Metal-organic frameworks for carbon capture

How the industrial-scale, cost-effective manufacture of MOFs and speciality nanomaterials could enable energy-efficient carbon capture and storage

James Stephenson
Promethean Particles

Leading scientific opinion increasingly points to human activity having a large, detrimental impact on our planet. One effect of this activity has been an unprecedented rise in global warming driven predominantly by increased emissions of greenhouse gases such as carbon dioxide (CO_2). The issues and consequences surrounding global warming have been well studied. Global surface temperatures have already reached 1.1°C above pre-industrial levels (IPCC, 2023). Exceeding a 1.5°C rise in average temperatures could risk the earth's stability and life support systems (IPCC, 2018).

This startling recognition has led to an acceleration in demand for new solutions to help tackle climate change and, with it, a particular emphasis on decarbonisation. There are multiple decarbonisation approaches that can be employed to reduce the overall carbon footprint, which we have coined the 'Decarbonisation Mix'. Many climate change proponents advocate strongly for the prioritisation of energy efficiency improvements and fuel switching to less carbon-intensive variants. However, many hard-to-abate industries (power generation, steel, cement, chemicals) cannot simply switch to different fuels or efficiently electrify their processes, at least in the near term. As such, a third element of the mix has to be carbon removals.

Carbon capture is therefore increasingly being recognised as a critical technology in the range of solutions needed to effect decarbonisation and help limit climate change. Despite the views of some, it is not an underhand way to 'greenwash' the continued use of fossil fuels. The UK government, the German government, and the Intergovernmental Panel on Climate Change (IPCC) have all recently opined that CO_2 removal and carbon capture are now necessary approaches for the world to have any chance of limiting global warming to the 1.5°C goal established in the Paris Agreement. The UK government's recent announcement of £20 billion in funding earlier this year to support the development of carbon capture and storage (CCS) projects highlights this emphatically.

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Current technological options for CCS systems are limited

The most widely used commercial carbon capture technology today is amine scrubbing. The first amine scrubbers were designed and implemented in the 1930s, and the process is largely the same today, despite some significant improvements in the performance of the amine solvents used.

A typical configuration for a CO_2 scrubbing system is shown in **Figure 1**. CO_2 containing flue gas enters the bottom of the absorber and rises upwards. The CO_2 is absorbed by the downward flowing amine, which then flows out of the bottom of the absorber and into the stripper. Here, the CO_2 rich amine is intensively heated to desorb and separate the CO_2. The reboiler at the bottom of the stripper provides

