New synthetic routes towards MOF production at scale

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The potential commercial applications for metal organic frameworks (MOFs) are tantalizing. To address the opportunity, many novel approaches for their synthesis have been developed recently. These strategies present a critical step towards harnessing the myriad of potential applications of MOFs by enabling larger scale production and hence real-world applications. This review provides an up-to-date survey (212 references) of the most promising novel synthetic routes, i.e., electrochemical, microwave, mechanochemical, spray drying and flow chemistry synthesis. Additionally, the essential topic of downstream processes, especially for large scale synthesis, is critically reviewed. Lastly we present the current state of MOF commercialization with direct feedback from commercial players.

1. Introduction

Metal organic frameworks (MOFs) have emerged as a focus of academic fascination and commercial opportunity due to their unprecedented structures that imply a plethora of potential applications. The initial report from Hoskins and Robson instigated a new field of coordination chemistry, combining the tenets of organometallic cluster chemistry with established coordination motifs to form coordination polymers, a.k.a. MOFs.1,2 Later reports from key instigators including Yaghi,3,4 Kitagawa,5,6 Ferey,7,8 and Long9,10 projected the potential applications of MOFs, utilising the combination of unprecedented porosity with periodicity and versatile chemistries. The applications envisaged were largely based on separation, storage, sensing or release characteristics.11–15 As a result, it is possible that MOFs could have revolutionary performance in areas that include natural gas storage,16–18 petrochemical separation,19,20 CO2 capture,21,22 or drug delivery.23,24

However, central to the translation of these new materials into disruptive technologies is the ability to manufacture MOFs at the required scale, purity and price for implementation.

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For example, the potential application of the enormous natural gas reserves globally as a fuel for vehicles, adsorbed in MOFs within the tank would immediately require megaton scale production of MOFs. Or in CO₂ capture, more than 8000 million tons of CO₂ are produced from coal-fired power stations annually, again requiring many millions of tons of MOF to capture it. In the laboratory, MOFs are most commonly produced in milligram scales, with multi-day reaction times in expensive organic solvents. Their synthesis is often the balance of a number of competing forces, with a range of kinetic and thermodynamic products possible, meaning that a narrow set of reaction conditions are often possible for a successful synthesis. The large gap between laboratory production and that required for commercial application has created a strong imperative to develop efficient and versatile means of producing MOFs at scale.

As scale up production methods are developed, parameters for assessing their viability have become important. Of these, the key parameter is the space-time yield (STY), a measure of

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the amount of MOF able to be produced per unit volume of reactor in a 24 hour period. In concert with this, we recently proposed that the absolute value (in g h\(^{-1}\)) is also important. Many new production techniques are still in the early stages, meaning that the calculated STY may be prone to over extrapolation. Other important factors are measures of product quality (such as surface area and phase purity), particle size control, yield, and the versatility of the technique. This article will seek to use these criteria in describing the prospective production methods featured herein.

There are several challenges common to the bulk of the prospective scale up methods:

(a) Use of organic solvents. At scale, their cost, toxicity and in some cases flammability become significant issues.

(b) Anion build up. Typically, metal salts are employed as precursor molecules. At scale, nitrates present a safety hazard, and anions such as chlorides can prove corrosive. Oxide and hydroxide metal precursors are preferable.

(c) Ligand availability. Many MOFs require bespoke organic ligands. Production methods that could also produce these starting materials are in development.

(d) Particle size control. Applications such as membranes require nanometre sized particles whereas in storage applications. Larger particles are desired to stop unwanted movement of the MOF particles. Control of this is an important attribute.

(e) Activation. MOFs require removal of non-volatile solvents and unreacted starting materials from their pores. This is a major consideration at large scale.

(f) Shaping of MOF powders produced is also required for using them in real industrial applications.

All these challenges, which are specific for each MOF family due to their different composition and coordination nature, together with their extreme porosity, make the synthesis of these materials more complex than zeolites; each MOF requires bespoke conditions. In recent years, a number of approaches for addressing these challenges have been considered, including electrochemical, microwave and mechanochemical syntheses as well as spray drying and continuous flow production. Electrochemical synthesis of MOFs was developed by BASF and their initial purpose was to exclude anions by using metal electrodes as metal sources. Microwave-assisted synthesis, flow chemistry and spray-drying synthesis allow for a faster crystallization rate and production of smaller MOF crystals. In mechanochemical synthesis, no external heating or solvent is needed, reducing the washing and activation labour after the synthesis.

Given the rapid progress in the development of these techniques, there has been a recent rise in commercial entities that seek to utilise and/or produce MOFs. This review seeks to provide an update on progress of these companies, with direct input from them. BASF pioneered large-scale, bespoke solvothermal techniques primarily for use in vehicular natural gas storage. Following this, spin-out companies have been established, often based upon novel reaction techniques originally developed in a research setting. Some spin-out companies also seek to develop MOF-based products in addition to the broader supply of MOFs to the research community.

In the following, we review the novel synthesis routes developed to date. We also discuss important downstream processing considerations and provide a summary of recent commercial developments.

2. Production of MOFs: from laboratory to industrial scale

In 1995, Nalco Chemical Company and Omar Yaghi claimed the use of solvothermal synthesis to obtain MOFs.\(^{28}\) Up until now, this synthetic approach is the most common way to obtain grams of MOFs in the laboratory around the world. This method involves mixing solutions of the inorganic salt with the organic linker in a sealed reactor vessel and subsequent heating to promote the growth of insoluble frameworks that precipitate as fine crystals.\(^{29,30}\) This sealed approach allows the reaction mixture be heated up to temperatures and pressures above the solvent’s boiling point to solubilize, partially or completely, otherwise insoluble reagents and form extended networks. It has become a benchmark in MOF chemistry, and a large variety of MOF families such as MIL series,\(^8,31\) MOF-74,\(^32,33\) UiOs\(^34–36\) and PCNs\(^37,38\) have been synthesized following this principle.

However, despite the tremendous academic interest that MOFs have generated in the last two decades, with thousands of new structures and with very promising applications, only very few of them are produced at large scale and used in real world applications.\(^18,22,23,19–41\) The main reasons for this are the lack of stability of most of the structures towards temperature and humidity, the high cost of the raw materials and, above all, the difficulty of scaling up the synthesis and the post-synthetic stages in a cost-effective way whilst maintaining the product quality and reproducibility between batches. In addition, while the solvothermal approach is a well-known industrial method for chemical synthesis, its application for large scale MOF production is not feasible as MOF synthesis relies on the nucleation at a reactor vessel surface. Up-scaling the reactor vessel significantly decreases the surface to volume ratio and consequently, reduces the efficiency of the reaction. Additional problems include: long reaction times (hours or days), large amounts of solvents used, low quality of materials obtained, high complexity and cost in the up-scaling.\(^42\)

In order for any production MOF process to be industrially viable a number of key aspects have to be considered: (i) a versatile method is crucial in order to accommodate the maximum number of MOF structures with the same piece of equipment; (ii) the possibility to avoid harsh processing conditions such as high temperature and pressure will reduce capital and operating costs and alleviate safety concerns; (iii) a switch from batch to continuous processing would be beneficial offering higher output per unit time and a continuous steady-state operation leading to significantly reduced downtimes, labour costs, reactor volumes, as well as constant and consistent production; and (iv) a high space-time-yield (STY) parameter which measures the amount of MOF produced per m\(^3\) of reaction mixture per day.
All these factors make the scale-up of MOF production challenging and have motivated many researchers and engineers to explore and develop novel and commercially viable routes to produce MOFs in an efficient, reproducible and cost-effective way. Fig. 1 shows the timeline of the most common synthetic processes developed in the last two decades. In this review, we will focus on energy-efficient processes with reduced reaction times that facilitate the up-scaling and the continuous operation. In the following sections, we will describe in detail the advances in electrochemical, microwave and mechanochemistry approaches and the more recent routes, the spray dryer and flow chemistry. 

### 2.1 Novel synthesis routes

#### 2.1.1 Electrochemical synthesis

Electrochemistry can be defined as the study of interconversion between chemical and electrical energy. It combines electricity and chemistry and deals with chemical changes caused by an electrical current.

Taking advantage of the potential of electrochemistry to synthesize materials and their large experience in the domain, the company BASF first patented the use of electrosynthesis to produce MOFs in 2005. The synthesis consisted on immersing a copper plate in a solution containing the organic linker, 1,3,5-benzenetricarboxylic acid (BTC), and an electrolyte. The copper plate, which acts as the electrode, was used as the source of Cu(II) ions. When a certain current or voltage was applied, the Cu(II) ions were released from the copper electrode to the solution and reacted with the dissolved linker. In this patent, a powder of electrochemically produced HKUST-1 that consisted of octahedral crystals (size: 0.5–5 μm) could be fabricated after applying a voltage of 12–19 V and a current of 1.3 A for 150 minutes. The surface area of this synthesized HKUST-1 was 1820 m² g⁻¹, which is higher than that reported for the solvothermally synthesized HKUST-1 (1550 m² g⁻¹).

Since this first patent, electrochemical synthesis of MOFs has attracted great attention because it can offer many advantages. One of them is the possibility to run the synthesis of MOFs in a continuous way. It also allows their synthesis under milder conditions than typical solvothermal or microwave syntheses, reducing the reaction time. Indeed, while solvothermal synthesis might take hours or days, electrochemical methods can produce the MOF material within minutes or hours. In addition to these, the electrochemistry method provides the ability to control the MOF synthesis directly during the reaction by controlling the passed current or applied voltage. Furthermore, the electrochemistry method offers the possibility to synthesize homogeneous thin films or coatings.

Electrosynthesis of MOFs can be classified in two main methods: (i) the anodic dissolution, which was the first route patented by BASF; and (ii) the cathodic deposition. In the anodic deposition, an applied electric potential induces the release of metal ions from the electrode, which then react with an organic linker present in the solution leading to the formation of a MOF film. In this case, the use of a metallic electrode (instead of metal salts) as the source of metal cations avoids the formation of any corrosive anions (mainly, nitrate and acetate anions) or any by-products. The anodic dissolution is typically carried out in a two-electrode set-up without a reference electrode, and the use of protic solvents is usually needed to ensure the evolution of hydrogen and avoid the reduction of metal ions at the counter electrode. In addition, the use of a sacrificial compound (e.g. acrylonitrile, acrylic or maleic esters) that are preferentially reduced or a counter electrode with a suitable overpotential for hydrogen evolution is recommended. In the cathodic deposition, a solution containing the organic linker, the metal ions, and a so-called probase is contacted with a cathodic surface. In this approach, the MOF film deposition results from increasing the pH near the cathodic surface, where the electrochemical reduction of the probase occurs. An example of a probase is the nitrite ions coming from the reduction of nitrates, which are able to deprotonate the organic linker and form the MOF.

