desorption endothermic processes result in a temperature drop and high amount of residual \(\text{H}_2\) gas. Generally, the adsorbent powders exhibit low thermal conductivity which presents heat transfer issues. Hence, there have been studies reporting various strategies of processing and enhancing thermal properties of adsorbents powders for practical \(\text{H}_2\) storage applications. Attempts to enhance an adsorbent’s thermal conductivity include mixing of a MOF with carbon materials or conductive polymers. The other approach is incorporating heat exchangers in \(\text{H}_2\) storage tank design [24]. According to simulation studies [24], an adsorbent bed with thermal conductivities in the range of 0.3–0.5 \(\text{Wm}^{-1}\text{K}^{-1}\) can offer fairly even heat distribution.

In addition to the above considerations, in order to store and release the maximum amount of hydrogen readily at close to ambient conditions as required according to the DOE criteria, the interactions between \(\text{H}_2\) molecules and the adsorbent needs to be improved to achieve the adsorption enthalpy required. The heat of adsorption is an important parameter for hydrogen storage, the higher the heat of adsorption; the stronger the adsorbent-hydrogen interactions, the less cooling and the pressure required for readily adsorbing/desorbing \(\text{H}_2\) molecules at close to ambient conditions as per DOE criteria. However, this high heat of adsorption can also lead to a high \(\text{H}_2\) residual amount at low pressures. The maximum delivery of \(\text{H}_2\) is defined as the difference between \(\text{H}_2\) in a charged and discharged material [25]. When \(\text{H}_2\) is charged/discharged at 30/1.5 bar pressures at 77 K, the optimal adsorption \((\Delta H^{\text{opt}})\) is calculated to be -6.3 kJ/mol which is close to -5.0 kJ/mol usually reported for porous materials at 77 K [26]. However, at 298 K and same pressures, the calculated \(\Delta H^{\text{opt}}\) is -15.1 kJ/mol. The heat of adsorption \((\Delta H^{\text{ad}})\) is optimal with respect to the affinity of \(\text{H}_2\). Thus, it
should be strong enough to store a large amount of \( \text{H}_2 \) at the charging pressure of 30 bar but also weak enough to release \( \text{H}_2 \) at the discharge pressure of 1.5 bar. Nevertheless, unfortunately for porous adsorbents, \( \Delta H_{\text{ad}} \) is much less than \(-15.1 \text{ kJ/mol} \). For example, \( \Delta H_{\text{ad}} \) for activated carbon is \(~-5.6 \text{ kJ/mol} \) [27] thus \( \text{H}_2 \) adsorption on carbon materials is too weak and not strong enough for storing large amount of \( \text{H}_2 \) at ambient temperature. The same applies for MOFs [28] and zeolites [29]. This explains why highly porous adsorbents can adsorb relatively large amount of \( \text{H}_2 \) only at cryogenic temperature but not at ambient temperature. Therefore, to increase \( \text{H}_2 \) physisorption at close to ambient temperature, the \( \Delta H_{\text{ad}} \) must be increased too.

1.2. Problem Statement
The biggest technological challenge hindering the large scale applications and commercialisation of a sustainable hydrogen technology, especially in mobile transportation, is lack of safe, reliable and efficient hydrogen storage systems. Besides the conventional storage methods, that is high pressure gas cylinders and liquid \( \text{H}_2 \), the physisorption of hydrogen on porous carbons and MOFs materials is emerging as a potential solution for hydrogen storage. However, the main research challenge is on improving the properties of the porous materials to enable storage at close to ambient temperatures and relatively lower pressures.

Furthermore, MOFs and carbon materials are always produced in powder or particulate forms which cause handling problems and contamination of the pipeline storage system when releasing hydrogen. Therefore, they need to be shaped into mechanically stable and application-oriented structures to reduce their powdery appearance. Even though, MOFs and carbon powders can be processed by various techniques using different binders, most of the commercially available binders such as non-porous polymers and inorganic materials do not adsorb \( \text{H}_2 \) and often result in pore-blocking effects of the original MOF or carbon materials.

Therefore, there is a need for fabrication of porous polymer-based carbon/MOF composites which are easy to handle (compared to the crystalline MOFs) without compromising their pore characteristics and \( \text{H}_2 \) uptake properties. In this study the solution processable porous polymers were used as binders for shaping powdery carbon and MOF powders to produce monolithic shaped composites. This is the knowledge gap through which this study will be contributing towards the existing literature. It is expected that the proposed strategy will take
advantage of the large surface area, the ability to incorporate binding groups and tuneable pore sizes of individual pristine porous materials. The developed approach could eventually allow a large amount of H₂ gas to be stored in the composite materials at safer lower pressure as a result of the enhanced synergistic properties of the composite.

1.3. **Rationale and Motivation**

The energy sector in South Africa is governed by a key enabling policy for renewable energy documented on a white paper adopted in 1998 [30]. Therefore, the rapid transition from consumption of fossil fuels (which cause climate change) toward clean and sustainable renewable energy has been driven mainly by a wide range of objectives, which include increasing access to affordable energy services, improving energy governance, stimulating economic development, managing energy-related environmental and health impacts and securing supply through diversity [30]. In comparison to other conventional fuels, hydrogen is mainly carbon neutral to carbon negative so it provides clean and sustainable energy, which is in agreement with the Department of Minerals and Energy’s policy. Furthermore, the use of hydrogen as a sustainable energy carrier is not only related to environmental concerns but it also offers security of supply, thus addressing the objectives of the policy.

There are plenty of reports on the usage of individual pristine MOFs and polymers for hydrogen storage. However, to the best of my knowledge, there are few studies on MOF-polymer and carbon-polymer composites that have been specifically dedicated for hydrogen storage applications. Therefore, the current project aims at investigating various innovative strategies for shaping micro-porous powder materials (carbon/MOFs) by fabricating polymer based carbon/MOF composites that are expected to have attractive and enhanced hydrogen uptake capacities. The shaping strategies to be applied in the study are expected to play an important role in transitioning porous MOFs from laboratory to application-specific properties that are aimed for real practical applications. The identified strategy provides a simple and versatile synthesis technique for producing highly porous monoliths of potentially any shape at relatively low costs.

1.4. **Scope and Delimitations**

There is a vast number of materials used for hydrogen storage and each has its own advantages and drawbacks. Only a few examples of materials such as carbons, MOFs and
porous organic polymers and their respective composites will be discussed in this study to emphasize their importance and the improvements made. In this case, the aim is not to cite all the existing literature on the topic, but to review the most relevant papers; highlighting their novelties and contributions that the current study will be adding to the existing body of knowledge. This study is focused on the synthesis, characterisation and the application of the solution-processable polymer of intrinsic microporosity (PIM-1) and 3D printable acrylonitrile butadiene styrene (ABS) polymer based carbon/MOF composites specifically in H₂ gas storage. ABS and polylactic acid (PLA) are the most common 3D printable polymers for desktop 3D printers; other polymers include polyvinyl alcohol (PVA), polycarbonate (PC) and high-density polyethylene (HDPE). However, in this study, the focus will be on ABS plastic because is cheap and easy to use in 3D printers. Moreover, ABS was chosen in order to reinforce MOFs and porous carbon due to its superior mechanical strength and chemical resistance. Due to time constraints and unavailability of specialised equipment for high pressure measurements, the H₂ uptake measurements were only carried out at low pressures of up to 1 bar. The study does not cover the performance testing of materials towards H₂ storage for simulation of real-life conditions due to time-constraints in completion of a home-made hydrogen testing unit.

1.5. The Aim and Objectives of the Research

This study aims at investigating various innovative strategies for shaping carbon/MOFs which are currently obtained in powder form by developing porous polymer-based carbon/MOF composites materials.

The objectives of this study include:

- Synthesis and modifications of organic polymeric binders together with MOF/carbon inclusion as a compositing strategy.
- Employing 3D printing as a strategy for fabricating polymer/MOF/carbon composites materials.
- Interrogating the morphology, structural, textural, thermal and mechanical properties of the porous materials and their composites using various characterisation techniques.
- Evaluating hydrogen sorption capacity of synthesised porous materials at liquid nitrogen temperature (1 bar and 77 K).
1.6. **Hypothesis**

The composites materials will exhibit enhanced synergistic H$_2$ storage properties resulting from large surface area and tuneable pore sizes of individual pristine materials allowing a large amount of H$_2$ gas to be adsorbed at safer lower pressures.

1.7. **Research Framework**

Below, Scheme 1.4 details the research plan and various steps followed towards achieving the set aim and objectives of the study. This starts by reviewing the relevant literature and doing a gap analysis, and this is followed by carrying out the synthesis and post synthetic modifications (PSM) of pristine materials and their corresponding composites. Subsequently, the prepared materials were characterised and optimised before being evaluated for H$_2$ adsorption.

**Scheme 1.4.** Research process flow chart showing methodology sequence, where PSM is post synthetic modification.
1.8. Outline of the Thesis

Chapter 1: A general background and motivation of the study is presented. Overview of the H₂ economy together with the main aspects involved in the H₂ energy chain such as production, delivery, storage, conversion and application are also discussed. This chapter concludes by presenting the research framework and stating the hypothesis, aim and objectives of the study.

Chapter 2: Presents an extensive literature review relevant to the scope of the work. The concepts discussed include the synthesis, modifications and performance of H₂ storage materials and recent developments in shaping of MOF powders into different configurations for better handling properties. Other processing techniques such as extrusion, mechanical pressing, electrospinning, granulation and 3D printing finalise the scope of discussion for this chapter.

Chapter 3: Outlines the principles and analysis conditions of characterisation techniques applied to achieve the objectives of the study.

The objectives outlined in Chapter 1 were investigated and the results obtained are revealed in subsequent Chapters 4-7. Chapter 4-6 presents the published or submitted work of this thesis in a chronological order. Each chapter has an introductory section with a separate brief statement providing an overview to link the results into the main context of this thesis, a statement presenting the author’s share of work and a separate list of references. The unpublished work is presented in Chapter 7, followed by Chapter 8 that contains concluding remarks and future outlook. Briefly:

Chapter 4: Reports the synthesis and optimisation of porous-based metal organic frameworks monolithic hybrid composite (PIM-1/MIL-101(Cr)) and the discussion of the results obtained during the characterisation and evaluation of the materials for hydrogen storage application.

Chapter 5: Details the preparation of PIM-1/UiO-66/ZTC composites as a shaping strategy for ZTC and discussion of the results from the characterisation and performance of composites in H₂ storage.

Chapter 6: Investigates the effect of inclusion of PIM-1/UiO-66 composite onto carbon foam on the thermal properties of MOFs. This chapter further discusses the results obtained from
characterisation and evaluation of the pristine and composite materials for hydrogen storage applications.

**Chapter 7:** Presents the fabrication of 3D printed ABS/UiO-66/ZTC monolithic composites, their characterisation and discussion of the obtained results.

**Chapter 8:** Summarises the main findings of the study with overall conclusions and future work recommendations.

**References:** The references are cited per chapter.
1.9. References:


CHAPTER 2: LITERATURE REVIEW

Summary Statement

This chapter presents an in-depth literature review of hydrogen storage technologies with a special focus on concepts, properties, synthesis protocols, activation methods and performance of hydrogen storage materials. This chapter further highlights the current developments in processing metal–organic frameworks powders into beads, thin films, fibers, foams and gel monoliths. Recent advances of fabricating porous carbon and MOFs based composites through technologies such as granulation and 3D printing for hydrogen storage applications are also presented.

2.1. Hydrogen Adsorption in Porous Materials

Recently, porous materials with ultrahigh surface areas are of great interest for potential applications in energy storage and environmental remediation. Most porous materials have nanometer-sized pores with a large internal surface area and pore volumes. These materials have found wide applications in gas storage, gas purification and separation as well as in catalysis. The porous materials can be categorised by their pore sizes. In this case microporous materials have pore diameters of less than 2 nm in diameter, mesoporous materials have pores between 2 and 50 nm, whereas macroporous materials have pore diameters greater than 50 nm [1]. On the other hand, the term “nanoporous materials” refers to porous materials with pore diameters of less than 100 nm. There are many types of both crystalline and amorphous nanoporous materials such as framework silicates and metal oxides, pillared clays, nanoporous silicon, carbon nanotubes and related porous carbons that have been reported in the literature [2]. Hydrogen physisorption on a variety of these porous materials is one of the hydrogen storage methods being investigated for use in transport applications. As a result, a wide range of carbons, silicas, aluminosilicates, aluminophosphates, covalent organic frameworks (COFs), microporous polymer and porous MOF materials with various porous structures, surface chemistry and structural flexibility have also been studied [3]. In this study only nanoporous MOFs, microporous polymers, porous carbon-based materials and their corresponding composites materials will be discussed.
2.1.1. Carbon Materials

Among other porous materials, porous carbons possess attractive properties for hydrogen storage, with the advantages that they are relatively cheap and easy to produce [4]. Both, natural and synthetic carbon materials can be activated to obtain microporous adsorbents exhibiting very large specific surface areas that range from 1000 to 3000 m$^2$g$^{-1}$ and large micropore volumes [5]. The reversible hydrogen uptake offered by carbons was reported to be almost proportional to the specific surface area and micropore volume at both 77 K and room temperature [6,7]. Usually the best linear correlation is obtained when relating hydrogen adsorption capacity to micropore volume [8,9]. Jordá-Beneyto and colleagues [9] have reported on an activated carbon (AC), obtained by chemical activation of anthracite coal with potassium hydroxide (KOH), which showed a surface area of 3183 m$^2$g$^{-1}$ coupled with a hydrogen uptake of 3.2 wt.% at ambient temperature and 200 bar. Surprisingly, even at reduced pressures (5-70 bar) and cryogenic temperature, only about 3–4 wt.% was attainable [7,8].

The early reports on H$_2$ storage on carbon nanotubes (CNTs) showed very high storage capacities at room temperature, but unfortunately the reproducibility of most of the reported data was very low [10]. For example, the reported H$_2$ uptake capacities varied from negligible amount (0.25 wt.%) to 20 wt.% [7, 11-13]. These large discrepancies in H$_2$ storage capacity in CNTs are due to impurities in the CNTs, difficulties in obtaining accurate measurements and poor understanding of the H$_2$ storage mechanism in CNTs [13]. Now it is confirmed that when all the volumetric and gravimetric experimental errors are eliminated from the measurements, the H$_2$ uptake capacities of purified CNTs are below 0.3 wt.% at 298 K and 100 bar [13]. Furthermore, Zhou and co-workers then showed that ACs and activated carbon fibers can store up to 5 wt.% of hydrogen at low temperature (77 K) and high pressures (30 to 60 bar) [14]. On the other hand, ordered porous carbons prepared using templates have displayed surface area of 3200 m$^2$g$^{-1}$ and hydrogen capacity of 7 wt.% was observed at 77 K and 20 bar [15]. Recent experiments on carbon aerogels, which is a class of amorphous porous carbon structures possessing high surface area, have showed 5 wt.% of hydrogen adsorption at 77 K and pressure 20-30 bar for surface area of 3200 m$^2$g$^{-1}$ [16]. In general, it is stated that the reversible hydrogen uptake of 1.5 wt.% per 1000 m$^2$g$^{-1}$ of specific area is achievable for graphitic nanofibers, single and multi-wall carbon nanotubes (MWCNTs), under ambient conditions [17].
Zeolite Templated Carbons (ZTCs)

Zeolites are a group of crystalline materials with a three-dimensional aluminosilicate structure built of TO$_4$ tetrahedrons sharing all four corners, where T represents Si$^{4+}$ and Al$^{3+}$ ions [18]. They have a general formula that can be written as M$_{x/n}$[(AlO$_2$)$_x$(SiO$_2$)$_y$]mH$_2$O, where M is an exchangeable cation like alkali or alkaline earth metal ion, n is the charge on the cation and m is the number of molecules of water of hydration [10]. Zeolites exhibit high thermal stability and large ion-exchange capacity. Moreover, they can have a very open microporous structure with different framework types depending on the assembly of the tetrahedral building units. To date, only a few zeolites have been considered for hydrogen storage applications because of their dense framework and low pore volumes resulting in less gravimetric hydrogen storage capacity as compared to carbons and MOFs. A gravimetric hydrogen capacity of about 0.1 wt.% has been reported for different zeolites at room temperature [19]. Although zeolites offer flexibility of the possible framework geometries, their use as hydrogen adsorbents materials is restricted by the theoretical upper limit on the hydrogen storage capacity and the need of cryogenic temperature for achieving high storage capacity. Theoretical calculations showed that the possible maximum hydrogen uptake of a zeolite is limited to 2.86 wt.% which could be achieved either at low temperature and high pressure or in the presence of ideal strong adsorption sites (high binding energy, negligible volume) [20].

The research advancement in improving the H$_2$ adsorption properties of zeolites have led to the discovery of zeolite templated carbons (ZTCs) which now forms part of the definition of porous carbon materials. The use of microporous zeolites as hard templates to generate ZTCs with well-defined porosity is also determined by the templating process conditions [21]. The traditional process of obtaining ZTC is via a chemical vapour deposition (CVD) method. ZTCs exhibit tunable structural characteristics, including controlled surface area, pore size, pore volume, particle size, and morphology [22-24]. The highest reported H$_2$ storage capacity for ZTCs so far are in the range of ~0.8 to 3.0 wt.% (at 77 K and 1 bar) [15, 25-27] and ~6.0 to 7.3 wt.% (at 77 K and 20 bar) [15, 25, 27-28] with the highest surface area of 3332 m$^2$g$^{-1}$ [25]. The study by Sevilla and co-workers [21] investigated the effects of chemical activation with KOH on the textural properties of ZTCs, particularly changes in pore size distribution and how they relate to the hydrogen storage capacity of the activated ZTCs. Their findings showed that KOH activation resulted in enhancement in surface area (increased from 1400–1650 m$^2$g$^{-1}$ to between 1850 and 3100 m$^2$g$^{-1}$), the pore volume (rose from 0.8–1.1
cm$^3$g$^{-1}$ to 1.5–1.75 cm$^3$g$^{-1}$) and hydrogen uptake capacity (increased from 2.4–3.5 wt.% to between 4.3 and 6.1 wt.%) at 77 K and 20 bar.

2.1.2. Metal Organic Frameworks (MOFs)

Metal-organic frameworks have been earmarked as one of the most promising materials for storing hydrogen mostly due to their attractive properties such as; ultra-high porosity (up to 90% free volume), high surface areas, synthetic controllability and their relative ease for incorporation of functional groups [29]. MOFs are three–dimensional coordination porous networks consisting of metal ions or metal clusters (nodes), connected by multidentate organic ligands which feature different geometries [30]. Owing to rich functionality and unique physical properties of the organic linkers and metal centres, MOFs have found various applications. Besides applications in drug delivery, gas separation and catalysis, gas adsorption and storage they can also be used as sensors, among other applications [31-34]. Significant progress has recently been achieved in the synthesis of various MOF types as potential hydrogen storage candidates owing to their ability to tune their pore structure and surface chemistry to meet the requirements for specific applications. They have easily tunable pore sizes ranging from micro (1-2 nm) to mesopores (2-50 nm), [35-36] resulting in surface areas as high as 6000 m$^2$g$^{-1}$ for MOF-210 or NU-100 [37]. The study by Farha et al. [35] reported the extraordinary and the highest ever reported surface area of 7140 m$^2$g$^{-1}$ for Nu-110E MOF. Additionally, Farha et al. [35] also proved that the upper theoretical limit for surface areas of MOF is 14600 m$^2$g$^{-1}$. On the other hand, the pore volume of MOFs is in the range of 0.2 to 0.8 cm$^3$g$^{-1}$, but even values well above 3.0 cm$^3$g$^{-1}$ were also reported for some MOFs [38].

Metal organic frameworks are usually synthesised from multidentate ligands and metal salts in solution by hydro or solvothermal treatment. There are also new synthetic approaches such as electrochemistry, microwave-assisted heating, mechanochemistry and sonochemistry which have extended the synthetic diversity of MOFs structures yielding different crystal sizes, morphologies and properties of MOFs [39]. Several MOFs, including MOF-177 [40-41], MOF-5 [42], isoreticular MOF (IRMOF-20) [41,43], Material d’Institute Lavoisier (MIL-101) [44-45] and [Cu$_2$(L$_2$)(H$_2$O)$_2$ (L$_2$ = terphenyl- 3,30,5,59-tetracarboxylate)] [38] were reported to show good reversible hydrogen uptake at 77 K and moderate pressure; ranging from 5.2 wt.% for MOF-5 to 7.5 wt.% for MOF- 177 at ~70 bar [41]. The IRMOF-20 has also showed the highest volumetric hydrogen capacity of 34 gL$^{-1}$ [41]. Furukawa and
co-workers [46] reported one of the highest gravimetric hydrogen capacity for MOF-210 which exhibited a Brunauer–Emmett–Teller (BET) surface area of 6240 m$^2$g$^{-1}$ and the highest gravimetric capacity of 8.6 wt.% at 77 K and 50 bar and that was attributed to its very low crystalline density of 0.25 gcm$^{-3}$ and large pore volume (3.6 cm$^3$g$^{-1}$).

Despite the many studies showing MOFs as best materials for H$_2$ storage at 77 K and moderate pressure (<100 bar) conditions, the H$_2$ storage at room temperature (298 K) is still very far below that seen at 77 K and 1 bar [36]. Moreover, selected MOFs especially the zinc-based ones are moisture sensitive which results in structural decomposition, poor reproducibility and reduced hydrogen storage capacity [47-48]. The other limitation is that MOFs are generally obtained as fine (micro) crystalline powders which are not easy to handle. Furthermore, the poor thermal conductivity of MOFs also adds to the challenges. However, there are other MOF materials which still possess good moisture, pressure, chemical and thermal stabilities like zirconium-terephthalate Universitetet i Oslo (UiO-66(Zr)) MOF [48], chromium (III) terephthalate (MIL-101(Cr)) [49] and copper-based MOF (HKUST-1) [50] which do not need modifications to improve their stability, thus they can be chosen for the system integration, as long as their water adsorption characteristics are tested over a large number of cycles. The zirconium and chromium based MOFs are amongst a group of MOFs with interesting properties towards hydrogen storage and their recent developments are discussed in greater details in the subsequent sub-sections.

2.1.2.1. Chromium (Cr)-based MOFs

As mentioned in the previous section, chromium-based MOF is one of the chemically stable MOFs and mostly studied with a well-known structure. At 1 bar and 77 K, the chromium-based MOF Cr(OH) (BDC) BDC= 1,4-benzenedicarboxylate also known as MIL-53 exhibits just 3.1 wt.% hydrogen uptake from a pore volume of 0.56 cm$^3$g$^{-1}$, BET and Langmuir surface areas of 1026 m$^2$g$^{-1}$ and 1500 m$^2$g$^{-1}$ respectively [51]. The other interesting chromium-based frameworks include Cr$_3$OF(BTC)$_2$; BTC = 1,3,5-benzenetricarboxylate, MIL-100 and CrOF(BDC)$_3$, MIL-101 [31, 44]. The MIL-101; (Cr$_3$F(H$_2$O)$_2$O[(O$_2$C)-C$_6$H$_4$-(CO$_2$)]$_3$) (Figure 2.1a) is a chromium MOF consisting of chromium trimers linked by terephthalate ligands [49]. The pore space is constructed from two cages with diameters of 2.9 and 3.4 nm which are connected with windows with diameters of 1.2 and 1.45 nm [52]. The MIL-101 MOF is thermally stable up to 500 ºC, it exhibits relatively high BET and Langmuir surface areas of 4100 and 5900 m$^2$g$^{-1}$; this is coupled with a pore volume of 1.9
cm$^3$g$^{-1}$ resulting in gravimetric hydrogen storage capacity of 6.1 wt.% at 80 bar and 77 K [44, 49]. The synthesis of Cr-MOF, MIL-101 is usually conducted in an autoclave at 200-220 °C for 8-20 hours by mixing a chromium salt with terephthalic acid, hydrofluoric (HF) acid and water. Thus, efforts have been dedicated on improving their synthesis procedures; like carrying out HF free synthesis to make the process greener even though that can sometimes be time consuming [53]. Ren et al. [54] reported a very promising green and reproducible approach for producing high yield of HF free modulated MIL-101(Cr) using formic acid as modulator and water as solvent at 120 °C for 8 hours. In this study the authors showed that when the molar ratio of formic acid/chromium chloride salt is 100:1 (100 equivalents formic acid) in the synthesis mixture, the Cr-MOF sample exhibits a relatively high H$_2$ storage capacity of 1.92 wt.% at temperature and pressure of 77 K and 1 bar respectively. Additionally, the synthesised MIL-101(Cr) crystals were thermally stable up to 350 °C and stable for several months in ambient air [54]. Chromium is one of the leading product of South Africa's mining industry and South Africa is also the second largest producer of zirconium [55]. South Africa can therefore benefit from this technology reducing the related costs by utilizing locally produced metals based technologies.

Figure 2.1. Molecular structure of the MIL-101(Cr) (Cr atoms are shown in dark blue) (a) and UiO-66(Zr) (Zr atoms are shown in grey) (b). Oxygen and fluorine atoms are shown in red, carbon atoms in black, and hydrogen atoms are omitted for clarity. Republished with permission of Royal Society of Chemistry, from ref. [56]; permission conveyed through Copyright Clearance Center, Inc.
2.1.2.2. **UiO-66(Zr) MOF**

The (UiO-66); (Zr₆O₂(OH)₂(O₂CCH₄CO₂))₃) (Figure 2.1b) is a zirconium containing MOF composed of hexameric Zr₆O₁₂ units linked by BDC linkers leading to a 3D arrangement of micropores in which each centric octahedral cage (free diameter: 11 Å) is connected to eight corner tetrahedral cages (free diameter 8 Å) through triangular windows (6 Å) [48]. The UiO-66 MOF has excellent stabilities which are not typically found in common porous MOFs, for instance it is thermally stable up to 540 ºC [48]. It was revealed that Zr-MOFs have high resistance against water and external mechanical pressure which is attributed to the strong Zr-O bonds present in the secondary building units and high extent of networking of the units [57-58]. Similar to studies by Ren et al. on Cr-MOF [54], other studies [59-60] on UiO-66(Zr) MOF also proved that the use of higher equivalents of modulator result in better UiO-66 crystals shapes with enhanced properties such as larger surface area (1367 m²g⁻¹) and pore volume (0.56 cm³g⁻¹), coupled with improved hydrogen uptake capacity (1.5 wt.%) at 77 K and 1 bar. In addition to improved structural properties and hydro-stability the synthesised UiO-66(Zr) exhibited high thermal stability, decomposing only above 500 ºC.

2.1.2.3. **Zr-fumarate MOF**

In addition to the earlier studies done by Wißmann’s group [61] where they synthesised a novel Zr-based MOF with fumarate (fum) dianions as linkers they also investigated the effect of varying the concentration of formic acid, a monocarboxylic modulator. In 2015, Ren et al. [62] reported the synthesis of highly crystalline Zr-fum MOF which was carried out using water as the solvent and formic acid as modulator at 120 ºC for 24 h. Based on their results the H₂ uptake capacity of 1.38 wt.% at 77 K and 1 bar was obtained. It was also revealed that the synthesised Zr-fum MOF sample has good thermal and moisture stabilities coupled with the potential to be up-scaled [62].

2.1.3. **Overview of Porous Polymers**

In the past, polymers were not considered for physisorption of hydrogen because most of them possess enough conformational flexibility to fill space efficiently (form densely packed amorphous solids) [63]. However, recently, microporous organic polymers (MOPs) have attracted enormous interest for practical use in hydrogen storage owing to their potential advantages over other common adsorbents. Firstly, the most attractive advantage of organic polymers over MOFs is that they have low a density because they consist only of light
elements such as carbon, hydrogen, nitrogen, and oxygen [64]. Secondly, they are less expensive than MOFs and can be easily modified to improve hydrogen binding affinities [65]. Thirdly, MOPs can easily be produced in large scale with good reproducibility. Lastly, porous organic polymers can also be fabricated in monolithic form. However, the main disadvantage is that there are few methods to produce primarily microporous organic polymers with high BET surface areas larger than 1000 m$^2$g$^{-1}$ [66]. Examples of porous polymers of interest in H$_2$ storage are presented in the subsequent sub-sections.

There are various types of microporous organic polymers that offer a possibility of storing hydrogen safely at moderate temperatures and pressures by means of physisorption. These include the hypercrosslinked polymers (HCPs), conjugated microporous polymers (CMPs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs) and porous aromatic frameworks (PAFs) [66]. The majority of the amorphous porous polymers are powders, while crystalline porous polymers are nanocrystals making processing of porous polymers very difficult. Owing to their unique structures, PIMs and CMPs are soluble in common solvents and they can be easily processed via solution methods. This serves as an advantage for expanding their applications. Before the development of CMPs, no porous polymers had combined extended $\pi$-conjugation along the cross-linked framework with porosity [67]. There is enormous diversity of synthetic methods and post synthesis modification that can be used for the synthesis of MOPs. Examples include Friedel-Craft alkylation [68] imidization, amidation [69], Sonagashira-Hagihara cross-coupling [70] and homocoupling [71]. However, most of these methods use volatile organic solvents which are associated with negative environmental impact.

### 2.1.3.1. Conductive Polymers: Polyaniline (PAni)

Polyaniline (PAni) and other conducting polymers such as polythiophene, polypyrrole, polyfuran and poly(3,4-ethylenedioxythiophene) have potential for various applications due to their light weight, conductivity, mechanical flexibility and low cost. Polyaniline is the most attractive and one of the most studied conducting polymers in the past years owing to its low cost, rich chemistry (three distinct oxidation states with different colours) and has an acid/base doping response which can increase its conductivity [72-73]. The acid treatment changes the texture of the polymer; which under certain conditions induces the formation of a microstructure with small nanosized pores (30 nm). This makes it desirable for adsorption of small molecules like hydrogen [74].
Polyaniline and polypyrrole have been proposed as candidates for H₂ storage systems due to their nanostructures and resultant abundance of physisorption and chemisorption sites [75-76]. The PANi and polypyrrole treated with hydrochloric acid (HCl) were mistakenly reported to have hydrogen storage capacities of 6-8 wt.% at room temperature and 90 bar [72]. This surprising H₂ uptake was explained to be attributed to molecular sieving phenomena resulting from doping-undoping and redoping processes creating micropores favourable for H₂ storage [72]. However, these results could not be reproduced and the real capacity of these materials was estimated to be less than 0.5 wt.% at room temperature and 94 bar [77]. The hypercrosslinked PANi was shown to exhibit surface area of 630 m²g⁻¹ [78]. Moreover, the isosteric enthalpy of adsorption of H₂ on PANi (−8 to −9 kJ mol⁻¹) [78] was found to be higher than that of hypercrosslinked polystyrene [66] but still below the optimum value (~ -15 kJ mol⁻¹) required for H₂ delivery at close to ambient temperature and in the pressure range of 1.5-30 bar [79]. However, the least attractive feature of PANi is lack of processability because is insoluble in common solvents.

