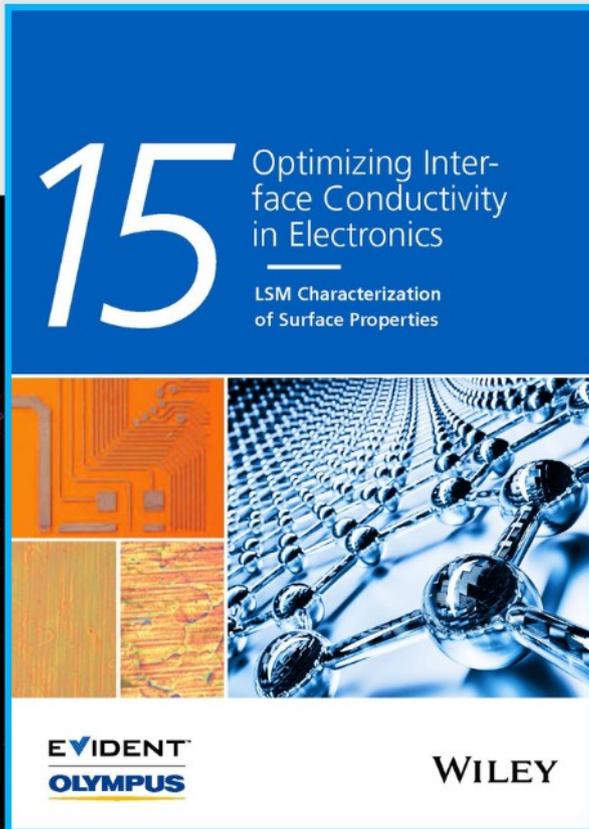




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# Green Synthesis of Reticular Materials

Aamod V. Desai, Erlantz Lizundia, Andrea Laybourn, Daniel N. Rainer, Anthony R. Armstrong, Russell E. Morris, Stefan Wuttke, and Romy Ettlinger\*

To help ensure a prosperous future on Earth for coming generations, academia and industry need to transform the way they plan and carry out the synthesis of novel materials to make them more environmentally sustainable. In particular, the field of reticular materials, i.e., metal-organic frameworks, zeolitic imidazolate frameworks, and covalent organic frameworks, has great potential to outperform other materials and revolutionize various fields of applications. This review highlights several key aspects from the choice of their starting materials, solvents and synthetic methodologies that fall under the umbrella of the Green Chemistry principles, and incorporates a Circular Economy perspective by providing relevant strategies such as reuse, regeneration, or recycling to maximize the value of the Earth's available resources. Moreover, it will shed light on the life cycle assessment results of selected reticular materials and consider how constraints imposed by Green Chemistry principles, life cycle assessment metrics, and circular patterns will shape the future rational sustainable design and discovery of reticular materials.

that counteract current environmental issues associated with the depletion of non-renewable resources, environmental pollution, global warming, and biodiversity loss.<sup>[1,2]</sup> In this context, reticular materials, such as metal-organic frameworks (MOFs), zeolitic imidazole frameworks (ZIFs), and covalent organic frameworks (COFs), are gaining attention due to their tailor-made multifunctional properties and potential applications. These range from gas storage and separation, water harvesting, catalysis, energy conversion and storage, sensing, to biomedicine, e.g., health-care, diagnosis, therapy, theragnostics, among others, as well as environmental remediation, and CO<sub>2</sub> capture.<sup>[3,4]</sup> To foster their syntheses in a “greener” and more environmentally “sustainable” fashion, it is essential to define what can be considered as “green” and how this can be maximized. For this, the 12 principles developed by Paul Anastas

and John Warner in 1998 should be considered.<sup>[5,6]</sup> Green Chemistry can be defined as follows: “*The design, development and implementation of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.*”<sup>[6]</sup> This

## 1. Introduction

In the 21<sup>st</sup> century, remarkable efforts are being made to find novel materials and environmentally friendly synthetic strategies

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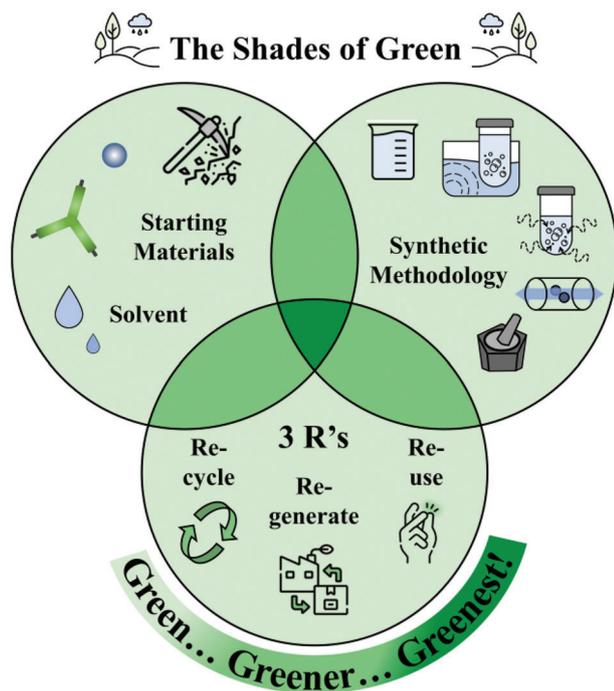
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**Figure 1.** Interplay between starting materials and solvents, the selected synthetic methodology and their reuse, regeneration, and recycling for the most environmentally friendly material preparation possible.

definition can be broken down to two core aspects: i) the importance of (wherever possible) designing, using, and producing only biocompatible building blocks and reaction media, and ii) focus on the utilization of synthetic methodologies with reduced energy input. Taking care of the two aspects individually clearly enables greener synthesis, but their combination would allow further improvements (Figure 1).