Since the electrochemical synthesis of HKUST-1 by BASF using the anodic dissolution was reported, there have been many efforts to understand and optimize this new route (Fig. 2a). Fransaer et al. recently proposed a mechanism for the anodic dissolution synthesis of HKUST-1 that consists in four phases: (i) initial nucleation; (ii) growth of HKUST-1 islands; (iii) intergrowth; and (iv) crystal detachment. When an electric potential is applied, the oxidation of the anode starts and the Cu(II) ions are released into the solution. The nucleation of the HKUST-1 phase starts once the critical ion concentration on the surface of the anode is reached. The nucleation is progressive and the dimensions of the crystals depend on the synthesis time and choice of the solvent. The HKUST-1 layers grow at the MOF-solution interface confirming that Cu(II) ions, which are dissolved at the interface, diffuse through the HKUST-1 crystals before they react.
with the organic linker. This migration of ions is accompanied by the creation of voids at the substrate–HKUST-1 interface, resulting in the formation of fragile layers of HKUST-1 crystals that are easily detached from the substrate. Simultaneously, van der Veen and Domke et al. described this anodic dissolution mechanism from a more chemical point of view. These authors identified that chemical species involved in the electro-synthesis of HKUST-1 are initially Cu$_2$O, which results from the oxidation of the copper plate in the presence of H$_2$O or O$_2$. Then, Cu$_2$O is further oxidized to CuO that can react with the organic linker and lead to the formation of HKUST-1 crystals.

To date, it is known that small variations of the applied electric potential and passed current, the nature of the solvent and its conductivity, and nature of the electrolyte have a strong influence on the anodic dissolution synthesis of HKUST-1. For example, the applied electric potential is important due to the influence on the anodic dissolution synthesis of HKUST-1. For instance, increase of conductivity by increasing the concentration and its conductivity, and nature of the electrolyte have a strong influence on the anodic dissolution synthesis of HKUST-1. For example, increase of conductivity by increasing the concentration of MTBS in the electrolyte solution reduced the ohmic drop of the solution and increased the production yield of HKUST-1. However, Deyaner et al. found some disadvantages related to the use of MTBS in the electrochemical formation of HKUST-1 thin films. They observed structural damages of the copper mesh and the generation of non-adhesive HKUST-1 crystals at the surface of the anode. On the contrary, they could get more control over the synthesis in the absence of MTBS because of lower current density in the system. Another disadvantage of using MTBS was reported by Hartmann et al., who observed a decrease in the surface area of HKUST-1 that was attributed to the presence of the electrolyte salt in its pores.

Beyond the archetypical HKUST-1, the syntheses of other MOFs have been envisaged using anodic dissolution. Remarkably, Gascón et al. demonstrated the possibility to electrochemically synthesize ZIF-8, MIL-53 and MIL-100(Al). Since then, De Vos and Fransaer et al. optimized the quality of the synthesized MIL-100(Fe) by performing the electrochemical synthesis under high pressure and high temperature. Also, Attfield and Dryfe et al. improved the synthesis of zeolitic imidazolate frameworks (ZIF) (e.g. ZIF-4, ZIF-7, ZIF-8, ZIF-14, and ZIF-67) coatings (Fig. 2d) by increasing the reaction times (a proxy for higher metal ion concentration), the organic linker concentration and the reaction temperature. With this anodic dissolution,
luminescent rare earth based MOFs were also prepared by Fransaer et al. on electrically conductive solid substrates. Here, Tb-BTC and Gd-BTC layers were electrochemically synthesized on terbium and gadolinium metal foils by immersing the foil in a water-ethanol solution containing the organic linker, the electrolyte (MTBS) and applying a constant current of 1 mA cm$^{-2}$.

Within this variety of MOFs, the electrochemical synthesis of MOF-5 has also been largely investigated. Cao et al. reported the anodic dissolution electrosynthesis of thin films of rod-like MOF-5 crystals. They could generate dense and thick MOF-5 films by using zinc electrodes in an aqueous solution containing H$_2$BDC and ammonium fluoride as the electrolyte salt and applying voltage (2 V) at 65 °C. Liang et al. synthesized MOF-5 in the form of flower shape by using molten salt in the electrolyte solution and 1-butyl-3-methylimidazole (BMIM) bromine as a template. This MOF-5 was synthesized using a zinc plate as the anode, a titanium plate as the cathode, and a DMF and BMIM bromide mixture containing H$_2$BDC and zinc nitrate hexahydrate as the electrolyte solution. The reaction was done in atmospheric conditions and applying a current density of 0.025 A cm$^{-2}$ for 2 hours.

As stated above, the second main route for the electrochemical synthesis of MOFs is the cathodic deposition. In 2011, Dinca et al. first investigated the cathodic deposition of MOFs to resolve two major limitations of the anodic dissolution (Fig. 3a): (i) the deposition surface (anode surface) is used to produce the metal cations and thus, it is eroded in a continuous manner throughout the synthesis; and (ii) the selection of the anode metal is limited since the anode is also used as the metal resource. In this cathodic deposition, the metal salt, which is dissolved in the electrolyte solution together with the organic linker and the probe, is used as the metal precursor. To show the potentiality of this approach, Dinca et al. showed the synthesis of HKUST-1 and MOF-5 in only 15 min at room temperature (Fig. 3b). For it, they used fluoride doped tin oxide (FTO) as the working electrodes, Ag/Ag(cryptand) as the reference electrode, and a DMF: water (100 : 1) (v : v) mixture containing the organic linkers and the metal salts as the electrolyte solvent. In these syntheses, it was found that the nature of the metal salt plays a crucial role. This importance is due to the nature of the counteranions, which act as a probase and can inhibit or favour the formation of the desired MOF.

For example, as the synthesis of MOF-5 starts with the formation of Zn$_5$(OH)$_6$(H$_2$O)$_2$(NO$_3$)$_2$, the use of chloride anions can inhibit its formation due to the formation of Zn$_5$(OH)$_6$(Cl)$_2$(H$_2$O)$_2$. On the contrary, the use of nitrate anions can help on its formation since they can act as the probase and participate in the formation of the intermediate specie.

The aptitude of the cathodic deposition to favour formation films was also exploited by the same authors to form more complex biphasic MOF thin films at room temperature from single deposition baths using potential bias as the main user input. In this case, bilayer structures of MOF-5 and (Et$_3$NH)$_2$Zn$_3$(BDC)$_4$ (applied potential: −1.7 V) (Fig. 3e), mixed structures of MOF-5 and (Et$_3$NH)$_2$Zn$_3$(BDC)$_4$ (applied potential: −1.1 V), and layers of only (Et$_3$NH)$_2$Zn$_3$(BDC)$_4$ (applied potential: −1.5 V) were fabricated tuning the applied potential.

Later innovations on the electrochemical synthesis of MOFs have been centered on the development of new methodologies such as electrophoretic deposition, galvanic displacement, anodic–cathodic deposition or bipolar electrochemistry. For example, Ameloot et al. combined both anodic and cathodic deposition to perform the modulated synthesis of UiO-66 simultaneously on both anode and cathode surfaces. For this synthesis, zirconium films were used as electrodes and H$_2$BDC was dissolved in a mixture of DMF, nitric acid (electrolyte), water and acetic acid (AA). AA was used as a modulator to increase the amount of linker defects and therefore, the BET surface area. However, increase of AA also decreased the crystallinity because of the increase of the competition between BDC and AA. It was found that denser packed films with smoother surfaces were formed on the anode when an AA concentration of 0.5 M or 1 M was used, and that larger octahedral UiO-66 crystals were obtained for AA concentrations higher than 5 M. In this process, when the AA concentration increased, the complexion of released Zr(IV) ions also increased leading to a decrease of the anodic deposition. On the contrary, when the concentration of AA decreased, the concentration of released Zr(IV) ions increased, thereby increasing the deposition on the cathode.

Another interesting example was reported by Bradshaw and Kuhn et al. who used bipolar electrochemistry (BE) to produce Janus-type MOF composites inducing the site selective ZIF-8 or HKUST-1 crystallization on a polarized metallic wire under an electric field. In BE, a conducting object is exposed to an electric field established between two electrodes in a solution this...
induces a positive and negative polarization between the two opposite sides of the object and a redox reactions can occur.77

2.1.2 Microwave synthesis. Microwave (MW) irradiation is a widely used method in organic chemistry. In recent years it has been used for the synthesis of inorganic nanomaterials – zeolites and MOFs, among others.78-81 The method is based on the interaction of electromagnetic waves with any material containing mobile electric charges, such as polar molecules in a solvent or conducting ions in a solid. Contrary to classical solvothermal methods, where thermal energy is transferred from the heat source to the solution through the reaction vessel, in MW synthesis the irradiation interacts directly with the reactants, resulting in more efficient and faster heating. Additionally, in MW synthesis crystallisation occurs at the hot spots that form due to the direct heating of the solvent, in contrast to the wall of the reactor vessel as with conventional heating methods. Consequently, it is much faster and results in a smaller particle size. In this section, we describe some remarkable examples of the preparation of MOFs via microwave irradiation.

The pioneering work on MW synthesis of MOFs by Jhung et al. reported the water-based synthesis of the chromium trimesate MIL-100 MOF in the presence of hydrofluoric acid.82 The synthesis was performed in a microwave oven at 220 °C for 1, 2 or 4 hours with the reaction mixture in a sealed Teflon autoclave. The results showed the presence of unreacted metallic chromium species for reaction times less than 2 hours. The crystal yield obtained after 4 h was 44%, which is comparable to the 45% achieved in the conventional synthesis in 4 days. Two years later, the same group reported the synthesis of spherical nanocrystals of chromium terephthalate MIL-101 MOF.83 In this work, they showed that crystal size increases with increasing irradiation time, ultimately allowing the isolation of particles with a high surface area.

The MW synthesis of IRMOF-1, IRMOF-2, and IRMOF-3 was reported by Ni et al. who obtained microcrystals with a relatively uniform size and identical cubic morphology in less than 2 minutes.84 They showed that the crystal size can be varied from micrometer to submicrometer by manipulating the concentration of the starting material. The same synthesis was conducted by Choi et al. who investigated how the power level, irradiation time, temperature, solvent concentration and substrate composition affected the crystallinity and morphology of MOF-5.85 The microwave irradiation lead to crystals after only 30 min of reaction time while 24 h were necessary with the conventional method. The optimum microwave conditions lead to uniform cubic crystals with average size of 20–25 μm and with a BET surface area of 3008 m² g⁻¹.