2.1.3.2. Hyper-Crosslinked Polymers (HCPs)

The hypercrosslinked polymers (HCPs) are amorphous polymers that can be produced either by direct step growth poly-condensation of appropriate monomers or crosslinking (intermolecular and intramolecular) of preformed linear or crosslinked polymer chains in an appropriate solvent. They usually have significant microporosity and as a result of that they tend to exhibit Type I nitrogen gas sorption isotherms. The most common HCPs are produced from polystyrene related polymers also known as Davankov resins mostly prepared through Friedel-Crafts alkylation [80]. For example, the crosslinking of linear polystyrene entails the use of monochlorodimethyl ether as a crosslinking agent to form a methylene bridge intramolecularly inside a single chain or between two chains [67]. The same method is used in the case of styrene-divinylbenzene gels wherein the methylene bridge can be formed in the pre-formed polymer such as poly(chloromethyl styrene) [81]. These materials can be produced in various forms as powders, monoliths, suspension polymerised beads or spherical particles with large diameters (500 nm) obtained by surfactant-free emulsion polymerisation [82]. In some cases, the BET surface areas of up to 2090 m²g⁻¹ can be achieved for hypercrosslinked polystyrene based polymers [81]. Direct polycondensation is another method of producing HCPs. For instance, polycondensation of dichloroxylene yields polyxylene networks with BET surface areas as high as 1431 m²g⁻¹ [66]. The other example is
a HCP network produced from bis(chloromethyl)biphenyl (BCMBP). The microporous hypercrosslinked polymer based on BCMBP has been reported to exhibit both the highest gravimetric hydrogen storage capacity (3.68 wt.% at 77 K and 15 bar) and the highest surface area (1904 m$^2$g$^{-1}$) in comparison to other organic polymers [66, 83]. Therefore, in general HCPs can be formed from polysulfones, polystyrene, polyanilines, poly(vinylpyridine), polyacrylates and small molecules such as dichloroxylene and dianaminobenzene [75]. The HCPs prepared by crosslinking 4,4’-dilithiobiphenyl and other multi-lithiated aromatic monomers with dimethylcarbonate to form polymeric carbinol networks were found to exhibit surface areas in the range of 400–1000 m$^2$g$^{-1}$, while the microporous hydrophobic polysilane networks obtained via an organolithiation approach for gas adsorption applications, also showed BET surface areas of 700–1100 m$^2$g$^{-1}$ [84]. The H$_2$ adsorption capacities of HCPs are typically lower than those of MOFs and porous carbons. For instance, a H$_2$ uptake of 3.68 wt.% at 77 K and 15 bar was reported for HCP [66]. Nonetheless, hypercrosslinked polymers are cheap yet stable, and readily scalable [80]. However, unlike the solvent processable linear PIMs, HCPs are insoluble networks [85], thus they cannot be easily processed and they swell in solvents and gases [86-87].

2.1.3.3. Conjugated Microporous Polymers (CMPs)

The conjugated microporous polymers (CMPs) are amorphous porous polymers consisting of extended conjugated networks. The synthesis methods and properties of CMPs and HCPs are very similar and thus CMPs can be considered as a sub-class of HCPs [80]. A range of CMPs exhibiting BET surface areas $\leq$ 1000 m$^2$g$^{-1}$ and H$_2$ adsorption capacity of about 1.0 wt.% at 77 K and 1 bar can be prepared from poly(aryleneethylene) (PAE) networks via Sonogashira Hagihara palladium (Pd)-catalysed cross-coupling chemistry [70, 88-89]. Like isoreticular MOFs, CMPs were reported to show a tuneable pore size and pore volume when varying strut length in the PAE network [70, 90]. It was found that the longer the linker between branching sites of the CMPs, the smaller the total surface area, thus CMPs with different specific surface areas and pore sizes were produced from phenyl monomers of varied length linkers [91]. For example, Jiang and co-workers, prepared HCMP-1 (BET surface area = 842 m$^2$g$^{-1}$) and HCMP-2 (BET surface area = 827 m$^2$g$^{-1}$) from 1,3,5-triethynylbenzene and 1,4-diethynylbenzene respectively [92]. The physical properties of CMPs can be further tuned by copolymerization of short and long struts of amorphous copolymers [90]. Moreover, the microporous conjugated poly(phenylene butadiynylene)s (PPBs) with complex structures.
produced from a homocoupling approach were reported to exhibit high surface areas of up to 842 m$^2$g$^{-1}$ and broader pore size distributions which were not observed in PAEs samples [70]. Typically, pure CMPs exhibit low H$_2$ adsorption at 77 K but the lithium (Li) doped CMP with a relatively low surface area of 795 m$^2$g$^{-1}$ has exhibited an enormously high H$_2$ uptake of 6.1 wt.% at 77 K and 1 bar [93]. This outcome was ascribed to an enhanced adsorption enthalpy resulting from the charge-induced dipole interaction between H$_2$ and Li atoms. Unfortunately, when other main group elements like nitrogen [94], chlorine and bromine [95] were investigated, the H$_2$ uptakes remained relatively low in contrast to findings obtained for Li$^+$ ion systems.

2.1.3.4. Covalent Organic Frameworks (COFs)

Unlike other MOPs, the covalent organic frameworks (COFs) are crystalline and are synthesised in the same manner as MOFs thus resulting in fixed porosity. However, the framework of COFs is made up of light elements and no heavy metals like in MOFs [96-97]. The first COF, COF-1 was synthesised by condensing boronic acid into a boroxine anhydride node followed by crosslinking with diboronic acid in sealed pyrex tubes [98-99] and it exhibited a BET surface area of 711 m$^2$g$^{-1}$ and a micropore volume of 0.32 cm$^3$g$^{-1}$. On the other hand, COF-102 has been reported to exhibit high H$_2$ adsorption capacity of 7.24 wt.% at 77 K and 35 bar [93]. Another member of the COF family, COF-103 was found to exhibit a very high BET surface area (4210 m$^2$g$^{-1}$), comparable to that of MOFs [100]. Additionally, COFs materials display very high thermal stabilities in the range of 500 – 600 °C.

2.1.3.5. Porous Aromatic Frameworks (PAFs)

Porous aromatic frameworks (PAFs) are synthetic polymers with diamond like structures constructed by organic building blocks through irreversible covalent cross-coupling reactions [101]. PAFs have shown very high surface areas, robust skeletons, excellent stabilities and H$_2$ uptakes exceeding those of PIMs, CMPs, HCPs and MOFs. To name a few, PAF-1 was reported to have high thermal stability (up to 520 °C) and an extremely high BET surface area (5600 m$^2$g$^{-1}$) coupled with high H$_2$ uptake (10.7 wt.% at 77 K and 48 bar) [93, 101]. Both PAF-3 and PAF-4 were shown to exhibit chemical and thermal stability similar to PAF-1. PAF-3 also exhibited a high surface area of 2932 m$^2$g$^{-1}$ and 5.50 wt.% H$_2$ uptake capacity at 77 K and 60 bar. These polymers are the smallest subcategory of MOPs. Nonetheless, introducing PAFs have led to the discovery of porous polymer networks (PPNs) with PAF-1
like structure. Surface areas higher than those of PAFs were observed for PPN-4 (6461 m²g⁻¹) coupled with a maximum excess H₂ uptake of 8.34 wt.% at 77 K and 55 bar [80, 93]. Additionally, PPN-4 and PPN-5 were also reported to show good stability towards heat and moisture. However, just like all PAFs, the PPNs are insoluble in common solvents thus limiting their processability [102]. Similar to CMPs, Li ion doping of PAFs enhanced their H₂ uptake capacity. For instance, 5% Li doped PAF-1 (Li@PAF-1) showed a significantly higher H₂ adsorption capacity (increase of 22%) than pure PAF-1 as well as enhancement in the ultra micropore content and enthalpy of adsorption [103]. In one recent study, PIM-1/PAF-1 membrane was reported for hydrogen storage application. The composite was prepared by mixing the PIM-1 and PAF-1 together in chloroform to achieve a desired solution mixture for casting a membrane [104]. The obtained lightweight hybrid material exhibited enhanced surface areas and pore volumes almost proportional to the amount of incorporated PAF-1. It showed promise to be used as a hydrogen storage material for applications where pressures up to 75 bar are required.

2.1.3.6. Polymers of Intrinsic Microporosity (PIMs)
Budd et al. [105] showed that when at least one of the monomers contains a site of contortion (e.g., a spiro-centre) or a rigid non-planar unit connected to a rigid backbone (e.g., a ladder polymer) then close packing is precluded, and polymers of intrinsic microporosity (PIMs) are obtained. PIMs are of interest for several applications including in separation membranes, sensors, catalysis and gas storage [106]. These polymers consist of interconnected cavities which provide large internal surface area; values in the range of 500 to 1000 m²g⁻¹ were reported [65]. PIMs exhibit good chemical and thermal stability, synthetic reproducibility and the potential to easily modify the micropore structure by choice of monomer precursors [65].

PIMs are divided into the soluble linear PIM chains that are solution processable and the insoluble PIM networks. PIMs are produced using a highly efficient dibenzodioxane forming reaction from bis-catechol type monomers. The insoluble PIM networks have shown surface areas and hydrogen uptake capacities that are higher than their linear counterparts [64]. This is due to their high micropore volume. PIM networks are made from the three-connected branching monomers named 9,10-diethyl-2,3,6,7,12,13-hexahydroxytriptycene (Trip) [64], cyclotricatechylene (CTC) [107] and hexaaazatrinaphthylene (HATN) [108]. The recent experimental work done on PIMs have shown that a hydrogen uptake of 1.4 wt.% and 1.7 wt.% was attainable at 1 bar and 10 bar respectively for the (CTC–PIM) [109]. It was also
reported that at 77 K a network-PIM (incorporating a Trip subunit) can store up to 1.6 wt.% of hydrogen at 1 bar and 2.71 wt.% at 10 bar [64, 110]. With further modifications hydrogen storage capacity at cryogenic temperature can be improved.

PIM-1 (Figure 2.2) was reported as the first from the PIM’s family that exhibited BET surface areas of up to 850 m²g⁻¹ (while other soluble PIMs were found to have surface areas of between 440 and 600 m²g⁻¹) with a total pore volume of 0.78 cm³g⁻¹ and hydrogen uptake of 1.04 and 1.40 wt.% at 1 bar and 15 bar respectively at 77 K [109]. So far, among a range of microporous organic polymers, PIM-1 appears to be the best candidate for hydrogen adsorption [111]. PIM-1, is soluble in common solvents such as chloroform and tetrahydrofuran, dichloromethane, dichorobenzene, 1,2,4-trichlorobenzene, and acetophenone and it forms robust, flexible films upon solvent casting [112-113]. For both network-PIM and hyper-cross-linked polymer a maximum hydrogen adsorption of 3 wt.% is obtained at 77 K and 10-15 bar [64]. However, at near ambient temperature hydrogen adsorption can be much lower than at 77 K owing to the weak interaction between hydrogen and the polymer. Therefore, to enhance the hydrogen adsorption on PIMs, their textural properties need further enhancement. By forming a composite with other porous materials, a higher hydrogen uptake at 77 K can be achieved and thus in general PIMs can be considered as good candidates for reversible hydrogen storage under cryogenic conditions.

![Figure 2.2](image)

**Figure 2.2.** Molecular model (left) and chemical structure (right) of PIM-1. Republished with permission of Royal Society of Chemistry, from ref. [106], [110]; permission conveyed through Copyright Clearance Center, Inc.

Various polymeric hydrogen storage media that have been investigated are summarised in Table 2.1 below.
Table 2.1. Surface areas and hydrogen uptake of porous polymers measured at different temperature and pressure.

<table>
<thead>
<tr>
<th>Number</th>
<th>Material</th>
<th>BET Surface area (m² g⁻¹)</th>
<th>H₂ uptake (wt.%)</th>
<th>Temperature (K)/Pressure (bar)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PIM-1 film</td>
<td>804</td>
<td>1.49 &amp; 1.66</td>
<td>77/10 &amp; 77/32</td>
<td>[114]</td>
</tr>
<tr>
<td>2</td>
<td>PIM-1</td>
<td>760</td>
<td>1.04 &amp; 1.44</td>
<td>77/1 &amp; 77/10</td>
<td>[65]</td>
</tr>
<tr>
<td>3</td>
<td>HATN-PIM</td>
<td>820</td>
<td>1.37 &amp; 1.56</td>
<td>77/1 &amp; 77/10</td>
<td>[65]</td>
</tr>
<tr>
<td>4</td>
<td>CTC-PIM</td>
<td>830</td>
<td>1.43 &amp; 1.70</td>
<td>77/1 &amp; 77/10</td>
<td>[65]</td>
</tr>
<tr>
<td>5</td>
<td>Porph-PIM</td>
<td>960</td>
<td>1.20 &amp; 1.95</td>
<td>77/1 &amp; 77/10</td>
<td>[110]</td>
</tr>
<tr>
<td>6</td>
<td>Trip-PIM</td>
<td>1065-1760</td>
<td>1.79 &amp; 2.71 &amp; 3.40</td>
<td>77/1 &amp; 77/10 &amp; 77/18</td>
<td>[64, 115]</td>
</tr>
<tr>
<td>7</td>
<td>PIM-7</td>
<td>680</td>
<td>1.00 &amp; 1.35</td>
<td>77/1 &amp; 77/10</td>
<td>[110]</td>
</tr>
<tr>
<td>8</td>
<td>Polystyrene nanospheres</td>
<td>1223</td>
<td>2.13</td>
<td>163/15</td>
<td>[116]</td>
</tr>
<tr>
<td>9</td>
<td>PAni</td>
<td></td>
<td>0.15</td>
<td>77/70</td>
<td>[117]</td>
</tr>
<tr>
<td>10</td>
<td>Nanoporous –Pani a</td>
<td>632</td>
<td>2.20</td>
<td>77/30</td>
<td>[78]</td>
</tr>
<tr>
<td>11</td>
<td>Nanoporous –Pani b</td>
<td>480</td>
<td>1.50</td>
<td>77/30</td>
<td>[78]</td>
</tr>
<tr>
<td>12</td>
<td>Nanoporous PAni (undoped)</td>
<td>439</td>
<td>0.80</td>
<td>77/1.2</td>
<td>[78]</td>
</tr>
<tr>
<td>13</td>
<td>Nanoporous PAni-HCl (doped)</td>
<td>439</td>
<td>0.30</td>
<td>77/1.2</td>
<td>[78]</td>
</tr>
<tr>
<td>14</td>
<td>HCP-polystyrene</td>
<td>1466</td>
<td>1.28 &amp; 2.75 &amp; 3.04</td>
<td>77/1 &amp; 77/10 &amp; 77/15</td>
<td>[118]</td>
</tr>
<tr>
<td>15</td>
<td>HCP-Polypyrroles</td>
<td>~20-700</td>
<td>0.60 -1.60</td>
<td>77/4</td>
<td>[75]</td>
</tr>
<tr>
<td>16</td>
<td>HCP-DCX</td>
<td>600-1900</td>
<td>0.90 -17.70</td>
<td>77/1</td>
<td>[66]</td>
</tr>
<tr>
<td>17</td>
<td>HCP-BCMA</td>
<td>921</td>
<td>1.41</td>
<td>77/1.13</td>
<td>[66]</td>
</tr>
<tr>
<td>18</td>
<td>HCP-BCMBP</td>
<td>1700-1904</td>
<td>1.63 &amp; 3.68 &amp; 4.00</td>
<td>77/1 &amp; 77/15 &amp; 77/100</td>
<td>[66, 119]</td>
</tr>
<tr>
<td>19</td>
<td>HCP-DCX</td>
<td>600-1900</td>
<td>0.90 -17.70</td>
<td>77/1</td>
<td>[66]</td>
</tr>
<tr>
<td>20</td>
<td>HCP-VBC</td>
<td>1466-1500</td>
<td>1.59 &amp; 3.04</td>
<td>77/1.13 &amp; 77/15</td>
<td>[120]</td>
</tr>
<tr>
<td>21</td>
<td>HCP-VBC-DVB</td>
<td>1300-1900</td>
<td>1.50 &amp; 3.00</td>
<td>77/1 &amp; 77/15</td>
<td>[121-122]</td>
</tr>
<tr>
<td>22</td>
<td>CMP-0</td>
<td>1018</td>
<td>1.40</td>
<td>77/1.13</td>
<td>[123]</td>
</tr>
<tr>
<td>23</td>
<td>CMP-1</td>
<td>834</td>
<td>1.20</td>
<td>77/1</td>
<td>[70, 90]</td>
</tr>
<tr>
<td>24</td>
<td>CMP-2</td>
<td>634</td>
<td>0.92</td>
<td>77/1.13</td>
<td>[90]</td>
</tr>
<tr>
<td>25</td>
<td>CMP (Li-doped)</td>
<td>795</td>
<td>6.10</td>
<td>77/1</td>
<td>[120]</td>
</tr>
<tr>
<td>26</td>
<td>HCMPC-1</td>
<td>842</td>
<td>0.95</td>
<td>77/1.13</td>
<td>[92]</td>
</tr>
<tr>
<td>27</td>
<td>HCMPC-2</td>
<td>827</td>
<td>1.16</td>
<td>77/1.13</td>
<td>[92]</td>
</tr>
<tr>
<td>28</td>
<td>COF-1</td>
<td>711</td>
<td>1.28</td>
<td>77/1</td>
<td>[98]</td>
</tr>
<tr>
<td>29</td>
<td>COF-5</td>
<td>1670</td>
<td>3.58</td>
<td>77/40</td>
<td>[99]</td>
</tr>
</tbody>
</table>
30 | COF-8 | 1350 | 3.50 | 77/40 | [99]
31 | COF-10 | 1760 | 3.92 | 77/40 | [99]
32 | COF-102 | 3620 | 7.24 | 77/35 | [99]
33 | COF-103 | 3530 | 7.05 | 77/40 | [99]
34 | PAF-1 | 5600 | 7.00 | 77/48 | [101]
35 | PAF-3 | 2932 | 5.50 | 77/60 | [124]
36 | PAF-4 | 2246 | 4.80 | 77/60 | [124]
37 | PPN-1 | 1249 | 3.30 | 77/45 | [125]
38 | PPN-2 | 1764 | 3.76 | 77/40 | [125]
39 | PPN-3 | 4221 | 4.28 | 77/42 | [102, 125]
40 | PPN-4 | 6461 | 8.34 | 77/55 | [80, 125]

PIM = polymer of intrinsic microporosity, HPC = hypercrosslinked, HATN = hexaazatrinaphthylene, CTC = cyclotricatechylene, Porph = porphyrin, Trip = triptycene, Monomers used for the synthesis of the hypercrosslinked polymer networks: DCX = dichloroxylene (ortho-, meta-, and para-isomers), BCMBP = 4,4'-bis(chloromethyl)-1,1'-biphenyl, BCMA = 9,10-bis(chloromethyl)anthracene, VBC = vinylbenzyl chloride, DVB = divinylbenzene, PAni = polyaniline, Nanoporous PAni \(^a\) = hypercross-linked with a diiodomethane cross-linker, Nanoporous PAni \(^b\) = hypercross-linked with a paraformaldehyde cross-linker, CMP = conjugated microporous polymer, POP = porous organic polymer, PAF = porous aromatic framework, PPN = porous polymer network.

2.2. **Activation of Porous Materials**

The most attractive properties of MOFs include an extraordinary high surface area and porosity. In most cases, any form of activation is always needed to remove chemicals and solvents used during synthesis from the pores without destroying the original morphology and porosity. This process is carried out as a last step after synthesis of porous materials. This section highlights some of the most commonly used activation strategies used for post synthetic modification of porous materials (**Figure 2.3**).
2.2.1. **Conventional Heating and Vacuum**

In a conventional activation method, liquid occluded in pores is removed by applying heat and vacuum treatment at atmospheric or low pressure. This drying method is commonly utilized to activate carbons, zeolites and certain MOFs. The thermal and structural stability as well as the conditions of fully outgassing porous materials vary significantly, and this is a very important aspect in adsorption studies. For instance, porous carbon must be heated at ~150 °C under high vacuum to remove adsorbed substances. Since the carbons have better stability than MOFs, activation of MOFs is more complex. Consequently, MOFs adsorption results are difficult to reproduce because of purity, stability and complicated activation procedures issues. However, certain MOFs like MIL-101(Cr) and UiO-66 have exceptional chemical and thermal stability and are therefore stable to conventional activation conditions [56]. In most cases, the capillary forces and surface tension effects which occur during liquid-
to-gas phase transition can lead to a complete or partial collapse of a porous framework structure; this effect is known as syneresis. The effects are very significant when the pores contain high boiling point solvents like N,N-diethylformamide, N,N-dimethylformamide (DMF) and dimethyl sulfoxide used to synthesise MOFs. Consequently, conventional heating yields materials with surface areas and porosity significantly lower than expected from simulations. Complete loss of crystallinity ascribed to inadequate activation, presents difficulties with assessing the full porosity in some materials [126-127].

2.2.2. Solvent Exchange and Chemical Treatment

To achieve effective activation, the high boiling point solvent can be substituted with lower boiling point solvents such as ethanol or chloroform after synthesis but before mild conventional activation [56]. This process is known as solvent-exchange. The lower boiling point solvents exhibit intermolecular interactions weaker than those of high boiling point solvents and this reduce capillary forces and surface tension. This method was shown to effectively activate MOFs resulting in enhanced surface areas. For an example, IRMOF-3 was activated after solvent exchange (DMF ↔ chloroform) and the surface area was increased from 10 m$^2$g$^{-1}$ to 1800 m$^2$g$^{-1}$ [128]. However, as much as this method has proven to successfully access full porosity and large internal surface area, the values obtained are still lower than the predictions (from single-crystal structures). Some MOFs are known for their exceptional chemical stability, therefore they can be treated in concentrated acidic solution and undergo subsequent conventional activation. For instance, activation of tetracarboxylate-porphyrin-containing (MOF-545) and Zr$_6$ containing (NU-1000) with hydrochloric acid chemical treatment resulted in a significant enhancement in pore volume [129-130].

2.2.3. Freeze Drying

Freeze-drying is another recently used method for activation of MOFs. The samples to be activated by this method must be exchanged and stored in benzene or cyclohexane [131]. During freeze-drying, the sample undergoes repeated freezing and defrosting cycles and only during the last freeze cycle is the sample exposed to vacuum at temperature and pressure below the triple point of the solvent [56]. Then, in the final step, the solvent (benzene or cyclohexane) is frozen and subsequently sublimed from the pores at low pressure thus avoiding the liquid-to-gas phase transition and its syneresis effects. In studies [132] where
this method was used, significant increases in BET surface areas were observed compared to the conventional solvent exchange method.

2.2.4. Supercritical Carbon Dioxide (scCO$_2$) Exchange

MOFs can be activated by solvent exchange with a low boiling point (volatile) solvent prior to heating in ultrahigh vacuum or by supercritical carbon dioxide extraction. It was found that supercritical carbon dioxide activation gave the best results, such as preserving the mesopore framework and enhancing the surface area, better than other activation methods. Just like in freeze-drying, prior activation the DMF trapped inside the crystals’ pores is exchanged with solvents (like acetone, chloroform or absolute ethanol) followed by washing in hexane [133]. During scCO$_2$ activation, the sample goes through repeated cycles of soaking in liquid CO$_2$ and gradual venting. Then the liquid CO$_2$ is heated above its critical point (31.0 ºC and 73.9 bar) conditions at 40 ºC and 80-200 bar and kept under supercritical treatment conditions for several hours. Subsequently, after the treatment, the material is removed while maintaining the high pressure [128, 134-135]. Many researchers around the globe have utilised the scCO$_2$ activation method on various MOFs with success [136-139]. For an example, effective activation of IRMOF-3 which showed about 285-fold increase in BET surface area (2850 m$^2$g$^{-1}$) over conventional activation was observed by Nelson and co-workers [128]. Liu et al. showed that flowing scCO$_2$ can also be used to activate microporous materials directly from DMF, thus eliminating the solvent exchange step. Directly after the scCO$_2$ treatment, most microporous materials exhibited exceptional high surface areas. For instance, the IRMOF-3 displayed a BET surface area of 3090 m$^2$g$^{-1}$ significantly better than 2850 m$^2$g$^{-1}$ obtained by scCO2 which involved a solvent exchanged step [138]. The effectiveness is not the only driving factor behind the use of scCO$_2$ but is also cost competitive, scalable and non-toxic in nature [140]. In some cases, the removal of adsorbed solvents may result in formation of open metal centres, which improves adsorption. Therefore, these characteristics (thermal, chemical, structural stability, framework flexibility and activation procedures) must also be considered when comparing adsorption properties of various porous materials. To show how drying methods affect the textural properties Table 2.2 presents the advantages and disadvantages of drying methods and the corresponding textural characteristics of some gels.
Table 2.2. Summarises physical properties, advantages and disadvantages of various drying methods.

<table>
<thead>
<tr>
<th>Drying method (material)</th>
<th>Porosity</th>
<th>Surface Area (m²·g⁻¹)</th>
<th>Density (gm⁻³)</th>
<th>Thermal Conductivity</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subcritical (Xerogel)</td>
<td>Low</td>
<td>Low (up to 200)</td>
<td>High (~1.9)</td>
<td>High</td>
<td>Simple &amp; cheap</td>
<td>High shrinkage</td>
<td>[141]</td>
</tr>
<tr>
<td>Freeze (Cryogel)</td>
<td>High</td>
<td>Large (&gt;800)</td>
<td>Low (0.08-0.18)</td>
<td>Low</td>
<td>Simple, low shrinkage</td>
<td>Requires solvent exchange</td>
<td>[142]</td>
</tr>
<tr>
<td>Supercritical (Aerogel)</td>
<td>High pore volume</td>
<td>Large (up to 1000)</td>
<td>Low (0.03-0.5)</td>
<td>Low</td>
<td>No shrinkage</td>
<td>Time consuming &amp; requires solvent exchange with CO₂</td>
<td>[143]</td>
</tr>
</tbody>
</table>

2.3. Shaping Strategies for MOFs (MOF/Carbon-Polymer Fabrication Strategies)

As previously mentioned, most MOFs are obtained as fine powders and lack processability, consequently, various processing routes which include mechanical pressing, coating, foaming, templating, slip/tape casting, granulation, extrusion and pulsed current processing are being investigated for processing MOF powders into shaped structures [144-145]. However, during the shape-forming step, compression results in a decrease in the outer surface area caused by a physical reduction in MOF’s surface area and loss of the porous structure within MOFs. This can be due to a very high pore volume in a highly fragile MOF framework, whereas in zeolite structures the walls surrounding the pores are thicker and mechanically stable. Furthermore, most MOFs still do not exhibit sufficient strength after extrusion. Hence, it is essential to apply binders and other substances that stabilize the materials to be agglomerated without decreasing their performance. These additives or binding agents help to efficiently compact MOF powders to form MOF-organic matrix composites with various shaped macroscopic bodies such as monoliths, pellets, membranes [146-150], beads [151], flexible sheets or fibers [152-154] ensuring maximal packing densities [145]. Recent works have also demonstrated the possibility of preparing MOFs in several substrates such as ceramic foams [155], mesoporous silica [156-157] and alumina [158]. The shaped bodies in a form of monoliths are advantageous compared to pellets or...
beads due to high mechanical stability coupled with reduced abrasion with insignificant decrease in pressure drop [135].

In one of the studies, a continuous shaping strategy for MOFs was investigated for shaping MOF powders into processable fluid, foams and other shaped bodies which are transformable among these phases [159]. During the shaping process it is crucial to ensure that the binder used occupies minimal volume and does not increase the density, without reducing the microporosity of MOF. Several studies have been published on the topic of MOF/carbon composites. However, there are very few studies reporting carbon/polymer or MOF/polymer composites specifically for hydrogen storage purposes. Therefore, this study presents recent advances made in the subject of carbon and MOFs-based polymeric composites that are aimed at hydrogen storage. The subsequent sections will provide a detailed discussion reviewing various strategies explored in the past years and recent advances on shaping of MOFs, the properties and applications of composites in hydrogen storage.

2.3.1. Monolithic MOF Gels

Fabrication of monolithic bodies of MOF gels without the use of any binders is one of the novel methods towards overcoming the MOF pore-blocking effects arising from non-porous binders. This is only possible through the use of sol-gel chemistry which was previously used for the synthesis of inorganic compounds like alumina, silica and titanium oxide. The common and frequently studied polymeric gel is the one based on resorcinol and formaldehyde monomers and was invented by Pekala and co-workers [160] in 1989. These materials are synthesised by a sol-gel method of resorcinol (1,3-dihydroxylbenzene) and formaldehyde in an aqueous medium [161]. Since this publication, numerous studies have been reported describing not only the various synthetic methods but also how processing conditions affect the final structure and properties of the resulting gels. The sol-gel step can either be base-catalysed (eg. activation of resorcinol) or acid-catalysed (eg. activation of formaldehyde). The catalyst helps in influencing the time of gelation and the porous nature of the material. Furthermore, the molar ratios of resorcinol to formaldehyde, resorcinol to water, resorcinol to catalyst, curing time, temperature and washing or drying procedures determine the latter properties of the hydrogels such as density, surface area, thermal conductivity, particle- and pore size in a sensitive way [134, 143, 162]. The versatility of the sol-gel approach is the most interesting feature, as the gels can have the same chemical composition but exhibit various porous textures (see Table 2.2). For instance, important properties of
resorcinol-formaldehyde gels such as high porosities (>80%), surface area (400 - 1200 m$^2$g$^{-1}$) and pore volumes depend on the synthesis and processing conditions [143].

The sol-gel approach is a six stage process [163] which includes hydrolysis, condensation, gelation, curing, solvent exchange and drying steps [143, 164]. The gel resulting from a sol-gel is a continuous network containing pores filled with solvent. Thus, various drying methods are employed to replace the continuous liquid phase occluded in the pores with gas and this is how different forms of gels are obtained. Depending on the drying method applied to remove the solvent, gels are classified into three main categories: aerogels, cryogels and xerogels when supercritical drying, freeze-drying and evaporative drying are employed, respectively [162] as illustrated in Figure 2.4 below.