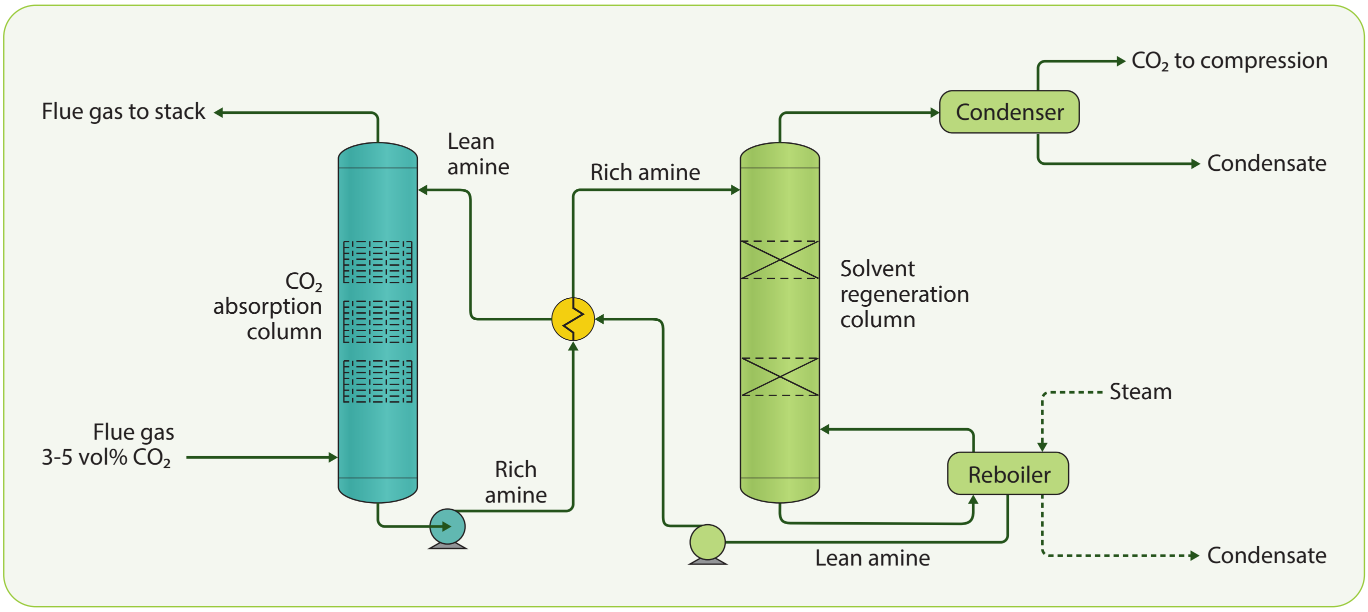

Figure 1 Typical configuration of an amine-based carbon dioxide scrubbing system

the necessary heating for the desorption of the CO_2. Reboiler bottoms are recycled back into the absorber, which provides regenerated lean amine ready to repeat the process.

Amine scrubbers have a high CO_2 uptake capacity and relatively low initial capital investment. However, they do suffer from some limitations. Firstly, the operational cost of amine scrubbers is expensive, mainly driven by the energy required to regenerate the amine once it is saturated with CO_2. Amines absorb CO_2 through a strong chemical reaction, forming very stable bonds that require significant energy to break during regeneration. Our customers in the power generation space have pointed to energy penalties in the 30-40% range, representing a significant drop in productivity regarding both Capex and Opex.

Due to the high energy input required, the reboilers are often large, further resulting in operational footprint restrictions. High-duty amine scrubbers have large space requirements, limiting their utility for smaller, more modular carbon capture duties.

Lastly, certain amines present challenges from a material handling perspective. Most amines undergo oxidative degradation and thermally degrade at solvent regeneration temperatures above 120°C (Vega et al., 2014). It is estimated that this degradation leads to an average monthly replacement requirement of 5% of the amine. Amines also tend to corrode the process equipment and pipework, leading to higher overall Capex and maintenance-driven downtime.

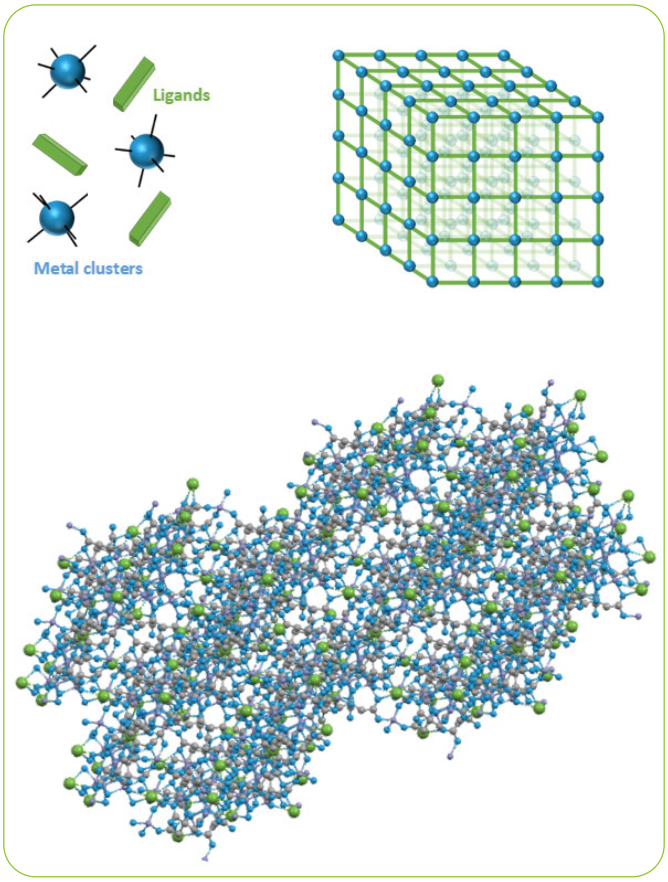

Figure 2 Simplified and modelled 3D representations of MOF structures comprising metal clusters and organic ligands (linkers)

Metal-organic frameworks (MOFs)

Initially discovered in 1965 as waste material from other chemical processes, MOFs are a class of materials with exciting chemical and structural properties. Well known for their ultra-high surface areas in excess of 7,000 m² per gram, MOFs also have uniform pore structures, tuneable porosity, and significant flexibility in network topology and chemical functionality. The first permanently porous MOF was discovered in the late 1990s, and the term 'metal-organic framework' was coined.