Although current research aims to establish more and more green pathways for reticular material synthesis considering the 12 fundamental principles of Green Chemistry,<sup>[7,8]</sup> the latest environmental policies and the pressures on our environment are requiring us to quickly implement constraints to reduce greenhouse gas emissions to at least 55% below 1990 levels by 2030 (EU's 2030 Climate Target Plan),<sup>[9]</sup> and strengthen the implementation of circular processes. The introduction of standardized environmental impact metrics methodologies such as life cycle assessment during the early design of reticular materials<sup>[10]</sup> could enable systematic understanding and discovery of novel environmentally sustainable materials with deep scientific, technological, and societal impact. Going beyond the classical green synthesis approaches and diving into a life cycle mindset considering all the life cycle stages, from raw material acquisition, synthesis, use/maintenance, and end-of-life will provide a bigger-picture of environmental sustainability.<sup>[11]</sup> Extending the use phase and closing loops through strategies such as reuse, regeneration or recycling ensures that the material and energy invested during the material synthesis are circulated at the highest value, the core idea behind the Circular Economy. Only by paying more attention to this aspect will it be possible to work in the "greenest" way (Figure 1).

The interest in the development of greener synthetic approaches for reticular materials has commanded much attention in recent years, and some excellent reviews have highlighted the different aspects therein.<sup>[7,12–16]</sup> In this review we aim to approach this topic by first briefly outlining the aspects of the 12 principles of Green Chemistry with respect to their applicability to the synthesis of reticular materials and introduce the different relevant synthetic methodologies. Second, we will shed light on all the efforts that have already been made in the field of reticular materials to replace hazardous chemicals by more environmentally friendly alternatives, e.g., by using water or Cyrene (C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>) as a solvent instead of *N,N*-dimethylformamide (C<sub>3</sub>H<sub>7</sub>NO), and to rather adopt less energy-consuming synthetic routes, e.g., room-temperature-, sonochemical-, microwave-assisted- or mechanochemical synthesis instead of solvothermal synthesis, to provide more green and sustainable syntheses in the future. Third, this review focuses on the importance of the introduction of a life cycle mindset for reticular materials and their environmental impact assessment. With these considerations in mind, researchers have a great opportunity to design greener and waste-free protocols that yield future materials with reduced toxicity<sup>[17]</sup> and improved transiency (degradability),<sup>[2]</sup> potentially limiting their environmental footprint caused by the disposal and subsequent accumulation of durable and potentially harmful materials in marine, river, and land environments.

## 2. Tutorial Session about the Importance of Green Synthesis

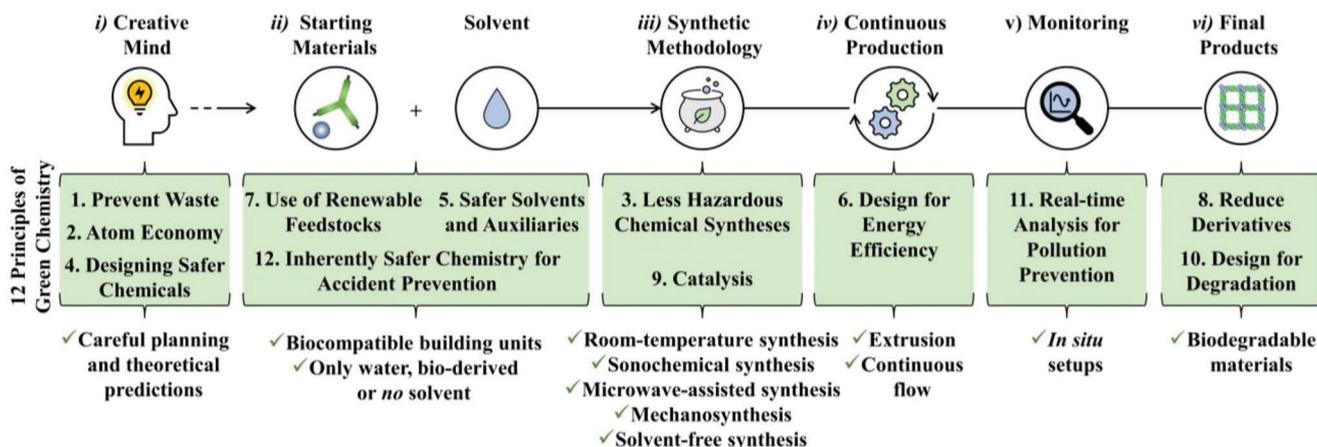
To boost the environmentally sustainable synthesis of reticular materials, we encourage consideration of various aspects prior to novel material design and synthesis. Figure 2 outlines some of the most important aspects: starting from i) the creative idea of a new synthesis, to ii) the choice of starting materials and solvents as well as iii) the best suited synthetic methodology, to considerations whether iv) the continuous production and v) monitoring are achievable, until ultimately vi) the final product is obtained. In the following, the individual aspects are discussed accounting for the corresponding principles of Green Chemistry. As the chosen synthetic methodology plays a crucial role in the overall environmental impact of producing a material, the different synthesis pathways are subsequently discussed in detail.

### 2.1. The 12 Principles of Green Chemistry in Design and Synthesis of Reticular Materials

Although the consideration of all 12 principles of Green Chemistry to the same synthetic procedure would be ideal and is strongly encouraged below, we believe it is worth noting that sometimes this is not achievable and the overall sustainability may benefit more from making trade-offs.

#### 2.1.1. The Creative Idea

Whenever designing a novel material and its synthesis, one should aim to maximize waste prevention, atom economy, and the creation of new materials in the safest manner possible.



**Figure 2.** Overview of the relevant aspects prior to novel synthesis, the 12 principles of Green Chemistry and their real-world translation.