![Figure 2.4](image)

**Figure 2.4.** Schematic representation of the steps involved in the synthesis of organic gels. Reprinted from ref. [165], Copyright 2017, with permission from Elsevier.

Aerogels and cryogels are usually preferred over xerogels owing to their excellent textural properties illustrated in Table 2.2 [134, 135]. However, the original process developed by Pekala [160] can be very time-consuming and difficult to apply at large scale. The synthesis of organic gels includes aging of the aqueous gels for seven days, acid washing to complete the polymerization reaction, solvent exchange and finally drying, thus the whole process can take up to two weeks. Other types of stimuli such as light and microwaves can be used as heating source for fast, simple and cost-effective production of monolithic gels.
Recently, the conventional sol-gel approach was also shown to be employable to organometallic materials like MOFs wherein gelation is favoured over crystallization. Monolithic MOF gels are amorphous and unlike the crystalline MOFs, they were reported to exhibit high adsorption rates coupled with high storage capacities in gas separation and storage applications; as a result of their hierarchical porosity advantage over the mono-modal pore size distribution of crystalline MOFs [166]. Yet, there is less information on the synthesis conditions as well as the mechanism involved in the formation of MOF gels. It is said that gel formation is triggered by conditions very specific to each metal-ligand pair [167]. Apart from being a shaping strategy, it is noteworthy that fabrication of MOF gels eliminates the use of harsh chemicals (toxic and corrosive acids) [168]. In a recent study, Bueken and colleagues [169] have presented xero- and aerogel monoliths of Zr⁴⁺ based nanoparticles MOFs (UiO-66-X (where X= H, NO₂, NH₂, (OH)₂), UiO-67, MOF-801, MOF-808) for the very first time. The UiO-66 gels were transformed to hierarchically (micro-meso) porous xero- and aerogels monoliths with pore volumes of 2.09 cm³/g and 1.66 cm³/g respectively which are exceptionally higher than those of the bulk UiO-66 powder. Thus, adopting the sol-gel strategy has provided a step towards shaping Zr MOFs without a use of a binder for adsorption or catalysis applications. Additionally, due to their optically transparent characteristic, the xerogels may be used in the fabrication of transparent films and coatings. Generally, in most cases a Soxhlet extraction set-up is often useful to preserve the original gel morphology during washing of gel monoliths [170].

2.3.2. **Formation of MOF Composites**

Even though significant progress has been made in the discovery of new MOF types, there is an emerging trend for the synthesis of MOF composite materials based on the already existing MOFs materials. The main driving force for this endeavour is to try to improve on the inherent MOF properties either by enhancement of their thermal conductivity, creation of new functionalities such as formation of new pores or to shape the loose MOF powders into application-specific shaped bodies that can easily be used in the real-world applications. Similar shaping approaches applied on MOFs can also be applied on carbon powder materials to enhance their mechanical strength without adversely altering their intrinsic H₂ adsorption properties. Fabrication of MOF-based composites materials like MOF/carbon and MOF/polymer composites offers improved synergistic properties [171-173]. MOF-based
composites are generally formed by physical or chemical mixing of MOFs with inorganic and/or organic additives as binders to shape the MOFs into monoliths [157, 174-175].

The obvious advantage of mixing MOFs with an organic polymer or inorganic material is that the resulting hybrid composite material exhibits the combined properties emanating from their individual counterparts. This also allows creativity to invent novel multifunctional materials with new properties which can consequently result in enhanced performance for various types of applications. In most cases organic polymers help with the reinforcement of the filler material due to their good mechanical properties such as plasticity, elasticity and rubbery nature (depending on the glass transition temperature) [71]. Last but not least, processable polymers also play a vital role in shaping powder filler materials like MOFs (low processability) because when dissolved in suitable solvents they can be molded and casted to result in composites with easy-to-handle properties. Polymers are light materials but they also exhibit attractive properties. The properties of hybrid materials are interesting and attractive for many applications, and processability is one of the properties which stands out. In previous years, MOF-composites have been fabricated as thin-films through layer-by-layer deposition of MOFs onto a series of templates [176], graphite [177], porous oxide supports [178-179] or through a seeding and growth method [180]. Most of these materials are used as gas separation membranes [148, 178-179] and have to date not been sufficiently exploited for gas storage applications.

2.3.2.1. MOF-Carbon Composites

MOF composites have been fabricated successfully with ACs, MWCNTs, zeolite templated carbons and with other MOFs specifically for hydrogen adsorption applications. Since carbon materials are known to exhibit many interesting features such as light weight, high mechanical strength, and high thermal and electrical conductivity, they are considered desirable for practical hydrogen storage [181]. Thus, in an attempt to improve moisture stability of MOF-5 a composite consisting of MWCNTs and MOF-5 was fabricated [172]. The composite material had an interpenetrating structure and hierarchical mesopores which helped in improving the storage capacity from 1.2 wt.% up to 2.02 wt.% at 77 K and 1 bar [172]. In a similar study, Yang et al. also showed a 50% enhancement in H₂ storage capability of MWCNTs/MOF-5 composite compared to pristine the MOF [182]. In a recent review by Prachi et al. [10] they suggested that cryogenic temperatures can be avoided if the hydrogen is more strongly coordinated with the substrate, with the ideal enthalpy of
interaction being around 30 kJ/mol for storage at room temperature. Since such high values cannot be obtained by physisorption, therefore other forms of modifications are necessary such as either bonding the hydrogen molecule to an active metal site or a spill-over effect (defined as dissociative chemisorption of H$_2$ on metal catalyst and migration of hydrogen atoms onto adjacent carbon adsorbent) [10].

In another study, a platinum (Pt)-loaded MWCNT/MOF-5 composite was reported to have improved H$_2$ storage from 1.20 wt.% in pristine MOF to 1.89 wt.% in the composite at conditions of 77 K and up to 1 bar pressure [183]. Thus, the incorporation of Pt metal resulted in secured porosity which acted as a H$_2$ spill-over receptor. The spill-over effect (shown in Figure 2.5) involves dissociation of hydrogen molecules in the presence of a metal or metal oxide catalyst and subsequent migration of atomic hydrogen into layers of the adsorbent [184-186]. Similar observations were published on this effect by Zhou et al. [187] wherein Pt decorated ZIF-8/GO hybrids (ZIF-8/GO-Pt) resulted in the specific surface area twice smaller (620 m$^2$g$^{-1}$) than that of pristine counterparts, that is ZIF-8 (1300 m$^2$g$^{-1}$) and ZIF-8/GO (1250 m$^2$g$^{-1}$). Surprisingly, H$_2$ adsorption capacity of ZIF-8/GO-Pt at 25 °C under 10 bar was twice larger than that of both ZIF-8 and ZIF-8/GO because of the spill-over effect. An analogous enhancement in the H$_2$ adsorption capacity at close to ambient conditions was observed for other graphene/MOF composites; MIL-101/GO-Pt (2.7 times higher than that of MIL-101) at 25 °C and 10 bar [188] and Cu-BTC/GO-Pt (increased from 0.41 wt.% to 0.77 wt.%) at 25 °C and 80 bar [189]. Additionally, both experimental and theoretical investigations have also proved that the H$_2$ adsorption capacities of MOFs can be improved significantly by doping the frameworks (preferably over the organic linker) with alkali-metal ions, in particular Li$^+$ ions because of its strong affinity towards H$_2$ molecules [190-191].

On the other hand, a study by Rallapalli et al. [192] investigated the in-situ incorporation of activated carbon in MIL-101(Cr) pores to enhance the volumetric H$_2$ uptake capacity of MOFs. It was revealed that with a low AC mass loading of 0.63%, a significant 58% increase in H$_2$ uptake can be achieved. A H$_2$ adsorption capacity of 10.1 wt.% (at 77.4 K and pressure of up to 60 bar) and a BET surface area of 3555 m$^2$g$^{-1}$ were obtained for the AC@MIL-101 composite compared to 6.39 wt.% and 2887 m$^2$g$^{-1}$ for pristine MIL-101, under the same conditions [192]. The observed increase in H$_2$ uptake was ascribed to the reduction of pore size of microporous MIL-101 and the formation of additional micropores 0.45–0.61 nm in MIL-101 framework. A recent study [193] still on MIL-101(Cr) and AC, suggested a green synthesis of MIL-101 (Cr) under mild conditions without hydrofluoric acid while also
incorporating AC to create hybrid materials with enhanced H\textsubscript{2} uptake properties. They reported a maximal excess H\textsubscript{2} uptake of 13.5 wt.% for a hybrid AC-MOF adsorbent (BET surface area = 3542 m\textsuperscript{2} g\textsuperscript{-1}) at 77 K and 100 bar while a maximal value of only 8.2 wt.% was reported for the pristine MIL-101(Cr) (BET surface area = 3223 m\textsuperscript{2} g\textsuperscript{-1}), under the same conditions.

![Figure 2.5. Schematic illustration of hydrogen spill-over effect on the ZIF-8/GO hybrid material doped with Pt nanoparticles. Reprinted from ref. [194], Copyright 2017, with permission from Elsevier.]

**2.3.2.2. MOF-Polymer Composites**

Researchers have investigated several approaches for addressing processability issues of MOFs. The incorporation of MOFs into polymer matrix is now a rapidly growing interdisciplinary research area. The resulting multifunctional hybrids usually exhibit novel properties that are unique and superior to those of the individual components due to a synergistic effect. Since MOFs are inorganic-organic hybrid porous materials that possess organic ligands; they have good compatibility with a polymer matrix [195]. However, features of the inorganic part often results in inevitable interfacial defects between MOF crystals and polymers and various strategies are used to improve the compatibility between the MOFs and polymer matrix [196]. Examples of strategies for synthesis of MOF-polymer composites are discussed in the subsequent sections.
2.3.2.2.1. Synthesis of MOF-Polymer Composites using Chemical Methodologies

There are various chemical ways of synthesising polymeric MOF composite materials that are classified as *ex-situ* or *in-situ* process (as seen in Scheme 2.1). During the *in-situ* process MOF crystals are grown in the pores of the pre-formed polymer. The in-situ approach usually produces homogenous filler distributions in the matrix unlike the *ex-situ* which suffers from filler particle sedimentation and agglomeration. The first report of a MOF-polymer composite through the *in-situ* growth of a MOF in a pre-formed polymer was published in 2008 [197]. In the *ex-situ* process, the MOFs powders which are already synthesised, following an external synthesis step, are added to an organic precursor solution which is then followed by a polymerisation step. The *ex-situ* process is the easiest and is the most applied composite formation method whereas the *in-situ* methods are more sophisticated. However, due to the differences in physico-chemical properties and differences in density of MOFs and polymers, precipitation of MOF particles may occur resulting in the composites displaying undesired properties. Therefore, several alternative techniques have to be employed to overcome these issues and improve the interfacial contact. The strategies that can be used to ensure homogenous blending include the preparation of highly concentrated (15-18%) solutions in order to increase viscosity and reduce sedimentation, surface modification of the MOF’s structure to have stronger interactions with the polymer or carbon, high composites formation temperature, use of coupling agents and post treatment of a polymer/MOF composite (e.g. annealing). Therefore, the use of dispersing technologies like ultra-sonication is a necessity when carrying out an *ex-situ* process. Otherwise, pre-polymerisation of the polymer prior to embedding of porous materials, as reported by Czakkel et al. [198], can be performed. Applying this method to polymer/MOF composites, the pore-blocking effects and inhomogeneity which are often observed in the synthesised composite could be easily avoided to retain the original porous properties of the MOFs [199]. The proceeding discussion below will present polymer/MOF based composites materials obtained through *in-situ* and *ex-situ* chemical synthesis routes used to fabricate films, beads, monoliths and foams structures.
Scheme 2.1. Schematic presentation of the in-situ and ex-situ synthesis of polymer/MOF based composites.

2.3.2.2.1. MOF Composites using Polymeric Beads

The use of polymeric binders for processing of MOF powders into shaped monolithic bodies has been identified as a promising method [200-201]. For example, in a synthesis of a PET-HKUST-1 composite, poly(ethylene terephthalate) (PET) and HKUST-1 MOF were dissolved in 1,1,1,3,3,3-hexafluoroisopropanol solvent. The resulting solution mixture was further mixed with a coagulant solvent in which the PET is insoluble. In the case of PET, acetone was used. The composite then solidified into small spheres with better mechanical stability [202]. Interestingly, 25 wt% of nonporous PET binder did not result in pore blocking but, a decrease in surface area was observed due to a contribution of non-porous binder. In a similar study, Neill et al. [151] reported a series of experiments in the fabrication of MOF composite materials where MOF crystals were deposited into mm-sized hydrophilic macroporous polyacrylamide (PAM) oxide or oxide-PAM beads through solvothermal methods or immersion in mother solutions. The researchers discovered that MOF growth tends to occur selectively on the exterior surface of PAM beads if these are pre-soaked in a reaction solvent before addition to the MOF synthesis precursors. This phenomenon arises due to large barrier to diffusion of the metal salt and ligands into the bead interior relative to
the rate of nucleation. Again in this study the compatibility between the polymer and MOF crystals have been highlighted. Here, the intrinsic hydrophilicity and processability nature of the PAM resulted in suitable interactions with the MOF. The stoichiometric ratio of MOF:Polymer was tunable by changing the concentration of precursors. HKUST-1@PAM composite with a maximum Cu-BTC loading of up to 62 wt% could be achieved with a BET surface area of 654 m²g⁻¹ (pristine HKUST-1: 1075 m²g⁻¹). The obtained HKUST-1@PAM composite beads showed improved mechanical stability and better handling over the bulk HKUST-1 MOF counterpart. Figure 2.6 below displays a photograph and a scanning electron microscopy (SEM) image of pristine PAM beads.

Figure 2.6. A photograph of the PAM beads (left) and a SEM image showing a cross-section of a single bead (right) with macroporosity throughout the structure. Republished with permission of Royal Society of Chemistry, from ref. [151]; permission conveyed through Copyright Clearance Center, Inc.

2.3.2.1.2. Use of Polymeric Foams in MOF Composites Formation

The MOF composite foams are emerging as promising materials following the report of Pinto et al. [203] who proposed an alternative to the shaping of MOFs by means of direct synthesis of UiO-66 over polyurethane foam (PUF) templates. They claimed that this novel method resulted in hierarchically porous composite materials displaying both macroporosity of the PUF support and microporosity of the UiO-66. Additionally, it exhibited high adsorption capacity for benzene and n-hexane and the composite can be designed into various shapes. However, the N₂ uptake capacity was comparatively lower due to UiO-66 growth inside the polyurethane matrix instead of forming at the surface. Consequently, the BET surface area of
511 m$^2$g$^{-1}$ was obtained for 71 wt% loading of UiO-66 (1175 m$^2$g$^{-1}$) on PUF matrix. In the case of HKUST-1@PAM beads [151] and HKUST-1@porous polymer high internal phase emulsion (polyHIPEs) monolith [197], selective growth of MOF crystals on the external surface of the polymer matrix was controlled by swelling a polymer in the reaction solvent. In comparing the performance of their materials against other composites reported in the literature, it was found that the surface area of the obtained UiO-66/PUF composites is higher than the values reported for MOFs anchored on ceramic foams [155], polyHIPEs [197] and pulp paper fibers [154], but lower than MOFs supported on mesoporous silicas [156-157]. It seems like that in the search for suitable templates and binders for MOFs, introducing hierarchical porosity into the MOFs has become a priority in many applications like catalysis and gas separation [204].

2.3.2.2.1.3. MOF Composites using Polymeric Films and Membranes

The other field where MOF-polymer composites have become popular over the past few years is mixed matrix membranes (MMMs). In most cases MOF-polymer MMMs are prepared by dispersing the already synthesised MOF crystals into a just prepared polymeric solution so that it fills the macropores of the polymer prior to casting and curing [146]. For example, a recent work by Khdhayyer et al. [205] demonstrated that embedding the MIL-101 in PIM-1 can improve the properties and performance of PIM-1 in MMM. In this study, different kinds of MIL-101 were dispersed in the PIM-1 matrix to investigate the effect of the chemical nature of amine- or ethylene diamine-functionalized MIL-101 and the effect of the particle size of MIL-101 on the MMM performance. The solubility, permeability and diffusion coefficients and corresponding selectivities of the obtained MMMs were measured for the He, H$_2$, O$_2$, N$_2$, CH$_4$ and CO$_2$ gases on the “as-cast” samples and after alcohol treatment. Their morphology analysis confirmed the absence of defects at the MOF-polymer interface (as illustrated in Figure 2.7).
Recently, a similar report by Tian and the team [206] reported a comparative study on different composite membranes based on a PIM-1 matrix embedded with nano-sized fillers: MIL-101 or activated carbon (AX21) to form PIM-1/AX21 and PIM-1/MIL-101 composite films of a range of filler compositions. Through a detailed evaluation of composites properties, it was revealed that the PIM-1/AX21 composite with 60 wt% AX21 exhibited a high BET surface area of 2034 m² g⁻¹, enhanced H₂ adsorption kinetics coupled with a total H₂ storage capacity of up to 6.36 wt% at 77 K and 10 MPa; which exceeds the U.S DOE hydrogen storage target (5.5 wt% for a complete system). These findings indicate that AX21 offers more favourable pore sizes and shapes for hydrogen adsorption than MIL-101 [207]. Furthermore, the PIM-1/AX21 displayed a higher ultimate stress and strain (sufficient for use in H₂ storage cylinders) than the MIL-101 or PAF-1 containing composites.

2.3.2.1.4. MOF-Polymer Monolith Composites
Schwab and co-workers [197] demonstrated, for the first time, successful in-situ loading of Cu₃(BTC)₂ MOF inside a monolithic macroporous hydrophilic polyHIPE template based on 4-vinylbenzyl chloride crosslinked with divinylbenzene. The polymeric support that was used maintained its monolithic nature even after repetitive impregnation steps under the harsh hydrothermal conditions used for the formation of the MOF. This study emphasised the importance of using hydrophilised polyHIPE over ordinary hydrophobic polyHIPE to
improve interactions between polymer matrix and MOF crystals and enabled direct crystallization of MOF inside the polymeric support [197]. In doing so, it resulted in HKUST-1@polyHIPE composites with hierarchical structures that resulted from a combination of macroporosity of polyHIPE and microporosity of the MOF which is an attractive property for applications involving diffusion-controlled processes. Figure 2.8a shows a scanning electron micrograph of octahedral HKUST-1 crystallites loaded in macropores of the polyHIPE. After three MOF impregnation steps, which has been estimated to be 62.3 wt%, a maximum surface area of 570 m²g⁻¹ was achieved for HKUST-1@polyHIPE composite relative to 1340 m²g⁻¹ of a pure HKUST-1 MOF. However, the authors did not mention what happens with the material’s properties after 3 cycles of impregnation. It is understandable that MOF loading was tunable depending on the number of impregnation steps, but it is expected that after several cycles the support material will reach saturation. Furthermore, a loss of about 32.63% in surface area was not accounted for in the report.

Figure 2.8. SEM image of HKUST-1@polyHIPE (a). Reprinted from ref. [197], Copyright 2008 with permission from John Wiley and Sons. Photographs of pristine poly(HEMA)HIPE material (b) and pp-MIL-101@HIPE composites with 38, 59 and 67 wt% of MIL-101 (c). Reprinted from ref. [207], Copyright 2014, with permission from Elsevier.

Wickenheisser and colleagues [208] reported similar monolithic composites prepared by embedding pre-synthesised MIL-101 (Cr) crystals into a polyHIPEs material based on crosslinked macroporous and monolithic 2-hydroxyethyl methacrylate (HEMA) foam. The BET surface area for the composite obtained by prepolymerisation was higher compared to the composite of the same loading wt% of MIL-101 that was obtained by the standard procedure of pre-polymerization viz. 990 m²g⁻¹ for prepolymerised and only 450 m²g⁻¹ for standard MIL-101(Cr)@poly(HEMA)HIPE. Additionally, the obtained hierarchical and mechanically robust MIL-101(Cr)@poly(HEMA)HIPE (Figure 2.8c) composite, with up to
59 wt% of MIL-101 (Cr) loading, exhibited higher methanol and water vapour uptake capacities compared to pristine HIPE (Figure 2.8b). According to the authors, the application of these composites is not only limited to water adsorption but they can also be utilised in other applications such as in adsorption chillers or heat pumps.

In continuous efforts towards achieving immobilisation of MOFs into macroscopic shaped bodies, the same authors [199] further enhanced their work by reporting the integration of MIL-101(Cr) in resorcinol-formaldehyde xerogels to produce monoliths. The monolithic MOF composites were based on different MOFs (MIL-100 and MIL-101 Fe and Cr based MOFs) and a polymerised resorcinol-formaldehyde xerogel which were fabricated for water adsorption applications. A maximum loading of up to 77 wt% of MIL powder material was achieved in monolithic bodies obtained by pre-polymerization of the xerogel solution. The optimised monolith exhibited good mechanical stability coupled with a reasonable surface area of 2530 m²g⁻¹ (pristine MIL-101: 3060 m²g⁻¹) and water vapour uptake which was close to the expected amount according to the MIL loading percentage. It is worth noting that from their study (mostly for the MIL-101 (Cr) composites) there was no significant loss of BET surface area, porosity and water uptake capacity. This demonstrates once again that the MIL-101 (Cr) was a good choice for use as a porous filler material.

2.3.2.2.2. Electrospinning Approach

Electrospinning is a method mainly used for fabrication of almost every ultrathin polymer fiber and is also a processing technique for supporting small particles on the surface of polymeric fibers [209-210]. In electrospinning, a polymer solution is polarized or melted in the presence of a strong electric field. In this case, the polymer solution is drawn from the syringe on one electrode to a counter electrode, where the solvent evaporates or solidifies if a polymer melt is used. The fiber then get deposited on the counter electrode. The electrospun fibers exhibit unique properties in comparison to fibers fabricated from other processing techniques like nonwovens which are obtained from a melt-blown method. Electrospinning in a laboratory scale is usually carried out using a syringe filled with a polymer or polymer-filler spinning solution connected to a syringe pump, as illustrated in Figure 2.9. The conducting needle on a syringe is connected to the high-voltage power source. The counter electrode is made of a metal plate covered with aluminium foil or textiles substrates. An industrial-scale electrospinning set-up consists of two conductive horizontal cylinders which are rotating and aligned parallel, during electrospinning; the lower cylinder is continuously impregnated with
the spinning solution while rotating and the upper cylinder is continuously transporting textile substrate resulting in large production of homogeneous layers of electrospun fibers.

Electrospinning is also used for introducing adsorptive properties in textiles for various applications such as gas adsorption or separation. The intrinsic porosity in electrospun fibers can be created by including AC into polymeric precursors [211] or carbon fibers derived from carbide [212]. Similar successful attempts showed that porous fibers can be produced from inclusion of zeolites, but the mechanical strength of the obtained fibers was too weak to be considered for applications on flexible textile substrates. To overcome this problem, an alternative strategy is inclusion of porous binders into polymeric fibers to improve the strength and required flexibility for use on textile substrates. Since electrospinning is a versatile method for the incorporation of any particles in fibers for enhanced properties, the integration of carbon nanotubes [213], salts [214], organic and inorganic particles [215] in electrospun fibers has been proven successful. In general, the integration of solid particles binders in electrospun fibers results in processed composite fibers with enhanced electrical conductivity, catalytic activity and mechanical strength properties. Only a few studies have been reported on the inclusion of porous additives in composite fibers for application on adsorptive processes. The porous materials like mesoporous silica SBA-15 and zeolites are the mostly used binders up to now [216-218].

![Schematic diagrams of a laboratory-scale electrospinning device with rotating metal plate as counter electrode used for production of the composite fibers.](image)

Figure 2.9. Schematic diagrams of a laboratory-scale electrospinning device with rotating metal plate as counter electrode used for production of the composite fibers. Reprinted from ref. [153] Copyright 2011 with permission from John Wiley and Sons.
2.3.2.2.2.1. MOF Immobilization by Electrospinning

MIL-100(Fe) and HKUST-1 were the first types of MOFs chosen to be investigated for application as adsorptive materials in protective clothing owing to their good mechanical stability during processing conditions [153]. The spinning solutions used for the fabrication of composite fibers consisted of polyvinylpyrrolidone (PVP) in ethanol, polystyrene (PS) in tetrahydrofuran and polyacrylonitrile (PAN) in dimethylformamide (DMF). All the solutions gave homogeneous layers of composites fibers. When PS binder was used, a maximum MOF loading of 40 wt% was achieved. On the other hand, when PVP and PAN binders were used, a much higher MOF loading (a maximum of 80 wt%) was achieved. These electrospinning experiments were carried out on a medium-sized industrial scale device. The obtained results showed that the structural integrity of MOFs was retained after electrospinning as illustrated in Figure 2.10. The nitrogen sorption measurements at 77 K, showed that both pore volume and surface area decreased by 20% for 80 wt% MOF loaded samples, which is due to the presence of 20 wt% of polymer binder in the electrospun fibers. No pore blocking was observed, so MOFs properties were not compromised after the electrospinning process. The polymeric feedstock to be used for supporting MOF particles on textile substrates must meet specific requirements such as being processable from a green solvent and must have good hydro-stability if is to be used in protective clothing. The immobilization of MOF powders by electrospinning using a polymer as a binder for fabrication of composite fibers is a simple and versatile method for shaping of MOFs.

Figure 2.10. SEM micrographs of electrospun composite fibers: HKUST-1/PS fiber from a solution in THF showing a pearl necklace-like morphology (a) and HKUST-1/PAN fibers from a solution in DMF showing a spider web-like morphology on a PAN non-woven (large substrate fibers in background) (b, c). Reprinted from ref. [153] Copyright 2011 with permission from John Wiley and Sons.
2.3.2.2.3. MOF Composites using 3-D Printing

In the near future, we will be living in the new revolutionary world of three dimensional (3D) printing where people can make almost anything. The 3D printing process is a powerful tool of design and manufacturing. In simple terms, a 3D printer can be described as a machine that produces three dimensional objects from computer drawings by adding layers of material one layer after another [219]. The revolutionary industrial manufacturing of 3D printing could be a breakthrough in addressing the processability issues of MOF powders by 3D printing monolithic structures that can be shaped or extruded into any desired application-specific shape. The use of 3D printing for shaping of powdered MOFs provides a simple and cost-effective alternative to traditional methods [220]. Acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) are the most common 3D printable polymers used for desktop 3D printers; other polymers include PVA, polycarbonate and high density polyethylene. The 3D printing process used with ABS is called fusion deposition modelling where the materials are heated and squeezed through a nozzle to build 3D structures [219].

The 3D printed composite monoliths do not only offer better handling properties, but also enable hierarchical pore size distribution to be implemented. Hence, additionally, the properties of a 3D printable polymer integrated in MOFs can result in complex multifunctional materials [221]. The first report on 3D printed MOF-based monoliths (MOF-74(Ni) and UTSA-16(Co)) was described by Thakkar et al. [222] for application in CO₂ removal from air. Here, the two mixtures of MOF powders and bentonite clay (binder and rheological modifier) and PVA in deionised water were combined to produce an extrudable paste, as illustrated in Figure 2.11a. The optimum maximum loadings of 80 and 85 wt% of MOF-74(Ni) and UTSA-16(Co) in PVA were achieved respectively. The obtained CO₂ uptake for both composites, correlated very well with the capacities of their MOF counterparts under the same conditions (5000 ppm (0.5%) CO₂ exposure at 25°C). However, the 3D-printed monoliths displayed a significant loss of surface area (see Figure 2.11(b-e)) of up to 30% (from 631 to 444 m²g⁻¹) for UTSA-16(Co) and 38% (from 1180 to 737 m²g⁻¹) for MOF-74(Ni), attributed to the low surface of non-porous bentonite clay and PVA binders. Prior to both N₂ and CO₂ adsorption isotherms analysis, UTSA-16(Co) and MOF-74(Ni) samples were outgassed at 110 and 250 ºC for 6 hours, respectively. Furthermore, the loss of porosity was also observed owing to the contact with water during preparation of the extrudable paste. Nonetheless, their findings showed that the MOF materials shaped with a 3D printing technique was suitable for gas separation applications with faster adsorption
kinetics than their MOF powder analogues. In a similar study presented by Bible and colleagues [223] a 10 wt% of ZIF-8 or HKUST-1 was successfully incorporated in ABS through 3D printing. The obtained ABS-ZIF-8 retained the MOF gas adsorption properties, however the ABS-HKUST-1 composite resulted in slower gas sorption profiles at room temperature and reduced gas adsorption uptake at 77 K. The poor performance of the latter indicates that the rate of adsorption in the composites was driven by N$_2$ gas–MOF interactions rather than N$_2$ gas-ABS with also the possibility of alteration of the ABS structure by HKUST-1.

The very recent study by Young et al. [224] also highlighted a pore occlusion problem in which the 3D-printed UiO-66-based monoliths were non-porous owing to the inclusion of a flexible acrylate polymer binder. To recover the UiO-66 pore accessibility, the composite was degassed at 150 °C for 12 hours and subsequently heated at 280 °C under air for 30 minutes (to selectively degrade the polymer binder), and then lastly, the obtained composite was washed twice with dichloromethane. The resulting material still maintained the printed structure, while N$_2$ physisorption results showed recovery of the microporous characteristics of UiO-66 and the presence of small additional mesopores was also observed. Furthermore, UiO-66 in this study was found to behave as a rheological modifier itself, avoiding the need for additives such as the bentonite clay employed in earlier studies [222].
The 3D printing approach was also employed to moisture sensitive MOFs. For instance, Kreider et al. [225] demonstrated successful inclusion of water-sensitive MOF-5 (10 wt%) in ABS. Interestingly, irrespective of the degradation of MOF-5 which was observed during production of the extrudable paste by solvent casting, the resulting ABS-MOF-5 still retained
the MOF-5 H₂ uptake properties even under humid conditions. The H₂ adsorption measurement was carried out by exposing ABS-MOF-5 (degassed at 103 °C for 3 days) to 0.6 bar of H₂ for 2 minutes followed by desorption measurement where a degassed ABS-MOF-5 composite was incubated at a H₂ pressure of 0.6 bar for 28 hours. The obtained results showed that ABS-MOF-5 monolith exhibited H₂ uptake higher than the pristine polymer counterpart. Furthermore, the physical and mechanical properties of the composite (Young’s modulus, glass transition temperature, stress and strain at the breaking point) remained the same with some hardening effects owing to polymer-MOF interactions. To this end, it means embedding MOFs in a polymer matrix through 3D printing could protect embedded MOFs from moisture degradation viz. the results by Kreider et al. [225] showed that the MOF-5 is not further degraded once it is incorporated into the polymer. However, it should be noted that these findings have not been proved by other studies yet. Thus, the 3D printing technique may be suited for MOF-5 but not for other MOFs which are for instance air sensitive, since the layer-by-layer printing process necessitates air exposure for long periods.