MW irradiation is an attractive method to synthesize MOFs with biomedical applications, such as iron-carboxylate MOFs, because uniform nanocrystals are easily achievable. For instance, in 2009, Lin and co-workers described the MW synthesis of 200 nm nanoparticles of iron-MIL-101 MOF and its amino functionalized version.86 The starting materials were dissolved in DMF and then rapidly heated to 150 °C and held at this temperature for 10 minutes.

Several studies have been performed comparing conventional electric (CE) heating, MW and ultrasound (US) methods in order to understand the accelerated US and MW syntheses.87-90 For example, in 2009, Haque et al. performed a kinetic study on the synthesis of MIL-53-Fe.91 They found that the crystallisation rate (both nucleation and crystal growth) decreased in the order: US > MW ≫ CE. These results suggested that physical effects, such as hot spots, are more important than chemical effects in the accelerated syntheses performed under US and MW conditions (see Fig. 4). A similar study was performed by Chalati et al. where the synthesis of iron fumarate MIL-88A nanoparticles was compared with the classical solvothermal, MW and US methods.92 With the CE heating a polydisperses sample of 200 nm nanoparticles was obtained, whereas 100 nm monodisperse nanoparticles but with very low yields were obtained with the US method and <100 nm monodisperse nanoparticle with high yields were obtained with the MW method.

The zeolitic imidazolate framework, ZIF-8, has been synthesized with MW irradiation and CE heating at 140 °C in 4 hours and 20 hours respectively.93 In addition to the reduced reaction time, the ZIF-8 obtained by microwave heating had a larger surface area and micropore volume compared with the ZIF-8 synthesized with CE heating.

There are a few reports available showing the effectiveness of MW irradiation for the synthesis of lanthanide–organic frameworks. For example, Silva et al. obtained quality single-crystals of the microporous cationic [Ce₂(pydc)₂(Hpydc)(H₂O)₂]Cl (where pydc corresponds to the 2,5-pyridinedicarboxylic acid) by applying MW heating for 20 min at 200 °C.94 In 2014, Vileda et al., synthesized a series of lanthanide (Eu, Gd and Tb) bisphosphonates using conventional hydrothermal synthesis (180 °C, 3 days), MW-assisted heating (40 °C, 5 seconds) and US-assisted
synthesis (room temperature, 5 minutes). Under CE heating, microcrystalline materials were obtained which did not possess any significant catalytic activity, whereas the application of MW and US resulted in nanocrystals that exhibited relatively high catalytic activity and excellent selectivity to 2-methoxy-2-phenylethanol (100% yield within 48 hours of reaction time). A recent work by Cao and co-workers showed the gram scale production of nine isostructural microporous lanthanide MOFs via a microwave over 5 min. The same synthesis but under conventional solvothermal reaction required seven days to produce the same materials with a similar yield. Moreover, with the solvothermal method only 10 milligrams of quality material could be obtained while MW synthesis yielded up to 2 grams.

In recent years, zirconium-based MOFs have attracted great attention due to their exceptionally high thermal and chemical stability. In 2013, D’Alessandro and co-workers reported the efficient synthesis of MIL-140A, MIL-140B and MIL-140A-NH₂ frameworks using MW irradiation. They obtained products with purer phase and higher quality in significantly less time than the CE heating method. Recently, a process optimisation for the UiO-66 MW assisted synthesis was presented by Taddei and co-workers. The optimized synthesis required 15 minutes of pre-mixture of the initial solutions and 15 minutes at 120 °C. The reaction yield was 83% and no significant negative effects on morphology, crystal size, or defects were found from the use of MW assisted heating in comparison with those synthesized by CE heating. One exciting area that it has been explored with MW in the last 2 years is the defect engineering of UiO-66. Babarao and co-workers presented an experimental and theoretical study showing the correlation between the defect concentration composition in UiO-66 and their carbon dioxide adsorption properties. They presented a detailed MW-assisted solvothermal synthesis protocol to prepare pure phases of high-quality crystalline UiO-66 frameworks with different defect concentrations. Highly crystalline UiO-66 octahedral shaped crystals were obtained in a short reaction time of 5 minutes using hydrochloric acid and formic acid as modulators.

### Mechnanochemical synthesis

Mechanosynthesis is a well-known technique in metallurgy and mineral processing but within the last few decades it has expanded rapidly into many areas of chemistry such as catalysis, inorganic chemistry and pharmaceutical synthesis. The central concept behind this synthesis method is to promote chemical reactions by milling or grinding solids without any or with only minimal amounts of solvents. With this approach the conventional solvothermal MOF reactors are substituted by a mortar and pestle or in a mechanical process by automated ball mills. In general, the mechanical milling process is higher in energy and ensures the reproducibility between batches. In addition to the solvent-free conditions, this approach leads to a faster and more efficient synthesis of MOFs obtaining quantitative yields and allows to use MOF precursors with low solubility such as oxides, hydroxides and carbonates. However, the big limitation lies in up-scaling mechanosynthesis, it is essentially a batch processing technique with a relatively low rate of production. Furthermore, it should be noted that despite a ‘solvent-free’ synthesis, purification may still be needed and may require a solvent. Nevertheless this synthesis approach is the most environmentally friendly process to produce MOFs, and hence could reduce significantly the cost of production.

The three different mechnanochemical approaches used for MOF production are Solvent-Free Grinding (SFG) which is the simplest method and avoids the use of solvent; Liquid-Assisted Grinding (LAG) which is more versatile, and quicker, as it uses catalytic amounts of liquid phases which increase the mobility of the reagents; and finally, Ion-and-Liquid Assisted Grinding (ILAG) which uses a catalytic liquid with traces of salt additives to accelerate the MOF formation. Using these techniques, the synthesis for almost all families of MOFs has been demonstrated, and selected studies will be explained in this section.

A first work by James and co-workers employed the SFG method, milling a dry mixture of copper acetate and isonicotinic acid (Hina) powder for 10 minutes resulting in the formation of copper(ii) isonicotinate MOF with acetic acid and water molecules occluded in the pores (see Fig. 5a). Using the same approach, the same group performed a screening study, grinding sixty different combinations of twelve different divalent metal salts, composed of copper, nickel and zinc together with five different carboxylate organic linkers for 15 minutes. As a result several crystalline structures, including two microporous metal–organic frameworks HKUST-1 and Cu(INA)₂, were obtained.

One important advantage of this approach is the possibility to synthesize MOF's with only water as a by-product allowing the complete elimination of the purification stage. This is achieved by using hydroxides or oxides as the metal source which then in combination with the protons generated from the organic ligand forms H₂O.

Following this strategy, Tanaka and co-workers presented the mechanical dry conversion of zinc oxide and an imidazole ligand into ZIF-8. The process was investigated for reaction times of 3 to 240 hours, yielding the best BET surface area (1480 m² g⁻¹) at 96 hours. The decrease of the BET surface area after 96 hours was due to the formation of amorphous domains during the mechananochemical reaction. The same year, Balema and co-workers reported the preparation of the yttrium based MIL-78 MOF under completely liquid-free conditions and using a metal hydride for the first time as a starting material and forming hydrogen as a by-product.

Very recently, Xu and co-workers reported the synthesis of MIL-101(Cr) without the addition of solvent and hydrofluoric acid. The chromium salt and the terephthalic acid were ground for 30 minutes at room temperature and then transferred into an autoclave at 220 °C for 4 hours, yielding a material with a BET surface area of 3517 m² g⁻¹ and with a reduced particle size compared to the batch process.

In 2006, Braga and co-workers demonstrated for the first time how the addition of small amounts of solvent to the powder mixture precursors could effectively improve the crystallisation of the compounds and accelerate the synthesis. They synthesized the CuCl₃(dace) [where dace is the trans-1,4-diaminocyclohexane] one-dimensional coordination polymer by grinding the starting materials for 5–10 minutes in the presence of water or DMSO.
which was then removed by thermal and vacuum treatment. In 2009, Frisˇcˇic´ and Fábián demonstrated the ability to selectively and quantitatively build different metal–organic architectures by simply changing the amount and type of solvent using the same starting materials. In this specific work, they presented the formation of four coordination polymers and two porous structures by grinding zinc oxide and fumaric acid in the presence of different types of solvents.116 In 2010, Klimakow et al. synthesized the well-known HKUST-1 and its benzenetribenzoate-based analogue MOF-14 via the LAG approach. The MOFs were obtained by grinding the copper acetate monohydrate salt with the corresponding organic linkers for 25 minutes. Acetic acid was formed as a by-product, which blocked the micropores and consequently resulted in a smaller BET surface area compared to other synthetic approaches.117 James and co-workers showed that by adding small amounts of liquid by-products, generated via the SFG method, before the mechanical process, that the synthesis could be accelerated.118 By adding small amounts of acetic acid into the precursor mixtures, the formation of Cu(INA)₂ MOF was dramatically accelerated, while for HKUST-1, due to the lower solubility of the trimesic acid, no improvement was reported. In 2010, the same group studied by X-ray diffraction the structural properties of [Zn₂(fma)₂(bipy)], where fma corresponds to fumaric acid and bipy to 4,4'-bipyridine, prepared by mechanochemistry (see Fig. 5b).119 The acetic acid and H₂O by-products occluded in the pores were removed by thermal treatment and the interpenetrated structure was refined using Rietveld methods.

In 2015, Prochowicz et al. described the “SMART” (SBU-based Mechanochemical Approach for pReCursors Transformation) strategy for the synthesis of IRMOFs.120 The successful mechanochemical synthesis was performed by mixing pre-assembled oxo-zinc amidate clusters with terephthalic acid in the presence of microlitres of N,N-diethylformamide (DEF) over 60 minutes. Additionally, the study showed the importance of the acid–base relationship between reagents in this type of approach.

Recent work by Frisˇcˇic´ and co-workers presented the synthesis of UiO-66 and UiO-66-NH₂ at gram scale by adding different amounts of N,N-dimethylformamide (DMF) and methanol to the solid mixtures of the reactants as well as exposing the powder mixture to methanol vapours at 45 °C for 3 days and 1 week respectively.121 The best BET surface area obtained for UiO-66 was 1020 m² g⁻¹ with 75 minutes grinding, and 945 m² g⁻¹ for UiO-66-NH₂ after 90 minutes grinding, both in the presence of methanol, for the materials exposed to methanol vapours.

The third mechanochemical methodology, ILAG, was demonstrated to be highly efficient for the synthesis of pillared-layered MOFs. For example, the zinc pillared material based on terephthalic acid and dabco (1,4-diazabicyclooctane) was synthesised after...
45 minutes reaction by adding catalytic amounts of an alkali metal or ammonium nitrate salt into the mixture (Fig. 5c).\textsuperscript{122} Using the same starting materials, but replacing the ammonium nitrate with sulphates, yielded the same pillared-layered structure but on a hexagonal grid. A second example was presented, showing the mechanochemical ILAG approach for the room-temperature synthesis of ZIF-8, using zinc oxide as the starting material and stoichiometric amounts of ammonium salts.\textsuperscript{123} In this case the use of salts enabled synthesis with imidazole enabling the selective ZIF topology formation by changing the type of ammonium salt and adjusting the reaction times.