**Prevent Waste (First Principle of Green Chemistry):** It is clearly preferable to prevent waste than to take care of it after its creation and material syntheses should be designed to avoid waste and non-desired by-products. In this sense, the choice of starting materials has a huge impact on the formation of resulting by-products. While metal salt precursors such as acetates, carbonates, hydroxides, oxides, and sulfates are considered as green, metal nitrate salts should be avoided as they can release corrosive and toxic  $\text{HNO}_3$ .<sup>[18]</sup> Ideally, the metal ions and organic ligands used should be selected so that they are non-toxic and do not pollute the environment after the material is degraded. The utilization of organic salts is of interest to avoid the formation of corrosive acids.<sup>[19]</sup> Moreover, the solvent and its potential decomposition during the synthesis play a crucial role. The widely used *N,N*-dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ ) should definitely be avoided as it decomposes into *N,N*-dimethylamine at elevated temperatures. It can be replaced by greener solvents such as bio-derived Cyrene ( $\text{C}_6\text{H}_8\text{O}_3$ ),<sup>[20]</sup> or even better, by water, alcohol, acetone, ionic liquids, or supercritical  $\text{CO}_2$ .<sup>[21–24]</sup> In addition, fine-tuning the synthetic protocol can minimize the formation of by-products. For instance, applying mechanochemistry for the preparation of the zeolitic imidazolate framework ZIF-8(Zn) can be performed with only water as a by-product.<sup>[25]</sup>

**Atom Economy (Second Principle of Green Chemistry):** To fully exploit the value of Earth's resources the incorporation of all materials involved in the synthetic process of a novel material should be maximized. As a result, carefully planned syntheses and syntheses using minimal or no solvent are desirable. In case solvents are needed, their capture and subsequent reuse should be pursued (this also applies to unreacted organic linkers). Additionally, reaction paths offering yields >80% result in lower environmental impacts per amount of synthesized material (the functional unit concept in life cycle assessment, as will be discussed later). For instance, the solvent-based microwave-assisted synthesis of the metal-organic framework HKUST-1(Cu) can render yields as high as  $\approx 96\%$  in only 30 min.<sup>[26]</sup> Changing the synthetic methodology of the zeolitic imidazolate framework ZIF-8(Zn) from a solvent-based precipitation in methanol to mechanochemistry can boost its yield from only 10% to 70%.<sup>[25]</sup>

**Designing Safer Chemicals (Fourth Principle of Green Chemistry):** Clearly, the overall (nano)toxicity of the final product can be lim-

ited by only considering certain metal ions and organic linkers that are known to be physiologically acceptable and have minimal  $\text{IC}_{50}$  (half maximal inhibitory concentration) values. Besides nontoxic building blocks, further aspects such as the morphology and size of a material must also be considered to avoid undesired toxicological effects as the likelihood of causing serious damages in living tissues may increase with decreasing size due to easier penetration into cells.<sup>[17]</sup> Interestingly, a targeted degradation into living tissues can avoid endogenous accumulation and toxicity issues.<sup>[27]</sup>

### 2.1.2. The Choice of Starting Materials and Solvents

**Use of Renewable Feedstocks (Seventh Principle of Green Chemistry):** To maximize the sustainability of a novel synthesis, ideally, the raw material or feedstock should be renewable and locally available rather than derived from finite and critical raw materials. Moreover, finite raw materials present supply chain bottleneck issues and their extraction can require intensive processing and refining, jeopardizing their environmental sustainability.<sup>[28]</sup> In this context, Dong et al. molecularly engineered wood to create cellulosic chains that can act as linkers. Upon coordination with  $\text{Cu}^{2+}$  (assisted by  $\text{OH}^-$  and  $\text{Na}^+$ ) these can compose a 3D hierarchically arranged cellulosic scaffold with highly aligned 1D open channels of  $\approx 10 \text{ \AA}$ .<sup>[29]</sup> This approach is scalable, cost-effective, and universally applicable to industrially relevant cellulosic materials such as wood, paper, or cotton textiles, paving the way towards a new exciting field of bio-based reticular materials. Likewise, greater use of bio-sourced building units such as furan-2,5-dicarboxylic acid (FDCA) should be promoted.<sup>[30,31]</sup> This molecule has already been used as a ligand for the preparation of several MOFs.<sup>[32–34]</sup> In the same vein, the utilization of other bio-based linkers that have shown potential as building blocks in MOFs is encouraged.<sup>[35–41]</sup>

**Safer Solvents and Auxiliaries (Fifth Principle of Green Chemistry):** As already mentioned, whenever possible the use of auxiliary substances, e.g., solvents or separation agents, should be reduced as far as possible. Switching from organic solvents to water-based reactions significantly reduces the toxicity and carbon footprint associated with solvent refining and discharge.

Nitrogen-containing petrochemical solvents that critically affect aquatic ecosystems should especially be avoided, and thus, checking the solvent sustainability guides for appropriate reaction media selection is encouraged.<sup>[42,43]</sup>

*Inherently Safer Chemistry for Accident Prevention (Twelfth Principle of Green Chemistry):* In agreement with all previously mentioned principles of Green Chemistry, the choice of substances and their form used in a chemical process should be in such way so that the potential for chemical accidents, including releases, explosions, and fires, is minimal. It is recommended to continuously shift the focus of synthesis towards aqueous-based protocols without strong acids/bases as modulator, preferably at ambient temperature and pressure.

### 2.1.3. The Best Suited Synthetic Methodology

*Less Hazardous Chemical Syntheses (Third Principle of Green Chemistry):* The choice of synthetic methodology should ideally be designed to only utilize and generate substances that possess little or no toxicity to human health and the environment. Until now, syntheses still involve reagents being notably harmful for both human and environmental health, with flammability and safety-related concerns. Research should strongly focus on fully aqueous-based syntheses or those using ionic liquids and deep eutectic solvents which can concomitantly act as solvents and structure-directing agents. Microwave-assisted syntheses under controlled pressure conditions and using greener and less hazardous solvents should be further explored. Moreover, the use of more mechano-synthesis that avoids the need for flammable, toxic/poisonous, or irritating solvents is desirable.

*Catalysis (Ninth Principle of Green Chemistry):* To increase the efficiency of the reactions, more attention should be paid to the use of catalytic reagents (as selective as possible) that are superior to stoichiometric reagents in the synthesis of reticular materials. It may even be an option to use substances that are considered hazardous, e.g., a strong mineral acid or base for MOF synthesis or for preparing COFs, if these are used in such small amounts that the overall benefit is positive.<sup>[44–47]</sup> Thinking about the entire process and sometimes accepting a trade-off might be more beneficial than strictly banning individual components.