MOFs are highly porous crystalline frameworks comprised of multivalent metals bonded to multitopic organic linkers (see **Figure 2**). The choice of metal ion and organic linker molecules is almost limitless, and it is estimated that more than 100,000 MOFs have so far been synthesised. Despite significant promise, the development of MOFs has been mainly the purview of academia, with novelty rather than utility being the main driver. This has resulted in MOFs acquiring a reputation for high-cost and low industrial-scale manufacturability.

Role of MOFs in energy-efficient CCS systems

Along with their high porosities and incredibly high surface areas, certain MOFs also have other advantageous properties for carbon capture applications. These include high thermal and chemical stabilities, tuneable selectivity, low energy of desorption, and recyclability (Britt et al., 2009). MOF-based CCS has the potential to deliver significant advantages over incumbent technologies, including increased energy efficiency, lower process complexity, and smaller operating footprints.

December 2022 represented a significant milestone for the technology. Promethean Particles and the University of Nottingham announced the completion of a MOF-based carbon capture pilot project at Drax's incubation facility in Selby, North Yorkshire. The aim of the project was to show how MOFs would perform outside of the laboratory and in relevant industrial conditions and, as such, demonstrate the achievement of technology readiness level (TRL) 5 (see **Figure 3**). The project was successful and not only showed that MOFs could capture the CO_2 from the flue gas, but also helped inform future process design.

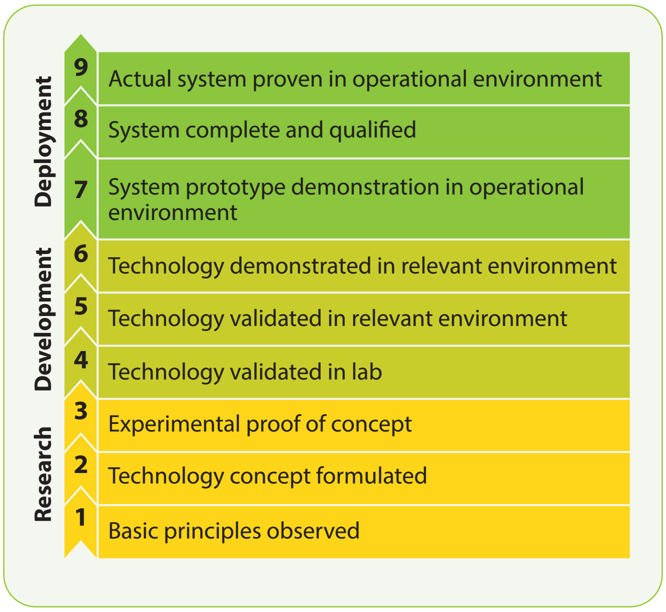

Figure 3 The technology readiness level scale (adapted by The Welding Institute [TWI])

Rapid progress of the technology has since been demonstrated. Further pilots have been completed, including a more sophisticated, automated system that meets TRL6 criteria. This system can be transported to customer sites to provide in-situ demonstrations of the technology against the customer's particular gas separation requirements. When not in use by customers, Promethean connects the system to its 1 megawatt (MW) gas-fired water boiler to help further inform process and application development activity.

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The Department for Energy Security and Net Zero recently announced financial support for Promethean to develop a TRL7 system capable of capturing 1-3 tonnes per day of CO_2 as a winner of the government's CCUS Innovation 2.0 competition. It is expected that these ever-increasingly sophisticated pilots will help de-risk this next-generation technological approach and lead to broader adoption of the technology across a range of point-source emitters in various industrial sectors. As highlighted in **Figure 4**, the operation