Mechanochemistry is a versatile method that allows the synthesis of most of the common MOF structures, however so far all examples described a production at less than one gram scale. As an alternative, extrusion techniques have been explored for the up-scaling of MOF production under solvent-free conditions. Extrusion is one of the major continuous manufacturing processes used in industries such as food, metallurgy, plastics and pharmaceuticals and has shown very promising results for the synthesis and shaping of MOFs. In 2015, James and co-workers showed the synthesis of HKUST-1, ZIF-8 and aluminium fumarate MOF with twin-screw extrusion (TSE) at the gram scale. Fig. 5d shows the TSE used for the synthesis of MOFs which consists of a feed port where the MOF precursors were introduced into a heatable barrel containing the screw and an exit port which a die can be attached to shape the final material. HKUST-1 was synthesized by extruding copper hydroxide and trimesic acid in the presence of methanol. The extrudate was stirred in ethanol and dried at 150 °C for 2 hours yielding a N\textsubscript{2} BET surface area of 1738 m\textsuperscript{2} g\textsuperscript{-1}. In the case of ZIF-8 the synthesis was performed by a single screw extrusion (SSE) where the zinc carbonate and the 2-methylimidazole ligand were extruded at 200 °C without the addition of any solvent. In this case, the activation was carried out by stirring the material in methanol and drying the material at 150 °C yielding a N\textsubscript{2} BET surface area of 1738 m\textsuperscript{2} g\textsuperscript{-1}. A last example was obtained by introducing a mixture of aluminium sulphate, sodium hydroxide and fumaric acid into the twin extruder at 150 °C. In this case the by-product was removed by washing the extrudates with water and N\textsubscript{2} BET surface area obtained was 1010 m\textsuperscript{2} g\textsuperscript{-1}. Extrusion is an efficient way to produce MOFs solvent free with high with very promising space-time-yield (STY) (see Fig. 5e). Kilogram scale production could be achieved by using a large-scale equipment and paired with a more detailed knowledge and understanding of the MOF synthesis by this methodology.

2.1.4 Spray-drying synthesis. Spray-drying (SD) process has been a well-established method in industry for decades. The basic idea behind this method is the production of dispersed powder from a liquid or slurry that is rapidly evaporated with a hot gas. The development of the SD method evolved over a period from 1870s through early 1900s. SD was first patented in 1872 by Samuel Percy,\textsuperscript{124} but it was not until the World War II when it gained importance due to transportation needs. SD was used to reduce the weight of food and other species by removing their liquid content (mainly, water). Since then, SD has been widely used for the production of dried pharmaceuticals, bone and tooth amalgams, beverages, flavors, milk and egg products, soaps and detergents, and many other products.\textsuperscript{125} More recently in history, SD has extended its use to the encapsulation and miniaturization of multiple species,\textsuperscript{126–128} with the idea of protecting them, controlling their release, and increasing their solubility and dispersability. It has also been employed for preparing very homogeneous mixtures of reactants,\textsuperscript{129,130} a crucial step that has facilitated the fabrication of certain materials.

Beyond the use of SD in these applications, the local heating of micro- and submicrometer droplets that occurs during the SD process can also be used to conduct chemical reactions. Thus far, this concept has mainly been utilized for discovering and isolating metastable phases of materials that can be only reached thanks to the fast drying conditions of the SD method.\textsuperscript{131}

In 2013, Maspoch \textit{et al.} expanded this concept to the synthesis of supramolecular materials and, in particular, MOFs.\textsuperscript{132} The main principle of the process was based on the fast drying of atomized microdroplets of a solution that contains the MOF precursors (Fig. 6a and b). Thus, the process starts with atomization of a solution of the MOF precursors into a spray of microdroplets. This step is accomplished by simultaneously injecting one or more solutions, at a certain rate, (hereafter, feed rate) and compressed air or nitrogen gas, at another certain rate (hereafter, flow rate). Thus, each precursor droplet contacts – and is suspended by – a gas stream heated to a certain temperature (hereafter, inlet temperature), causing the solvent to be heated and evaporated and inducing the MOF precursors (e.g. metal ions and organic ligands) to react forming

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Fig. 6 Spray-drying method for the production of MOFs. (a) Photograph of the spray-dryer while it is used to fabricate HKUST-1. (b) Schematic illustration of the spray-drying synthesis of MOFs. The MOF precursor solution can be introduced into the spray drier using a: (c) two-fluid nozzle; (d) three-fluid nozzle; (e) T-junction; and (f) continuous flow rector coupled to a two-fluid nozzle. (i) Springer Nature and The Royal Society of Chemistry, adapted with permission from ref. 132 and 134).
MOF nanoparticles inside each droplet. At this moment, the newly formed MOF nanoparticles accumulate and merge into compact or hollow spherical MOF superstructures/beads while the solvent is fully evaporated. These MOF superstructures/beads are finally collected inside a collector located at the end of the spray drier instrument.

Table 1 lists all MOFs – together with the optimized conditions and yields – that have been synthesized using the SD method so far. Besides the optimization of the synthesis parameters such as type of reagents/solvents, feed/flow rates and inlet temperature, a very important aspect that needs to be carefully selected when one wants to synthesize a specific MOF by SD is how the precursor solution is introduced into the spray drier (Table 2). To date, there are four major modes for introducing the MOF precursor solution: (i) use of a two-fluid nozzle (Fig. 6c); (ii) use of a three-fluid nozzle (Fig. 6d); (iii) use a T-junction (Fig. 6e); and (iv) use a continuous flow coupled to a reactor (Fig. 6f).

The use of two-fluid nozzle is the simplest process. It is based on the preparation of a homogeneous solution or suspension that contains all MOF precursors, which is then injected through a two-fluid nozzle. This two-fluid nozzle allows the simultaneous injection of this precursor solution at a certain feed rate and compressed air or nitrogen gas at another certain flow rate. In general, this method is very useful to synthesize MOFs that are built up from mononuclear metal ions or smaller metal clusters or secondary building-units (SBUs). An archetypical class of MOFs that can be fabricated using this approach is the large family of MOFs constructed from Cu(II) paddlewheel units and polycarboxylate linkers. For example, HKUST-1 (also known as Cu-BTC or BasoliteC300) can be synthesized by spray-drying a solution of Cu(NO3)2·2.5H2O and trimesic acid (H3BTC) (3:2 molar ratio) in DMF, ethanol and water (1:1:1) with a feed rate of 4.5 mL min−1, a flow rate of 336 mL min−1 and an inlet temperature of 180 °C. They could be obtained as hollow spherical MOF superstructures (size: 2.4 ± 0.4 µm) or nanoparticles (size: 75 ± 28 nm) (Fig. 7a).

Second and third routes for introducing the MOF precursors inside the spray drier instrument are very similar. They are based on using multi-fluid nozzles, to independently atomize the solutions containing the MOF precursors, or additional channels,

| MOF Substrates | Solvent | Electrolyte | BET surface area (m² g⁻¹) | Ref. |
|----------------|---------|-------------|---------------------------|------|
| Anodic deposition | HKUST-1 | Copper electrode | MeOH | — | 1820 | 50 |
| | | Copper electrode | EtOH:H2O | MTBS | — | 57 |
| | | Copper mesh | EtOH:H2O | — | — | 59 |
| | | Copper electrode | EtOH:H2O | MTBS | 1440 | 58 |
| | | Copper electrode | EtOH:H2O, organic solvents | MTBS | — | 61 |
| | | Copper electrode | ETOH, ETOH:H2O | MTBS | 1309 | 63 |
| | ZIF-8 | Zinc electrode | AcN:H2O | MTBS | 1300 | 64 |
| | ZIF-4 | Zinc electrode | DMF:H2O | MTBS | 1730 | 65 |
| | ZIF-14 | Zinc electrode | DMF:H2O | MTBAMS | 598 | 65 |
| | ZIF-7 | Zinc electrode | DMF:H2O | MTBAMS | 358 | 65 |
| | ZIF-64 | Cobalt electrode | DMF:H2O | MTBAMS | 1521 | 65 |
| | MIL-53(Al) | Aluminium electrode | DMF:H2O | KCl or NaCl | 1200 | 58 |
| | MIL-100(Al) | Aluminium electrode | EtOH:H2O | — | 969 | 58 |
| | MIL-100(Fe) | Iron electrode | EtOH:H2O | MTBS | — | 64 |
| | Tb-BTC | Terbium foil | EtOH:H2O | MTBS | — | 66 |
| | Gd-BTC | Gadolinium foil | EtOH:H2O | MTBS | — | 66 |
| | MOF-5 | Zinc plate | EtOH:H2O, NH4F | — | 67 |
| | | Zinc plate and titanium plate | DMF | BMIM | 914.7 | 68 and 69 |

| MOF Substrates | Method | Ref. |
|----------------|--------|------|
| Cathodic deposition | MOF-5 | FTO | Cathodic | 70 |
| | UiO-66 | Zirconium foil | Anodic and cathodic | 76 |
| | MOF-5 | FTO | Cathodic | 71 |
| | MOF-5/[Er2(NH3)16]3[Zn6(BDC)12] | FTO | Cathodic | 72 |
| Others | ZIF-8 | Zinc wire | BE | 77 |
| | UiO-66 | FTO | Electrophoretic deposition | 74 |
| | HKUST-1 | FTO | Electrophoretic deposition | 73 |
| | Glass | Galvanic displacement | 75 |
| | Porous stainless steel | Electrophoretic deposition | 73 |
| | Cu bead | BE | 77 |
| | MIL-53 | FTO | Electrophoretic deposition | 74 |
| | NU-1000 | FTO | Electrophoretic deposition | 74 |

Abbreviations: MTBS, methyltributylammonium methyl sulfate; MTBAMS, methyltributylammonium methyl sulphate; BMIM, 1-butyl-3-methylimidazole; FTO, fluorine doped tin oxide; BE, bipolar electrochemistry.
to independently inject them. Both approaches enable mixing of the precursor solutions just before they are heated into the atomized droplets. In the first approach, mixing occurs inside the drying chamber, thanks to the coalescence of the atomized droplets. In the second one, mixing is done through a connector inserted before the two-fluid nozzle. Using either variation decreases the probability that unwanted species or bases) to accelerate MOF formation, thus increasing yields and purities and enabling the synthesis of new hollow MOF superstructures and related nanocrystals. To date, both approaches have allowed the synthesis of several MOFs, including MIL-88A,132 ZIP-8132,133 and Fe-BTC/MIL-100133 (Fig. 7b and c).