### 2.1.4. Continuous Production

*Design for Energy Efficiency (Sixth Principle of Green Chemistry):* The requirements of energy during a synthesis should carefully be considered to minimize their environmental and economic impacts. As a result, synthesis at ambient temperature and pressure is preferable. This is also of special interest and benefit for the large-scale production of reticular materials. For instance, electrochemical and microwave heating are quick and have been up-scaled commercially for the metal-organic framework HKUST-1(Cu).<sup>[48,49]</sup> Continuous, large-scale production of metal-organic frameworks through electrochemical, microwave-assisted or mechanosynthesis, spray drying, and flow chemistry synthesis and the comparison of their energy efficiency are becoming increasingly important.<sup>[22,50,51]</sup> For the preparation of some well-known MOFs and COFs, using newer methods such

as liquid-phase plasma, was found to reduce reaction time to a few minutes, which reduced the energy input.<sup>[52,53]</sup> Comparing the energy efficiency regarding purification and activation of metal-organic frameworks considering calcination, solvent exchange, supercritical CO<sub>2</sub> drying, freeze-drying, microwave heating, ultrasound, UV/Vis irradiation, induction heating and acid treatment, revealed that ultrasound, induction heating and targeted heating technologies such as microwave and photo-thermal methods offer potential energy savings.<sup>[54]</sup>

### 2.1.5. Monitoring

*Real-Time Analysis for Pollution Prevention (Eleventh Principle of Green Chemistry):* To reduce the formation of hazardous substances and optimize the efficiency of synthesis, further analytical methodologies are required that enable real-time, and in-process monitoring. Although the nucleation and growth of reticular materials are still relatively understudied, more and more in situ X-ray diffraction,<sup>[55–57]</sup> X-ray scattering techniques,<sup>[58–60]</sup> as well as NMR studies,<sup>[61]</sup> with reticular materials are being introduced to provide better understanding.<sup>[62]</sup>

### 2.1.6. The Final Product

*Reduce Derivatives (Eighth Principle of Green Chemistry):* In order to reduce the risk of additional purification steps due to derivatization and potentially generated waste, the utilization of blocking groups, protection/deprotection, and temporary modification of physical/chemical processes should ideally be avoided in the synthesis of reticular materials. However, the resulting properties of the final product need to be carefully evaluated to ensure the best possible material performance.<sup>[62]</sup>

*Design for Degradation (Tenth Principle of Green Chemistry):* Already during the development of a new material, care should be taken to ensure that it is readily biodegradable into innocuous degradation products at the end of its life that circumvent the contaminant leakage/accumulation into the environment.<sup>[63,64]</sup>

By designing reticular materials that are fully based on edible building blocks,<sup>[65]</sup> physiologically acceptable metals<sup>[66]</sup> or naturally available polymers,<sup>[29]</sup> researchers have the great opportunity to mainly develop novel materials that do not persist in the environment.

## 2.2. Comparison of Synthetic Methodologies

Besides optimizing the starting materials (**Figure 3** left), the selected synthetic route plays a major role in making the syntheses of reticular materials greener and more sustainable.<sup>[12,66–68]</sup> To date, the “playground” of reticular materials has expanded to more than 90 000 structures that have been synthesized—and more than 500 000 structures are predicted.<sup>[69]</sup> These materials were obtained by methods referred to as “shake and bake,” “mix and wait,” and “heat and beat.”<sup>[70]</sup>

Enormous efforts have been made to move from the most common solvothermal synthesis of reticular materials at high temperatures to room-temperature and more energy-efficient methods

Starting Materials	Volume of Solvent	Synthetic Methodology	Metal-Organic Frameworks	Zeolitic Imidazolate Frameworks	Covalent Organic Frameworks
<p><b>Metal source</b> → Impact on formation of by-products ✓ Acetates, carbonates, hydroxides, oxides, and sulfates</p> <p><b>Metal ions</b> ✓ Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, V<sup>4+</sup>, Mn<sup>4+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, and Zr<sup>4+</sup></p> <p><b>Organic ligand</b> ✓ Amino acids, peptides, nucleobases, saccharides, porphyrins, and proteins</p> <p><b>Use of Bases / Modulators</b> → Enables deprotonation of ligand → Impact on crystallization</p> <p><b>Solvent</b> → Impact on speed of crystallization and formation of by-products ✓ Water, alcohol, acetone, ionic liquids, Cyrene, supercritical CO<sub>2</sub>, ethyl acetate, and ethyl lactate</p>	 0.2–2 μL mg <sup>-1</sup> 0 mL	 <b>Solvothermal Synthesis</b>	since 2014: 80 publications	since 2021: 4 publications	since 2018: 10 publications
		 <b>Room-Temperature Synthesis</b>	since 2014: 126 publications	since 2015: 27 publications	since 2014: 15 publications
		 <b>Sonochemical Synthesis</b>	since 2008: 19 publications	since 2012: 4 publications	since 2012: 4 publications
		 <b>Microwave-assisted Synthesis</b>	since 2009: 23 publications	since 2012: 1 publication	since 2021: 1 publications
		 <b>Mechano-synthesis / Solvent-free Synthesis</b>	since 2012: 55 publications	since 2012: 5 publications	since 2020: 8 publications

**Figure 3.** Overview of possibilities regarding the starting materials and the synthetic methodologies at hand to make the synthesis reticular frameworks more environmentally sustainable. The number of publications was determined with *Scopus* in April 2023, based on searching for “metal-organic framework”/“zeolitic imidazolate framework”/“covalent organic framework” and “green” and “solvothermal synthesis”/“room-temperature synthesis”/“sonochemical synthesis”/“microwave-assisted synthesis”/“solvent-free synthesis” in the title or the abstract.

such as sonochemical synthesis, microwave-assisted synthesis, and solvent-free synthesis (Figure 3). So far, clearly most work has been done in the field of metal-organic frameworks (303 publications), followed by zeolitic imidazolate frameworks (41 publications) and finally covalent organic frameworks (38 publications). Comparing the ratio of the different synthetic methodologies, unsurprisingly, most publications that were published using the keyword “green” are room-temperature syntheses for all three reticular material classes.