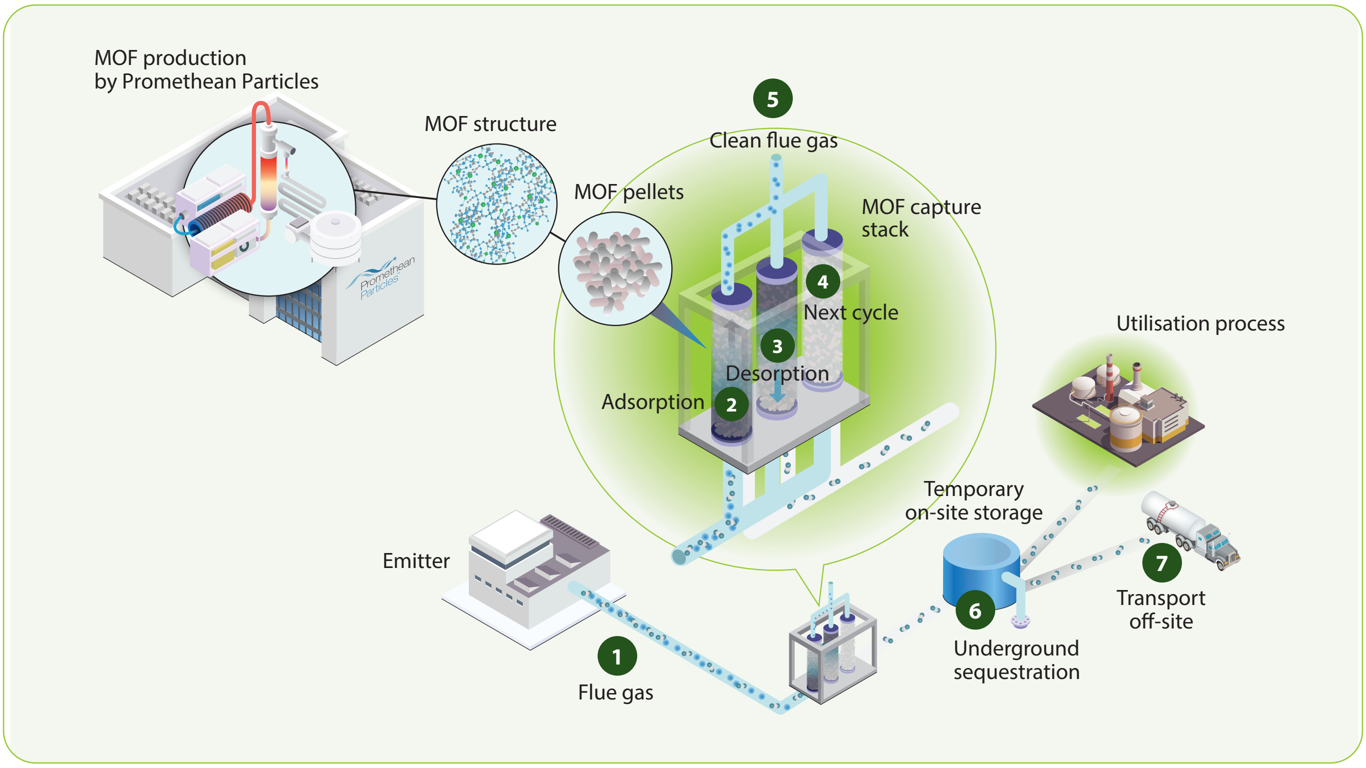

Figure 4 Infographic of a MOF-based carbon capture system

of a MOF-based carbon capture system is relatively simple:

❶ Having installed a new MOF-based CCS system, the emitter no longer vents their CO_2 containing flue gas to the atmosphere. It is instead piped to the MOF capture stack (MCS).

❷ The MCS contains a number of contactor beds that are operated in a sequence. CO_2 rich flue gas enters the first bed that contains MOF pellets which adsorb the CO_2.

❸ Just prior to the first bed becoming saturated (determined by an array of CO_2 sensors), flow is switched to a second bed. Once the flow is established at the second bed, automated valves switch the first bed into regeneration mode, which is effected by either a controlled swing of temperature or pressure (depending on the system design).

❹ Following regeneration/desorption, the bed is left ready for when it is needed for the next cycle.

❺ At all times, 'clean' flue gas is either vented directly from the MCS or is returned to the site's existing vent stack (if present)

❻ The stripped CO_2 is sent to temporary on-site compression and storage.

❼ The stored CO_2 can then be transported off-site for further downstream use or sequestration.

> **There are currently several different approaches to the manufacture of MOFs, and not all approaches are suitable for the efficient production of every MOF**

Commercial viability of MOFs

MOFs have historically suffered from perceptions of only being available in gram quantities and at exorbitant prices. This has rightly led many to question if it is remotely feasible and viable for a MOF-based technology to be deployed at the scale necessary to make an impactful dent in the global decarbonisation need in the fight against climate change.