In the last approach, the MOF precursor solution is passed through a continuous-flow reactor just before the entrance of the spray dryer.134 This process begins by injecting the precursor solution into a continuous coil flow reactor encased in a thermostatic oil tank, where it is heated at a certain temperature ($T_1$) to promote the SBU formation and nucleation. Here, the residence time of the precursor solution in the coil flow reactor is controlled by the rate of the pump (the feed rate). Since the outlet flow of the reactor is connected directly to the nozzle of the spray-dryer, the pre-heated solution is automatically injected into the spray-drier at the same feed rate. The solution is then atomised using a two-fluid nozzle, and is dried at a certain inlet temperature and flow rate, such that the MOF growth is confined to the atomised microdroplets.

In most of the cases, this last continuous process enables the collection of dried MOFs shaped in the form of compact micrometre superstructures/beads instead of the hollow ones usually obtained in the first three strategies. This difference is attributed to the formation, inside the reactor, of a suspension containing a primary nucleus. In a general spray-drying process, the atomised droplets are exposed to hot air, the solvent evaporates and consequently, the droplet surface shrinks. During this process, hollow superstructures are formed when there is a non-linear change in precursor concentration at the droplet: specifically,
The main advantage of this last SD approach is that it allows the synthesis of multivariate or multi-metallic MOFs;\textsuperscript{135,136} the mixture of multivariate or multi-metallic MOFs;\textsuperscript{112,117} and the mixture of MOFs with other materials to make composites.\textsuperscript{132,138} With this aim, the use of SD has been extended to the synthesis of porous materials that are not based on coordination bonds but on hydrogen bonds.\textsuperscript{136} For instance, MPM-1-TIFSIX, a porous material based on the hydrogen-bonded assembly of \([\text{Cu}_2(\text{ade})_4(\text{TiF}_6)_2]\) (ade = adenine) paddlewheels (Fig. 8a), was synthesized by spray-drying an aqueous solution of \([\text{Cu(NO}_3]_2\cdot 2.5(\text{H}_2\text{O})\) and \(\text{TiF}_6(\text{NH}_4)_2\) along with a solution of adenine in water/acetonitrile mixture using a 2-fluid nozzle and an inlet temperature of 150 °C. Moreover, SD was also very recently found to be a fast method to post-synthetically modify MOFs using conventional covalent chemistry (Fig. 8b).\textsuperscript{135} To perform this modification, a suspension of pre-synthesized MOF crystals is spray-dried together with the desired reagent. With this simple method, two MOFs, the amine-terminated \(\text{UiO-66-NH}_2\) and the aldehyde-terminated ZIF-90, were rapidly post-synthetically modified with aldehydes and amines, respectively, using the well-known Schiff-base condensation reaction and achieving conversion efficiencies up to 20% and 42%, respectively. Moreover, it was demonstrated that the aldehyde groups of ZIF-90 could be cross-linked using a diamine molecule with a conversion efficiency of 70%.

Another advantage of SD as a synthetic method in the MOF field is the possibility to synthesize multi-metallic and multivariate MOFs. From an experimental point of view, the synthesis of these multi-component MOFs does not require technological changes. Its main principle is based on mixing different metal ions or organic linkers in the MOF precursor solution that is spray-dried. With this approach, Wang \textit{et al.} showed the synthesis of lanthanide-based MOF nanoparticles in which the ratio of \(\text{Tb(III)/Eu(III)}\) was controlled (Fig. 8c).\textsuperscript{137} They proved that the resulting MOF nanoparticles could be used as promising nanothermometers with high detection sensibilities, spatial resolutions and short acquisition times. Similarly, multi-variate \(\text{UiO-66s}\) were synthesized by mixing different ratios of two (benzenedicarboxylic acid and 2-bromobenzenedicarboxylic acid) or three (benzenedicarboxylic acid, 2-aminobenzenedicarboxylic acid and 2-bromobenzenedicarboxylic acid) organic linkers in the MOF precursor solution (Fig. 8d).\textsuperscript{134} The resulting \(\text{ UiO-66 Materials}\) showed tunable pore surface area. For example, the surface area decreased with increasing equivalents of 2-bromobenzenedicarboxylic acid: 818 \(\text{m}^2\ \text{g}^{-1}\) for 0.6; 678 \(\text{m}^2\ \text{g}^{-1}\) for 1.3; and 570 \(\text{m}^2\ \text{g}^{-1}\) for 2.3.

Finally, SD is also a very simple and fast method to produce MOF-based composites. As above, these MOF-based composites can be created by just mixing other materials – pre-synthesized or their precursors for \textit{in situ} synthesis – in the MOF precursor solution. With this basic idea, Maspoch \textit{et al.} demonstrated that different substances such as magnetic inorganic nanoparticles (Fig. 8e),\textsuperscript{132} inorganic salts (\(\text{NaCl, CaCl}_2\) and \(\text{LiCl}\))\textsuperscript{132,139} (Fig. 8f) and fluorescent molecules\textsuperscript{132} can be combined with MOFs, thereby creating different types of composite materials that combine the intrinsic properties of MOFs and these other materials. Finally, the same authors showed that SD method can be also used to combine MOFs with organic polymers.\textsuperscript{138} In this

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_7.pdf}
\caption{SEM and TEM images of several MOFs synthesized by spray-drying. (a) Hollow spherical superstructures of HKUST-1 synthesized using a two-fluid nozzle. Inset shows a TEM image of a single HKUST-1 nanoparticle. (b) Spherical superstructures of MIL-88A synthesized using a T-junction. Inset shows a SEM image of a single bead. Scale bars: 10 \(\mu\text{m}\) (c), 5 \(\mu\text{m}\) (a and d), 2 \(\mu\text{m}\) (b, inset d), 200 \(\text{nm}\) (inset b), and 50 \(\text{nm}\) (inset a and c). (c) Springer Nature and The Royal Society of Chemistry, reprinted with permission from ref. 132 and 134).
\end{figure}
specific case, pre-synthesized HKUST-1 nanocrystals were encapsulated into polystyrene spheres to improve the hydrolytic stability of HKUST-1.

2.1.5 Flow chemistry. Flow chemistry is a continuous processing technology used in the pharma and agrochemical sectors over the last two decades. Recently, its application to the synthesis of functional nanomaterials such as inorganic nanoparticles, quantum dots, metal oxides and MOFs has shown great promise. Contrary to batch reactions, in a flow chemistry setup, the chemical reactions occur in a continuously flowing stream in a tube or pipe rather than in a reaction vessel. This results in several main advantages: (a) the surface area-to-volume ratio for a reaction mixture in a flow reactor is much higher than in a batch-type reactor giving inherent improvements to heat and mass transfer leading to a much rapid syntheses; (b) flow chemistry allows for precise control over the reaction parameters which facilitates the synthesis optimization and the reproducibility between batches; (c) harsh reaction conditions can be safely reached due to excellent transport intensification properties of the reactors; (d) typically less solvent is used and the energy consumption is lower; (e) downstream processes and quality control methods can be easily integrated in the flow processes and (f) these type of reactors are readily scaled-up. Flow chemistry is thus a cost-effective method that follows the green principle and satisfies the requirements for industrial production. Not surprisingly, several researchers have started to use flow chemistry to synthesize MOFs (Table 3). In the last year, numerous works have been reported in the literature and in this review we will classify such reports into three different categories: (a) microfluidic reactors (MR), which manipulate the reagents in channels that are geometrically constrained at the microscale; (b) plug flow reactors (PFR) where the reagents are pumped through a tube or pipe and consumed as they flow down the length of the reactor and (c) stirred tank reactors (CSTR) where the MOF precursor are introduced into a tank reactor while products are continuously removed. Table 3 lists all MOFs – together with the optimized conditions and space-time-yields – that have been synthesized using the flow chemistry method so far.

In 2011, Ameloot and co-workers were first to show that microfluidics could be used for the synthesis of metal–organic materials. They synthesized metal–organic crystals in a microscale reactor, in which the reagent phases were injected into an immiscible carrier fluid, causing the spontaneous formation of droplets where the reaction occurs (Fig. 9b). In this case, the immiscibility of the water and oil phases was exploited as a template for the controlled formation of hollow metal–organic copper trimesate HKUST-1 microcapsules. The authors described the crystallisation process as a dynamic on-going process of nucleation and crystal growth that resulted in the
formation of crystalline MOF membranes with a uniform wall thickness.

Two years later, Faustini et al. reported the solvothermal and hydrothermal synthesis of MOFs and MOF-composite superstructures using oil microdroplets as a reactors.\textsuperscript{141} Four representative MOF structures, copper trimesate HKUST-1, zinc terephthalate MOF-5, zinc aminoterephthalate IRMOF-3 and zirconium terephthalate UiO-66, were synthesised, yielding substantially faster kinetics in comparison to the conventional batch processes (see Fig. 9a). In addition, they reported the possibility of creating MOF heterostructures using imidazolate frameworks (ZIFs) in a two-step process. Firstly, the iron oxide precursor solution and the oil phase were injected and reacted in a microreactor at 80 °C for 2 minutes. Then, the resulting iron oxide particles were transported downstream to a second microreactor, where they merged and reacted with a mixture of ZIF-8 precursor (zinc nitrate and 2-methylimidazolate in methanol, and polystyrenesulphonate). This lead to the creation of core–shell Fe₃O₄@ZIF-8 composite superstructures.

The same year, Coronas and co-workers demonstrated the feasibility of the droplet-based microfluidic approach for the crystallisation of the iron fumarate MIL-88B MOF.\textsuperscript{137} In this study, they confirmed that the size of the resulting crystals was dependent of the temperature and residence time. They observed a continuous increase in particle size with average sizes increasing from 90 to 900 nm with higher residence times and/or higher temperatures. In addition, D’Arras and co-workers demonstrated the possibility of synthesizing new structures using microsystems.\textsuperscript{142} They reported the structure of a new cerium(III)–terephthalate MOF which was synthesized flow-type reactor at high temperature and pressure with a very short residence time.

Moving to the PFR reactors the first work was reported in 2012 by Gimeno-Fabre et al. showed the synthesis of HKUST-1 and Ni-CPO-27 in a counter current mixing reactor where the MOF precursors were mixed with a preheated supercritical water stream at high pressures.\textsuperscript{145} The high temperatures were used in order to increase the rate of crystal growth, with a limitation in that heating beyond 300 °C could lead to the formation of metal oxides as a waste-product. Three years later, the same reactor was used to demonstrate the large scale production of ZIF-8 and the control of the size and shape of the crystals.