2.3.2.3. Industrial Perspectives in the Formation of MOF Composites

2.3.2.3.1. MOF-containing Paper Sheets

The immobilization of MOFs in paper sheets stands a good chance to be considered as a convenient method of shaping MOF powders because the paper industry is well advanced. This approach can provide a reliable and affordable large scale production of MOF containing paper sheets. Other substrates such as α-alumina or copper mesh can also be used for immobilization of MOF powders [226-227]. Paper is considered as the most suitable substrate because of its flexibility. The filter element or paper sheet properties can be modified accordingly to be suitable for any type of applications such as in air and liquid filtration by the use of additives. MOF particles are one of the additives that can be included into the paper sheets using the common processes for introducing pigments or fillers in paper [170]. MOF-paper sheets composite can be fabricated by adding MOF powder to pulp slurry using a Rapid Kothen sheet mold [228]. The results obtained from the study of immobilization of 6.5-14.6 wt% Cu₃(BTC)₂ on paper sheets [228] showed that incorporation of MOFs in paper sheets is a feasible practical strategy for immobilization of MOFs. However, the inhomogeneity of MOF crystals in the fibrous network of paper sheets resulted
in a low surface area (170 m²g⁻¹). Consequently, further modifications or rather the use of more advanced synthetic approaches are required to solve the inhomogeneity issue.

2.3.2.3.2. MOF/Pulp Fibers

Another method for fabrication of paper sheets is the direct crystallization of MOF crystals on the surface of pulp fibers. The obtained hybrids can be processed into paper sheets or filter elements. This method is an alternative solution to the inhomogeneity issues experienced with the ex-situ slurry method discussed above. The direct crystallization approach results in homogeneous distribution of MOF crystals within paper sheet and improved fixation of MOF at the surface of pulp fibers substrate. Previous attempts on immobilization of powder materials on fibers by Valtchev and colleagues [229] involved deposition of zeolites on vegetable fibers. In a similar study [154], the Cu₃(BTC)₂ MOF was grown directly onto two different types of pulp fibers to produce MOF/pulp fibers composites. The two pulp samples containing different residual lignin content were prepared from the Kraft process and chemo thermomechanical pulping (CTMP) process respectively. It was found that the composition and quality of used pulp significantly affects the dispersion of MOF crystals on the pulp fibers. According to the reported results, the pulp fibre sample containing the highest amount of lignin obtained from the CTMP process exhibited largest BET surface area (315 m²g⁻¹) owing to the high content of lignin residue. This also resulted in enhanced uniform distribution of MOF crystals on the fiber surface. The pulp fiber with a smaller amount of lignin prepared by the Kraft method showed a surface area of only 165 m²g⁻¹. The in-situ synthesis showed enhanced surface adhesion as compared to paper sheet samples prepared through an ex-situ slurry approach. The observation was explained to be attributed to the carbonyl and carboxylic acids functional groups present in lignin which facilitate better affinity and binding towards Cu₃(BTC)₂.

2.3.2.3.3. Extrusion

Extrusion and mechanical pressing are the most common processing techniques used to shape MOFs under high pressure conditions which usually require addition of binders or additives [230-231]. Nonetheless, and in most cases, the use of a binder results in pore blocking which adversely affects the performance of MOFs. Küsgens and co-workers [175] fabricated Cu₃(BTC)₂ MOF monoliths through a two-step extrusion process. The process involved mixing pre-synthesised MOF crystals with a liquid binding agent (methyl siloxane) and a
commercially available, non-toxic and highly soluble plasticizer (methylcellulose) in a lab-scale kneader. Subsequently, the molding batch was extruded to produce a monolith which was cut into smaller 200 mm pieces. Figure 2.12 shows the final monolith of Cu$_3$(BTC)$_2$ MOF. Alternatively, montmorillonite, bentonite, attapulgite and kaolin can also be used as binders. A specific surface area of 484 m$^2$g$^{-1}$ and a high mechanical stability of 320 N were obtained for monolithic HKUST-1 structures but the surface area decreased to 287 m$^2$g$^{-1}$ after several months. Despite the efforts made towards shaping of HKUST-1, there are still some uncertainties in terms of storage stability under hydrothermal or humid conditions [232].

Figure 2.12. Photograph of Cu$_3$(BTC)$_2$ monolith obtained by extrusion. Reprinted from ref. [175]. Copyright 2010 with permission from John Wiley and Sons.

2.3.2.3.4. Mechanical Pressing

Recently, mechanical compression of MOFs into pellets without significant loss of hydrogen storage capacity has attracted much attention owing to a huge enhancement of the volumetric hydrogen capacity. For instance, the recent study by Bambalaza et al. [233] reported compaction of UiO-66 at ~700 MPa into dense pellets with enhanced total volumetric H$_2$ uptake capacity. It was found that the obtained pellets had retained about 98 % of the microporosity and surface area of its powder counterpart without collapsing the MOF structure. The densified pellets obtained in this study exhibited a total gravimetric H$_2$ uptake of 5.1 wt.% which is equivalent to its powder analogue under the same conditions (77 K and 100 bar). On the other hand, volumetric H$_2$ uptake was found to increase from 29 gL$^{-1}$ (UiO-66 powder) to 74 gL$^{-1}$ (UiO-66 pellet) at 77 K and 100 bar. In this case, the authors had achieved an adequate balance between porosity and packing density to improve the
volumetric H₂ uptake of UiO-66. These findings also provide an insight in transitioning MOFs from laboratory to real practical applications.

In the past, the MOF field has received significant criticism owing to hydro sensitivity of some MOFs. This was confirmed by Kusgens et al. [232] showing that both HKUST-1 and DUT-4 are not stable towards water, while the MIL series of MOFs and ZIF-8 are stable as illustrated in Figure 2.13 below. Hence, among various densified monoliths of MOFs such as MOF-5 [234], MIL-177 [235], and MIL-101 [236] which have been investigated so far, the monoliths based on MIL-101 (Cr) can be considered as promising adsorbents due to their high hydro stability and good hydrogen uptake capacity [49] compared to zinc-based MOFs [237].

![Figure 2.13](image.png)

**Figure 2.13.** Steam stability map for various types of MOFs, wherein the position of the structure for a given MOF represents its maximum structural stability by XRD measurement. Reprinted with permission from ref. [237]. Copyright 2009 American Chemical Society.

Lupu and co-workers, [238] conducted an experimental assessment of the physical upper limit of hydrogen uptake for both powder and compressed pellet MIL-101. Wherein, the pellets achieved a maximum hydrogen uptake of 9.6 wt.% and 42 g L⁻¹ at 20 K, P/P₀ = 0.9 and the nitrogen BET of 2745 m² g⁻¹. Another report by Raj et al. [239] investigated the effect of applying different compression pressures (5, 10 and 15 tonnes; where 1 tonne per square metre = 9.80665 kPa) on the MIL-101 (Cr) pellet properties and its correlation with hydrogen uptake capacity. The MIL-101(Cr) used in their study was synthesised in bulk (25
g/batch) using acetic acid as a modulator instead of HF acid. The MIL-101 (Cr) powder was moulded into a pellet using binders such as the sodium salt of carboxy methyl cellulose, starch and polyvinyl alcohol (PVA). The performance of the obtained pellets obtained using binders was compared with pellets prepared without binder. The surface area and micropore volume were found to decrease with the increasing compression pressure. The MIL-101(Cr) pellets prepared using 10% PVA, as a binder, at 10 tonnes compression pressure showed a maximum hydrogen storage capacity of 2.54 wt.% (at 77 K and 4500 kPa). On the other hand, the MIL-101(Cr) pellets compressed at the same pressure without binder, showed 3.10 wt.% hydrogen storage capacity when measured under similar conditions [239]. The low hydrogen uptake was ascribed to the reduction in the surface area after densification. The binder also decreased the microporosity of the material by blocking its pores. However, it was concluded that the use of binder can effectively increase the bulk density and provide ease of handling of the MIL-101(Cr) sample. Peterson et al. [240] also investigated the effects of pelletisation pressure on the physico-chemical properties of the UiO-66 and Cu₃(BTC)₂ because in some cases the pressure resulted in unwanted losses of crystallinity and microporosity [241].

2.3.2.3.5. Granulation Strategy
Granulation is a common and one of the significant shaping processes used in the pharmaceutical industry to enhance compressibility of powders during the production of pharmaceutical oral dosage forms like tablets and granules. In simple terms, granulation is a size enlargement process in which small fine or coarse particles are converted into physically stronger and larger clusters called granules. The particles size of the granules is determined by the quantity and feeding rate of granulating liquid. Granulation normally starts after initial dry mixing of the powdered ingredients to ensure that a uniform distribution of each ingredient is achieved. Generally, there are three methods of granulation, the dry granulation, direct granulation and wet granulation. The wet granulation method (displayed in Figure 2.14) requires fine-tuning of several parameters including liquid content, type of binder, surface tension and viscosity of liquid binder/powder mixture to increase mechanical strengths of shaped MOFs without a significant loss of the porosities [242].
The recent granulation technologies (granulators) include steam granulation; moisture activated dry granulation, moist granulation, thermal adhesion granulation, foam granulation, freeze granulation, melt or thermoplastic granulation and pneumatic dry granulation, etc. Each technique has its unique characteristics, advantages and disadvantages. Granulation is used to minimize handling problems and hazards associated with toxic dust particles during handling, transporting and application of powders. Thus, shaped materials are convenient for storage and shipment because granules can occupy less volume per unit weight as opposed to loose powders which have low packing densities. Moreover, granulation helps with adhesion and cake formation of moisture sensitive materials. In this way granules will absorb some moisture but still retain flow-ability because of their size [244].

The granulation processing method is by far one of the best shaping strategies in comparison to other pressurised methods which can often cause a partial collapse of MOF pore structures or even a significant loss of crystallinity [244]. This approach has been employed in a few studies for shaping of MOF powders [235, 245-246]. Recently, Ren and his co-workers [246] employed a centrifugal granulation process for shaping of MOF powder. Through this process they demonstrated successful shaping of a Zr-MOF powder (in the presence of 10 wt% sucrose as a binder) into a kilogram batch of spherical pellets within 30 min operation time. This shows that the granulation method offers a more efficient approach to shape MOF powder materials in comparison to the mechanical pressing method [246]. The study of breakage is considered very important in the granulation process as it affects the subsequent
processing, transport, handling and final use of granular products [247]. Therefore, in their study the mechanical stability and breakage of the Zr-MOF pellets was evaluated by conducting a drop test and simulated tumbler drum test. It was found that after 70 consecutive drops at a height of 0.5 m, no breakage of the pellets was recorded and only 5% breakage was recorded after 60 min of tumbling time at a speed of 25 rpm. Even though, the shaping resulted in a significant decrease in surface area and hydrogen storage capacity of the Zr-MOF, it is expected that with the use of a more suitable choice of binder higher values can be obtained.

2.4. Concluding Remarks and Novelty Statement

In this review, a detailed discussion on a wide range of fabrication techniques for processing carbon and MOF materials into mechanically stable composite configurations and their performance in hydrogen adsorption and other related applications has been provided. As shown in the review, some highly promising H₂ uptake capacities have been achieved on activated carbons and their respective MOF and polymer composites particularly via the spill-over effect. In addition to inclusion of porous filler materials in polymers through in-situ and ex-situ chemical synthesis, other processing techniques such as extrusion, mechanical pressing, electrospinning and granulation and 3D printing have shown a great potential in shaping MOFs for industrial applications. Although 3D printing has shown promise in fabrication of mechanically stable MOF composites with high reproducibility, the post-synthetic activation methods required to retain accessible pores for gas adsorption remain a challenge and therefore need to be considerably improved. It can be summarised that scalable and solvent-dispersible microporous polymers like PIM-1 are indeed promising materials for compositing with powder materials and casted into free standing films and monoliths for hydrogen storage. The fact that most of PIM-1/MOF composites have been utilised for gas separation membranes, and not much on H₂ storage, opens a room for development of novel adsorbents for H₂ storage. However, substantial improvements in both gravimetric and volumetric hydrogen capacities, other properties like enthalpy of adsorption, thermal conductivity and a better understanding on hydrogen storage process when adsorbents materials are featured in a H₂ tank are necessary to meet the DOE targets.

Additionally, the literature reviewed above reveals the gap in the application of monolithic shaped MOF-polymer composites prepared through various processing methods for hydrogen storage. In this case, several MOF/carbon composites have been well investigated and
reported but without demonstrating how the carbon materials affect the thermal conductivity of MOFs. To the best of my knowledge, there are few studies on MOF/polymer and carbon/polymer composites that have been specifically reported for hydrogen storage applications. Additionally, most processing techniques often neglect carbon materials since the focus is mostly on MOFs. For instance, there is no evidence of a PIM-1/UiO-66/ZTC or PIM-1/ZTC composites being used as adsorbents for H₂ storage. The novelty of the present thesis is related with the fact that the current project has investigated various innovative strategies for shaping powdered materials (carbon/MOFs) by fabricating hierarchical porous monoliths of PIM-1/MIL-101(Cr), PIM-1/UiO-66(Zr), PIM-1/ZTC and PIM-1/UiO-66/ZTC composites exhibiting attractive and enhanced hydrogen uptake capacities. Furthermore, the effect of the inclusion of carbon materials on the thermal properties of MOF/polymer composites was also investigated in an attempt to improve the thermal conductivity of MOFs when practically applied as an adsorbent bed in H₂ storage units. The improvement in thermal conductivity will help with fast thermal dissipation during an exothermic H₂ adsorption process. Therefore, the ability of shaping MOF and carbon powders without adversely compromising their essential properties as shown in this project should help in accelerating the transition of porous MOFs from laboratory to application-specific properties that are aimed for real practical applications.
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CHAPTER 3: CHARACTERISATION TECHNIQUES

Summary Statement

This chapter presents an overview of the principles and analysis conditions of the characterisation techniques applied in this study to interrogate the morphology, structural, textural, thermal and mechanical properties and gas sorption analysis of the porous materials and their composites.

3.1. Characterisation Techniques for Porous Materials

The following section gives a brief overview of the theoretical framework and analysis conditions of the analytical characterisation techniques and gas sorption analysis techniques applied in this study.

A broad range of characterization methods were used in the analysis of the morphology, composition, chemical and physical properties of nanoporous hybrid materials. However, only a small selection of the most important techniques used in this study are discussed with more emphasis on nitrogen and hydrogen physisorption employed to characterise the adsorption properties of pristine and composites materials. Unlike MOFs, polymers and their composites are often amorphous so some of the conventional techniques like X-ray diffraction are limited. Of course, the fact is since a composite is a hybrid of two different materials it means that various analytical characterization methods must be used for complete investigation. The generated pristine and composites materials were thoroughly characterised, and their properties were compared to those of the existing literature. The following characterization techniques were used to guide the research direction in terms of informing whether further modifications of the synthetic approach would be necessary.

3.1.1. Scanning Electron Microscopy (SEM)

Electron microscopy is one of the important techniques used to interrogate the morphology of materials at the atomic and nanometer scale. This technique provides an image of the sample under analysis and additional details like elemental distribution and other information can be obtained when the microscopy is coupled with other analytical techniques. However, just like
many other methods it has advantages and disadvantages. For instance, the micrograph obtained only shows a small part of the sample analysed which means it may not be a true reflection of the whole sample. The high energy electron beam can also destroy the nature of the highly sensitive sample. Therefore, the results from this technique should always be confirmed by other characterisation methods.

The scanning electron microscope (SEM) is a technique used for surface imaging of materials to obtain highly magnified images down to a resolution of less than 2 nm. The SEM consists of two main parts, the column and the cabinet [1]. The electron column is the extension consisting of the electron source, where electrons pass through from their emission and narrowed to a diameter of 0.4-5 nm by one or two condenser lenses until they reach the sample [2]. Subsequently, the installed detectors (energy transducers that transform one type of signal to electrical signal) will capture the scattered signals resulting from the interaction between the electrons and the sample and send the resulting electrical signal to the control cabinet. Upon receiving the electrical signals, the control cabinet quantifies the electrical signals and turn them into images and graphs [1-2]. The working principle of a SEM is shown in Figure 3.1.b

Figure 3.1. A picture of Zeiss FIBSEM (a) and a schematic diagram showing the components of SEM and how it works (b). Reprinted from ref. [2].

In this study, the SEM was used to study the morphological appearance of the porous filler materials and their interaction with a polymer matrix in the composites. This information was also used to complement the gas adsorption studies. All the SEM images were recorded using a Carl Zeiss Auriga Cobra focused-ion beam scanning electron microscope (FIBSEM) at an
accelerating voltage of 3 kV (Figure 3.1a). Prior to imaging, the samples were mounted on specimen stubs with a carbon adhesive tape, and then sputter-coated with chromium under vacuum to prevent electrostatic charging effects using Quorum sputter coater. Prior to cross-section imaging of 3D-printed monolithic samples, the samples were cryogenically fractured by immersing in liquid nitrogen for a few minutes and were mounted on the stubs with conductive carbon cement.

3.1.2. Powder X-ray Diffraction (PXRD)

Spectroscopic methods of analysis are expanding with time and are no longer just limited to absorption; therefore, Fourier transform infra-red (FTIR) spectroscopic analysis and X-ray photoelectron spectroscopy are surface analysis techniques while powder X-ray diffraction (PXRD) is a grazing technique. Here PXRD and FTIR were used to study and confirm the structure and crystallinity of samples to supplement the observations made with SEM. The X-ray diffraction is a useful and non-destructive technique used to interrogate the crystallinity, lattice spacing parameters and crystal structure of materials. The XRD phenomenon originates from firing a sample with a beam of X-rays which then interact with electrons within the material through an elastic and coherent scattering process [3]. In the case of crystal diffraction, well-defined XRD peaks are generated by constructive interferences effects at specific scattering angles, whereas the patterns of an amorphous material present a broad intensity maximum that spans several degrees along 2θ [3-4]. The relationship between the angle of reflections and the wavelength of radiation is expressed by Bragg’s law:

\[
\lambda = 2d_{hkl} \sin \theta_{hkl}
\]  
(Equation 3.1)

where \( \lambda \) is the X-ray wavelength, \( d \) is the interplanar distance between a set of parallel planes defined by the Miller indices \( h \ k \ l \), and \( \theta \) is the angle of incident beam, which is equal to half of the scattering angle \( 2\theta \). Bragg’s law can be derived from the scheme in Figure 3.2.
Figure 3.2. Schematic illustration of derivation of Bragg’s law where, from set crystallographic planes drawn, constructive interference occurs when the optical path difference of the different beams (marked in red) is equal to an integer number of wavelengths (nλ). Reprinted from ref. [3], Copyright 2017, with permission from Elsevier.

PXRD was used in this study to confirm the crystal structures of crystalline MIL-101 and UiO-66 MOFs. The effect of polymer matrix inclusion on the filler’s (MOF or carbon) structural stability was monitored by PXRD. This technique is essential in confirming successful synthesis of MOFs crystals and determining whether the crystallinity of the MOF material was retained after forming the composite. All the PXRD patterns reported in this study were recorded at ambient conditions on a PANalytical X’Pert Pro powder diffractometer equipped with a pixel detector using Ni-filtered Cu Kα radiation (0.154 nm) between $3^\circ \leq 2\theta \leq 60^\circ$, at a scanning rate of $2^\circ \text{min}^{-1}$. For sample preparation before each measurement, samples were well-ground into a fine powder with an agate mortar and pestle.

3.1.3. Fourier Transform Infra-Red (FTIR) Spectroscopic Analysis

Fourier transform infra-red (FTIR) spectroscopy is a powerful technique for probing and confirming the chemical functional groups of molecules which absorb light in the infra-red region of the electromagnetic spectrum. Therefore, FTIR spectroscopy is particularly useful for identification of organic compounds due to the range of functional groups, cross-links and side chains involved, which will be observed by characteristic vibrational frequencies in the infra-red range [5]. During infrared spectroscopy analysis, the IR radiation energy emitted from the source is passed through an aperture which controls the energy to the sample and the detector [5-6]. The beam enters the interferometer where the “spectral encoding” takes place.
to produce the interferogram (a pattern formed by wave interference) signal. The beam subsequently enters the sample compartment where it is transmitted through or reflected off the surface of the target sample [5]. This is where specific frequencies of energy measured as wave numbers, typically over the range 4000–600 cm\(^{-1}\), are absorbed. This absorption corresponds specifically to the bonds present in the molecule and is the unique characteristic of the sample [7]. Finally, the beam passes to the detector designed to measure special interferogram signal for final measurement. The measured signal is digitised and sent to the computer where a Fourier transform converts the interferogram into an actual spectrum which is plotted against the corresponding wave number against transmittance values [5, 7]. The scheme summarising the components of the FTIR and its working principle is shown in Figure 3.3 below.

![Figure 3.3](image)

**Figure 3.3.** The schematic diagram showing the instrumental process for FTIR measurements. Reprinted from ref. [5].

To complement the PXRD and SEM results, FTIR spectroscopy was used to identify the chemical composition, types of chemical bonds and functional groups present within the composite materials. All Fourier transform infra-red (FTIR) spectra were obtained using a Perkin-Elmer Spectrum 100 FTIR spectrometer, working in the range from 4000 to 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) in attenuated total reflection (ATR) mode. Prior to each FTIR measurements, 8 scans of the background were collected and four spectra were obtained for each sample.
3.1.4. **Thermal Gravimetric Analysis (TGA)**

Thermogravimetric Analysis (TGA) is a technique in which the weight of a material is measured using a microgram balance as a function of temperature or time as the sample is heated at a specific heating rate in a controlled atmosphere [8]. Since it measures mass changes, it is used for composition analysis of the inorganic and organic content present in the sample, determination of thermal stability and decomposition kinetics [8-9]. A sample purge gas controls the sample environment and this gas may be inert or a reactive gas that flows over the sample and exits through an exhaust [8]. The components of the TGA instrument are shown in **Figure 3.4** below.

![TGA instrument scheme](image)

**Figure 3.4.** TGA instrument scheme. Reprinted from ref. [9].

Since thermal stability of the synthesised adsorbents materials is important when designing and selecting materials for hydrogen storage, TGA was conducted to understand the thermal properties of the pristine and composites materials. In the current study, thermal gravimetric analysis curves were measured on Mettler, Toledo, TGA/SDTA 851 e instrument; about 10 mg of the tested sample was prepared and loaded onto a platinum pan and heated to 1000 °C at a heating rate of 10 °C min⁻¹ under air. Determining the thermal degradation temperatures of the samples in this study helped with choosing safe degassing temperatures to use (in gas sorption experiments) to preserve the structural integrity of the studied materials.
3.1.5. Thermal Conductivity Tester
In addition to thermal stability, the other heat properties (thermal conductivity, thermal diffusivity and volumetric heat capacity) were measured to investigate the effect of incorporating carbonaceous materials in MOFs and polymers. Thermal conductivity of a material is defined as a measure of materials’ ability to conduct or transfer heat. Fourier’s law [10-11] describes thermal conductivity (equation 3.2)

\[ q = -\lambda \frac{dT}{dx} \]  
\[(Equation 3.2)\]

Here \( q \) is the heat flux (Wm\(^{-2}\)K\(^{-1}\)), \( \lambda \) is thermal conductivity (Wm\(^{-1}\)K\(^{-1}\)), \( \frac{dT}{dx} \) is the temperature gradient, where \( T \) is the temperature in K or °C and \( x \) is the distance or thickness in m. The negative sign indicates that heat flows from higher to lower temperature.

Thus, the rate of heat transfer is faster in materials of high thermal conductivity than in materials of low thermal conductivity. In hydrogen storage systems, thermal management is an essential component of tank design for enabling fast refuelling for adsorption which relies on temperature or pressure swing [12].

Thermal diffusivity determines the rate at which the material temperature adapts to the surrounding temperature. A material with high thermal diffusivity conducts heat quickly and thus it rapidly adjusts its temperature to that of its surroundings. It is the ratio of thermal conductivity and volumetric heat capacity [11]. Therefore, it is defined by equation 3.3:

\[ a = \frac{\lambda}{c_v} \text{ [m}^2\text{s}^{-1}\text{]} \]  
\[(Equation 3.3)\]

where \( \lambda \) is thermal conductivity (Wm\(^{-1}\)K\(^{-1}\)), \( a \) is thermal diffusivity (m\(^2\)s\(^{-1}\)) and \( c_v \) is volumetric heat capacity (Jm\(^{-3}\)K\(^{-1}\)).

The last thermal property closely related to the aforementioned is the heat capacity which is a measure of a material’s capability to store energy [12]. The specific heat capacity and volumetric heat capacity are related, wherein informally, the former is the amount of heat energy needed to heat a material of a certain unit of mass to a certain temperature whereas the latter dictates the amount of heat energy that must be applied to heat a material of certain
volume to attain a certain temperature. Heat capacity represents the relation between heat content and resulting temperature change and is calculated using equation 3.4

\[ c_v = \frac{Q}{V \Delta T} \]  

(Equation 3.4)

Here \( c_v \) is volumetric heat capacity (Jm\(^{-3}\)K\(^{-1}\)), \( Q \) is heat transferred to a material (J), \( V \) is the volume of a material (m\(^3\)) and \( \Delta T \) is the resulting temperature change in K or °C. Therefore, because volumetric heat capacity is related to specific heat capacity \( c_m \) and density \( p \), their relationship can be expressed by:

\[ c_v = p \cdot c_m \]  

(Equation 3.5)

Where \( c_m \) is the specific heat (Jg\(^{-1}\)K\(^{-1}\)) and \( p \) is the density of the material (kgm\(^{-3}\)or gm\(^{-3}\)) [11]. Materials with high specific heat capacity absorb more heat energy than materials with low specific heat capacity.

In this study, the volumetric heat capacity, thermal conductivity and thermal diffusivity measurements were carried out using a Hot Disk transient plane source (TPS) 500 thermal constant analyser. The TPS sensor (Figure 3.5b) is fabricated in the shape of continuous double spirals of nickel (Ni) enclosed with Kapton (polyimide film) for electrical insulation and protection [13]. As electrical current passes through the nickel-spiral the sensor temperature increases, the heat then flows into the material at a rate dependent on the heat transfer properties of the material tested. The thermal properties of the material can then be calculated by the temperature versus time response registered in the sensor. The sensor (Hot Disk no. 5465) used for all samples has a diameter of 3.2 mm with a temperature coefficient of resistance is 0.004672 K\(^{-1}\). The sensor was sandwiched between two pieces of the same material as illustrated in Figure 3.5a. The settings of the instrument were 80 s measurement time, 94.34 mW heating power. The measurements were carried out at room temperature (about 24 °C).
3.1.6. Mechanical Stability Testing

The mechanical characterisation of porous adsorbents materials is of interest in their optimisation for potential application as H₂ storage tank liners as they must be able to withstand the internal pressure and have sufficient mechanical properties to withstand the mechanical strains of the tank that occur during hydrogen charging [15]. In simple terms, tensile testing is pulling a test specimen in a straight line to measure how it changes up to the point of yield or breaking, whether gradual or sharp [16]. Even where performance to ultimate failure is not required, characteristics of deformation, elongation and relaxation can be accurately recorded, as in springs and elastomers. The specimen under test may be a synthesised material sample, or a manufactured product.

In the Instron Tensile Tester (Figure 3.6), one end of the test specimen is clamped in jaws, which are mounted on a movable cross-head that is moved at a constant rate by a mechanical drive. The drive comes from a computer-controlled stepper motor and is connected to the recorder drive. The other end of the test specimen is clamped in jaws which are mounted on a fixed load cell containing a strain-gauge [16-17]. The electronic circuits of the load cell lead to deflection of the recorder pen. Finally, the elongation and load are digitally transferred to a computer [17]. Then, the obtained data is plotted in stress-strain graphs and analysis is done based on plotted graphs to determine the tensile strength of a specimen under observation as either low or high.

Figure 3.5. TPS sensor sandwiched between test samples (a) and kapton sensor (b). Reprinted from ref. [14], Copyright 2017, with permission from Elsevier.
The mechanical tensile strength tests of the 3D printed dog-bone shaped specimens (100 mm in length, 13.05 mm in width and 3.23 mm thickness) as defined by the American Society for Testing and Materials (ASTM) D638 were conducted using Instron tester 5966 at an extension rate of 5 mm/min at 23 ºC. The reported results are an average of at least 4 tests per sample.

3.1.7. **Nitrogen and Hydrogen Sorption Analyses**

To complement the physico-chemical properties of the adsorbent materials, the nitrogen and hydrogen gas sorption studies of pristine porous powders and monolithic composites were performed at 77 K and pressures up to 1 bar. Nitrogen gas was used to probe the surface areas of solid or porous materials and their pore size distribution. These properties are of great importance when fabricating materials with enhanced hydrogen uptake capacities. Surface area analysis is one of the most widely used methods in characterisation of porous materials as properties such as gas adsorption capacity, catalytic activity and pore volume are often associated to a material’s surface area. Physisorption is best described by the Brunauer Emmett and Teller (BET) theory while the chemisorption is explained by Langmuir theory. The BET theory assumes that a gas can form multiple layers on the surface of the solid during adsorption and the second and other layers are more weakly adsorbed than the first.
layer, whereas the Langmuir theory assumption is that adsorption occurs in one layer on the surface of the solid [18]. Through BET surface area measurements, it can be discovered if the polymer matrix is trapped inside the filler’s pores which could reduce the accessible pore volume.