There are currently several different approaches to the manufacture of MOFs, and not all approaches are suitable for the efficient production of every MOF. The classical, most widely used production method is solvothermal batch synthesis, where all raw materials are simultaneously loaded into a vessel and heated to initiate the synthesis reaction(s). However, batch synthesis, while well understood, is not without its challenges. The need to safely load all materials into a vessel and consistently heat,

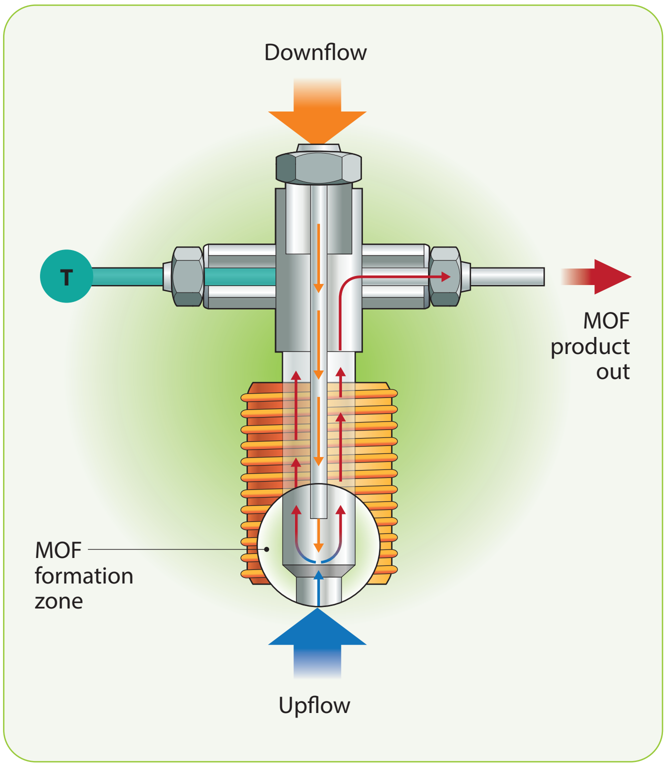

Figure 5 Schematic representation of a continuous flow MOF reactor

hold, and cool the reaction mixture provides little processing flexibility. Additionally, batch chemical processing can be much less efficient to scale and considerably more Capex intensive.

Continuous flow manufacturing of MOFs

It is broadly recognised in the chemical industry that continuous flow manufacturing is a more efficient, cost-effective production methodology where the volumes are sufficiently high and product changeovers are infrequent. Promethean is a global pioneer in the continuous flow manufacture of advanced materials, including MOFs. It operates the largest continuous multi-nanomaterial manufacturing plant in the world that utilises proprietary, patented reactors (see **Figure 5**).

The continuous flow manufacturing process is a considerable advantage in large-scale, low-cost manufacturing of MOFs. Continuous flow hydrothermal synthesis provides a huge amount of process flexibility not afforded by other manufacturing methods. Each reaction stream can be independently controlled, including flow rate, temperature, pressure, and concentration. This process control yields quality advantages and the ability to tune MOF morphology as well as a significant input on cost performance.

The continuous manufacturing process helps achieve orders of magnitude lower costs, and essentially renders Capex and conversion costs insensitive to the final product cost, a critical consideration when assessing how to efficiently scale into the millions of tonnes.

Conclusion

There are numerous technological approaches to address climate change, including energy efficiency improvements, fuel switching, and carbon capture. There is no single panacea solution to address a problem of