Table 3  MOFs synthesized by flow chemistry with different approaches and conditions

| Method | MOF | Residence time | Temperature (°C) | STY (kg m⁻³ day⁻¹) | SA BET (m² g⁻¹) |
|--------|-----|----------------|-----------------|--------------------|-----------------|
| MF     | HKUST-1\textsuperscript{140} | —              | RT              | —                 | 620             |
|        | HKUST-1\textsuperscript{141} | 1 min          | 90              | 5.8               | 1105            |
|        | MOF-5\textsuperscript{141}  | 3 min          | 120             | —                 | 3185            |
|        | IRMOF-3\textsuperscript{141} | 3 min          | 120             | —                 | 2428            |
|        | UiO-66\textsuperscript{141} | 15 min         | 140             | —                 | 1509            |
|        | MIL-88B\textsuperscript{137} | 4 min          | 95              | —                 | —               |
|        | ZIF-8\textsuperscript{143}  | 15 s           | RT              | 210 000           | 1770            |
|        | Ce-BDC\textsuperscript{142} | 30 s           | 230             | —                 | —               |
|        | UiO-66\textsuperscript{144} | 0.44–2.2 min   | 120             | —                 | 922–1206        |
| PFR    | HKUST-1\textsuperscript{149} | 1.2 min        | 85              | 4533              | 1805            |
|        | UiO-66\textsuperscript{149} | 10 min         | 130             | 1186              | 672             |
|        | NOTT-400\textsuperscript{149} | 15 min         | 85              | 1078              | 741             |
|        | Al-Fum\textsuperscript{150} | 1 min          | 65              | 97 139            | 1054            |
|        | HKUST-1\textsuperscript{148} | 5 min          | 60              | —                 | 1673            |
|        | MIL-53[Al]\textsuperscript{147} | 20 min         | 250             | 1021              | 919             |
|        | MIL-53[Al]\textsuperscript{147} | 20 min         | 250             | 1300              | 1010            |
|        | STA-12(Cd)\textsuperscript{151} | 5–20 min       | 70              | —                 | 134             |
|        | ZIF-8\textsuperscript{146} | < 5 s          | 100             | 11 625            | 1806            |
|        | ZIF-8\textsuperscript{146} | < 5 s          | 100             | —                 | 1780            |
|        | CAU-13\textsuperscript{151} | 20 min         | 130             | 3049              | 401             |
|        | CPO-27\textsuperscript{145} | < 5 s          | 300             | 1501              | 1030            |
|        | HKUST-1\textsuperscript{147} | 20 min         | 250             | 730               | 1574            |
|        | HKUST-1\textsuperscript{145} | < 5 s          | 300             | 4399              | 1950            |
|        | UiO-66\textsuperscript{151} | 45 min         | 120             | 428               | 1263            |
|        | STA-12\textsuperscript{151} | 20 min         | 70              | 428               | 134             |
|        | HKUST-1\textsuperscript{155} | 1 min          | 360 W           | 64 800            | 1550            |
|        | MIL-53[Al]\textsuperscript{153} | 4 min          | 200 W           | 3618              | 1376            |
|        | UiO-66\textsuperscript{153} | 7 min          | 200 W           | 7204              | 1052            |
|        | MOF-74[Ni]\textsuperscript{152} | < 1 s          | 150             | 2160              | 840             |
| CSTR   | UiO-66\textsuperscript{154} | 8–40 h         | 100–120         | —                 | 810             |
|        | MOF-5\textsuperscript{155} | 5 h            | 140             | 1000              | 2302            |
by adding ammonium hydroxide or trimethylamine in the reaction mixture.\textsuperscript{146} The STY obtained in this process was 11.625 kg m\textsuperscript{-3} day\textsuperscript{-1} and with a surface area of 1800 m\textsuperscript{2} g\textsuperscript{-1}.\textsuperscript{148} Retaining the use of supercritical water and an ethanol stream, Bayliss et al. developed a system to produce MIL-53(Al) and HKUST-1 under continuous flow conditions obtaining a STY of 1300 kg m\textsuperscript{-3} day\textsuperscript{-1} and 730 kg m\textsuperscript{-3} day\textsuperscript{-1}, respectively.\textsuperscript{147} These last two methods produced high quality materials with high STY, however high temperatures and pressures were still required, which increase the overall cost of the process and could limit the practicality of the technique at industrial scale.

In 2013 Chang et al. reported the proof-of-concept mesoscale flow production of HKUST-1 using 5 minutes as a residence time and with a surface area of 1673 m\textsuperscript{2} g\textsuperscript{-1}.\textsuperscript{148} The particle size of the MOF could be adjusted by changing the relative ratios of the solvents and reaction temperatures from 150 nm to 4 μm. To demonstrate the versatility and efficacy of flow reactors to produce MOFs, Rubio-Martinez and co-workers used a PFA reactor to synthesize the copper trimesate HKUST-1, the zirconium terephthalate UiO-66 and the scandium biphenyl-tetracarboxylate NOTT-400, all with different reaction requirements (see Fig. 9).\textsuperscript{149} The materials were obtained in 5, 10 and 15 minutes, respectively, without loss in yield or product quality. It was demonstrated that the results could be up-scaled 30-fold using a bench-top reactor, allowing a production rate greater than a kilogram per day and a STY of 4533 kg m\textsuperscript{-3} day\textsuperscript{-1} using a bench-top reactor. The successful up-scaling of this process was demonstrated in a second publication where the production of the aluminium fumarate MOF was proved in 4 different stainless-steel tubular flow reactors: a 10 mL coil tubing at laboratory scale, two intermediate stages with 107 mL and 374 mL reactor volume, and a pilot-scale 1.394 L reactor, delivering unprecedented production rates and STYs (97 159 kg m\textsuperscript{-3} day\textsuperscript{-1}) while maintaining the product quality.\textsuperscript{150} To our best knowledge, this is the highest reported value of STY for a MOF produced by continuous methods. Additionally, the reactor design used in this work demonstrated the possibility to readily translate reaction parameters from the laboratory scale to pilot scale without any re-optimization of the reaction conditions, while maintaining the STY values within the same range.

The last work using PFR comes from Stock and co-workers who presented the synthesis of UiO-66, CAU-13 and STA-12 – a new cadmium phosphonate network using a 16 mL PTFE reactor yielding a STY of 428 kg m\textsuperscript{-3} day\textsuperscript{-1} and 3049 kg m\textsuperscript{-3} for UiO-66 and CAU-13, respectively.\textsuperscript{151} One year later, the same was group reported the water-based synthesis the zirconium fumarate and UiO-66-NH\textsubscript{2} starting from a slurry of the starting solutions.

In a slightly different reactor design, two recent works reported the combination of microwave assisted heating with a PFR system. The first study from 2015 by Albuquerque et al. reported on a system where the microwave reactor was attached to the flow reactor in order to accelerate the nucleation of the MOFs and to improve the reproducibility of the synthesis.\textsuperscript{152} The MOF precursors of MOF-74(Ni) were introduced first into the nucleation zone that consisted of a microwave reactor and consequently the material was introduced into a PFA coil for 8 min to growth the final crystals. As a result, they obtained a better crystallinity in a shorter reaction time and achieved a STY of 2160 kg m\textsuperscript{-3} day\textsuperscript{-1}. The second work by Taddei et al. presented the synthesis of UiO-66, HKUST-1 and MIL-53(Al) in a 6.2 and 53 mL PTFE flow reactors heated by microwave.\textsuperscript{153} The materials were obtained in 7, 1 and 4 minutes of residence time, while maintaining the product quality and resulting in high STY of 7204 kg m\textsuperscript{-3} day\textsuperscript{-1}, 64 800 kg m\textsuperscript{-3} day\textsuperscript{-1} and 3618 kg m\textsuperscript{-3} day\textsuperscript{-1} for UiO-66, HKUST-1 and MIL-53(Al) respectively.

The use of stirred CSTR was showcased by two groups, synthesizing NH\textsubscript{2}-UiO-66 and MOF-5. The first work in 2013
by Schoenecker and co-workers who synthesized the amine-functionalised UiO-66 in DMF by convention heating.\textsuperscript{154} In this system the MOF precursors were pumped into a pre-mixing tank over 15 min and then introduced into a 2 litre flow crystallisation reactor over 8 to 40 hours during which time small aliquots of the intermediate product were collected at different times to bulk reaction kinetics. The product obtained had good crystallinity but the BET surface area and the yield were below the values reported in batch. A later study by McKinstry \textit{et al.} presented the synthesis of MOF-5 in a CSTR at atmospheric pressure obtaining the desired quality and with a STY of 1000 kg m\textsuperscript{-3} day\textsuperscript{-1} (see Fig. 9c).\textsuperscript{155}

### 3. Downstream processes

After any MOF synthesis, careful processing is required to obtain the final functional material. Directly after the synthesis, the product slurry needs to be washed with the reaction solvent to remove any unreacted and by-products, \textit{e.g.} using a centrifuge or a Buchner filter. Subsequently, an activation process is required to remove guest molecules, trapped within the framework, to obtain the expected surface area of the structure. Depending on the MOF structure, these two stages can be the most time-limiting stages of the process and become hugely significant in the large-scale production. The last stages of the process consist in drying and shaping the MOFs as well as a heat activation step before testing. Fig. 10 shows a diagram of the typical downstream processes for the synthesis of a MOF.