Consequently, to encourage the more intensified utilization of alternative energy-efficient routes such as sonochemical-, microwave-assisted-, and mechano-synthesis their advantages will be discussed below. However, it has to be noted that the discussed methodologies also suffer from a few different limitations:<sup>[8,71]</sup> i) (Hydro)solvothermal syntheses may take several days and the solvents used, such as ionic liquids, may be trapped in the pores of the resulting material; ii) the ultrasound waves applied in sonochemical syntheses may break crystallites and prevent the growth of large crystals; iii) similarly, also microwave-assisted syntheses often fail to produce large crystals and are difficult to translate into industrial settings; and iv) mechano- and solvent-free syntheses generally offer less control over crystal morphology, the resulting particle size and the formation of secondary phases.

### 2.2.1. Solvent-Based Synthesis

The term solvent-based synthesis covers various synthesis routes that can be based either on organic solvents or on water, at ambient or high pressures and temperatures. Usually, these syntheses are optimized with respect to the used starting materials and

their solubilities to allow the crystallization of extended, porous frameworks through strong directional bonds. Because the solubility may decrease with decreasing temperature/pressure and when changing from organic solvent to water, syntheses at ambient conditions often require the additional use of modulators or bases that guarantee the deprotonation of the organic ligands. This also applies to sonochemical-, microwave-assisted-, and mechano-synthesis.

### 2.2.2. Sonochemical Synthesis

Sonochemical synthesis refers to reactions that are driven by high-energy ultrasonic waves. The effect is mainly caused by the formation of acoustic cavitation, which is a consequence of formation, growth, and the collapse of bubbles in the liquid. This phenomenon is responsible for creating very high temperatures and pressures, forming local hotspots that function as a reactor. The liquid constantly expands and contracts, generating a large number of reaction centers. Typically, in chemical synthesis, frequencies up to 1 MHz are employed with short reaction times ranging from minutes to few hours. Broadly, reactions can occur in three regions—inside the bubble, at the interface of the bubble and bulk solvent, or in the vicinity of the bubble. In the last case, the formation of free radicals in the hot region can lead to the initiation of reaction in the bulk. Likewise, dissolved gases in the liquid can affect the reaction and its yields. Also, the temperature of the liquid has an effect, as the surface tension influences the formation of reaction centers.<sup>[72]</sup>

Sonochemical synthesis has picked up over the last few years, particularly in organic synthesis, owing to wide availability of equipment, ease of operation, and shorter reaction times. In the

domain of reticular frameworks, the emphasis has been on using this technique to obtain the products quicker with smaller particle sizes. Apart from modulating frequencies, the effects of time, temperature, concentration, solvents on the yields, and quality of products have been examined.<sup>[73,74]</sup>

### 2.2.3. Microwave-Assisted Synthesis

Since the early 2000s, microwave technology has been used to prepare a wide range of reticular materials. Compared to traditional solvothermal methods, microwave-assisted syntheses enable exceptionally faster reactions within  $\text{min s}^{-1}$  rather than  $\text{h d}^{-1}$  and consequently, they feature substantially reduced energy consumption.<sup>[75]</sup> In microwave heating, energy is delivered through the interaction of the alternating electromagnetic field with the material under treatment rather than by convective, conductive, or radiative heat transfer.<sup>[76]</sup> The propensity for individual components (or a reaction mixture) to be heated by microwave radiation is characterized by their dielectric properties. These indicate which reagents interact more strongly with the electric field and thus heat more effectively.<sup>[77]</sup> Large variations in the dielectric properties of individual components within the bulk reaction mixture are indicative of a selective heating mechanism whereby individual components are selectively heated and become hotter than the bulk.<sup>[77–79]</sup> In the context of green and sustainable syntheses of reticular materials, selective heating enables the improvement in yield of the final product, control over the reaction pathway, and importantly the potential for a substantial reduction in energy requirements as the energy is absorbed into the critical components rather than heating the bulk, opposite to conventionally heated process(es).<sup>[80]</sup>

To further optimize microwave-heated reactions, high-speed synthesis using microwave-heating technology has attracted extensive and continually increasing interest. Most reports involve “off the shelf” batch microwave reactors which typically possess multi- or single-mode cavities featuring direct bulk temperature control using either infra-red or fiber-optic probes, agitation devices, and software that enables online bulk temperature/pressure regulation by controlling microwave power output.<sup>[81,82]</sup> There are even examples in which domestic kitchen microwave ovens (including with modification) are used.<sup>[49,83,84]</sup> The optimization of microwave synthesis of reticular materials historically involves altering chemical (type of metal salt, solvent, concentration, pH, presence of modulators) and process parameters (microwave power, treatment time, temperature, pressure, mixing) with the aim of increasing yield, phase purity, crystallinity, and surface area whilst reducing reaction time, particle size distribution, and production of unwanted by-products. However, most approaches do not consider the minimum amount of energy required to perform these reactions which is essential for producing the optimum quality of products in an economically viable and sustainable way.<sup>[78,80]</sup> Quantifying energy absorbed into specific components of the reaction is not simple because it relies on the performance of the microwave reactor which is dependent on a wide range of factors including the reactor itself (cavity geometry, configuration of microwave feed(s)/supply) and the material under treatment (dielectric properties, which are functions of frequency of the electromagnetic field, temperature, state of