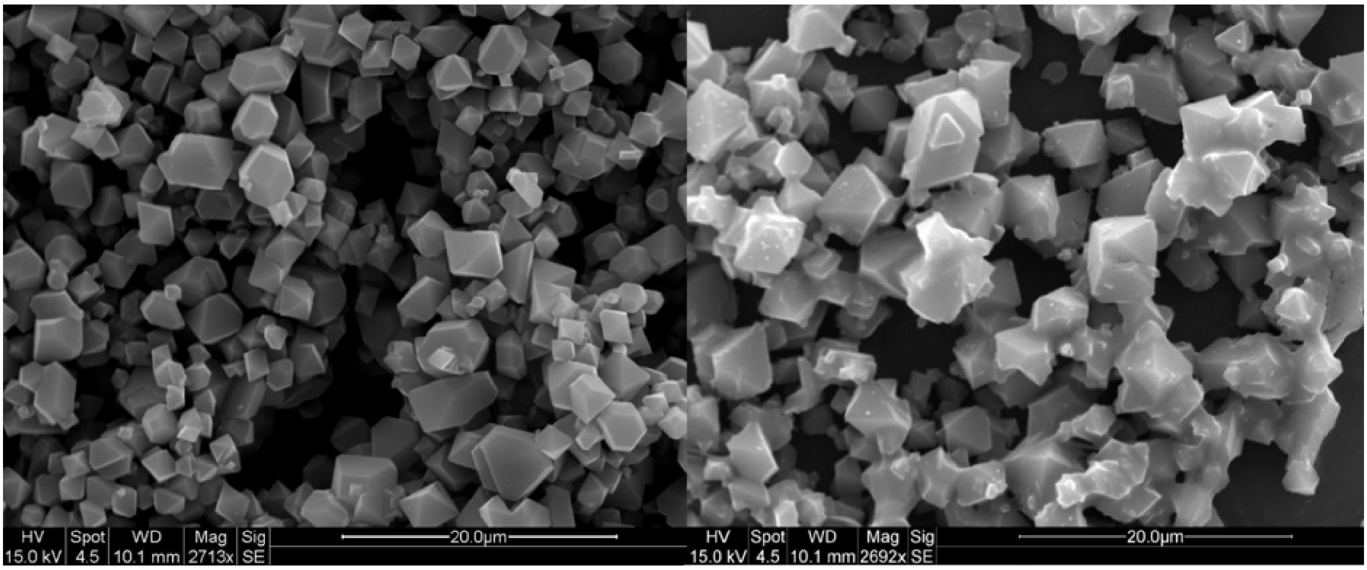

Figure 6 Scanning electron microscope (SEM) images of inconsistent particle size, left, and incomplete growth and agglomeration, right *(Images obtained at The nmRC, University of Nottingham)*

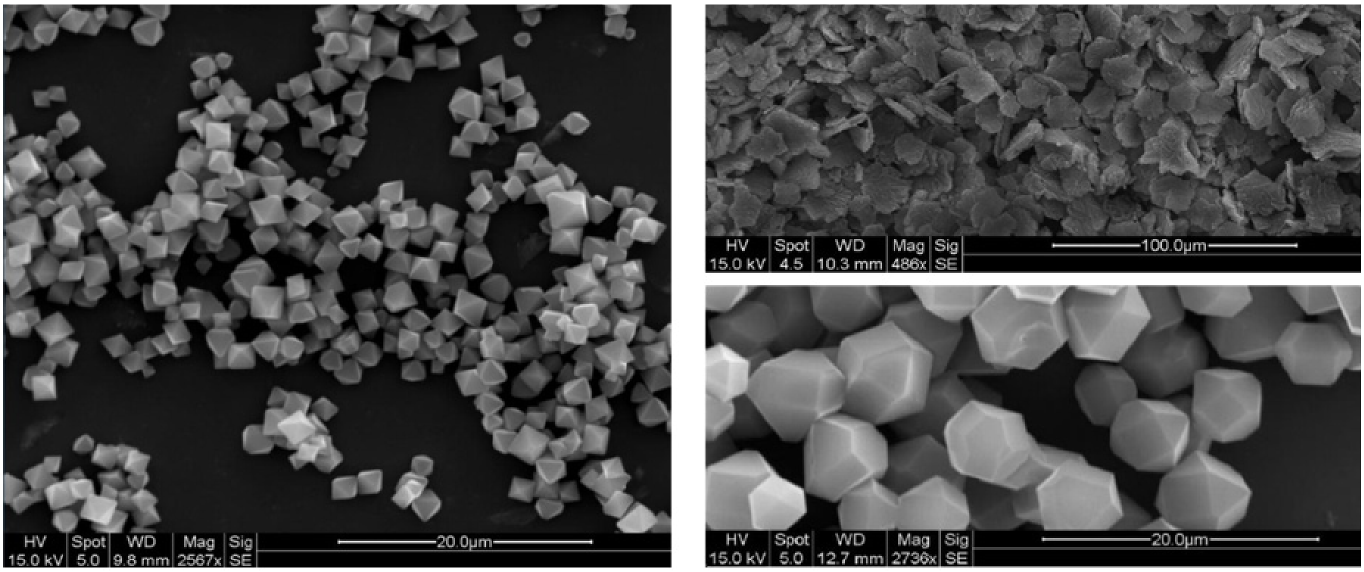

Figure 7 SEM image of clean, uniform particle size distribution, left, and SEM images of different morphologies of the same MOF structure, right *(Images obtained at The nmRC, University of Nottingham)*

this magnitude, so multiple approaches must be deployed.

MOFs continue to show a lot of potential as adsorbent materials for carbon capture. However, their industrial viability is predicated on an ability to manufacture at an industrial scale and at orders of magnitude lower costs than those currently reported.

Promethean is pioneering the industrial-scale, cost-effective manufacture of MOFs and speciality nanomaterials via its proprietary synthesis process.

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