Despite promising advances in MOF synthesis, there are still challenges remaining related to the downstream processing. On the laboratory scale these processes are well established and sufficient to obtain milligram amounts of quality materials. However, these conventional downstream methods are not well-suited to high production rates. The first stage, the washing and separation of the small crystals from the mother liquor still is a major obstacle for the large scale production MOFs. There are many well established types of equipment for solid–liquid separation such as centrifuges, cyclones, settling chambers, classifiers or filters, in addition to the direct evaporation of the mother liquor. However, the small size of the MOF particles, their low concentration in the solvent, as well as their density approaching that of the solvent (due to the high porosity), makes separation \textit{via} most conventional methods inefficient or expensive at an industrial scale.\textsuperscript{156}

Once the MOF slurry has been cleaned of the excess linkers and by-products, the activation stage is the next step of the process in order to obtain the highest porosity and BET surface area of the framework. Several strategies exist to remove the unreacted and solvent molecules trapped in the pores of the MOFs without collapsing the framework.\textsuperscript{157} The most common procedure is a simple heating of the MOF to certain temperature under vacuum. Each MOF has its optimal protocol in order to obtain the highest surface area but generally the temperature should be between the boiling point of the solvent and the decomposition temperature of the structure. However, in most cases this strategy leads to a lower surface area, or to a collapse of the structure due to the high surface tension and capillary forces imposed on the structure by the liquid-gas phase transition of the trapped solvent molecules. An alternative strategy is to exchange the solvent used for the synthesis with one that has a lower-boiling point such as methanol, chloroform or acetone prior to heating the sample under vacuum. This strategy is laborious as generally most MOFs require soaking for a long period of time to ensure that the new solvent infiltrates. For example, in the case of MOF-74 and UiO-66 both MOFs require a soaking in daily refreshed methanol for 3 and 7 days respectively to ensure the complete removal of DMF (solvent used for the synthesis and washing stage) from the pores.\textsuperscript{36,158} Some frameworks, such as ZIF-8 and MIL-53(Al) require a solvent exchange process with methanol with an additional thermal treatment, 300 °C for 2 hours and 330 °C for 72 hours respectively to obtain the BET surface areas of 1630 m\textsuperscript{2} g\textsuperscript{-1} and 1590 m\textsuperscript{2} g\textsuperscript{-1}, respectively.\textsuperscript{31,159}

An attractive substitute for the solvent exchange method is the use of supercritical CO\textsubscript{2}. This relatively new strategy consists of exchanging the synthetic solvent for a one that is miscible with liquid CO\textsubscript{2} such as ethanol or methanol and then subsequently exchanging this second one for liquid CO\textsubscript{2} at high pressure and temperature for several hours. The difference here is that the CO\textsubscript{2} supercritical phase eliminates surface tension and capillary forces making this activation method much milder than the conventional and solvent exchange methods. There are several MOFs that have been effectively activated with this strategy. For example, MOF-200 and MOF-210, where a simple solvent exchange followed by pore evacuation under vacuum was not effective, were successful activated, without losing the porosity, by a full solvent exchange with liquid CO\textsubscript{2}.\textsuperscript{4} The surface areas obtained were 4530 and 6240 m\textsuperscript{2} g\textsuperscript{-1}, respectively. Another example is the supercritical CO\textsubscript{2} activation of bio-MOF-100 were the DMF solvated samples were soaked in
ethanol for 48 hours, and an exchange/activation with CO$_2$ liquid over a period of 8 hours yielded a BET surface area of 4300 m$^2$ g$^{-1}$.\textsuperscript{160} In a variant of this method the sample is placed in a column and the supercritical CO$_2$ flows through the sample instead of using static CO$_2$ exchange. This method was presented by Koh and co-workers who activated UCMC-9 microporous coordination polymers via supercritical CO$_2$ flow activation yielding a surface area BET of 4970 m$^2$ g$^{-1}$.\textsuperscript{161}

Later novelties on the activation have been based on freeze-drying activation techniques which uses thermal cycling and the vacuum sublimation of solvents (benzene and cyclohexane) at low temperatures to avoid the impact of capillary forces on porous structures in order to control the stability of frameworks and improve its porosity.\textsuperscript{162} Recently Rubio-Martinez \textit{et al.} presented for the first time the use of megasonics as an alternative strategy for the simultaneous separation and activation of MOF crystals.\textsuperscript{163} Its operating principle is based on the application of high frequency ultrasound to the MOF solution, leading to the separation of the solid MOF particles from the solvent. Additionally, the megasonic treatment leads to an activation by the simultaneous removal of occluded reagents from the MOF crystals. This one-step process showed an improvement of up to 47% the surface area of the final product compared to conventional methods. The method removes one stage from the downstream processing and is readily scalable and thus capable of producing commercially usable product at a large scale.

Shaping of MOF powders produced in any of the fabrication methods explained above is also mandatory for using them in real industrial applications. For instance, extruded or compact MOFs in the form of beads, pellets and monolithic bodies are required if MOFs want to be used for gas separation and storage applications. In methane storage (e.g. Adsorbed Natural Gas or ANG), for example, it is of utmost importance to fill the storage tanks with the largest amount of adsorbent; a condition that can only be achieved if MOF powders are densely packed. Furthermore, powdered MOFs are usually more difficult to be handled and can potentially contaminate pipes during charge/discharge cycles. For other applications such as functional textiles,\textsuperscript{164} alternative shaping and/or integration methods that process MOFs into paper sheets,\textsuperscript{165} fibers,\textsuperscript{166} membranes,\textsuperscript{167,168} foams\textsuperscript{169} or coatings\textsuperscript{170} are also needed (Fig. 11).

Considering the potential adsorption-related applications of MOFs, most of the efforts done in shaping MOFs have been dedicated to their densification. The objective of densification is to pack the maximum amount of an active MOF on a certain volume without losing its integrity and adsorption capacity. Daily \textit{et al.} calculated that doubling the density of HKUST-1 powder would result in an adsorbent with performances comparable of those of the state-of-the-art carbons at intermediate pressures (30–100 bars).\textsuperscript{171} However, despite the high industrial importance of shaping MOF powders, the interest of academic research groups to face this problematic is quite recent. In fact, the structuration of MOFs into shaped bodies was initiated by some companies (mainly, BASF), which tend to keep these shaping processes as in-house know-how or are only disseminated in patents. In this context, BASF published the first patent application concerning “shaped bodies containing metal–organic frameworks” in 2002. This patent was centered in the fabrication of MOF-2 and MOF-5 pellets using an eccentric press. In this process, both MOFs were mixed with graphite that acts as a binder improving their mechanical strength.\textsuperscript{172}

Pelletization under pressure is probably the most common method used for densifying MOFs. In this process, a fine powder is pressed at a certain pressure to give pellets that can be crushed or fractionized by sieving. In some cases, before MOF powder is pressed, it can be blended with a binder to improve the cohesion between crystals and their mechanical strength. There are however two factors of this method that tend to affect the final adsorption properties of the pellet shaped MOFs. From one side, the pressure applied can crush the structure of the MOF due to its low mechanical stability. From the other side, the use of binders can dilute the porous

![Fig. 11 Examples of shaped MOFs. (a) Functional textiles; (b) paper sheets; (c) pellets; (d) extruded monolith; (e) fibers; (f) membrane; (g) foams; and (h) granules. (© Nature Publishing group, American Chemical Society, Royal Society of Chemistry, Elsevier with permission from ref. 163–165, 167, 180 and 184).](image-url)
powder and/or cause pore blockage, resulting in a reduced performance per unit mass (or volume) of the adsorbent.

As shown in Table 4, the influence of the pressure applied during pelletization of MOF powders was studied in some representative MOFs. However, systematic studies that correlate the pelletization conditions with the resulting adsorption properties of MOFs are very limited, and some discrepancies can be found. A general tendency when compressed pellets are processed is a decrease of the BET surface area and porosity of MOFs. This is specially the case for HKUST-1 that is mechanically fragile. For HKUST-1, it has been described that a significant loss of its BET surface area occurs at moderate pressures. Ahn et al. reported a loss of 50% of its BET surface area when the applied pressure was around 10 MPa, whereas Bazer-Bachi et al. and Peterson et al. found a similar decrease when pressures of 80 MPa and 70 MPa were applied, respectively. Other MOFs have shown better mechanical resistance. For example, UiO-66 and analogues, which are known for their high mechanical and thermal stability owing to their 12-fold connected clusters in the three spatial directions, were shown better stability during the compression process. Here, Peterson et al. observed a loss lower than 10% of the BET surface area of UiO-66 when it was pelletized under a pressure of 70 MPa. Dietzel et al. also reported the total conservation of the BET surface area of CPO-27 after tabling it at 100 MPa, whereas its porous character totally disappears at 1 GPa. In the case of ZIF-8, the BET surface area was well preserved until a pressure of 700 MPa. Above this pressure, different reports revealed some discrepancies. While Bazer-Bachi et al. observed a loss lower than 20% of its BET surface area, Chapman et al. observed a loss of 50% at pressures above 1 GPa. This difference can be attributed to non-reported parameters, such as the pressure increase rate and the dwell time, which can dramatically influence the integrity of the final pellet.

Binders are sometimes utilized during this pelletization process. As state above, they basically serve to improve the cohesion between MOF crystals and their mechanical stability. Some tested binders include graphite, polyvinyl alcohol (PVA) and cellulose ester. To our knowledge, however, there is no a systematic, rational study on the influence of the nature and concentration of these binders on the BET surface area and general properties of MOFs during their pelletization.

The presence of binders is also necessary in other shaping processes, including foaming, extrusion, granulation and cake crushing. In all these procedures, MOF powders are initially dispersed in a solvent/binder mixture. The choice of the binder gives a certain texture and property to the mixture, which is then manipulated in different ways to obtain the desired MOF shapes. For example, in the extrusion process, the MOF solvent/binder

| Table 4 | Examples of shaped MOFs using pelletization, foaming and extrusion methods |
|---------|---------------------------------|
| MOF | Pressure | Binder | Property |
| Pellet HKUST-1 | 70 and 700 MPa | Alox C and graphite | Very high adsorption capacity for CO₂ |
| | 0.24–40 MPa | Cellulose ester, K15M | 50% decrease of the BET surface area (after 700 MPa) |
| MIL-53(Al) | 1–8 bar | Polyvinyl alcohol | Maintained ammonia removal capacity |
| UiO-66 | 70 and 700 MPa | Graphite | Below 5 bar, constant selectivity |
| ZIF-8 | 398–1432 MPa | Cellulose ester, K15M | Above 5 bar, selectivity decreased |
| SIM-1 | 40–398 MPa | Cellulose ester, K15M | 22% decrease of the BET surface area |
| CPO-27-Ni | 0.1–1 GPa | Without binder | Suitable material for o-xylene over p- and m-xylene separation at low concentrations |
| Foam MIL-101(Cr) | — | Ni foam | Decrease in hydrogen storage capacities (19%) |
| | — | Polyurethane | Maintaining more than 70% of the adsorption capacity for benzene and n-hexane |
| Zr-MOF | — | Carboxymethylcellulose | High catalytic activity in C–H oxidation |
| Extrusion HKUST-1 | Silres MSE 100 | Culling MHPC 20 000 P | 70% decrease of the BET surface area |
| | Zr-MOF | Sucrose and water | 50% decrease of the BET surface area |
mixture forms a paste that can then be extruded to induce shaping of the MOF into different morphologies (Table 4). Following this latter method, Kaskel et al. mixed HKUST-1 crystals with a silicone resin and a plasticizer to form a paste that was subsequently extruded into monolithic HKUST-1 strings in a ram extruder. In this case, the decrease of the BET surface area was significant (70% of its initial BET surface area) due to the presence of binders and heating conditions, but the performance of the extruded monolith was higher than the monolith obtained by in situ synthesis of HKUST-1 in cordierite honeycombs. The extrusion method was also used by Ren et al. to prepare UiO-66 spherical pellets (with a BET surface area of 674 m² g⁻¹ that corresponds to 50% of its initial value) from a paste made of UiO-66 and 10 wt% sucrose/H₂O mixture using a granulator.