Hydrogen adsorption measurements for porous materials require stringent experimental protocols and validation using extensive reproducibility studies to establish the accuracy. These measurements can be obtained using either direct gravimetric instruments of adsorption or indirect volumetric (or manometric) measurements using a Sievert apparatus [19]. The H₂ storage capacity is usually determined from hydrogen adsorption isotherms measured gravimetrically or volumetrically, where in both cases the pressure is increased incrementally and a plot of the adsorbed hydrogen quantity versus pressure is produced [20]. Gravimetric measurements are usually used up to ~ 20 bar whereas volumetric analysis can be performed up to 200 bar pressure although results have usually only been reported up to 100 bar [21]. The instruments used for volumetric measurements have a simpler design, which is cheaper to construct for high-pressure instruments. Hence, adsorption/desorption in volumetric instruments is driven by pressure differences which provides accurate adsorption/desorption kinetics whereas, the gravimetric measurements are carried out under isobaric conditions (constant chemical potential). However, in terms of maintenance both techniques require ultraclean high-vacuum systems with all metals seals with diaphragm and turbo pumps, which are evacuated to 10⁻¹⁰ bar to completely degas the sample. Moreover, a gas purification system is needed to remove trace impurities from hydrogen [21]. In the case of volumetric measurements ensuring that the sample is completely degassed is more difficult in comparison to gravimetric measurements wherein, the equilibrium degassed state for porous material is easily determined [22]. The hydrogen sorption measurements error issue is a great concern and it has been addressed in several studies. It has been emphasised that sufficient care and attention should be paid to factors such as; insufficient sample degassing before analysis, dead volume and buoyancy corrections [23], moisture contaminated H₂ supply [23-25] and wrong representation of the real gas behaviour of H₂ at high pressure [26-27]. Unfortunately, due to unavailability of the specialised equipment for volumetric measurements, only gravimetric measurements were carried out in the various sections of the current study.
In this study, both the N$_2$ and H$_2$ gases (ultra-high purity grade, (99.9990%)) sorption isotherms were measured using a Micromeritics accelerated surface area and porosimetry (ASAP) 2020 HD analyser at 77 K (Figure 3.7). Prior to the measurements, the samples (0.2–0.5 g) were transferred into a glass sample tubes capped with a seal frit (of known mass, cold and warm free space). Thereafter, these sample tubes were attached to the degassing port of the ASAP, where the samples were outgassed at elevated temperature (100–200 °C) under vacuum (down to 10$^{-7}$ bar) for at least 8 hours to remove any humidity and physisorbed gases. Subsequently, the data was modelled and analysed by the BET method for calculating surface areas from the N$_2$ sorption isotherms in the relative pressure ($p/p^o$) range of 0.01-0.14. Density functional theory (DFT) and Horvath-Kawazoe (H-K) methods were used for determining the pore size distribution curves and total pore volumes (from N$_2$ sorption isotherm at $p/p^o = 0.99$) with MicroActive software.

Additionally, other tests like energy-dispersive X-ray spectroscopy and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can be used to study the elemental analysis of the material and to check the dispersion of the dopant/modifier.
Elemental analysis can also be used to determine the exact formula of the porous material, but in the case of MOFs it can be difficult to interpret the data as there may still be solvent molecules inside the framework.
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CHAPTER 4: RESULTS AND DISCUSSION (I)

THE SYNTHESIS OF POLYMER-BASED METAL-ORGANIC FRAMEWORKS MONOLITHIC HYBRID COMPOSITES (PIM-1/MIL-101(Cr)) FOR HYDROGEN STORAGE APPLICATION


Summary Statement

This chapter discusses the results obtained when a polymer/MOF composite was prepared using PIM-1 as a binder for MIL-101(Cr) MOF powder. The chapter begins by interrogating the characteristics of pristine materials (PIM-1 and MIL-101(Cr)) and their respective composites. The resulting composites exhibited enhanced specific surface areas coupled with improved hydrogen uptake capacities with the highest MOF loading (80 wt %) showing the best properties.
Abstract

Herein, we report a simple method for the preparation of cross-linked polymer of intrinsic microporosity (PIM-1)/Materials Institute Lavoisier chromium (III) terephthalate (MIL-101(Cr)) monoliths which involves direct impregnation of PIM-1 with MIL-101(Cr) powder by physical mixing in tetrachloroethane solvent. This procedure yields monoliths with high metal organic framework (MOF) loading weight percentages of up to 80 wt % of MIL-101 powder with little loss of composite mechanical strength. From the nitrogen adsorption isotherms, it was observed that the PIM-1/80wt%MIL-101(Cr) had good retention of MOF filler surface area and accessibility of its micropores with nearly no pore blocking effects. The hydrogen adsorption was also not far from the estimated hydrogen uptake capacity based on the MIL-101 weight percentage estimation. As a consequence of the highly porous nature of the hybrid material, PIM-1/MIL-101(Cr) composite has been considered as a promising material for inclusion in hybrid hydrogen storage cylinders. Moreover, these composites provided better handling compared to the crystalline powder MOFs without compromising the properties of MOF.

Keywords: Polymer of intrinsic microporosity; MOF composites; hydrogen storage; adsorbents.

4.1. Introduction

The biggest technological challenge hindering the large scale applications and commercialisation of a sustainable hydrogen fuel, especially in mobile transportation, is due to the absence of efficient, reliable and safe hydrogen (H2) storage systems [1]. Besides conventional hydrogen liquefaction and highly pressurised hydrogen gas tanks storage methods, which are limited by very high energy consumption for achieving compressed gas or liquid H2, the physical adsorption of hydrogen on highly porous materials possessing high surface area is emerging as a potential solution for hydrogen storage [2]. Metal-organic frameworks (MOFs), zeolites, porous organic polymers, and various carbons have been thoroughly investigated as adsorbents for hydrogen storage applications [2, 3]. The new 2020 United States Department of Energy (US DOE) gravimetric and volumetric storage targets for H2 are 4.5 wt. % and 0.030 kg H2/ L, respectively [4]. These targets are particularly set for a system; that is, calculations of H2 storage capacity should include pressure containment, cooling systems, valves, etc. Therefore, the storage materials with gravimetric capacities
significantly greater than 4.5 wt % are required to achieve these targets. However, the previously mentioned materials are yet to meet all the US DOE 2020 targets set for hydrogen storage materials [2]. Furthermore, for intended practical applications these materials needs to be processed into mechanically stable and easy to handle structures due to the drawbacks associated with their powdery appearance [3, 5]. Therefore, this study aims at investigating novel methods and processes that incorporate powders into structures by producing monoliths of polymer/MOFs composites without adversely compromising the key intrinsic characteristics of the parent materials. To date, there are a very limited number of reports that describe composite materials that meet all the US DOE specified performance necessary for H₂ storage applications. Although powdered MOFs can be processed with various suitable binders, there are limitations in terms of H₂ storage applications; such as, most commercially available inorganic and polymeric binders do not adsorb H₂ and usually block certain pores of the MOF powder materials [5, 6]. One of the current advancements towards processing MOF powders includes their incorporation into polymer films and spheres [7-16]. For instance, Wickenheisser and co-workers fabricated a MOF composite material based on a polymerized resorcinol-formaldehyde xerogel in monolithic form for water adsorption applications [17]. In an extension of their study, they also showed that MOF monoliths can also be shaped by inclusion of Materials Institute Lavoisier chromium (III) terephthalate (MIL-101(Cr)) inside the macropores of poly(2-hydroxyethyl methacrylate) high internal phase emulsion (HIPE) foam. When the composite was tested for vapour adsorption applications, it showed higher water vapour and methanol uptake capacities compared to pristine HIPE [18].

Recently, it has also been shown that MOFs can be incorporated into three dimensional (3D) printed polymers [19]. However, in most cases these composites are fabricated as mixed matrix membranes for water and gas adsorption applications. The choice of the polymer used for composites fabrication is an extremely important aspect and preference is often given to materials which possess reasonable surface area and are able to adsorb hydrogen. This is done so that a polymer matrix does not compromise the hydrogen storage capacity or even other significant properties of the MOF filler material. One of the best porous polymers which exhibit desired properties are polymers of intrinsic microporosity (PIMs) [20-21]. Although PIMs have previously been applied in hydrogen storage as films, there is a need for development of easy and efficient methods for fabrication of free-standing porous MOF-based composites. In this study, monolithic MOF/polymeric composites were fabricated using the PIM-1 as a matrix for embedding MIL-101(Cr) MOF crystals. Different MOF
powder loadings ratios were investigated and the resulting composites were tested for hydrogen storage application.

4.2. Experimental

4.1.1. Materials and Chemicals

For the experiments, the following chemicals were used: formic acid (HCOOH, 99.5+%, Sigma-Aldrich), 1,1,2,2-tetrachloroethane (TCE, 98.0+%, Sigma-Aldrich), terephthalic acid (98%, Sigma-Aldrich), chromium chloride hexahydrate (CrCl$_3$.6H$_2$O, 99.5+%%, Sigma-Aldrich), tetrafluoroterephthalonitrile (C$_6$F$_4$-1,4-(CN)$_2$, 99%, Sigma Aldrich), 5,5’,6,6’-tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-spirobisindane (C$_{21}$H$_{24}$O$_4$, Sigma Aldrich), potassium carbonate (K$_2$CO$_3$), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), chloroform (CHCl$_3$) and de-ionized water. These chemicals were purchased and used without additional purification. Nitrogen (N$_2$) and hydrogen (99.999%) ultra-high purity grade gases were purchased from Afrox Company, South Africa.

4.1.2. Synthesis of MIL-101(Cr) MOF

MIL-101(Cr) MOF was synthesised following the previously described procedure with some minor modifications [22]. In a typical procedure, terephthalic acid (1.66 g) was dissolved in deionised water (45 mL) with the aid of ultra-sonication. Chromium chloride hexahydrate (2.66 g) was also dissolved separately in 55 mL of deionised water. Then a mixture of the two reactants was transferred to the 250 mL teflon-lined high-pressure autoclave reactor (Berghof, Germany). Formic acid (30.2 mL, 80 eq) was added to the resulting solution and the contents were heated to 210 °C and maintained at that same temperature for duration of 8 hours. After the 8 hours, the reaction was stopped and left to cool to room temperature. The obtained MOF precipitate was dissolved in DMF and the solution was heated to 80 °C under magnetic stirring and kept there for 3 h, followed by centrifugation. Then the recovered precipitate was further dissolved in ethanol and heated to 60 °C under magnetic stirring for 24 h. The final precipitate was collected by centrifugation and the obtained product was finally dried overnight at 90 °C in a conventional oven.
4.1.3. **Synthesis of PIM-1**

PIM-1 was synthesised according to the procedure reported by Budd et al. [23]. Briefly, a mixture of precursors; 5.11 g of 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane (15×10⁻³ mol), 16.59 g of anhydrous K₂CO₃ (120×10⁻³ mol) and 3.00 g of tetrafluoroterephthalonitrile (15×10⁻³ mol) were added into a 250-ml three-neck round-bottom flask fitted with a reflux condenser. Then the resulting synthesis mixture was purged and backfilled with nitrogen for 3 times, subsequently a 100 ml anhydrous DMF was added. Soon, a yellow precipitate appeared and the mixture was then subjected to vigorous stirring for 72 h at 65 °C under N₂. The resulting synthesis mixture was left to cool to room temperature. Thereafter, 300 ml of water was added to the mixture under stirring for another 1 hour. The raw solid product was collected by filtration and was dried at 80 °C under vacuum for 2 days. The raw PIM-1 solid was dissolved in 300 ml chloroform under magnetic stirring and once completely dissolved it was transferred into a separating funnel, which was fixed over a conical flask containing 800 ml methanol which was stirred vigorously. The polymer solution was slowly dripped into the stirred methanol to re-precipitate the PIM-1. Once all the polymer solution had dripped into the conical flask, the yellow precipitate was again vacuum filtered and dried at 80 °C under vacuum. This re-precipitation procedure was repeated up to three times. The final product was collected and dried under vacuum at 60 °C overnight.

4.1.4. **Ex-situ Synthesis of the PIM-1/MIL-101(Cr) Monolithic Composite Materials**

The direct impregnation of PIM-1 with MIL-101(Cr) powder by physical mixing in tetrachloroethane solvent can readily lead to cross-linked PIM-1/MIL-101(Cr) monolith bodies. This was achieved by preparing separate tetrachloroethane-based solutions of PIM-1 and suspension of various loadings of pre-dried MIL-101(Cr) powder (40, 60 and 80 wt %). The solutions were mixed with each other in a 20 ml cylindrical glass vial and further subjected to a vigorous magnetic stirring overnight to achieve a desired homogeneous mixture of PIM-1/MIL-101(Cr). The resulting viscous mixture was thereafter heated to 150 °C to evaporate the solvent and a monolith was obtained. PIM-1 has good solubility in tetrachloroethane such that it helped in forming a homogenous mixture with MIL-101 and readily produced monolithic gels.

The following formula was used to calculate the wt. % of MOF in PIM-1/MIL-101(Cr) composite:
\[ \text{wt} \% = \frac{M_{\text{MIL-101}}}{M_{\text{MIL-101}} + M_{\text{PIM-1}}} \times 100 \]

Where \( M_{\text{MIL-101}} \) and \( M_{\text{PIM-1}} \) represent the masses of MIL-101 and PIM-1 powders, respectively.

A summary of the procedure used for synthesis of pristine PIM-1 and MIL-101(Cr) together with the MOF composite is shown in Scheme 4.1 below.

**Scheme 4.1.** Schematic procedure to prepare molecular cross-linked PIM-1/MIL-101(Cr) monoliths.

**4.1.5. Sample Characterisation**

The powder X-ray diffractometer (PANalytical X’Pert Pro), coupled to a Pixcel detector (Cu-K\( \alpha \) radiation \( \lambda = 0.154 \) nm) was used to obtain powder X-ray diffraction (PXRD) patterns at scanning rate of 2 ° min\(^{-1}\). The samples were measured at room temperature. The morphological analysis of the obtained samples was conducted using focused ion beam scanning electron microscope (Carl Zeiss Auriga Cobra). TGA/SDTA 851\( ^e \) instrument (Mettler, Toledo) was used to carry out the thermogravimetric analysis (TGA), in a temperature range of 46-1000 °C and heating rate of 10 °C min\(^{-1}\) under air (60 ml min\(^{-1}\)) and nitrogen flow (40 ml min\(^{-1}\)) as a balance gas. The nitrogen and hydrogen sorption (up to 1 bar) measurements were obtained from a Micrometrics ASAP 2020 HD analyser at 77 K. The
specific surface areas by BET theory and pore size distributions (PSDs) were obtained from the nitrogen physisorption isotherms. Before any gas sorption experiment, the samples were outgassed in the degassing port under vacuum (down to $10^{-7}$ bar) for at least 8 h at 200 °C for removal of moisture or other volatile contaminants.

4.3. Results and Discussion

PXRD plots of PIM-1/MIL-101(Cr) composite materials (Figure 4.1a) demonstrate unchanged crystalline phase of as-synthesised MIL-101 (with all major characteristic peaks of MIL-101(Cr) at around $2\theta =$ 5.2, 8.5 and 9.1°) as earlier reported [21]. The broad peak observed for the PIM-1 sample depicts its amorphous nature. It could also be observed that as the quantity of MIL-101(Cr) filler was increased in the hybrid materials there was some corresponding increase in the intensity of the main characteristic peaks of the MOF. Simultaneously, there was reduction of the amorphous hump that was related to the PIM-1 material. The TGA curves (Figure 4.1b) of both pristine PIM-1 and MIL-101(Cr) materials compare well with previous reports [23,24], showing PIM-1 and MIL-101(Cr) to be stable up to ~430 °C and ~350 °C, respectively. The high thermal stability observed for PIM-1 is attributed to intense dipolar interactions of the cyano- (-C≡N) functional groups in the polymer chains [25]. The first continuous weight loss step (~150 - 200 °C) for the MOF and PIM-1/80wt%MIL-101(Cr) can be ascribed to the evaporation of DMF and water absorbed in the pores of the MOF. However, the observable difference at the lower temperatures (where PIM-1/80wt%MIL-101(Cr) suffered an excessive mass loss compared to MIL-101(Cr)) could possibly be due to evaporation of residual tetrachloroethane solvent. The mass loss observed at around 350–470 °C for the MIL-101(Cr) can be assigned to the disintegration of the MOF structure [22].
**Figure 4.1.** Stacked PXRD patterns (a) and TGA profiles (b) of PIM-1, MIL-101(Cr) and PIM-1/MIL-101(Cr) composites samples.

Scanning electron micrographs in **Figure 4.2(a-b)** show the porous nature of the PIM-1 sample and the octahedral shaped crystals for the MOF sample. Even though PIM-1 powder is a microporous material, the observed porosity in the macro scale together with the high roughness can be attributed to the evaporation of the solvent during the synthesis process. Polak-Krašna et al. [21] had also attributed the chaotic nature of the solvent evaporation process as the main responsible factor in the non-uniform distribution of the observed macropores. In the PIM-1/MOF composite samples (**Figure 4.2(c-e)**), the respective morphologies of pristine materials after the physical mixing was maintained. Furthermore, it was observed that most of MOF particles were well dispersed in PIM-1 matrix although some agglomeration had been observed at high 80 wt % MOF loading. The mechanical strength of the composite was observed to decrease as the MOF loading was increased. The samples with loading above 80 wt % of MIL-101 (Cr) were observed to crumble easily and for future experiments this will be avoided by adding a surface modifier to improve the compatibility between PIM-1 and the MIL-101(Cr).
Figure 4.2. High resolution scanning electron micrographs of pristine PIM-1(a) and MIL-101(Cr) (b) and respective MIL-101(Cr) embedded PIM-1 composite with various MIL-101(Cr) loadings of 40 wt % (c), 60 wt % (d) and 80 wt % (e) and pictures of pristine PIM-1 powder, MIL-101(Cr) powder and PIM-1/MIL-101(Cr) monolith (f).

The nitrogen sorption isotherms for PIM-1 and MIL-101(Cr) presented in Figure 4.3a share similar patterns with those previously reported, where PIM-1 isotherm revealed both Type I for microporosity and Type IV for mesoporosity indicating hierarchical porosity behaviour [26]. The presence of a relatively large hysteresis was also reported by Polak-Kraśna et al [21] and was attributed to occur either due to the presence of narrow pore channels or possible pore swelling. On the other hand, the N\textsubscript{2} sorption isotherms for MIL-101(Cr) and composites materials displayed Type IV behaviour with smaller hysteresis loop which indicates that samples were more microporous than mesoporous. This is corroborated by their pore size distribution curves based upon DFT model presented in Figure 4.3b and as well as the data shown in Table 4.1. From the DFT pore size distribution, the 40 and 60 wt % composites showed a broad multi-modal pore size distribution at 1.1, 1.7, 2.3 and 3.5 nm. Whereas for the 80 wt % composite, pore sizes displayed some narrow distribution almost similar to that of MIL-101(Cr) centered at 1.1 - 2.1 nm. In summary, the PSD curves confirmed the increasing micropore characteristics of composites as the MIL-101(Cr) content increased.
**Figure 4.3.** N$_2$ adsorption-desorption isotherms of pristine and composites materials at 77 K (a) and corresponding DFT pore size distribution (insert) of pristine MIL-101(Cr) MOF and their respective PIM-1 composites (b).

The surface area and total pore volume of hybrid materials were found to increase proportionally to the weight percent loading of MIL-101 as displayed in Table 4.1. However, the actual measured surface area of PIM-1/80wt%MIL-101(Cr) is slightly higher than estimated from a rule of mixtures calculations as shown in equation 4.1.

Surface area (composite) = $W_{PIM-1} \times surface\ area\ (PIM - 1) + W_{MIL-101} \times surface\ area\ (MIL - 101)$  
(Equation 4.1)

Wherein the property of a composite is a weighed mean of the characteristics of its individual components and where $W_{MIL-101}$ and $W_{PIM-1}$ are the weight fractions of MIL-101 and PIM-1, respectively such that; $W_{PIM-1} + W_{MIL-101} = 1$

It is noteworthy that the measured specific surface area of pristine PIM-1 increased from 784 to 2347 m$^2$ g$^{-1}$ upon preparation of the PIM-1/MOF composite, which represents a significant 3-fold increase. The anomaly observed in the measured versus predicted surface areas of PIM-1/80wt%MIL-101(Cr) can be due to the possibility of an increased external surface area.
which led to some exposed MOF crystal surface when the sample was almost saturated due to the high MOF loading. There is also a possibility that the earlier observed mesoporosity in the pristine powder PIM-1 (SEM images) due to reprecipitation had been eliminated and thus amplifying the intrinsic microporosity which interacted synergistically with the MOF physical properties. The inability to obtain complete N\textsubscript{2} desorption isotherms was due to the impractical long times that the samples took to achieve equilibration in the low-pressure ranges. Similar observations were also reported earlier \cite{21}.

**Table 4.1.** Physical properties of pristine and composites materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured BET SSA (m\textsuperscript{2} g\textsuperscript{-1})\textsuperscript{a}</th>
<th>Estimated BET SSA (m\textsuperscript{2} g\textsuperscript{-1})\textsuperscript{b}</th>
<th>Micropore area (m\textsuperscript{2} g\textsuperscript{-1})\textsuperscript{c}</th>
<th>Pore size (nm)\textsuperscript{d}</th>
<th>Total Pore vol. (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>H\textsubscript{2} uptake (wt. %)\textsuperscript{f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine MIL-101(Cr)</td>
<td>2720</td>
<td>-</td>
<td>2636</td>
<td>1.2 – 2.2</td>
<td>1.39</td>
<td>1.76</td>
</tr>
<tr>
<td>PIM-1/80wt%MIL-101(Cr)</td>
<td>2347</td>
<td>2333</td>
<td>2290</td>
<td>1.1 – 2.1</td>
<td>1.20</td>
<td>1.73</td>
</tr>
<tr>
<td>PIM-1/60wt%MIL-101(Cr)</td>
<td>1821</td>
<td>1946</td>
<td>1781</td>
<td>1.1 – 2.7</td>
<td>0.89</td>
<td>1.50</td>
</tr>
<tr>
<td>PIM-1/40wt%MIL-101(Cr)</td>
<td>1331</td>
<td>1558</td>
<td>1273</td>
<td>1.1 – 3.6</td>
<td>0.70</td>
<td>1.32</td>
</tr>
<tr>
<td>Pristine PIM-1</td>
<td>784</td>
<td>-</td>
<td>693</td>
<td>1.1 – 3.5</td>
<td>0.53</td>
<td>1.02</td>
</tr>
</tbody>
</table>

\textsuperscript{a}BET surface area measured from N\textsubscript{2} adsorption isotherms at 77K.\textsuperscript{,} \textsuperscript{b}BET surface area calculated as the sum of the mass-weighted surface areas of the MOF and PIM-1 from this formula:

\[
\text{BET (estimated)} = \frac{\text{wt\% of MIL-101}}{100} \times 2720 m^2 g^{-1} + \frac{\text{wt\% of PIM-1}}{100} \times 784 m^2 g^{-1}
\]

\textsuperscript{c}From t-plot, \textsuperscript{d}Pore size determined by DFT analysis, \textsuperscript{e}Total pore volume determined from H-K analysis by uptake at p/p\textsubscript{0}~0.99, \textsuperscript{f}Hydrogen adsorbed at 77 K and 1 bar.

The H\textsubscript{2} storage capacities (Figure 4.4) were observed to follow a similar trend to the specific surface areas, where the H\textsubscript{2} uptake increased from 1.02 wt % for pristine PIM-1 to 1.73 wt % in PIM-1/80wt%MIL-101(Cr). This was expected as the H\textsubscript{2} adsorption capacity and specific surface area are directly correlated \cite{3, 27}. Unlike other polymeric materials that have been used to shape MOFs \cite{6}, the use of PIM-1 clearly shows advantages due to the fact that the obtained hydrogen storage capacity for the PIM-1/MOF is almost similar to that of the MOF. Furthermore, the shaping of the MOF through composite formation with PIM-1 leads to better handling while simultaneously is retaining the MOF’s hydrogen storage capacity. Importantly, all the H\textsubscript{2} adsorption isotherms indicated a sharp rise at low pressure up to 1 bar.
without reaching a point of saturation (plateau). Consequently, higher hydrogen uptake would be expected at pressures higher than 1 bar [28].

![Graph of H₂ adsorption isotherms of pristine and composites materials at 77 K and 1 bar.](image)

**Figure 4.4.** H₂ adsorption isotherms of pristine and composites materials at 77 K and 1 bar.

### 4.4. Conclusion

We successfully fabricated self-standing PIM-1/MOF composite monoliths containing various loadings of MIL-101(Cr) filler. The obtained composites exhibited enhanced specific surface areas coupled with improved hydrogen uptake capacities with the highest MOF loading (80 wt %) showing the best properties. Based on the adaptation of the estimation formula used for calculating estimated BET surface area, the obtained H₂ uptake capacity of the composite derived from 40 wt % and 60 wt % loadings of MIL-101(Cr) was found to be close to the estimated values. However, for 80 wt % loading, a hydrogen uptake of 1.73 wt % was obtained which is 7.5 % higher than the estimated value (1.61 wt %). The use of PIM-1, as a binder, proved advantageous since it did not show any signs of MIL-101(Cr) micropore blockage. The work presented here contributes towards the ongoing efforts to improve the hydrogen storage conditions for future application in light-duty vehicles by demonstrating that MIL-101(Cr) can easily be embedded into PIM-1 for better handling while maintaining
its functionality. Future work will include mechanical strength experiments, high pressure H₂ uptake measurements, kinetics and heat of adsorption studies.

**Author contributions**

Lerato Y. Molefe contributed in carrying out experimental work and writing of the manuscript. Nicholas M. Musyoka and Patrick G. Ndungu supervised and reviewed the manuscript. Jianwei Ren, Henrietta W. Langmi, Robert Dawson and Mkhulu Mathe reviewed the manuscript and provided some comments.
4.5. References:


CHAPTER 5: RESULTS AND DISCUSSION (II)

POLYMER-BASED SHAPING STRATEGY FOR ZEOLITE TEMPLATED CARBONS (ZTC) AND THEIR METAL ORGANIC FRAMEWORK (MOF) COMPOSITES FOR IMPROVED HYDROGEN STORAGE PROPERTIES


Summary Statement

In this chapter, a different type of MOF which has better synthesis reproducibility and potential for up-scalability (UiO-66(Zr)) was used as a porous filler material in the synthesis of a MOF/polymer composite. The polymer identified in the previous study (PIM-1) was used as the binder. Additionally, a zeolite templated carbon (ZTC) was included in the composite with the intent to improve the thermal conductivity properties of the resulting ternary composite (PIM-1/UiO-66(Zr)/ZTC). The optimised filler loading (80 wt%) that had been obtained in the previous chapter was also used in this study. The findings from this study showed that the resulting composites still maintained their pristine textural properties (surface area, pore size distribution and pore volumes) and some exhibited enhanced H₂ uptake properties.
Abstract

Porous materials such as metal organic frameworks (MOFs), zeolite templated carbons (ZTC) and some porous polymers have endeared the research community for their attractiveness for hydrogen (H\textsubscript{2}) storage applications. This is due to their remarkable properties, which among others include high surface areas, high porosity, tunability and high thermal and chemical stability. However, despite their extraordinary properties, their lack of processability due to their inherent powdery nature presents a constraining factor for their full potential for applications in hydrogen storage systems. Additionally, the poor thermal conductivity in some of these materials also contributes to the limitations for their use in this type of application. Therefore, there is a need to develop strategies for producing functional porous composites that are easy-to-handle and with enhanced heat transfer properties while still retaining their high hydrogen adsorption capacities. Herein, we present a simple shaping approach for ZTCs and their MOFs composite using a polymer of intrinsic microporosity (PIM-1). The intrinsic characteristics of the individual porous materials are transferred to the resulting composites leading to improved processability without adversely altering their porous nature. The surface area and hydrogen uptake capacity for the obtained shaped composites were found to be within the range of 1054 – 2433 m\textsuperscript{2}g\textsuperscript{-1} and 1.22 - 1.87 H\textsubscript{2} wt. %, respectively at 1 bar and 77 K. In summary, the synergistic performance of the obtained materials is comparative to their powder counterparts with additional complementing properties.

Keywords: Hydrogen storage, physisorption, polymers of intrinsic microporosity, zeolite templated carbon, metal organic frameworks.

5.1. Introduction

The current state-of-the-art for hydrogen (H\textsubscript{2}) storage in fuel cell vehicles is compression at 700 bar of which the storage tank is heavy, expensive and can also cause safety problems. Typically, a type IV cylinder in a fuel cell vehicle can store ≥ 5 wt. % of H\textsubscript{2} at 700 bar and 20 °C [1]. Therefore, strategies for developing alternative effective and efficient methods for storing H\textsubscript{2} still remain a challenge. The proposed 2020 United States Department of Energy (DOE) targets for on-board H\textsubscript{2} storage systems (include valves, pressure containment, cooling systems, etc.) are 4.5 wt. % and 0.030 kg H\textsubscript{2}/L for gravimetric and volumetric storage respectively [2]. The tremendous research progress made in nanoporous materials for
hydrogen storage applications shows great promise. Materials with high surface areas such as metal organic frameworks, carbons and porous polymers can store hydrogen through physisorption at safer low pressures and possess good reversibility as well as fast kinetics [3]. Moreover, high gravimetric H₂ capacities up to 8.9 wt. % at 77 K and 30 bar on ACs [4] and a maximum total of 10 wt. % on NOTT-112 MOFs can be achieved at 77 K and 77 bar [5]. Whereas, at low pressures, maximum amounts of H₂ adsorbed on MOFs are slightly lower and have been reported to be around 2.5 wt. % [6] while carbons such as CA-4700 have 3.9 wt. % at 77 K and 1 bar [4]. However, volumetric capacities remain low at the same conditions [7]. Therefore, the properties of these adsorbents must be improved to achieve high gravimetric and volumetric capacities at both low and ambient temperatures to become practically viable for their inclusion into an on-board H₂ storage system. Furthermore, nanoporous materials need modifications in order to enhance other physical properties such as thermal conductivity that is required for fast heat dissipation and mechanical strength required for better handling. These additional properties are crucial in practical applications.

Metal organic frameworks (MOFs) are a class of crystalline and highly porous hybrid materials consisting of metallic ions and organic ligands [8]. The properties of MOFs can be tuned by using a variety of metal ions and organic linkers during synthesis [9]. Besides application in drug delivery, gas separation and catalysis, MOFs not only exhibit interesting properties for gas adsorption and storage but can also be used as sensors, among other applications [10-13]. In this study, the interest of zirconium-carboxylate Universitetet i Oslo (UiO-66(Zr)) MOF was due to its excellent mechanical, chemical, and thermal stabilities [14]. In addition to MOFs, conductive carbon nanostructured materials such as zeolite templated carbons (ZTCs) whose structure consists of a three-dimensional network of buckybowel-like nanographene [15] have emerged as attractive materials for H₂ storage applications due to their high surface area, high porosity, light weight and high thermal conductivity [16].

The synthesis of porous composites has emerged as an attractive strategy for enhancing the intrinsic properties of the individual materials. For instance, Musyoka et al. [17] investigated the in-situ compositing of the zirconium based UiO-66 MOF with reduced graphene oxide (rGO) and observed an increased surface area coupled with enhanced hydrogen uptake capacity for the rGO/Zr-MOF composite in comparison to pristine Zr-MOF. The mechanism of hydrogen adsorption in a carbon material was reported to be through dissociation and chemisorption of hydrogen on the carbon sites with isolated hydrogen atoms being easier to
diffuse on the carbon materials [18]. Particularly, composites of MOFs with carbon materials are of great interest because carbon materials have high thermal conductivity, which is beneficial for heat management during hydrogen cycling [19]. However, despite their enhanced hydrogen sorption behaviour, MOF/Carbon composites still have processing challenges. Hence recently, fabrication of various types of polymer-based carbon and MOF composites have been investigated and identified as an interesting strategy not only for improving the performance but also for shaping of these materials.