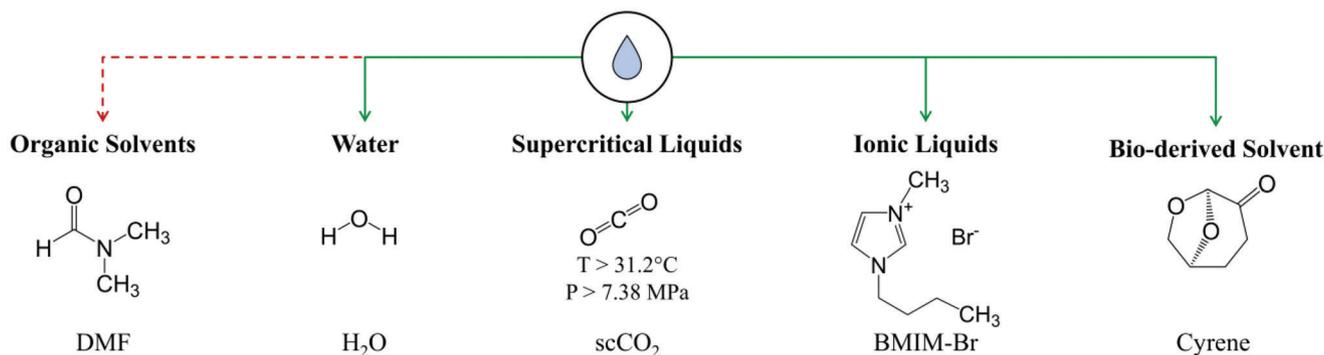
matter, composition and concentration; penetration depth; power density in the heated phase), the vessel material and internals (e.g., stirrer bars, fiber optic), and stirring.<sup>[76,80,82]</sup> To understand the mechanisms of microwave synthesis it is essential to design a toolbox that includes electromagnetic simulations, ideally underpinned by machine learning for material characterization, and rigorous experimental protocols able to quantify the absorbed energy in the heated phases.<sup>[78,80,82]</sup>

### 2.2.4. Mechanochemistry and Solvent-Free Synthesis

In contrast to the comparatively recent adoption of ultrasound irradiation and microwave heating to aid in the synthesis of chemical compounds, energy input through mechanical means is arguably one of the oldest methods humans have employed to purposefully and intentionally alter materials.<sup>[85]</sup> Deliberate use of mechanical energy for chemical synthesis has seen a resurgence in the last few decades in a wide variety of research areas, including medicinal chemistry,<sup>[86,87]</sup> organic chemistry,<sup>[88–90]</sup> and functional materials science,<sup>[91–93]</sup> among others. Success in these areas has also prompted investigation into the applicability of mechanochemical methodologies for the synthesis of reticular materials. A direct way of exposing chemicals to mechanical energy is by simple grinding using a pestle and mortar. This has been used in several studies but suffers from poor reproducibility and a lack of parameter control. Thus, mechanochemical treatments on laboratory scales are often carried out using mills of different kinds, typically ball mills such as vibratory mills (also known as mixer mills) or planetary mills. Such mills are commercially available as benchtop devices and owing to their size and straightforward and simple basic design can even be adapted and altered to suit specific needs such as in situ characterization. From the 2000s onwards, many different examples of mechanochemistry of reticular materials have been reported by several groups around the world.<sup>[94–96]</sup> Compared to other synthetic methods, these syntheses have the huge advantage of a significantly reduced volume of solvent of only  $0.2\text{--}2\ \mu\text{L mg}^{-1}$ . While a reduction of the required volumes is beneficial, avoidance of solvents altogether is an even more intriguing thought and should be pursued where possible. To date, several ways have been devised to adapt the synthesis conditions of reticular materials to accommodate the lack of a liquid phase and to fulfill the solvents' other roles in the synthesis. Inspired by these reports, solvent-free synthesis is strongly encouraged for the preparation of reticular materials.<sup>[97]</sup>

## 3. Different Synthetic Methodologies for Reticular Materials

In the following section, different solvent-based and solvent-free synthesis of reticular materials as well as their optimization with respect to greener synthesis will be discussed. Considering the sheer volume of work, the following chapter is not intended to be comprehensive and only illustrative examples are discussed. The selection of solvent for synthetic methodologies, including solvothermal-, room-temperature-, sonochemical-, microwave-assisted, and mechanochemistry, is highly relevant, and ideally



**Figure 4.** Overview of different types of solvents available for the solvent-based synthesis of reticular materials. Abbreviations: *N,N*-dimethylformamide (DMF); supercritical CO<sub>2</sub> (scCO<sub>2</sub>); 1-butyl-3-methylimidazolium bromide (BMIM-Br); dihydrolevoglucosenone (Cyrene).

commonly used organic solvents like *N,N*-dimethylformamide should be substituted by more environmentally friendly solvents such as water, supercritical and ionic liquids, and bio-derived solvents (Figure 4).<sup>[42]</sup>

### 3.1. Solvent-Based Synthesis

Although solvent-based synthesis can be performed at ambient or high pressures and temperatures in organic solvents, water, supercritical liquids, ionic liquids, or bioderived solvents, in the following section the main focus lies on making syntheses more environmentally friendly. Therefore, solvothermal syntheses as well as those using organic solvents will be neglected.

#### 3.1.1. Water

Using water as a solvent eliminates the disadvantages of organic solvents such as high cost and their flammable and hazardous nature. To continue to ensure the deprotonation of the organic ligand, this environmentally friendly alternative often requires the addition of modulators.

**Metal-Organic Frameworks and Zeolitic Imidazolate Frameworks:** Already in 1995, Yaghi and Li reported the hydrothermal synthesis of a Cu-based metal-organic framework.<sup>[98]</sup> Thereafter, numerous metal-organic frameworks were prepared in water-based systems. For instance, for the MOF-74 family high space-time yield reflux synthesis was reported without any cosolvents and at large scales.<sup>[99,100]</sup> Reinsch et al. revealed that also the well-known UiO-66 family can be synthesized via hydrothermal synthesis.<sup>[101]</sup> It is worth mentioning that in the early development of metal-organic frameworks, the use of hydrothermal methods was emphasized.<sup>[102–105]</sup> The huge potential and importance of water-based synthetic protocols have also recently been demonstrated by Zheng et al. with MOF-303(Al).<sup>[22]</sup> In this study, four synthetic methods (solvothermal, reflux, vessel, and microwave) are compared and an easy scale-up giving 3.5 kg of high-quality material per batch with a yield of 91% is presented from a vessel-based method. The corresponding space-time yield (STY) was estimated to be 179.5 kg m<sup>-3</sup> day<sup>-1</sup>. The synthesis optimization of another Al-based metal-organic framework, namely MIL-160(Al),<sup>[106]</sup> delivered water-based preparation with high yields