Starting from the binder-solvent-MOF mixture, monolithic MOF foams can also be formed (Table 4). In this case, the nature of the binder tends to form macroporous foam-type solids in which the MOF can be entrapped. Similar MOF foams can also be produced by synthesizing the MOF in the presence of pre-formed foam. Using both approaches, foams with MIL-101, HKUST-1, and UiO-66 were prepared. For example, Wang et al. synthesized a foam monolith composed of HKUST-1@Fe₃O₄-MF (MF means magnetic fluid) by dispersing HKUST-1@Fe₃O₄-MF particles in an aqueous carboxymethylcellulose solution. The treatment with acetonitrile and finally drying led to the formation of monolithic foams with high catalytic activity for C–H oxidation.

Other shaping processes require the formation of a dried MOF cake that is crushed. Here, the MOF powder is mixed with a certain amount of a binder (typically, polyvinyl alcohol (PVA)) and the resulting mixture is dissolved in a solvent forming a paste. This paste is then dried, crushed, and sieved into the wanted particle size fraction. Denayer et al. used this method to prepare MIL-53(Al) pellets using PVA as the binder. As revealed by N₂ adsorption isotherms, the MIL-53(Al) pellets showed a loss of BET surface area of 32% but maintained good CH₄/CO₂ selectivity capacities. Finally, other methodologies have also started to be explored to incorporate MOFs into fibers and papers, and shape them into alginate-based spherical beads or ceramic beads.

These few examples indicate that the shaping of MOFs for specific applications is still in an embryonic stage and strong efforts have still to be dedicated to the rational study of this process if we want to be able to access to the real commercial applications. It is also clear that, in adsorption-related applications, this shaping process must respect the relatively low thermal, chemical and mechanical stability of MOFs so that their adsorption capacities are mostly preserved. For other applications, however, this latter condition is not so important. In catalysis, for example, Bazer-Bachi et al. observed that, even though pelletization of ZIF-8 decreased its adsorption properties, it did not change its catalytic activity.

4. Perspectives and commercial developments

Since the first patent filed in 1995 and assigned to the Nalco Chemical Company, commercialisation of MOFs progressed gradually until the first MOF-based products released in 2016 by MOF Technologies and Numat Technologies (see Fig. 12). MOF production at scale is now underway which will help secure customer confidence and open the door for other MOF-based products. However, the growing market will push the MOF suppliers for further cost-efficiency, reproducibility and environmental sustainability to remain competitive. Here is a brief summary of companies working with MOFs in production, technology development and retail to date.

MOF Technologies was founded in 2012 based on patented mechanochemical manufacturing technology invented at the Queen’s University of Belfast. This innovative process allows the production of MOFs using little or no solvents. Solvent-free synthesis has advantages in both waste and energy management. Solvent waste is a major issue in the chemical industry. The energy required to initiate reaction can sometimes be reduced using mechanical energy rather than thermal energy. Recently this method has been configured for continuous production through extrusion which is scalable.

It is unknown how many MOFs can be manufactured using mechanochemical synthesis, however MOF Technologies offer a wide catalogue for direct purchase. At the end of 2016 they sold around 100 kg of MOFs from their catalogue: magnesium formate, Cu-BTC (HKUST-1), ZIF-8, Al(OH)₃ fumarate, ZIF-67, Mg-MOF-74 and Zn-SIFIXI-pyrazine. See Table 5 for a summary of MOFs for sale from each manufacturer.

MOF Technologies were the first to announce a MOF-based commercial product available through fruit and vegetable supplier Decco Worldwide Post-Harvest Holdings. The product has been registered with the U.S. Environmental Protection Agency under the proprietary name NT-7815 (EPA reference: 2792-79). NT-7815 is described as a micro-adsorbent delivering 0.7 wt% of 1-MCP, which is a gas that blocks postharvest ethylene responses, extending the storage life and quality of many fruits and vegetables. MOF Technologies has not released any details regarding the MOF incorporated within the product. With the announcement of the new product, MOF Technologies have expanded their production facility capable of producing 15 kg h⁻¹ in preparation for full scale between 5 and 10 tonnes per year from 2018 depending on which MOF.

NuMat Technologies established in 2013, have also released a MOF-based product called ION-X based on a proprietary set of MOFs for storing gases such as arsine, phosphine and boron.
MoF Apps, founded in 2013, are the exclusive licensee for UiO-66 and the zirconium-based family of MOFs. With a focus on MOF Application Services, the company aims to bring research and development of reliable production methods of nanoporous materials for a number of applications including medical devices, wound-healing and consumer healthcare. Framergy own the license for PCN-250 which can be used for spray-drying synthesis. The company is setting up a facility in Asia that will receive MOF-filled tanks from the United States. NuMat has a partnership with one of the top gas companies in Asia who will fill the tanks with gas which will then be distributed to customers. Asia which contains most of the major manufacturers of electronics in the world and therefore this position will likely offer direct access to this market which is 70% of the total demand. NuMat will lead the initial development of the proprietary set of MOFs for ION-X and have explored multiple manufacturing methods including flow, mechanochemical, solvothermal and others.

MOF Apps develops and offers integrated solutions using MOFs which are cost-competitive and which outperform state-of-the art systems. MOF Apps have sold the most amount of MOF to a leading vehicle manufacturer in August 2015 to test as adsorbed natural gas fuel platform.193

ProDia is a Horizon 2020 project funded through the European commission. It is a consortium of over 15 parties focused on the development of reliable production methods of nanoporous materials and their applications. Pilot-scale production of up to 100 kg will be led by Johnson Matthey for water-based synthesis, MOF Technologies for mechasynthesis and Axel One for spray-drying synthesis.194

ProfMOF founded in 2015 by a group of scientists at the University of Oslo, Inven2 and Kongsberg, focused on the commercialization of the MOF-material. ProfMOF prefer water-based and continuous flow production of MOFs. Prof Norbert Stock, inventor of CAU series and advisor for ProfMOF, has developed the water-based synthesis method for some of the zirconium MOFs and CAUs series.31,195,196 The ProfMOF catalogue includes: CAU-10, UiO-66, UiO-66-ADC, UiO-66-FA, UiO-66-BDC, UiO-66-BDC-NH3, UiO-66-BDC-COOH and UiO-66-BPDC/UiO-67.197

STREM Chemicals Inc. has become a distributor of MOFs manufactured in agreement with various MOF companies including KRICT, Inven2 and Framergy. Their catalogue includes: [CuI]6(DABCO)6, (CuI)6(C6H14N2)2, C6H12N4(CuCN)6, PCN-250(Fe) CONEKTC™ F250 by Framergy, MIL-100(Fe) KRICT F100 by KRICT, ZIF-8 and UiO-66 by Inven2.198

Sigma-Aldrich is a distributor of MOFs supplied by BASF under the product names Basolite® and Basosiv™. Fig. 13 shows the total number of academic publications that reference these products. The actual number of sales or quantities is unavailable and therefore these numbers represent the minimum. According to this data, Sigma-Aldrich has made at least a total of 1198 sales for research purposes. Their catalogue includes: Cu-BTC Basolite®, C300 by BASF, MIL-53 Basolite® A100 by BASF, Fe-BTC Basolite®, F300 by BASF, ZIF-8 Basolite® Z1200 by BASF, MOF-177 Basolite®, Z77 by BASF, Mg-Formate Basosiv™ M050 by BASF and Al-fumarate Basolite®, A520 by BASF (no longer available).199

Pseudo-startup MOFWORX from CSIRO Australia is commercializing MOFs based on patented flowchem manufacturing technology together with a diverse material and application-based portfolio. The group have built a reactor called Mindi (the aboriginal name for a mythological serpent that spits out white powder) that is capable of 10 kg h⁻¹ production. The company aims to become a product development house for MOF-based technologies supported by their own manufacturing capability.200

Other companies are working towards the commercialization of MOFs such as the MOF company, MOFGen, Framergy, ACSY-NAM and Promethean particles.201–204 MOFGen are developing nanoporous materials for materials for a number of applications including medical devices, wound-healing and consumer healthcare. Framergy own the license for PCN-250 which can be used

### Table 5

| MOF                        | Manufacturer       |
|----------------------------|--------------------|
| Al(OH) fumarate            | MOF Apps           |
| CAU-10                     | ProfMOF            |
| Cu-BTC                     | BASF               |
| Mg-MOF-74                  | MOF Technologies   |
| MIL-100                    | KRICT              |
| MIL-101-NH2                | MOF Apps           |
| MIL-53                     | BASF               |
| MIL-68                     | BASF               |
| MIL-177                    | BASF               |
| ZIF-67                     | MOF Apps           |
| ZIF-8                      | BASF               |
| Zn-SIFIX-pyrazine          | MOF Technologies   |

![Fig. 13](https://example.com/f13.png)

Fig. 13 Number of publications referring to the Basolite® and Basosiv™ products supplied by Sigma-Aldrich.
for natural gas capture and storage, and currently sold through STREM Chemical Inc. Promethean particles have commissioned a continuous flow reactor based on super critical water capable of producing 1000 tonnes per year. The company has focused on nanoparticle production for inks electronics industry but are capable of shifting to MOF production if the market becomes more attractive.

5. Conclusions and future priorities

The last two decades have seen great progress in the field of metal organic frameworks both in the discovery of new structures and the development of new functional properties of these nanomaterials. However, a crucial pre-requisite for accessing this potentiality in real world applications is the ability to routinely synthesize these materials in large quantities with high efficiency. It is only within the last five years that interest has arisen in the scientific community to develop novel synthetic methods and explore the scale up the synthesis of MOFs, focusing on economically viable strategies that do not rely on expensive or rare raw materials and also consider safety and environmental issues.

In this review, the advances in several synthetic methodologies were discussed. These new synthetic methods allow an unprecedented level of control over the reaction conditions, which in turn lead to a better control over particle size morphology, and reproducibility between batches. However, there are still a few issues remaining before MOF production reaches the level of a mature commercial technology. The solvent free approach and water-based synthesis are the most likely strategies to succeed in becoming economically and environmentally feasible for large ton scale production. Aside from the development of synthesis routes, another critical area is downstream processing, as the conventional downstream methods used at the laboratory scale are not well-suited to high production rates. This means that large scale application of MOFs will be limited by their commercial availability and thus most likely also the sustainability of the synthesis procedure until these methods are further developed. This future research, which will involve researchers of many different fields, will certainly introduce metal–organic materials up to their use for real practical applications.

Efforts in MOF commercialization have lead to the creation of several spin off companies, and the two new MOF markets recently released open a new and exciting time.

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