On the other hand, a highly processable polymer of intrinsic microporosity (PIM-1) is an attractive adsorbent material that is soluble in common solvents and it can be casted into mechanically stable structures [20]. However, most focus has been on improving the adsorptive properties of these materials for high uptake capacities and very little effort has been done on tailoring the materials for large scale applications properties. In a recent study by Tien-Binh et al. [21] defect-free mixed matrix membranes (MMM) made up of PIM-1 and UiO-66-NH₂ filler were prepared by in-situ chemical cross-linking of UiO-66-NH₂ with PIM-1 during polymer synthesis to improve the poor polymer-filler adhesion. It was reported that the in-situ chemical reaction between 1,4-dicyanotetrafluorobenzene monomer and amine groups of UiO-66(Zr) MOF led to direct grafting of PIM-1 onto the MOF surface and thus enhancing polymer-filler adhesion and gas separation performance (higher permeability and selectivity for all the gases tested).

There have been other studies on PIM-1/UiO-66 MMM [21-23] however their scope was limited to membranes for gas separation applications. Several other studies have also reported on other types of MOF/carbon composites such as MOF-5/expanded natural graphite (ENG) [24], MIL-101(Cr)/ZTC [25] and HKUST-1/graphene platelets [26]. Additionally, other MOF/polymer composites such as PIM-1/MIL-101 (Cr) [27], PIM-1/UiO-66 [22], PIM-1/UiO-66-NH₂ [21], PIM-1/UiO-66-CN [23] and Matrimid/UiO-66 MMMs [28] have been reported. However, no work has been done on composites materials consisting of the three pristine materials (carbon/polymer/MOF) for H₂ adsorption applications. In our previous work [29] we reported that upon increasing the MOF loading in PIM-1/MIL-101(Cr) composites, the surface area, pore volume and H₂ adsorption capacity increased significantly. Our findings showed that 80 wt% loading of MIL-101(Cr) onto PIM-1 exhibited enhanced H₂ uptake with no pore blocking effects. Hence, the optimised filler loading of 80 wt% was also chosen for the current study. However, the polymer/MOF composites still lacked thermal
conductivity. Therefore, it is on this basis that the current study presents the merging of physico-chemical properties of ZTC, PIM-1 and UiO-66(Zr) MOF into mouldable functional composites. In as much as all the three pristine materials can serve as individual H₂ adsorbents, ZTC in this case serves as the thermal conductivity enhancer whereas the PIM-1 also serves as the binder material.

5.2. Materials and Methods

5.2.1. Chemicals

In this study, the following chemicals were used: Potassium carbonate (K₂CO₃, Sigma-Aldrich, 99+%), N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%), 5,5’,6,6’-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, Sigma-Aldrich), 1,2,2-tetrachloroethane (TCE, Sigma-Aldrich, 98.0+%), 2,3,5,6 tetrafluoroterephthalonitrile (TFTPN, Sigma-Aldrich, 99%), 13X powder (Sigma-Aldrich, ~2 μm average particle size), furfuryl alcohol (FA, Sigma-Aldrich, 97%), hydrofluoric acid (HF, Ace chemicals, 97+%), hydrochloric acid (HCl, Ace chemicals, 37%), Anhydrous chloroform (CHCl₃, Sigma-Aldrich, 99.9+%), zirconium chloride (ZrCl₄, Sigma-Aldrich, 99.5+%), terephthalic acid (BDC, Sigma-Aldrich, 98%), formic acid (HCOOH, Sigma-Aldrich, 99.5+%), methanol (CH₃OH, Sigma-Aldrich, 99.9+%), ethanol (Ace chemicals, 90%) and de-ionized water were purchased and used without further purification. Hydrogen and nitrogen (N₂) gases of ultra-high purity grade purchased from Afrox Company, South Africa were used for sample analysis.

5.2.2. Experimental Procedure

5.2.2.1. Synthesis of ZTC

In this study, the synthesis of ZTC was prepared based on the previously reported two step procedure involving furfuryl alcohol impregnation of zeolite 13X followed by its chemical vapour deposition [25, 30]. In summary, zeolite 13X (24 g) was dried in the vacuum oven at 120 °C under vacuum for 12 h prior to its impregnation with 80 ml of furfuryl alcohol (FA) at room temperature. After subjecting the FA/zeolite mixture to magnetic stirring for 24 h, the mixture was filtered and washed with a few drops of ethanol to remove the excess furfuryl alcohol. Subsequently, the FA /zeolite mixture was placed in a high purity quartz crucible and transferred into an alumina ceramic tube furnace where it was polymerised at 80 °C for 24 h
under argon gas flow (100 mL min\(^{-1}\)). Thereafter, polymerisation was continued by heating the mixture at 150 °C for a further 8 h. The resulting hybrid was further heated up to 700 °C under an argon flow to allow stabilisation of the composite. After 3 h, still at 700 °C, the gas flow composition was switched to a mixture of ethylene/argon (10% ethylene in argon) and held for 3 h. The gas flow was switched back to argon only, while the temperature was being ramped up to 900 °C and carbonisation occurred for 3 h. Still under argon flow, the resulting product, referred to as zeolite/carbon composite was then cooled down to room temperature. The sample was washed in 10% aqueous solution of hydrofluoric acid for 24 h, followed by diluting the aqueous solution to 2 L with deionised water and filtered. The sample was further refluxed in 10% aqueous solution of hydrochloric acid for 24 h. Finally, the resulting carbonaceous materials called ZTC was collected by filtration and washed with 2L of deionised water and dried in a vacuum oven maintained at 120 °C and 40-50 mbar pressure for 12 h.

5.2.2.2. Synthesis of Uio-66(Zr)

The synthesis method for Uio-66(Zr) was as reported in a previous study [31] with some changes. In a typical procedure, 1.06 g of ZrCl\(_4\) and 0.68 g of BDC were dissolved in 50 mL of DMF and sonicated for 30 min. The resulting mixture along with 17.13 mL of formic acid was transferred into a 250 mL round bottom flask connected to a reflux system. Subsequently, the system was placed in an oil bath pre-heated at 120 °C and kept for 4 h. Finally, the obtained white precipitate was collected by centrifugation. Following centrifugation, the precipitate was dissolved in ethanol and heated at 60 °C under magnetic stirring for 24 h. Then the final precipitate was collected by centrifugation and was dried at 90 °C in a conventional oven.

5.2.2.3. Synthesis of PIM-1

PIM-1 was prepared through a double nucleophilic aromatic substitution reaction between two monomers (TTSBI and TFTPN) in the presence of anhydrous K\(_2\)CO\(_3\) catalyst as per typical procedure reported by Budd and co-workers [20]. In this case, a mixture of equimolar ratio amounts of TTSBI and TFTPN and a certain amount of anhydrous K\(_2\)CO\(_3\) catalyst (8 equivalent with respect to monomers) was evacuated and backfilled with nitrogen gas prior to dissolving in 100 ml of anhydrous DMF. The mixture was kept under nitrogen flow and heated to 65 °C under vigorous magnetic stirring. After 72 h, the resulting yellow precipitate
was cooled and dispersed in 300 ml of deionised water and stirring continued for 1 h. The obtained solid was collected by vacuum filtration followed by dissolving in chloroform and re-precipitated in methanol. The final product was dried at 80 ºC for 12 h in a vacuum oven.

5.2.2.4. Synthesis of PIM-1/UiO-66(Zr)/ZTC Composites

Different composite samples of PIM-1/80 wt% UiO-66(Zr), PIM-1/80 wt% ZTC and PIM-1/UiO-66(Zr)/ZTC (80 wt%) were prepared by physical mixing of pre-synthesised polymer and MOF/carbon powders using TCE solvent. The UiO-66(Zr) and ZTC powders were degassed at 200 ºC for 4 h prior to an experiment to remove any adsorbed solvent or water. In the case of PIM-1/80 wt% UiO-66(Zr), a procedure similar to the recently reported method for PIM-1/80 wt% MIL-101(Cr) composite [29] was followed but using a different type of MOF. By modifying the synthetic method for PIM-1/80 wt% UiO-66(Zr) through substitution of UiO-66(Zr) with ZTC, a black monolith with 80 wt% of ZTC and 20 wt% PIM-1 was obtained. On the other hand, the PIM-1/UiO-66(Zr)/ZTC (80 wt%) composite consisting of 20 wt% PIM-1, 40 wt% ZTC and 40 wt% UiO-66(Zr) in TCE solvent was prepared through the same solvent impregnation method. The resulting mixture was then heated at 150 ºC for 12 h to remove the residual solvent inside the monolith composite.

5.2.2.5. Sample Characterisation

The crystallinity analyses of the samples were conducted using the powder X-ray diffractometer (PANalytical X’Pert Pro), with a Pixcel detector (Cu-Kα radiation λ= 0.154 nm). The powder X-ray diffraction (PXRD) patterns were measured at scanning rate of 2 º min⁻¹ at room temperature. TGA/SDTA 851e instrument (Mettler, Toledo) was used for thermogravimetric analysis (TGA). The samples were heated at a heating rate of 10 ºC min⁻¹ from 46-1000 ºC. The analyses were carried out under air (60 mL min⁻¹) and nitrogen flow (40 mL min⁻¹) as a balance gas. All Fourier transform infra-red (FTIR) spectra were obtained using a Perkin-Elmer Spectrum 100 FTIR spectrometer, working in the range from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹ in attenuated total reflection (ATR) mode. Prior to each FTIR measurements, 8 scans of the background were collected. The morphology of the obtained samples was observed using the focused ion beam scanning electron microscope (Carl Zeiss Auriga Cobra). The nitrogen and hydrogen sorption (up to 1 bar) isotherms were obtained from a Micrometrics ASAP 2020 HD analyser at 77 K. The specific surface areas by BET theory were obtained from the nitrogen physisorption isotherms. Prior to the gas
sorption experiment, the samples were degassed in the degassing port under vacuum (down to $10^{-7}$ bar) at 200 °C for at least 8 h for removal of moisture or other volatile residues.

5.3. Results and Discussion

The PXRD pattern for the prepared UiO-66 (Zr) exhibited the main characteristic peaks which are consistent with the previous reported studies [31] and confirms the formation of pure crystalline MOF. The observed crystallinity complemented the respective SEM image (Figure 5.4d), showing highly defined octahedral shaped crystals with sharp edges as an attribute of the presence of 100 equivalent of modulator (formic acid) used during their synthesis. The ZTC sample showed a diffraction peak at 6.2° 2-theta similar to that of the zeolite 13X template, indicating a replication of zeolite 13X-type structural pore ordering in ZTC and also confirms the successful templating process [32, 33]. After incorporating the UiO-66 (Zr) and ZTC into the PIM-1 matrix to obtain PIM-1/80 wt% UiO-66(Zr) and PIM-1/80 wt% ZTC composites materials, the characteristics peaks of fillers were still present and dominant (as seen in Figure 5.1). Thus, indicating that the crystal structures of fillers were retained upon the crosslinking process between the polymer matrix and filler materials. As observed in Figure 5.1, the diffraction patterns of composite materials are dominated by strong diffraction peaks resulting from UiO-66(Zr) and ZTC respectively, coupled with some amorphous character associated with the presence of PIM-1, which is not prominent because of its low weight percentages (20 wt%). On the other hand, for PIM-1/UiO-66(Zr)/ZTC (80 wt%), the characteristic peaks of UiO-66(Zr) are dominant and clearly observed compared to those of ZTC and the amorphous nature of PIM-1, and the crystal phase structure of UiO-66(Zr) is still maintained.
To further investigate the properties of the obtained composites, the thermal behaviour of all the pristine and composites materials was investigated. As depicted in the TGA curves (Figure 5.2), the thermal stability was found to follow the order of ZTC>PIM-1/80 wt% ZTC> UiO-66(Zr)> PIM-1/80 wt% UiO-66(Zr)> PIM-1>PIM-1/UiO-66(Zr)/ZTC (80 wt%). Even though the incorporation of ZTC led to the improvement of thermal stability of PIM/80 wt% ZTC composite, it was interesting to note that the inclusion of UiO-66(Zr) in the composite containing the 3 filler materials (PIM-1/UiO-66(Zr)/ZTC (80 wt%)) had a lower thermal stability but still within the attractive ranges for most porous materials. In general, the thermal stability of PIM-1 (up to 415 °C) is known to be due to the presence of strong interactions of the nitrile groups [34]. On the other hand, UiO-66(Zr) weight loss at temperatures below 150 °C is often ascribed to the evaporation of adsorbed solvent and/or water molecules. The additional weight loss appearing in the range of 150 to 362 °C is attributed to the dehydroxylation of Zr<sub>6</sub> clusters before the commencement of the final weight loss starting from 475 °C until the MOFs finally degrades to ZrO<sub>2</sub>. This trend in weight loss is observed in all the MOF-containing composites synthesized in this study.

**Figure 5.1.** Stacked PXRD patterns of PIM-1, ZTC, UiO-66 (Zr) and their corresponding composites samples.
Figure 5.2. TGA thermograms of PIM-1, UiO-66 (Zr), ZTC and their corresponding composites samples.

Fourier transform infra-red spectroscopy was used for probing and confirming the chemical composition of the resulting composites and the cross-linking between the PIM-1 matrix and the filler materials (ZTC and UiO-66(Zr)). In Figure 5.3, the FTIR spectrum of pristine PIM-1 displays the C=O stretch (1213-1250 cm\(^{-1}\)) \[35\], and the characteristic nitrile (–C≡N) stretch (around 2229 cm\(^{-1}\)) \[36\]. The intense peak around 1446 cm\(^{-1}\) is due to C=C stretch vibrations and the other peaks observed at 1105-1015 cm\(^{-1}\) can be assigned to C-C stretching vibrations. On the other hand, the IR spectrum of pristine UiO-66(Zr) showed characteristic vibration peaks of the benzene ring at 1510 and 1403 cm\(^{-1}\) which agrees with reported literature data \[37\]. The intense doublet peaks at 1657 and 1581 cm\(^{-1}\) could be attributed to the in- and out-of-phase stretching modes of the carboxylate groups that are present in the terephthalic acid linker \[38\]. The peaks at around 811, 748 and 658 cm\(^{-1}\) corresponds to the O-H and the out of plane bending of the C-H group of the benzene ring of the BDC ligand \[39\].

A strong broad peak observed in the range of 3300-3500 cm\(^{-1}\) is attributed to the presence of hydroxyl groups from moisture adsorbed onto the surface of UiO-66 and composite materials. According to Nishihiara et al. \[15\], the idealised molecular structure of ZTC has edge sites of the buckybowl units containing different types of functional groups and a
significant amount of oxygen. In this case, spectra of the pristine ZTC and PIM-1/80 wt% ZTC composite (Figure 5.3 insert) showed a peak at around 1720 cm\(^{-1}\) which can be ascribed to a C=O stretching mode and a distinct band at 1600 cm\(^{-1}\) is assigned to the presence of carbonyl groups. The weak broad band in the ranges of 1000–1400 cm\(^{-1}\) for the ZTC sample was also observed by Nishihara et al. [15] and can be attributed to a C-O stretch. At the high carbonisation temperature of 900 °C, during chemical vapour decomposition process, phenolic OH groups are completely decomposed and hence leads to the absence of the typical broad band in the range of 3200-3400 cm\(^{-1}\) in the pristine ZTC [40]. On the other hand, the effect of PIM-1 on the composites (PIM-1/80 wt% UiO-66(Zr) and PIM-1/UiO-66(Zr)/ZTC (80 wt%)) was found to be minimal and the expected PIM-1 peaks were masked by the prominence of UiO-66(Zr) peaks. However, in PIM-1/80 wt% ZTC composite all of the PIM-1 peaks were clearly observed. Due to the absence of new peaks in the resulting PIM-1/MOF/ZTC composite, it was inconclusive to confirm whether there was cross-linking that occurred between the polymeric binder and filler materials.

Figure 5.3. FTIR spectra of UiO-66(Zr), PIM-1/80 wt% UiO-66(Zr), PIM-1/UiO-66(Zr)/ZTC (80 wt%) in comparison with pristine PIM-1 and an insert showing the ZTC and PIM-1/80 wt% ZTC spectra.
The SEM images of both parent zeolite and resulting ZTC neat materials (as seen in Figure 5.4(a-c)) clearly show almost similar octahedral pyramidal morphologies as earlier reported by Musyoka et al. [25, 41]. The octahedral shaped crystal morphology for the UiO-66(Zr) was also observed and is consistent with the previous reports [31]. On the other hand, SEM images for composites materials confirm that the ZTC and UiO-66(Zr) are well dispersed and embedded in the PIM-1 matrix phase. In Figure 5.4f, the dominating MOF and ZTC particles are seen closely attached together by PIM-1, indicating a good distribution of filler materials on the matrix as earlier reported [22]. Furthermore, the SEM images of the three composites do not show a sieve-in-a-cage morphology which is a characteristic for poor surface adhesion of filler particles to PIM-1. Thus, dissolving PIM-1 in TCE solvent leads to fluoride chain-ends of PIM-1 interacting with the hydroxyl functional groups of the BDC linker on the surface of UiO-66(Zr) MOF and this prevents the polymer from blocking the MOF pores [42].

Figure 5.4. High resolution SEM images (mag. 20000×) of zeolite 13X (a), ZTC (b), PIM-1/80 wt% ZTC (c), UiO-66(Zr) (d), PIM-1/80 wt%UiO-66(Zr) (e) and PIM-1.UiO-66(Zr)/ZTC (80wt%) (f).

Figure 5.5 presents the N₂ adsorption-desorption isotherms of the pristine PIM-1, powder fillers and the resulting composite materials measured at 77 K. The nitrogen sorption isotherms of ZTC and UiO-66 (Zr) show a steep/linear adsorption rise at low pressure ranges (0.0- 0.1), indicating their microporous nature. The same type I isotherm with microporous characteristics was maintained after the inclusion of PIM-1 and this is in agreement with
SEM and PXRD results, wherein neither the morphology nor the crystal structure of MOF was destroyed. PIM-1 and PIM-1/80 wt% UiO-66(Zr) exhibited a type I isotherm coupled with type IV isotherm behaviour, indicating the presence of both micropores and mesopores.

Figure 5.5. N₂ sorption isotherms of pristine and composites materials at 77 K.

The surface area of PIM-1 increased significantly from 785 m²g⁻¹ to 1767 m²g⁻¹ and to 2433 m²g⁻¹ upon addition of 40 wt% UiO-66 (Zr)/40 wt% ZTC mixture and 80 wt% ZTC fillers respectively, which is equivalent to a three-fold increase as shown in Table 5.1. On the contrary, PIM-1/80 wt% UiO-66(Zr) exhibited a slight increase which is a < 2 fold increase. In most studies, MOF-polymer composites can only achieve about 60% of the expected BET values due to pronounced pore blocking effects as was reported by other researchers such as found for MIL-101(Cr)@NIPAM [43], HKUST@HIPE [44] and UiO-66@polyurethane [45]. Whereas our composites have reached over 80% of the estimated surface areas with the exception of the PIM-1/80 wt% UiO-66(Zr) sample which achieved 62.8% suggesting that there are reduced pore blocking effects in ZTC containing samples. This can be attributed to ZTC’s high level of stability towards PIM-1 disturbance, whereby it was seen that the ZTC-
based composites retained most of its physical properties as compared to PIM-1/80 wt% UiO-66(Zr). Similar observations were reported in a recent study for PIM-1/MIL-101 MOF and PIM-1/AX21 activated carbon [40], wherein the activated carbon-based composites materials showed enhanced physical properties and better H₂ storage properties at both 0.1 MPa and 10 MPa adsorption measurements.

**Table 5.1.** Summary of the physical properties of pure materials and their respective composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th><strong>Measure BET SSA (m² g⁻¹)⁸</strong></th>
<th><strong>Estimate BET SSA (m² g⁻¹)⁹</strong></th>
<th><strong>Micropore area (m² g⁻¹)⁸</strong></th>
<th><strong>Total Pore vol. (cm³ g⁻¹)⁹</strong></th>
<th><strong>Measured H₂ uptake (wt. %)⁹</strong></th>
<th><strong>Estimated H₂ uptake (wt. %)⁹</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine ZTC</td>
<td>3206</td>
<td>-</td>
<td>3004</td>
<td>1.54</td>
<td>2.38</td>
<td>-</td>
</tr>
<tr>
<td>PIM-1/80 wt% ZTC</td>
<td>2433</td>
<td>2722</td>
<td>2262</td>
<td>1.18</td>
<td>1.87</td>
<td>2.11</td>
</tr>
<tr>
<td>PIM-1/UiO-66(Zr)/ZTC (80 wt%)</td>
<td>1767</td>
<td>2200</td>
<td>1668</td>
<td>0.83</td>
<td>1.65</td>
<td>1.70</td>
</tr>
<tr>
<td>Pristine UiO-66(Zr)</td>
<td>1903</td>
<td>-</td>
<td>1882</td>
<td>0.75</td>
<td>1.36</td>
<td>-</td>
</tr>
<tr>
<td>PIM-1/80 wt% UiO-66(Zr)</td>
<td>1054</td>
<td>1679</td>
<td>1014</td>
<td>0.48</td>
<td>1.22</td>
<td>1.29</td>
</tr>
<tr>
<td>Pristine PIM-1</td>
<td>785</td>
<td>-</td>
<td>707</td>
<td>0.54</td>
<td>1.02</td>
<td>-</td>
</tr>
</tbody>
</table>

⁸BET surface area measured from N₂ adsorption isotherms at 77 K. ⁹BET surface area calculated as the sum of the mass-weighted surface areas of the MOF/ZTC (fillers) and PIM-1 (matrix) from this formula:

\[
\text{BET (estimated)} = \frac{\text{wt}\% \text{ of filler}}{100} \times \text{BET}_{\text{filler}} \times m^2 g^{-1} + \frac{\text{wt}\% \text{ of matrix}}{100} \times \text{BET}_{\text{matrix}} \times m^2 g^{-1}
\]

\[c\] From t-plot, \[d\] Total pore volume determined from H-K analysis by uptake at p/p° ~0.99, \[e\] Hydrogen adsorbed at 77 K and 1 bar, \[f\] The estimated H₂ uptake calculated as the sum of the mass-weighted H₂ adsorption capacity of the MOF/ZTC (fillers) and PIM-1 (matrix) from this formula:

\[
\text{H₂ uptake (estimated)} = \frac{\text{wt}\% \text{ of filler}}{100} \times \text{H₂ uptake}_{\text{filler}} \text{ wt.\%} + \frac{\text{wt}\% \text{ of matrix}}{100} \times \text{H₂ uptake}_{\text{matrix}} \text{ wt.\%}
\]

The hydrogen adsorption curves of PIM-1/80 wt% ZTC, PIM-1/UiO-66(Zr)/ZTC (80 wt%) and PIM-1/80 wt% UiO-66(Zr) presented in **Figure 5.6** showed a slight decrease (≤ 11% loss) in H₂ uptake which is still at acceptable high capacity values (1.87, 1.65 and 1.22 wt. % respectively) and comparable to the estimated values (2.11, 1.70 and 1.29 wt. % respectively). The relatively high H₂ uptake can be attributed to the resulting high surface area and microporous network resulting when micropores of PIM-1 interconnect with the inner pores of UiO-66 (Zr) and ZTC forming an inter-connected micropore network.
Figure 5.6. $H_2$ adsorption isotherms of pristine PIM-1, UiO-66 (Zr), ZTC and their corresponding composites materials at 77 K and 1 bar.

The studies shown in Table 5.2 are not the only ones where PIM-1 was considered as polymer matrix in carbon and MOFs composites. A wide range of PIM-1 based composites have been reported for other applications, mostly in MMMs for gas separation applications. Some examples include a combination of PIM-1 with fillers such as GO [48], carbon nanotubes [49], MOF-74 [42], ZIF-67 [50], ZIF-8 [51], and COFs [52] MMMs. It is only recently, that there seems to be a growing interest of PIM-1 composites fabrication towards $H_2$ storage applications. Our MOF composites exhibited $H_2$ uptake values which are within the same range as reported in the literature. Table 5.2 demonstrates that the $H_2$ uptake for all composites materials increased with the loading amount of fillers and it correlates well with the BET surface areas of all samples. Another observation common in all composites, is that their $H_2$ uptake capacities are equal to the pristine materials or in some cases (PIM-1/MIL-101(Cr) (80 wt%) [29] and PIM-1/PAF (37.5 wt%) [47] found to exceed the expected values.
which signify good retention of intrinsic properties of the fillers. Nonetheless, just like many other previously reported materials, our composites are also yet to meet all the United States Department of Energy (DOE) 2020 targets set for on-board automobile hydrogen storage systems [53].

**Table 5.2.** Comparison of N\(_2\) and H\(_2\) sorption data of PIM-1 based composites materials from literature.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Measured BET surface area (m(^2) g(^{-1}))</th>
<th>Experimental H(_2) uptake (wt. %) at 77 K and 1 bar.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1/MIL-101(Cr) (80 wt%)-Monoliths</td>
<td>2333</td>
<td>1.73</td>
<td>[29]</td>
</tr>
<tr>
<td>PIM-1/AX21 (60 wt%)</td>
<td>2075</td>
<td>1.90</td>
<td>[46]</td>
</tr>
<tr>
<td>PIM-1/MIL-101 (40 wt%)-Films</td>
<td>1580</td>
<td>1.11</td>
<td>[46]</td>
</tr>
<tr>
<td>PIM-1/PAF-1 (37.5 wt%)</td>
<td>1639</td>
<td>1.15</td>
<td>[47]</td>
</tr>
<tr>
<td>PIM-1/80 wt% UiO-66(Zr)</td>
<td>1054</td>
<td>1.22</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/80 wt% ZTC</td>
<td>2433</td>
<td>1.87</td>
<td>This work</td>
</tr>
<tr>
<td>PIM-1/UiO-66(Zr)/ZTC (80 wt%)</td>
<td>1767</td>
<td>1.65</td>
<td>This work</td>
</tr>
</tbody>
</table>

**5.4. Conclusion**

In summary, the PIM-1 based composites consisting of a UiO-66(Zr), ZTC, and UiO-66(Zr)/ZTC mixture were successfully fabricated. Our results showed that after compositing, the obtained monoliths still maintained their meso-microporosity and other favourable H\(_2\) uptake properties. All the composites materials showed better hydrogen storage performances which are in agreement with the predicted values with negligible loss of < 12%. The results also suggest that the ZTC-based composites materials (BET surface areas 1767 m\(^2\) g\(^{-1}\) - 2433 m\(^2\) g\(^{-1}\)) were more stable and managed to retain most of the pristine ZTC intrinsic properties, with less pore blocking effects when compared to the MOF based materials (BET surface area 1054 m\(^2\) g\(^{-1}\)). It was found that the interactions between UiO-66(Zr) and the PIM-1 matrix were more physical rather than chemical in nature since no bond formation was observed. This study presented an easy-to-fabricate PIM-1/80 wt% ZTC, PIM-1/UiO-66(Zr)/ZTC (80 wt%) composites that had not been reported before. However, these composites materials still need further modifications to improve their H\(_2\) uptake capacities as
gravimetric capacities significantly greater than 4.5 wt. \% are required to achieve the set DOE targets, at pressures slightly higher than 1 bar. Future work will focus on thermal conductivity measurements of the composites and to compare the data to other closely similar materials.

Author contributions

LY was responsible for synthesis, characterisation of samples and drafting of the manuscript. NM and PG supervised and reviewed the work. HW and MM reviewed the final manuscript.
5.5. References:


CHAPTER 6: RESULTS AND DISCUSSION (III)

EFFECT OF INCLUSION OF MOF-POLYMER COMPOSITE ONTO A CARBON FOAM MATERIAL FOR HYDROGEN STORAGE APPLICATION


Summary Statement

The objective of this study was to use carbon foam as a support for UiO-66 MOF powder using PIM-1 as a binder. This chapter also presents a discussion of the structural, textural and H\textsubscript{2} adsorption results acquired from the immobilization of the MOF-polymer. In addition to the improved processability, the effect of carbon foam on the thermal conductivity of the MOF-polymer composite was further investigated.
Abstract

Despite the extensive studies done on the remarkable characteristics of metal organic frameworks (MOFs) for gas storage applications, several issues still preclude their widespread commercial light weight applications. In most cases, MOF materials are produced in powder form and there is always a need to find ways of shaping them to attain application-specific properties. Fabrication of MOF-polymer composites is considered an attractive approach for shaping MOF powders. In most cases, the final hybrid material retains the intrinsic adsorbing properties of the pristine MOF coupled with other interesting synergistic properties which are superior to their pristine counterparts. In this regard, use of porous polymers of intrinsic microporosity (such as PIM-1) has proved to be of interest. However, most of these polymers lack some other important properties such as conductivity which is of paramount importance in a hydrogen storage system. It is on this basis that our study aimed at direct anchoring of a PIM-1/MOF viscous solution onto a carbon foam (CF) substrate. Unlike the in-situ MOF crystallization approach under optimized solvothermal reaction conditions; the obtained composite materials from an ex-situ route was shown to exhibit better MOF anchoring and mechanical stability for the PIM-1/Universitetet i Oslo zirconium-carboxylate (UiO-66(Zr)) composite. The effects of CF inclusion in PIM-1/Uio-66(Zr) and on related thermal properties (thermal conductivity, thermal diffusivity and volumetric heat capacity) of UiO-66(Zr) were also investigated. Among other properties, the presence of micro- and mesoporosity together with enhanced surface areas endowed the resulting composite foam with characteristics that are attractive for enhanced hydrogen storage applications.