(93%) and high STY values (185 kg m<sup>-3</sup> day<sup>-1</sup>). To date, various zeolitic imidazolate frameworks have been synthesized in water and alcohol mixtures, but fully aqueous systems are rarer. Kida et al. investigated the formation of ZIF-8(Zn) in water depending on the ratio of metal to ligand.<sup>[107]</sup> The authors found that the resulting pH value plays a crucial role, and that using more ligand increases the formation rate of ZIF-8(Zn), while the particle size decreases. Similar trends were found for water-based synthesis of ZIF-90(Zn), where increasing ligand excess caused decreasing particle sizes.<sup>[108]</sup> It is worth noting that the initial reports on the preparation of other subclass of metal-organic frameworks such as those based on phosphonate ligands were demonstrated under hydrothermal conditions.<sup>[109–115]</sup>

**Covalent Organic Frameworks:** To date, almost all established synthesis protocols for covalent organic frameworks require high temperature, organic solvents, and hazardous additives. However, in 2021, Kim et al. successfully established a geomimetic hydrothermal reaction that gave access to polyimide-based covalent organic frameworks.<sup>[116]</sup> In 2022, Maschita et al. reported another (alcohol-assisted) hydrothermal synthesis which yielded two imide-linked covalent organic frameworks.<sup>[117]</sup> These pioneering works pave the way towards more water-based synthesis of covalent organic frameworks in the future.

#### 3.1.2. Supercritical Liquids

Using supercritical liquids, especially supercritical carbon dioxide, as reaction medium represents a green choice since it is abundant, inexpensive, non-flammable, non-toxic, and environmentally benign.<sup>[118]</sup> To reach the supercritical conditions of carbon dioxide, a mild critical temperature of 31.2 °C and a critical pressure of 7.38 MPa is necessary. Providing considerably faster mass transfer rates than liquid solvents as well as the ability to easily penetrate the pores of reticular materials, supercritical carbon dioxide can also be exploited for purification purposes.

**Metal-Organic Frameworks and Zeolitic Imidazolate Frameworks:** In 2014, Peng et al. revealed the impact on the porosity of mesoporous HKUST-1(Cu) synthesized in CO<sub>2</sub>-expanded *N,N*-dimethylformamide at different pressures.<sup>[119]</sup> When only working in supercritical CO<sub>2</sub> without the addition of a cosolvent, or greatly reduced amounts of a dimethyl sulfoxide/methanol solution 1D-Cu-MOF<sup>[120]</sup> and highly crystalline HKUST-1(Cu)<sup>[121]</sup>

could be obtained, respectively. López-Periago et al. also optimized their syntheses by mixing supercritical CO<sub>2</sub> with ionic liquids, i.e., 1-ethyl-3-methylimidazolium tetrafluoroborate or 1-ethyl-3-methylimidazolium bromide, which yielded highly porous MIL-100(Fe), HKUST-1(Cu) and ZIF-8(Zn).<sup>[122]</sup> To further minimize the environmental impact of their synthesis, López-Domínguez et al. employed the supercritical CO<sub>2</sub> synthesis of ZIF-8(Zn).<sup>[123]</sup> High yields of empty-pore ZIF-8(Zn) could be obtained without using organic liquids or excess of organic ligand. Also, Marrett et al. reported the rapid, clean, and scalable conversion of ZnO to various ZIFs.<sup>[124]</sup> Although these examples show that supercritical CO<sub>2</sub> represents an alternative solvent, it is more frequently used for the mild activation of reticular materials.<sup>[125]</sup>

**Covalent Organic Frameworks:** Xu et al. optimized the synthetic conditions for the 2D COF TAPB-TA (where TAPB-TA is 1,3,5-tris(4-aminophenyl)benzene/terephthalaldehyde) by using supercritical CO<sub>2</sub> and  $\gamma$ -valerolactone as a cosolvent.<sup>[126]</sup> While this structure is usually highly sensitive to harsh activation processes, their as-made material showed excellent high surface area and accessible pores. Corresponding theoretical calculations indicate that COF–COF interactions during the activation process prevent structural collapse.

The benefits of mild activation procedures of layered covalent organic frameworks with supercritical CO<sub>2</sub> have also been reported by Chen et al.<sup>[127]</sup> Similar to metal-organic frameworks, supercritical CO<sub>2</sub> treatments have so far been mainly attractive for unprecedentedly mild activation of covalent organic frameworks rather than for their synthesis.<sup>[128]</sup>