Keywords: Carbon foam, hydrogen storage, metal organic frameworks, polymers of intrinsic microporosity

6.1. Introduction

The harmful gaseous and particulate emissions from the combustion of fossil fuels has led to global warming and poor air quality which have detrimental effects on the environment and human health. Therefore, in order to address this challenge, there is a need to develop and embrace alternative low emission, cost effective and efficient energy technologies. Over the recent past, there has been a growing interest in the use of hydrogen (H\textsubscript{2}) as the future energy carrier. Hydrogen is considered a viable alternative fuel due to its abundant sources and clean combustion in which only water is released as a by-product [1]. However, H\textsubscript{2} gas has very
low volumetric energy density, making compression at very high pressures (~ 700 bar) difficult. In this regard, on-board storage of hydrogen gas presents the main obstacle for applications of H\textsubscript{2} fuel in automobiles. Research in this area is mainly driven by the proposed criteria set by United States Department of Energy (U.S DOE) for an on-board H\textsubscript{2} storage system for the year 2020, where the required volumetric and gravimetric storage capacities are set at 0.030 kg H\textsubscript{2}/L and 4.5 wt.% respectively [2] Unfortunately, at the moment, none of the current H\textsubscript{2} storage technologies have met the aforementioned U.S DOE specifications.

Nanoporous sorbent materials such as Metal organic frameworks (MOFs), zeolites, carbon and porous polymers play a significant role in industrial applications such as catalysis, gas storage and separation membranes [3-6]. Amongst these materials, MOFs exhibit attractive properties which are excellent for their application in H\textsubscript{2} storage. For instance, MOFs possessing surface areas exceeding 6000 m\textsuperscript{2}g\textsuperscript{-1} such that MOF-210 [7] and NU-100 [8] have been found to be excellent for H\textsubscript{2} storage. However, since MOFs crystals are obtained as fine powders, they suffer from poor processability and low thermal conductivity. To address these drawbacks, various types of carbon-based MOF composites including carbons such as graphene, carbon nanotubes, and templated carbons have also been investigated as H\textsubscript{2} storage materials owing to their electrical and thermal conductivity, flexibility and chemical and mechanical stability properties [5-8].

Fabrication of MOF-Carbon composites have been proposed and attempted to overcome conductivity limitations, but the issue of structural integrity still remains a challenge [13-15]. Conversely, thermoplastic additives such as polystyrene, acrylonitrile butadiene styrene, polymethyl methacrylate and many others have been used as binding agents for processing of MOF powders, but this is often associated with pore blocking effects which results in reduced MOF surface areas [16]. However, the processable polymer of intrinsic microporosity (PIM-1) with surface area ~700 m\textsuperscript{2}g\textsuperscript{-1} has been investigated for H\textsubscript{2} storage and its use as a MIL-101(Cr) binder was reported to exhibit a high surface area (2347 m\textsuperscript{2}g\textsuperscript{-1}) and H\textsubscript{2} uptake (1.73 wt.%) at 77 K and 1 bar, thus showing great promise in H\textsubscript{2} storage [17]. Carbon foam (CF) is a three-dimensional material consisting of interconnected macropores forming an open cell structure [18]. Due to its very attractive properties such as a 3D hierarchical porous structure, light weight and other aforementioned properties characteristic for carbons, it has been widely applied in catalysis, carbon monoxide and carbon dioxide gas adsorption and thermal storage [19-21]. Thus, CF can be used as a solid support for immobilizing MOFs.
In a previous study by Pinto and co-workers [22], attempts were made to support Universitetet i Oslo zirconium-carboxylate (UiO-66(Zr)) MOF crystals on polyurethane foam (PUF) but this did not completely solve the conductivity issue of MOFs because polyurethane is an insulator. Moreover, their in-situ approach resulted in slightly altered PUF composites structures. Nonetheless, the composites only retained about 55–60% of the initial surface area and microporous volume. Whilst the direct growth of a MOF onto a macroporous template is more common than the ex-situ immobilisation approach, a study by Ren and co-workers [23], employed a macroporous nickel foam from which multi-layers of MIL-101(Cr) powder were spray coated onto it. Composites with a maximum loading of 81 wt% of MIL-101(Cr) were obtained and found to exhibit a H₂ uptake capacity of 1.5 wt.% at 77 K and 1 bar. This study demonstrated a facile method for processing MOF powders for practical applications in H₂ storage systems, but the thermal conductivity studies were not reported. Hence, in this study, we explore a similar approach of the immobilization of PIM-1/UiO-66(Zr) on a conductive carbon foam (CF) through ex-situ inclusion of UiO-66(Zr) and PIM-1 inside the macropores of the CF. The chemically stable UiO-66 MOF was chosen in this study because it is one of the mostly studied MOFs and the structure is well-known. Furthermore, it has a high surface area, is robust and its hydro-stability makes it a highly competitive MOF in hydrogen storage applications.

In this context, the effect of inclusion of CF in polymer-based MOF composites on its physical properties was investigated for hydrogen storage. This novel hierarchical porous material possessed synergistic properties brought about by the increased amount of micromeso pores inside the macropores of CF. The inclusion of PIM-1/UiO-66(Zr) in CF not only increased the specific surface area and H₂ uptake of the CF but also allowed for the assembly of a mechanically robust composite material.

6.2. Experimental Section

6.2.1. Materials and Chemicals

Porous materials presented in this study were prepared using the following chemicals and were used as-received without further purification: terephthalic acid (BDC, 98%, Sigma-Aldrich), dimethylformamide (DMF, 99.8%, Sigma-Aldrich), formic acid (HCOOH, 99.5+% Sigma-Aldrich), ethanol (CH₃CH₂OH, 90%, Ace chemicals), potassium carbonate (K₂CO₃, 99+, Sigma-Aldrich), zirconium tetrachloride (ZrCl₄, 99.5+, Sigma-Aldrich), and polyurethane foam (PUF).
5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, Sigma-Aldrich), tertrafluoroterephthalonitrile (TFTPN, 99%, Sigma-Aldrich), anhydrous chloroform (CHCl₃, 99.9+%, Sigma-Aldrich), methanol (CH₃OH, 99.9+%, Sigma-Aldrich), 1,1,2,2-tetrachloroethane (CHCl₂CHCl₂, 98.0+%, Sigma-Aldrich), de-ionized water and activated carbon-based foam (CF). Nitrogen (N₂) and Hydrogen (H₂) gases of ultra-high purity grade, purchased from Afrox Company in South Africa, were used for sample analyses.

6.2.2. **PIM-I Synthesis**

The synthesis of PIM-1 was carried out according to the method reported by Budd et al. [24]. Briefly, a mixture consisting of an equimolar composition of 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane (5.11 g) and tertrafluoroterephthalonitrile (3.00 g) in the presence of anhydrous K₂CO₃ (16.59 g) catalyst was transferred into a 250 mL three-neck round-bottom flask. The mixture was then evacuated and back filled with nitrogen gas and anhydrous DMF (100 mL) was subsequently added. The resulting solution mixture was heated under reflux conditions at 65 °C, under N₂ gas and constant vigorous magnetic stirring for 72 h. The recovered yellow precipitate was cooled down to room temperature and added to 300 mL of water while stirring for an hour without heat. The resulting solid was vacuum filtered, dried at 80 °C under vacuum and then dissolved in anhydrous chloroform before re-precipitation in methanol. The re-precipitation cycles were repeated for three times and the final product collected by filtration was dried at 60 °C for two days in a vacuum oven. The simplified synthesis method is also presented in **Figure 6.1**.

6.2.3. **Synthesis of UiO-66(Zr)**

UiO-66(Zr) MOF crystals were synthesized following an optimised solvothermal synthesis method reported elsewhere [25] but with some minor amendments. Briefly, the method involved the mixing of 1.06 g (4.54 mmol) of zirconium tetrachloride, 0.68 g (4.09 mmol) of terephthalic acid in 50 mL of DMF. The resulting solution was ultrasonicated for 30 minutes and 17.2 mL (0.454 mol) of formic acid modulator was subsequently added to the mixture. The resulting mixture was then transferred into a 250 mL round bottom flask that had been fitted with a reflux system, placed in a hot oil bath and then heated to 120 °C. The reaction mixture was kept at this temperature for 4 h, under static conditions. After the reaction, the resulting white precipitate product was collected by centrifugation at 10000 rpm for 15 minutes. To remove the unreacted BDC reagent, the precipitate was further washed with
ethanol at 60 °C under stirring for 3 h and subjected to another cycle of centrifugation. Finally, the MOF crystals were dried at 90 °C in a conventional drying oven for 12 hours. The schematic illustration of the synthesis procedure is also presented in Figure 6.1 below.

6.2.4. Fabrication of Carbon Foam Immobilised PIM-1/UiO-66(Zr) Composite Structure

Unlike in the context of PUF/UiO-66(Zr) study [22], the carbon foam (CF) could not withstand the solvothermal conditions for UiO-66(Zr) synthesis due to the chemical instability of CF in acidic media at high temperatures. Additionally, when MOF powder was dusted onto the CF, it was found to be still loose and fell off easily from the foam. Therefore, the direct impregnation of the CF with PIM-1/UiO-66(Zr) solution mixture was found to be a viable route for retaining the structure of CF. In addition, the processability of PIM-1 made the binding and immobilization of the MOF onto CF relatively easy. A solvent impregnation method was used, and in this case small cubic shaped pieces of treated CF substrate (washed, sonicated in deionized water and dried in a vacuum oven maintained at 50 °C and 40-50 mbar pressure for 12 hours) were immersed in a mixture of PIM-1/UiO-66(Zr) in tetrachloroethane (TCE) solvent. The foam was left to soak in the mixture for 12 hours to ensure maximum infiltration of PIM-1/UiO-66(Zr) into the macro-pores of the CF. Subsequently; the CF/PIM-1/UiO-66(Zr) composite sample was heated on a heating plate at 150 °C, for 12 hours to evaporate the trapped TCE solvent.
Figure 6.1. Schematic representation of the chemical reactions for the synthesis of the pristine UiO-66(Zr) MOF and PIM-1 materials.

6.2.5. Sample Characterisation

Powder X-ray diffraction (PXRD) patterns were obtained at room temperature using a PANalytical X’Pert Pro powder diffractometer, coupled to a Pixel detector with Cu-Kα radiation (0.154 nm) and scanning rate of 2° min⁻¹. Carl Zeiss Auriga Cobra Focused ion beam scanning electron microscope (FIB-SEM) was used for morphological analysis of samples. The thermogravimetric analysis (TGA) curves were measured on a Mettler, Toledo, TGA/SDTA 851® instrument, the samples were heated to ~1000 °C with heating rate of 10 °C min⁻¹ under air (60 ml min⁻¹) and nitrogen flow was maintained at 40 ml min⁻¹ as a balance gas. The thermal conductivity, thermal diffusivity and specific heat of the CF samples were measured using a Hot Disk TPS 500 thermal constant analyser (ThermTest Inc.) with the transient plane source method at room temperature (24 °C). Measurements were carried out by sandwiching two flat pieces of samples with a Kapton disk sensor (3.2 mm) with a heating power of ~ 94.34 mW. Brunauer, Emmett and Teller (BET) surface areas and pore size distributions (PSDs) were determined from nitrogen (N₂) isotherms, which were obtained using a Micrometrics ASAP 2020 HD analyser 77 K. Before any gas adsorption experiment,
the samples were outgassed in the degassing port under vacuum (down to 10^{-7} \text{ bar}) for at least 8 h at 200 °C in order to remove any humidity and other physisorbed gases. Low-pressure hydrogen isotherms (up to 1 bar) were obtained using a Micrometrics ASAP 2020 HD analyser. All gas sorption experiments were performed at 77 K, using liquid nitrogen.

6.3. Results and Discussion

The comparative diffraction patterns of pristine materials and their corresponding composites are presented in Figure 6.2a. The crystalline structure of pristine UiO-66(Zr) was obtained, as confirmed by the presence of the two main characteristic diffraction peaks (2-theta = 7° and 9°) which are consistent with results reported in the literature [26, 27]. The two broad diffraction peaks centered at 2-theta = 20° and 2-theta = 43° which are characteristics peaks for graphite corresponding to the (002) and (100) lattice planes respectively, were observed for the carbon-based CF [28-31]. This pattern indicates a predominantly amorphous structure. Similarly, the diffraction pattern of CF and PIM-1 presents amorphous characteristics (Figure 6.2a). The CF and PIM-1 structures were retained in diffractogram of the CF/PIM-1 composite. It can be easily seen that the diffractograms of CF/UiO-66(Zr) and CF/PIM-1/UiO-66(Zr) display a diffraction pattern similar to that of UiO-66(Zr) with a slight peak broadening effect coming from the presence of CF. This indicates successful immobilization of the UiO-66(Zr) onto the CF as the UiO-66 (Zr) MOF crystalline structure was retained and no other new structure was formed.

The thermal degradation behaviour of the pristine materials (UiO-66 and PIM-1) and the CF/PIM-1/UiO-66(Zr) composite was studied using TGA and the thermograms are presented in Figure 6.2b. The TGA results of PIM-1 reveal two weight-loss steps whereas UiO-66(Zr) and CF/PIM-1/UiO-66(Zr) exhibited three mass-loss steps. The first weight loss which occurred below 150 °C for all samples relates to dehydration and the loss of solvent molecules. The TGA profiles of UiO-66(Zr) and CF/PIM-1/UiO-66(Zr) showed a second thermal degradation step between 150 and 362 °C resulting from dehydroxylation of Zr₆ clusters and the decomposition of the BDC linker [22, 32]. Then the last thermal degradation step above 475-545 °C was attributed to the final decomposition of the MOF structure to ZrO₂ residue [22, 33]. Consequently, pristine UiO-66(Zr) was stable up to 475 °C, whereas PIM-1 was only stable up to 415 °C. On the other hand, the thermal degradation temperature of the CF/PIM-1/UiO-66(Zr) composite; as was found to be slightly higher (434 °C) than that
of the pristine PIM-1 which indicates the contribution of high thermal stability of UiO-66 within the composite.

**Figure 6.2.** Stacked PXRD patterns (a) and TGA curves (b) of CF/UiO-66/PIM-1 based composites and their pristine counterparts.

SEM image of pristine CF (Figure 6.3a) shows an open cell/skeleton of highly interconnected large macropores surrounded by carbon walls throughout the structure. In Figure 6.3c, the well dispersed octahedral crystals of UiO-66(Zr) were observed, while the magnified image shown in Figure 6.3d clearly shows that both the MOF crystals and polymer are anchored to the pore wall/boundary. The PIM-1 and UiO-66 crystals did not completely infiltrate through the open cell macropores of the foam as observed in Figure 6.3e. Thus, the octahedral shaped UiO-66(Zr) in PIM-1 matrix forming a sieve-in-a-cage morphology of PIM-1/UiO-66(Zr) was dominant and quite dense on the CF surface. Therefore, the SEM images indicated successful incorporation of UiO-66(Zr) crystals and PIM-1 on the CF, which is in accordance with the PXRD and TGA findings.
Figure 6.3. High resolution SEM images of carbon foam (CF) (a), PIM-1(b), (c) UiO-66, CF/UiO-66/PIM-1 (d-e).

The sorption capabilities of the pristine and composite materials were confirmed by nitrogen adsorption at cryogenic temperature, from which the porosities and specific surface areas were also calculated (Figure 6.4a). The N\textsubscript{2} isotherms, at 77 K, for pristine UiO-66(Zr)
exhibited a type I isotherm which is indicative of the microporous nature of the adsorbent (< 2 nm). On the other hand, PIM-1 powder and CF/PIM-1/UiO-66(Zr) samples exhibited a type IV isotherm with almost similar hysteresis loops in which case the initial part of the isotherm (at low P/P₀ axis) indicates a complete monolayer coverage on mesopores (< 50 nm) surfaces. For the pristine CF, a type V isotherm with a desorption curve having a type H1 hysteresis loop (IUPAC classification) was observed which suggested presence of macropores (> 50 nm), which was confirmed with the SEM observations (Figure 6.3) [3]. This observation is normally common for water adsorption on activated carbon, which therefore makes sense since the analysed sample is an activated carbon-based foam [34]. The PSD curve (Figure 6.4b) of the CF/PIM-1/UiO-66 showed a relatively narrow multimodal pore size distribution centered at 1.9 nm (from UiO-66), 2.5-3.3 nm (of PIM-1) and a series of peaks at 4.4–9.9 nm (matching with CF peaks). The PSD, confirmed the earlier observations of the SEM and XRD analysis further indicating the co-existence of all the components present in the composite and a hierarchical characteristic as anticipated.

![Figure 6.4](image)

**Figure 6.4.** N₂ adsorption-desorption isotherms of pristine and composites materials at 77 K (a) and corresponding DFT pore size distribution of pristine materials and the respective CF/PIM-1/UiO-66(Zr) composite (b).

A summary of the textural properties of the pristine and composite samples is presented in **Table 6.1**. From the results, the CF/PIM-1/UiO-66(Zr) composite sample had a specific surface area of 766 m²g⁻¹ which was about 16 times that of the CF (47 m²g⁻¹). The surface area of the pristine materials (UiO-66(Zr); 1367 m²g⁻¹ and PIM-1; 784 m²g⁻¹) was found to be notably higher than that of the resulting composite. The observed reduction of surface area of
the composite could be ascribed to the poor infiltration of the PIM-1 and MOF into the CF macropores. Bearing in mind that the loading wt% of MOF is less when compared to the combined mass of PIM-1 and CF, this could also explain the decrease of surface area of the resulting composite material. Furthermore, the nitrogen sorption isotherm and pore size distribution curve (Figure 6.4(a-b)) of the composite sample displayed a hierarchical porous characteristic which correlates with the morphology of the composite displayed in SEM images (Figure 6.3d).

**Table 6.1.** Summary of textural properties and H$_2$ sorption capacities of pristine and composite materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured BET SSA (m$^2$ g$^{-1}$)$^a$</th>
<th>Micropore area (m$^2$ g$^{-1}$)$^b$</th>
<th>Pore size (nm)$^c$</th>
<th>Total Pore vol. (cm$^3$ g$^{-1}$)$^d$</th>
<th>Measured H$_2$ uptake (wt. %)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>47</td>
<td>6.58</td>
<td>5.1 – 9.9</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>PIM-1</td>
<td>784</td>
<td>687</td>
<td>1.1 – 10.4</td>
<td>0.53</td>
<td>1.02</td>
</tr>
<tr>
<td>UiO-66(Zr)</td>
<td>1367</td>
<td>1303</td>
<td>1.3 – 1.9</td>
<td>0.60</td>
<td>1.38</td>
</tr>
<tr>
<td>CF/PIM-1/UiO-66(Zr)</td>
<td>768</td>
<td>645</td>
<td>1.9 – 9.9</td>
<td>0.43</td>
<td>1.05</td>
</tr>
</tbody>
</table>

$^a$ BET surface area estimated from the N$_2$ sorption data at 77 K. $^b$ From t-plot. $^c$ Pore size determined by DFT analysis. $^d$ Total pore volume determined from H-K analysis estimated at p/p$_0$~0.99. $^e$ Hydrogen adsorbed at 77 K and 1 bar.

From Figure 6.5 the H$_2$ uptake capacities of PIM-1 (1.02 wt.%) and CF/PIM-1/UiO-66(Zr) (1.05 wt.%) were found to be almost similar. Furthermore, the H$_2$ adsorption capacities of UiO-66(Zr) and PIM-1 were retained which could indicate that no-pore blocking effect was experienced from the CF matrix. From the comparison of textural properties presented in Table 6.1, the surface areas were found to correlate well with the H$_2$ uptake capacities. This is in agreement with Chahine’s rule [35] which states that for every 500 m$^2$g$^{-1}$ of surface area there is 1 wt.% H$_2$ adsorption. According to Panella et al. [35], theoretically the maximum H$_2$ storage capacity per specific surface area of a carbon material can be calculated to 2.28×10$^{-3}$ mass%m$^{-2}$g. However, experimentally the measured value was found to be 1.91×10$^{-3}$ mass%m$^{-2}$g which corresponds to an occupancy of one H$_2$ molecule per 17.5Å$^2$ of carbon surface. Nijkamp et al. [36] have obtained similar results of a linear relation between H$_2$
uptake and specific surface area of carbon materials at 1 bar and 77 K. Additionally, these materials must be of low cost, low density and exhibit good thermal and mechanical properties. Nonetheless, so far, our results have shown that anchoring high loadings of PIM-1/UiO-66(Zr) on CF can potentially result in improved surface area if more infiltration into CF is achieved and the H$_2$ uptake is comparable to that of pristine UiO-66(Zr). Thus, the overall properties (textural and H$_2$ uptake) of the composite were reasonably compromised between the individual pristine counterparts (see Table 6.1). Notably, the H$_2$ adsorption isotherms of the pristine and composite materials exhibited a steep increase at low pressure up to 1 bar and did not attain adsorption saturation (plateau). Therefore, more H$_2$ would be adsorbed at higher pressures above 1 bar [37].

![Figure 6.5. H$_2$ adsorption isotherms of pristine and composites materials at 77 K and 1 bar.](image)

Table 6.2 presents thermal conductivities of pristine UiO-66(Zr) and PIM-1 as 0.2915 Wm$^{-1}$K$^{-1}$ and 0.0759 Wm$^{-1}$K$^{-1}$ respectively at 24 °C. The obtained thermal conductivity value for UiO-66(Zr) is reasonably consistent with the recently reported values for UiO-67 (0.19 Wm$^{-1}$K$^{-1}$), UiO-66 (0.11 Wm$^{-1}$K$^{-1}$) and Cu-BTC (0.39 Wm$^{-1}$K$^{-1}$) which were measured using a transient hot wire method with 30% uncertainty [38]. Although the value obtained in this
work for UiO-66 is slightly higher than the one reported in literature, this may be attributed to the sample preparation method. Differences in sample compaction density were previously reported to impact thermal conductivity values. For example, increasing the pellet density from 0.3 to 0.7 g.cm\(^{-3}\) increased the thermal conductivity of compacted MOF-5 from 0.07 to 0.14 Wm\(^{-1}\)K\(^{-1}\) [39, 40]. The thermal conductivities of the pristine carbon foam and CF/PIM-1/UiO-66(Zr) were 0.0703 and 0.1189 Wm\(^{-1}\)K\(^{-1}\) respectively when tested under the same conditions (as seen in Table 6.1.). The thermal conductivity of CF was found to be comparable with that of the activated carbon-based CF (prepared by thermo-foaming of dispersions of activated carbon powder in an aqueous sucrose resin) reported in literature (i.e. 0.036–0.049 Wm\(^{-1}\) K\(^{-1}\)) [41]. Surprisingly, the inclusion of CF did not enhance the thermal conductivity of MOFs in CF/PIM-1/UiO-66(Zr) composite as was initially hypothesised. According to the analytical relations of effective thermal conductivity for highly porous solids, comparison of predictions by Ashby [42] for open cellular structures to those by Maxwell-Eucken [43] or Hashin-Shtrikman [44] corresponding to closed cell structures has confirmed that open cells are more insulating than closed cells. Hence, we observed a low thermal conductivity for an open cell CF structure. These results indicate that CF does not have the potential to improve the thermal conductivity of MOFs for managing thermal effects during the H\(_2\) charging and discharging processes due to the large volume insulating pore framework (large spherical pores with thin walls). Therefore, in this case a high pore volume fraction and low densities of the CF and CF/PIM-1/UiO-66(Zr) were limiting factors towards improving the thermal conductivity of the UiO-66(Zr) MOF powder.

**Table 6.2.** The three related thermal properties (thermal conductivity, thermal diffusivity and specific heat) of pristine UiO-66(Zr), CF and PIM-1 and hybrid material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal conductivity (Wm(^{-1})K(^{-1}))</th>
<th>Thermal diffusivity (mm(^2)/s)</th>
<th>Specific heat (MJ/m(^3)K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>0.0703</td>
<td>0.4705</td>
<td>0.1528</td>
</tr>
<tr>
<td>PIM-1</td>
<td>0.0759</td>
<td>0.0904</td>
<td>0.8391</td>
</tr>
<tr>
<td>UiO-66(Zr)</td>
<td>0.2915</td>
<td>0.8797</td>
<td>0.3314</td>
</tr>
<tr>
<td>CF/PIM-1/UiO-66(Zr)</td>
<td>0.1189</td>
<td>0.1662</td>
<td>0.7166</td>
</tr>
</tbody>
</table>
6.4. Conclusion

Immobilization of MOF onto an inexpensive carbon foam substrate in the presence of a PIM-1 binding agent was attempted with the expectation of fabricating conductive, lightweight and cost-effective H$_2$ storage composites materials. The textural properties and hydrogen storage properties of the pristine and composite materials were assessed and compared. The carbon foam-immobilized PIM-1/UiO-66(Zr) composite material exhibited a hydrogen adsorption capacity of 1.05 wt.% at 77 K and pressure up to 1 bar. Thus, the intrinsic H$_2$ sorption properties of a MOF were retained. Unfortunately, the results have shown that the activated carbon-based foam used in this study is not conductive due to the high void volume. Thus, incorporation of PIM-1/UiO-66(Zr) into CF only offered better handling but no enhancement of thermal properties as was anticipated. It was revealed that the actual thermal conductivity of pristine CF (0.0703 Wm$^{-1}$K$^{-1}$) is less than that of UiO-66(Zr) MOF (0.2915 Wm$^{-1}$K$^{-1}$). Future-work will include interrogating various loadings of PIM-1/UiO-66(Zr) and other conductive adsorbent to obtain higher BET surface areas, high pressure H$_2$ uptake capacity and better thermal conductivity.

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Lerato Y. Molefe. The first draft of the manuscript was written by Lerato Y. Molefe and all authors reviewed and commented on previous versions of the manuscript. Nicholas M. Musyoka and Patrick G. Ndungu supervised and reviewed the work.
6.5. References:


CHAPTER 7: RESULTS AND DISCUSSION (IV)

3D PRINTED ABS/UiO-66/ZTC MONOLITHIC COMPOSITES FOR INTENDED HYDROGEN ADSORPTION STUDIES

Summary Statement

The aim of this work was to interrogate the feasibility of 3D printed ABS-MOF based composites to be used as hydrogen adsorbent when incorporated in a high pressure cylinder. This chapter is presented as a manuscript format and features experimental procedures used for materials fabrication and their characterisation. A discussion of the obtained results (physicochemical, thermal and mechanical characteristics) of 3D printed composites materials is fixed. The chapter then concludes by summarizing the main findings of the study.

Abstract

Despite the promising potential for metal organic frameworks (MOFs) in energy storage applications, until now their transition from laboratory research to commercial applications still remains a challenge. In this case, limitations such as poor hydro-stability of selected MOFs, low thermal conductivity and weak interactions with small molecules such as hydrogen (H$_2$) must be addressed. Moreover, there is a need to shape MOF powders into “easy to handle” configurations (e.g., monoliths, thin films, etc.) prior to their application. Recently, fabrication of MOF-polymer composites has been identified as an interesting route for shaping MOF powders. In this regard, 3D printing technique has shown a great promise for fabricating shaped functional blocks of polymer based MOF composites for a variety of applications. However, the research covered so far has only focused on MOFs and neglected porous carbon materials. It is on this basis that the current study presents results on fabrication of 3D printed composites with loadings of 5 wt% MOFs and 5 wt% zeolite templated carbon (ZTC). The XRD data showed that the MOF retained its crystalline structure within the composite as well as exhibiting enhanced mechanical stability. However, contrary to our expectation, the 3D printing process compromised the porosity of the resulting composite material.

Keywords: 3D printing, Hydrogen storage, Metal-organic frameworks
7.1. Introduction

Currently, combustion of fossil fuels remains the main source of energy which contributes to climate change and other localised deleterious environmental impacts. Thus, research interest in clean renewable energy systems is growing every day. Hence, the use of clean hydrogen (H₂) as an alternative energy carrier has been considered attractive as a fuel for transportation applications. However, the low volumetric energy density of H₂ makes its storage difficult. Therefore, to make H₂ storage practical for everyday use in mobile and other small scale power systems, compression into a much smaller volume that is lightweight, low-cost containment or materials at safe pressures and close to ambient temperature is required [1]. In this regard, the United States Department of Energy (U.S DOE) has set forth the targets; 0.030 kg H₂/ L (volumetric capacity) and 4.5 wt.% (gravimetric capacity) to be met by 2020 for on-board H₂ storage systems for light-duty vehicles [2].

There has been increased efforts and developments towards considering metal organic frameworks (MOFs) and porous carbons for H₂ storage. However, there are a couple of bottlenecks to overcome before they can be realized for large scale applications. The great potential of porous material’s applications is limited by their lack of immediate processability since in their as-synthesised form, they are obtained as a loose powder [3-4]. Therefore, there is always a need to process them into highly mechanically stable shaped macrostructures for various applications. Both the Universitetet i Oslo zirconium-carboxylate (UiO-66(Zr)) MOF and zeolite templated carbon (ZTC) used in this study are common and well interrogated porous materials that have been used for H₂ storage, high surface areas (1434 m²g⁻¹ and 3341 m²g⁻¹ respectively) and with hydrogen uptake as high as 1.6 wt.% and 2.5 wt.% respectively at 77 K and 1 bar [5-6]. Most importantly, ZTC is a conductive carbon material while the UiO-66(Zr) was chosen because it is chemically and thermally stable and easy to produce in large quantities. Conventionally, catalysts and adsorbent powders have been shaped into pellets and films. Although these forms may be suitable for some applications, other applications may require more complicated structures to solve issues such as high pressure drop, and low mass and transfer properties [7-9]. Researchers have found that monolithic structures tend to solve these problems resulting in an improved low pressure drop and enhanced mass and heat transfer properties [9-10].

Intensive research in the fabrication of three dimensional (3D) printable MOF/polymer composites has shown great promise in processing MOF powders for industrial applications.
Moreover, the recent advances on the implementation of 3D printing for numerous applications are steadily being exploited and further research will certainly open new opportunities and bring advantages in terms of product versatility, performance and low cost. The aim of this study is to address the processability of MOFs by fabricating a composite consisting of acrylonitrile butadiene styrene (ABS), UiO-66(Zr) MOF and the ZTC which was printed using a standard commercial thermoplastic 3D printer. ABS plastic is a cheap and easy to use material in 3D printers. Moreover, ABS was chosen in this work in order to reinforce MOFs due to its superior mechanical strength and chemical resistance [11]. ABS is also known to be highly soluble in ketones, esters and ethylene dichloride resulting in ease of processing and like many plastics, ABS is recyclable.

A previous study done on ABS-MOF-5 reported increasing MOF/polymer phase-separation challenges for MOF loadings above 10 wt% and due to weak mechanical properties associated with high MOF loadings they could not be printed [9]. Additionally, the degradation of moisture sensitive MOF-5 was observed during the solvent casting step of the filament feedstock preparation. Surprisingly, the ABS-MOF-5 monolith was still able to achieve H₂ uptake capacity higher than the pristine ABS counterpart irrespective of the MOF degradation problem. Most importantly, in MOF processing methods, the MOF must still retain its gas adsorption properties after processing. For instance, Evans and co-workers [12] investigated the influence of rigidity and flexibility of the polymer matrix on the porosity of the resulting MOF composite. In their study, the incorporation of a high loading of 50 wt% of ZIF-8 into rigid PLA and flexible thermoplastic polyurethane (TPU) polymer matrices were investigated. It was revealed that the incorporation of polylactic acid (PLA) resulted in a hierarchical MOF monolith (surface area = 531 m²g⁻¹) whereas the semiflex polymer matrix resulted in pore occlusion (surface area = 68 m²g⁻¹), concluding that improved flexibility blocks micropores and limits potential applications of the material. Amazingly, not much work has been performed on the incorporation of carbons. Another issue is that although thermoplastics offer mechanical stability, the lack of functional pores and intrinsic functionality can significantly affect the performance of MOFs and thus limit their applications [12]. Here we demonstrate that ABS/5 wt% UiO-66(Zr)/5 wt% ZTC retained the crystallinity of pristine materials while exhibiting enhanced mechanical stability.
7.2. Experimental Section

7.2.1. Material and Chemicals

The pristine and composites materials were synthesised using the following as-received chemicals that were used without further purification. Formic acid (HCOOH, Sigma-Aldrich, ≥ 99.5%), hydrofluoric acid (HF, Ace chemicals, ≥ 97%), N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%), furfuryl alcohol (FA, Sigma-Aldrich, ≥ 97%), 1,2,2-tetrachloroethane (TCE, Sigma-Aldrich, ≥ 98.0%), hydrochloric acid (HCl, Ace chemicals, ≥ 37%), Zirconium chloride (ZrCl₄, Sigma-Aldrich, ≥ 99.5%), ABS beads (3D printing store), 13X powder (Sigma-Aldrich, ~2 μm average particle size), terephthalic acid (BDC, Sigma-Aldrich, 98%), methanol (CH₃OH, Sigma-Aldrich, ≥ 99.9%), ethanol (Ace chemicals, 90%), acetone (Sigma-Aldrich, ≥ 99.8%) and de-ionized water.

7.2.2. Synthesis of UiO-66(Zr)

UiO-66(Zr) powder was prepared by modification of the optimised synthesis procedure described by Dyosiba et al. [13]. A mixture of anhydrous zirconium (IV) chloride (1.06 g), 1,4-benzenedicarboxylic acid (0.68 g) and DMF (50 mL) was placed in the ultrasonic bath for 30 minutes and transferred into a 250 mL round bottom flask along with 17.2 mL of formic acid. The reaction apparatus was placed in an oil bath heated at 120 °C, without stirring and kept under reflux for 4 h. After the reaction, the mixture was cooled to room temperature and the white precipitate of UiO-66(Zr) crystals were collected by centrifugation and repeatedly washed with ethanol at 60 °C (under magnetic stirring) for 3 h to remove the unreacted BDC residues. The purified white crystals were then collected by centrifugation and thereafter dried at 90 °C for 12 hours.

7.2.3. Zeolite Templated Carbon (ZTC) Synthesis

The synthesis of ZTC was conducted following a two-step procedure, namely impregnation of zeolite 13X with furfuryl alcohol followed by chemical vapour deposition (CVD) process as described in earlier reported studies [14-15]. Briefly, 24 g of zeolite 13X powder (pre-dried at 120 °C under vacuum for 12 h) was impregnated with 80 mL of furfuryl alcohol (FA) and stirred for 24 h at room temperature. The obtained mixture was then filtered and washed with a few drops of ethanol. Subsequently, the FA/zeolite mixture was placed in a quartz crucible and transferred into an alumina ceramic tube in a CVD furnace system where polymerisation at 80 °C took place for 24 h under argon gas flow (100 mL min⁻¹). The polymerisation temperature was ramped up to 150 °C and maintained at this temperature for
a further 8 h. To stabilise the composite, the resultant composite was heated up to 700 °C in argon flow and maintained for 3 h. Thereafter, the gas flow was switched from argon to a mixture of ethylene/argon (10% ethylene in argon) at the flow rate of 100:400 mL min⁻¹ while the temperature was kept at 700 °C, and held there for an additional 3 h. Subsequently, in the carbonisation step, the gas flow was switched back to argon gas, while the temperature was raised to 900 °C. After 3 h of carbonisation, the resulting zeolite/carbon hybrid product was left to cool down to room temperature. The zeolite/carbon product was then crushed using a mortar and pestle, followed by washing in 10% aqueous solution of hydrofluoric acid for 24 h and the solution was diluted to 2 L with deionised water and collected through vacuum filtration. The recovered sample was then refluxed in 10% aqueous solution of hydrochloric acid for 24 h. The resulting carbonaceous material (called ZTC) was filtered, washed with 2 L of deionised water and finally dried in a vacuum oven at 120 °C for 12 h.

7.2.4. Solvent Casting of ABS and UiO-66(Zr)/ZTC
The ABS beads (18 g) were dissolved in acetone (50 mL) while stirring at room temperature until a homogenous solution was obtained. Meanwhile, a mixture of 1 g of UiO-66(Zr) (5 wt% loading) and 1 g of ZTC (5 wt% loading) was dispersed in 50 mL of acetone and subjected to vigorous magnetic stirring for 12 hours at room temperature to obtain a well-dispersed suspension. Subsequently, the dispersed UiO-66(Zr)/ZTC mixture and ABS solution were mixed and further stirred for 12 hours. The resulting mixture (ABS/UiO-66(Zr)/ZTC, 90:5:5 wt%) was cast on a non-stick baking pan and the solvent was slowly evaporated by placing the pan in a conventional drying oven at 60 °C to obtain a few millimetres thick film. For composites with 10 wt% composition of individual powders, that is the ABS/ZTC and ABS/UiO-66(Zr) samples were prepared by following the same procedure.

7.2.5. Extrusion and Filament Formation
The as-synthesized composite films were chopped into small pieces and loaded into the heating barrel of the Noztech Pro desktop extruder. The heating element was firstly switched on and left to heat to 190 °C and then the motor (rotating at 40 revolutions per minute) was turned on and maintained for at least 15 min to allow the barrel, screw and nozzle to thoroughly heat up. The composite materials were then extruded through a 1.75 mm die to produce the feedstock filaments for 3D printing.
7.2.6. **3D Printing of Composite**

A commercially available thermoplastic 3D printer (CRON P300S) was used in this study. The monolithic structures (rectangular strips and dog-bone shapes used for mechanical testing) were printed through a 0.4 mm diameter nozzle heated to 240 °C on a glass bed (ABS juice coated) set to 110 °C. Prior to BET surface area and H$_2$ uptake measurements, all the printed samples were soaked in a methanol solution for a minimum of 48 h and activated under vacuum at 75 °C. **Figure 7.1** presents a schematic for the steps followed during the fabrication of 3D printed MOF composites objects.

![Schematic illustration of the 3D-printed MOF/Polymer composites preparation procedure.](image)

**Figure 7.1.** Schematic illustration of the 3D-printed MOF/Polymer composites preparation procedure.

7.2.7. **Sample Characterisation**

Powder X-ray diffraction (PXRD) patterns were obtained at room temperature using a PANalytical X’Pert Pro powder diffractometer, coupled to a Pixedl detector (Cu-Kα radiation $\lambda=0.154$ nm). A Mettler Toledo, thermogravimetric analyser (TGA)/STDA 851e instrument was used to analyse the thermal degradation behaviour of the pristine materials and their respective composites samples. The samples weighing about 10 mg were heated from 25 to ~1000 °C at a heating rate of 10 °C min$^{-1}$ in air (60 ml min$^{-1}$) and nitrogen flow was maintained at 40 ml min$^{-1}$ as a purge gas. Surface morphologies of the pristine materials and 3D printed monoliths were examined by using a Carl Zeiss Auriga Cobra focused ion beam...
scanning electron microscope (SEM). Before imaging the samples, they were firstly coated with a thin layer of chromium using Quorum Q150T ES turbo-pumped sputter coater. The mechanical tensile strength tests of the 3D printed dog-bone shaped pristine ABS and ABS/5 wt% UiO-66(Zr)/5 wt% ZTC composite specimens (100 mm in length, 13.05 mm in width and 3.23 mm thickness) as defined by the American Society for Testing and Materials (ASTM) D638, were determined using Instron tester 5966 at an extension rate of 5 mm/min at 23 ºC. The reported results are an average of five independent measurements for reproducibility of the results. The thermal conductivities of the 3D printed samples and pristine compacted UiO-66(Zr) and ZTC powder were measured based on transient plane source technique. In details, 3.2 mm Kapton insulated sensor with a heating power of 94.34 mW was sandwiched between two flat samples and the thermal conductivity was measured using a Hot Disk TPS 500 thermal constant analyser (ThermTest Inc.) at room temperature (24 ºC).

7.3. Results and Discussion
The XRD pattern of the pristine ABS (Figure 7.2a) revealed a broad peak centered at 2-theta = 15º with a shoulder peak at 2-theta = 7º and a small hump with less intensity at 2-theta = 43º, which signifies the amorphous nature of the ABS polymer similar to the reported results in literature [16-17]. The PXRD patterns of pristine UiO-66 (had two main diffraction peaks at 2-theta = 7 and 9º) matched well with previously reported studies by Ren et al. [18]. The ZTC sample had a diffraction peak centered at 2-theta = 6º which is due to the inverse replication of zeolite 13X pore ordering that indicated a successful templating process as described by Xia et al. [19]. On the other hand, the PXRD patterns of the corresponding composites samples (Figure 7.2b) displayed both peaks of the pristine porous material as well as that of the ABS polymer. However, the peaks of the UiO-66 were more prominent in the ABS/5 wt% UiO-66/5 wt% ZTC sample since the ZTC single peak was masked by the MOF peaks. This observation confirmed successful inclusion of both ZTC and MOF powders in the ABS matrix.
The thermal stability of the pristine porous materials and the corresponding composites was evaluated by TGA and the resulting thermograms are presented in Figure 7.3. Since ABS is a hydrophobic polymer, it does not adsorb any moisture and hence no mass loss was observed at temperatures below 200 °C. The UiO-66(Zr), did lose some residual moisture and adsorbed solvent molecules as exhibited by the weight loss in the low temperature regions. Additionally, the UiO-66(Zr) displayed two other mass loss stages that corresponded to the decomposition of the BDC linker due to the dehydroxylation of Zr$_6$ clusters (150–362 °C) [20]. The MOF structure completely decomposed to ZrO$_2$ at temperatures between 475 and 550 °C [21-22]. The ABS polymer remained stable up to 400 °C and, above this temperature, the polymer started to decompose into its constituents: acrylonitrile, butadiene and styrene [11, 23]. The corresponding composite material followed a similar trend as observed for the pristine materials, except that weight loss of the ABS constituent began at 420 °C, slightly above 400 °C, owing to its enhanced thermal decomposition behaviours due to the synergistic interactions with the porous additives. The thermal properties of the UiO-66 MOF such as MOF decomposition to ZrO$_2$ residues were not that evident due to very small loading amount (5 wt%) added in ABS.
Figure 7.3. TGA profiles of UiO-66, ZTC, ABS and ABS/5 wt% UiO-66/5 wt% ZTC.

The SEM micrograph of the ABS polymer (Figure 7.4a) displays a rough amorphous surface of the non-porous polymer, which correlates with the PXRD results (Figure 7.2a). The incorporation of UiO-66 and ZTC crystals was further evidenced by SEM images (Figure 7.4 (d-f)), in which case there is a degree of porosity created by the presence of octahedral shaped UiO-66(Zr) crystals and the relatively bigger octahedral pyramidal ZTC particles observed on the surface of ABS polymer matrix. The morphological features of the pristine UiO-66(Zr) and ZTC (Figure 7.4 (a-b)) are also consistent with observations from previous studies [6, 24]. The incorporation of MOF and ZTC filler into the ABS polymer matrix introduced formation of pores within the ABS polymer thus increasing the pore volume of the monolith composite. Figure 7.4 (d-f) clearly shows the presence of the pores on the surface of ABS matrix when the two filler materials were incorporated.
Figure 7.4. High resolution SEM images (mag. 20,000 ×) of ABS (a), ZTC (b), UiO-66 (c), ABS/10 wt% ZTC (d), ABS/10 wt% UiO-66 (e), ABS/5 wt% UiO-66/5 wt% ZTC (f).

Thermal conductivity

The thermal conductivity of pristine ABS is known to be 0.1 Wm⁻¹K⁻¹ [25] but it has also been reported as 0.187 Wm⁻¹K⁻¹ in another study [26]. Nevertheless, our 3D printed ABS showed a thermal conductivity value of 0.18 Wm⁻¹K⁻¹ (Table 7.1) which is comparable to the earlier value reported in the literature. This low heat conductivity is a typical characteristic of polymers and is associated with their relatively low atomic density, complex structure in their molecular vibrations and weak chemical interactions [27]. On the other hand, the thermal conductivity of UiO-66(Zr), ABS/10 wt% UiO-66, ABS/10 wt% ZTC and ZTC are 0.29 Wm⁻¹K⁻¹, 0.14 Wm⁻¹K⁻¹, 0.18 Wm⁻¹K⁻¹ and 0.06 Wm⁻¹K⁻¹, respectively. Contrary to other studies in the literature, the thermal conductivity of the UiO-66(Zr) used in this study had a high value (2.6 times) than the value reported by other researchers (0.11 Wm⁻¹K⁻¹) [28]. This difference could be due to the method used for acquiring the data. Even though, ZTC was expected to have a high thermal conductivity, the technique of data acquisition necessitated the use of a pelletized sample which was not possible for the powdery ZTC and hence the obtained value may not be reliable. However, the thermal diffusivity values are of interest to the study since they inform on the heat dissipation effect when the adsorbent is incorporated in a H₂ storage system. In this case, the ABS/5 wt% UiO-66/5 wt% ZTC rapidly dissipates more heat than its pristine counterparts and other composites materials which have very low thermal diffusivities. Since the thermal diffusivity of a material determines how fast the
material can adapt to the surrounding temperature or transfer thermal energy, the ABS/5 wt% UiO-66/5 wt% ZTC will rapidly adjust to any temperature fluctuations. Unfortunately, the obtained results are contrary to the postulated hypothesis that ZTC based composites will have thermal conductivities higher than that of the UiO-66(Zr) MOF. Nonetheless, by finding alternative methods to pelletize ZTC powder, then accurate thermal conductivity value could be obtained. The ZTC based composites have shown a potential to be applied as an adsorbent bed inside the H₂ storage tank since the current values are close to the thermal conductivities range (0.3–0.5 Wm⁻¹K⁻¹) that simulation studies have indicated to potentially offer good heat distribution in a H₂ storage system [29-30].

**Table 7.1.** Thermal properties (thermal conductivity, thermal diffusivity and specific heat) of pristine porous materials and their respective composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal conductivity (W/m⁻¹K⁻¹)</th>
<th>Thermal diffusivity (mm²/s)</th>
<th>Specific heat (MJ/m³K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>0.1813</td>
<td>0.1137</td>
<td>1.5965</td>
</tr>
<tr>
<td>UiO-66</td>
<td>0.2915</td>
<td>0.8797</td>
<td>0.3314</td>
</tr>
<tr>
<td>ZTC</td>
<td>0.0622</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ABS/10 wt% UiO-66</td>
<td>0.1435</td>
<td>0.3927</td>
<td>0.3655</td>
</tr>
<tr>
<td>ABS/10 wt% ZTC</td>
<td>0.1778</td>
<td>1.271</td>
<td>0.1399</td>
</tr>
<tr>
<td>ABS/5 wt% UiO-66/5 wt% ZTC</td>
<td>0.2192</td>
<td>19.54</td>
<td>0.0112</td>
</tr>
</tbody>
</table>

**Figure 7.5** presents the stress-strain curves of the pristine ABS and the corresponding ABS/UiO-66/ZTC composite. The tensile strength of ABS ranges from 45.1 MPa to 49.1 MPa with an average of 47.6 MPa. This value is similar to the value reported in literature (39 MPa) [9]. The tensile strength of ABS/5 wt% UiO-66/5 wt% ZTC composite ranges from 22.2 MPa to 36.7 MPa with an average of 30.9 MPa.
Table 7.2 summarises tensile properties (tensile strength, elongation at break and Young’s modulus) of the ABS and the corresponding composites. The obtained results showed that incorporation of additives (10 wt% mixture of UiO-66 and ZTC) to pristine ABS, resulted in a 17.8% and 35.1% decrease in modulus and in tensile strength respectively. Additionally, the elongation at break value for ABS/5 wt% UiO-66/5 wt% ZTC is also 53.4% lower, compared to that of pristine ABS (5.8%) (see Table 7.2) making it more brittle than ABS. This observation may be attributed to the presence of pores and relatively weaker interactions between the polymer chains and the additives in ABS/5 wt% UiO-66/5 wt% ZTC (10 wt%) in comparison to the pristine ABS, as seen in the SEM images (Figure 7.4). In general, the incorporation of UiO-66 and ZTC powders in an ABS polymer matrix induced mechanical properties of the powders although the tensile properties of ABS were affected, as expected. In this case, pristine ABS can withstand a higher tensile stress before breaking than ABS/5 wt% UiO-66/5 wt% ZTC. However, a study by Kreider, et al. [9] reported the enhancement of the tensile strength and modulus and elongation at break of the composite upon addition of MOF-5 due to high adhesion between MOF-5 and the ABS matrix. The mechanical
properties of ABS/5 wt% UiO-66/5 wt% ZTC are satisfactory since the aim was to improve the handling properties of powder materials and not that of ABS.

**Table 7.2.** Tensile properties of pristine ABS and ABS/5wt % UiO-66/5 wt% ZTC composite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine ABS</td>
<td>47.6 ± 1.8</td>
<td>5.8 ± 1.2</td>
<td>1778 ± 126</td>
</tr>
<tr>
<td>ABS/5 wt% UiO-66/5 wt% ZTC</td>
<td>30.9 ± 5.4</td>
<td>2.7 ± 0.3</td>
<td>1462 ± 232</td>
</tr>
</tbody>
</table>

*Gas sorption studies*

Recovering the micropores of MOF after 3D printing is still a huge challenge because the thermoplastic polymers and other binders which are currently used in 3D printing are not porous and therefore result in pore blocking and reduced performance. A number of studies [31-33] have reported similar difficulties in pore accessibility of filler materials (MOFs, zeolite and carbon) in composites and the use of post-printing thermal removal of organic binders from the composite structure (by thermal activation at temperatures above the thermal degradation of binders but below that of the filler material) as a strategy to recover gas adsorption capabilities.

In this study, even after methanol treatment and activation, the 3D printed samples still showed BET surface areas less than 3 m$^2$g$^{-1}$. This may be attributable to surface pore occlusion as similar findings were obtained by Evans et al. [12] for the composite of flexible polyurethane polymer matrix and 50 wt% ZIF-8 MOF which resulted in a low surface area of 68 m$^2$g$^{-1}$. Here, the pores of the MOF were unblocked by formulating a ternary composite consisting of the parent flexible polymer (polyurethane), the MOF crystals (ZIF-8) and a second polymer additive (PVDF-HFP) used as a template followed by printing and later removal of the sacrificial polymer (PVDF-HFP) by chemical treatment. A similar method of restoring MOF microporous was recently applied by Young et al. [31] where a flexible
acrylate-based polymer matrix was degraded from its composite with UiO-66 so as to recover porosity.

Moreover, according to the simulations and experimental finding by Semino and colleagues, [34] rigid polymers are unable to conform to the MOF surface resulting in poor matrix-filler interactions and appearance of microvoids at the interface. The flexible polymers conform to the morphology of the MOF surface, hence partial (forming smaller pore sizes) or complete pore blocking may occur as there are no interfacial microvoids. The flexural modulus of ABS (1.60–2.46 GPa) is less than that of PLA (3.80 GPa), making ABS a flexible material compared to rigid PLA. Therefore it appears that the ABS polymer blocked most of the UiO-66 and ZTC micropores and hence gas was unable to diffuse through.

However, these results are in contradiction with the morphology analysis which showed voids created within the ABS matrix. Therefore, the presence of hierarchical porosity observed from SEM images (Figure 7.4(d-f)) and the retained crystal structure of MOF within the composite rules out the possibility of complete pore blockage and alteration of MOF structure respectively. Since the N\textsubscript{2} isotherm could not be obtained for pristine ABS as well, then the likely cause for such low gas adsorption may be that the printed samples were too thick and presented a large barrier to gas diffusion for isotherm data collection on the time scale allowed by the instrument parameters. The same observations were made by Bible et al. [35] in N\textsubscript{2} sorption isotherms at 77 K and gas sorption kinetics study at room temperature for ABS-HKUST-1 composite filaments.

7.4. Conclusion

In summary, the 3D printed hierarchical porous and mechanically stable monoliths have successfully resolved the processability issues of MOFs and carbon powder materials. An important feature of 3D printed materials is that they exhibit high strength and light weight which are commonly required in many applications. The incorporation of UiO-66 and ZTC into an ABS polymer matrix has revealed good effects related to mechanical strength without altering their crystallinity. The characterisation results revealed that, the ABS/5 wt%UiO-66/5 wt% ZTC composite has a better degree of crystallinity and a higher thermal stability than pristine ABS. However, without both N\textsubscript{2} and H\textsubscript{2} gas sorption data for ABS and the composites materials, no concrete conclusion can be drawn on the accessibility of pores in
3D printed materials. Although accurate gas adsorption measurements could not be obtained given the challenges with recovering the porosity of filler materials and the possibility of instrument limitations (related to the long diffusion times on printed samples), the 3D printing approach demonstrates that it is promising processing technique for both MOFs and porous carbons with the potential to enable fabrication of hierarchical monoliths with complex structures. Therefore, in future studies the use of supercritical CO₂ will be used to activate the 3D printed materials and following the success of recovering microporosity, high loadings of ZTC and UiO-66(Zr) crystals exceeding 10 wt% in ABS will also be investigated. Moreover, the addition of porous polymers like polymers of intrinsic microporosity (PIM-1) as a binding agent and ABS as plasticizer for MOF and ZTC structures may help in further enhancing the porosity, mechanical properties and H₂ storage performance of 3D printed composites.
7.5. References:


CHAPTER 8

OVERALL CONCLUSIONS AND FUTURE-WORK RECOMMENDATIONS

Summary Statement

This chapter presents a summary of the main findings of the study in correspondence with the specific research objectives. The achievements, challenges encountered, and limitations of the study are further discussed. This chapter terminates by presenting suggestion for future work.

8.1. Overall Conclusion

In this thesis, various strategies for shaping MOF and porous carbon powders for H\textsubscript{2} storage applications have been investigated. Specifically, a facile synthesis approach that is based on physical mixing of MOF or porous carbon with solution processable PIM-1 polymer has been used to produce PIM-1/MIL-101(Cr), PIM-1/UiO-66(Zr), PIM-1/ZTC, PIM-1/UiO-66(Zr)/ZTC and CF/PIM-1/UiO-66 composites materials. The PXRD, FTIR, SEM, TGA, nitrogen gas sorption analyses, determination of thermal conductivity and tensile strength testing were some of the procedures used to characterise the structural, chemical bonding, morphological, porosity, thermal and mechanical properties of the pristine and resulting composite materials. Both the pristine and composites materials were further tested for low pressure H\textsubscript{2} adsorption at 77 K and 1 bar.

From the experiments carried out towards achieving the aim and objectives listed in Chapter 1, then the following conclusions can be drawn:

The synthesis of the pristine powder MOF materials (MIL-101 (Cr) and UiO-66 (Zr)) and ZTCs were successfully synthesised with slight or minimal modification of procedures reported in the literature. The polymer materials were also synthesised by following the conventional methods reported in literature except for the synthesis of BCMBP and PIM-1 which required the use of anhydrous solvents under nitrogen flow. This was a challenging task, but the training offered by an experienced research group specialising in polymer
chemistry (University of Sheffield) was used. Obtaining high molecular weight PIM-1 still remains a challenge.

At first the effect of using different polymers (hyper-crosslinked organic polymer based on resorcinol and formaldehyde, bis(chloromethyl)biphenyl, polyaniline) and PIM-1 were investigated to choose the best polymeric feedstock for the composites fabrication. Of all, the PIM-1 was found to be the most suitable matrix for embedding fillers, hence the fabrication of free-standing PIM-1/MIL-101(Cr), PIM-1/UiO-66(Zr), PIM-1/ZTC, PIM-1/UiO-66(Zr)/ZTC and CF/PIM-1/UiO-66 composites was then achieved through adopting a simple direct impregnation method using a suitable solvent. This method is commonly used in mixed matrix membranes for gas separation studies, but the strategy was applied in this study to develop polymer-based composites for H$_2$ storage.

Chapter 4: The PIM-1/MIL-101(Cr) study at different mass loading of MIL-101(Cr) revealed that up to 80 wt% of filler material can be loaded on PIM-1 without altering the intrinsic properties of the filler wherein, textural, structural and morphological analyses confirmed the retention of porosity and crystallinity of MIL-101. The study additionally demonstrated that the BET surface areas and H$_2$ uptake of composites with low MOF loadings (40 and 60 wt%) agreed with the theoretical estimates based on the amount of respective components in the composite. Both the surface area and H$_2$ uptake for PIM-1/80 wt% MIL-101(Cr) were slightly higher than the estimated values. A hydrogen uptake of 1.73 wt % was obtained for PIM-1/80 wt% MIL-101(Cr) which is 7.5 % higher than the estimated value (1.61 wt %). The use of PIM-1, as a binder, proved advantageous since it did not show any signs of MIL-101(Cr) micropore blockage.

Chapter 5: Detailed studies were carried out with the optimal 80 wt% loading of UiO-66(Zr) and incorporation of ZTC to harness the advantage of both the fillers and matrix materials. The composites in this study were also found to retain accessibility of micropores, which led to a corresponding enhancement in H$_2$ storage performance. All the composites materials showed hydrogen storage performances which are in agreement with the predicted values with negligible loss of < 12%. The results also suggest that the ZTC-based composite materials (BET surface areas 1767 m$^2$g$^{-1}$-2433 m$^2$g$^{-1}$) were more stable and managed to retain most of the pristine ZTC intrinsic properties, with a lower pore blocking effect when
compared to the MOF based materials (BET surface area 1054 m²g⁻¹). Due to the absence of new peaks in the resulting PIM-1/MOF/ZTC composite, no confirmation of any cross-linking that occurred between the polymeric binder and filler materials was noted. Nonetheless, this study presented an easy-to-fabri cate PIM-1/80 wt% ZTC, PIM-1/UiO-66(Zr)/ZTC (80 wt%) composite that had not been reported before.

Chapter 6: The PIM-1/UiO-66(Zr) composite was anchored on carbon foam to obtain a CF/PIM-1/UiO-66 which had ease-to-handle properties. The carbon foam-immobilized PIM-1/UiO-66(Zr) composite material exhibited a hydrogen adsorption capacity of 1.05 wt.% at 77 K and pressure up to 1 bar. Thus, the intrinsic H₂ sorption properties of a MOF were retained. Unfortunately, it was revealed that CF is non-conductive due to its high void volume and its actual thermal conductivity (0.0703 Wm⁻¹K⁻¹) is less than that of UiO-66(Zr) MOF (0.2915 Wm⁻¹K⁻¹). As a result, no thermal conductivity enhancement in CF/PIM-1/UiO-66 was observed.

Chapter 7: This chapter aimed to employ 3D printing as a strategy for fabricating polymer/MOF/carbon composites materials. 3D printing as a relatively new processing technique was successfully used to fabricate ABS/10 wt% UiO-66, ABS/10 wt% ZTC and ABS/5 wt% UiO-66/5 wt% ZTC monolithic composites. The incorporation of UiO-66 and ZTC powders into an ABS polymer matrix proved to have good effects on the mechanical properties of powders without altering their crystallinity. The tensile strength of ABS (47.6 MPa) in ABS/5 wt% UiO-66/5 wt% ZTC composite (30.9 MPa) was slightly affected as expected. The characterisation results revealed that, the ABS/5 wt% UiO-66/5 wt% ZTC composite has a better degree of crystallinity and high thermal stability than pristine ABS. Unfortunately, there were challenges in performing the N₂ and H₂ adsorption isotherms due to pore blockage of MOF and ZTC by the ABS polymer.

In general, the results obtained from this thesis have established a facile shaping strategy for MOF and porous carbon powders for hydrogen applications without altering their gas adsorption properties. Therefore, these results further demonstrate the potential of hierarchical porous monolithic composites as adsorbents for H₂ storage applications. This is promising and opens new insights in that the properties and shapes of monolithic composites
can further be optimised with other porous polymer binders for enhanced H₂ storage and other related applications.

8.2. Future-work Recommendations

In general, the main objectives of the study were met. However, since the physical mixing of MOF powders with polymers presents some issues related to phase homogeneity, it is recommended that the polymer and MOF will need to be functionalised prior to mixing. This pre-synthesis modification will facilitate favourable chemical interactions between the filler and the matrix which will result in improved phase homogeneity and enhanced synergistic properties.

Furthermore, there are still a number of scientific and technological aspects that must be considered in future studies. In this case the following further studies are recommended;

- The incorporation of other types of polymers of intrinsic microporosity (except PIM-1) in MOFs and porous carbons can be explored in order to attain adequate balance between bulk packing density and high porosity to achieve both high volumetric and gravimetric H₂ uptake that will meet the US DOE targets.
- The post-synthetic activation of 3D printed composite monoliths with supercritical carbon dioxide for pore expansion.
- The thermal conductivity values obtained in this work were not consistent. Therefore, the use of a more appropriate and reproducible method for acquiring thermal conductivities of porous powders and their respective composites is required.
- Since the mechanical properties of the PIM-1/MIL-101(Cr), PIM-1/UiO-66(Zr)/ZTC and CF/PIM-1/UiO-66 composite materials have not been tested owing to the difficulties in synthesising large quantities of MOFs, ZTC and PIM-1, future studies should focus on upscaling these materials to allow the testing of their mechanical properties of their respective composites.
- Apart from solvent impregnation and 3D printing methods of fabricating MOF and porous carbon-based composites, other techniques such as granulation can be investigating using porous polymers such as PIMs and bis(chloromethyl)biphenyl polymers as binders.
• Evaluation of high pressure hydrogen uptake capacities of the porous composite materials is indispensable for real practical applications and therefore it is highly recommended for future work.

• Lastly, the feasibility studies need to be undertaken wherein the storage performance (cycle-life stability, kinetics, thermodynamics etc.) of the adsorbents can be interrogated by incorporating the shaped composites in a prototyped hydrogen storage tank. These tests will enable interrogation of their performance in simulated real-life conditions for hydrogen storage and hence should be considered in future studies.