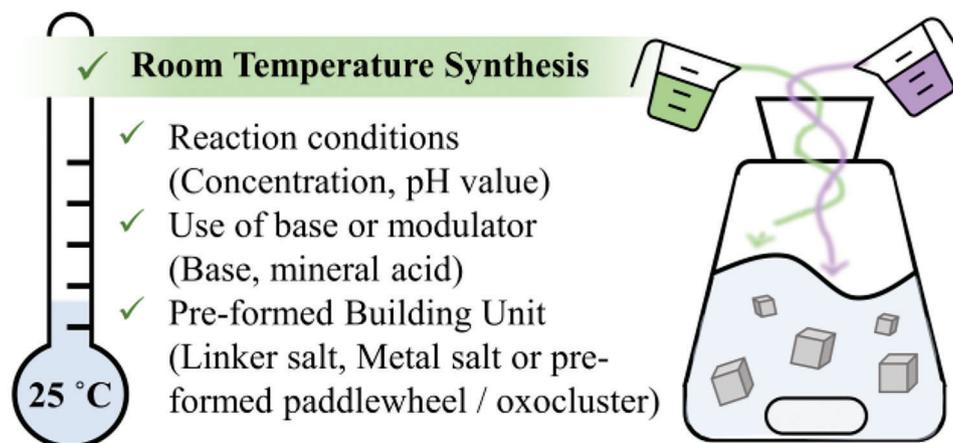
### 3.1.3. Ionic Liquids

Ionic liquids can be of several different types. Room-temperature ionic liquids are liquid at ambient temperature and generally comprise an organic cation with an anion that can be a halide or other inorganic ion or a more complex organic anion. Near room-temperature ionic liquids are often defined as liquids below 100 °C and there are also molten salts that are liquid at higher temperatures. In addition, mixtures of compounds that become liquid in certain ratios, such as deep eutectic solvents are also classified as ionic liquids. Whether ionic liquids are truly green solvents has been the subject of some debate. They are often claimed to be green and safe owing to their ability to dissolve a wide range of organic and inorganic compounds and their extremely low vapor pressure.<sup>[129–131]</sup> However, they are still organic in nature and have many of the same issues as other organic solvents and there is no doubt that the "greenness" of ionic liquids is sometimes overplayed. There are many possible binary ionic liquids now available, and care must be taken to choose those that can withstand the synthesis conditions without decomposing (and potentially interfering with the reaction). In addition, as both the components of a binary ionic liquid are charged, they can act as powerful structure-directing agents in the formation of porous solids, which can be beneficial in the synthesis of zeolites but is less useful for green synthesis of reticular materials because they then need an extra step to remove them from the final material.<sup>[132]</sup> If the reticular material is stable enough, this extra step is often a high-temperature calcination in air to com-

bust the occluded ion, but this of course is dependent on the thermal stability of the reticular material itself. Bystrzanowska et al. completed a systematic multicriteria analysis of the sustainability of ionic liquids.<sup>[133]</sup> In general, they are ranked similarly to many organic solvents, but the dearth of toxicity information for many means that there are still remaining question marks about whether it is correct to call them true green solvents. Even so, there are situations when the use of ionic liquids may lead to a greener synthesis when replacing, for example, a very volatile organic compound. The use of ionic liquids as solvents in the preparation of materials is called ionothermal synthesis, by analogy with solvothermal synthesis. Since its invention in the 2000s, it has been used to prepare a wide variety of solids, including metal-organic frameworks, coordination polymers, and covalent organic frameworks.<sup>[132,134–136]</sup> A particularly interesting aspect of ionothermal synthesis is the opportunity for induction to produce chirality in solids.<sup>[137,138]</sup> In terms of sustainability however, the most interesting aspect of ionic liquids is that they are often excellent microwave absorbers, making microwave-assisted synthesis an appropriate and green choice (Section 3.4).<sup>[139,140]</sup>

**Metal-Organic Frameworks and Zeolitic Imidazolate Frameworks:** Exploiting the advantages of ionic liquids, Sang et al. reported the rapid crystallization of UiO-66(Zr) in 1-hexyl-3-methylimidazolium chloride in only 30 min.<sup>[141]</sup> Martins et al. used similar methods to produce ZIF-type materials.<sup>[142]</sup> Systematically screening the deprotonation performance of various ionic liquids, Fan et al. prepared crystalline HKUST-1(Cu) utilizing *N,N,N',N',N'*-hexakis(2-hydroxyethyl)ethane-1,2-diaminium bromide at room-temperature.<sup>[143]</sup> Using the ionic liquids 1-propyl-3-methylimidazolium bromide or 1-butyl-3-methylimidazolium bromide, a novel Zn-MOF<sup>[144]</sup> and five unique Keggin-type polyoxometalate-based metal-organic frameworks (Zn or Cu-based) could be prepared.<sup>[145]</sup> Even though the solvent used can be considered as green, the other reaction conditions cannot, as these syntheses were performed in a Teflon-lined stainless-steel autoclave at 160 °C and 170 °C, respectively, for 5 d. Ye et al. proposed another approach: after an anion exchange of the ionic liquid forming 1-butyl-3-methylimidazolium hexafluorophosphate, ionic liquid microemulsion could be prepared that yielded Zn-MOF at room-temperature.<sup>[146]</sup>

**Covalent Organic Frameworks:** The benefits of working with ionic liquids have also successfully been transferred to covalent organic frameworks. Guan et al. could prepare a series of 3D ionic liquid-containing covalent organic frameworks with high reaction speed of only three min in 1-butyl-3-methylimidazolium bis[(trifluoro-methyl)sulfonyl]imide at room-temperature.<sup>[147]</sup> Using 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate, Dong et al. successfully synthesized multiple 2D keto-enamine-linked covalent organic frameworks, but their reaction conditions required 120 °C for 3 d.<sup>[148]</sup> As already expected from the previous works of metal-organic frameworks with ionic liquids, Gao et al. investigated the influence of the counter anion of 1-butyl-3-methylimidazolium in great detail, including bromide, trifluoromethanesulfonate, tosylate, trifluoroacetic, dicyanamide, nitrate, thiocyanate and bis[(trifluoro-methyl)sulfonyl]imide. The authors showed that polycondensation of high quality crystallites of TFPPy-PDA-COF and TFPPy-PyTTA-COF (where TFPPy is 1,3,6,8-tetrakis(4-formylphenyl)pyrene, PDA *p*-phenylenediamine, and PzTTA is FPPy with 4,4',4'',



**Figure 5.** Figure showing the different aspects of room-temperature synthesis of reticular frameworks.

4''-(pyrene-1,3,6,8-tetrayl)tetraaniline) was only triggered when having bis[(trifluoro-methyl)sulfonyl]imide as counter ion.<sup>[149]</sup> Using 1-butyl-3-methylimidazolium with hydrogen sulfate as counter ion, Zhao et al. synthesized further 2D keto-enamine-linked covalent organic frameworks.<sup>[150]</sup> This clearly demonstrates the huge design versatility ionic liquids can provide as a solvent. In addition to acting as solvent, ionic liquids can also become part of covalent organic frameworks, either on the main linkers, the nodes, or the side chains, thereby boosting their properties.<sup>[151]</sup>

### 3.1.4. Bio-Derived Solvents

Hazardous organic solvents such as *N,N*-dimethylformamide, which decomposes into *N,N*-dimethylamine at elevated temperatures, can be substituted with more environmentally friendly alternatives like Cyrene, i.e., dihydrolevoglucosenone, which can be bio-derived in two simple steps from cellulose.<sup>[152]</sup> Zhang et al. were able to verify the universal application of Cyrene as a solvent by synthesizing highly crystalline HKUST-1(Cu), UiO-66(Zr), Co-MOF-74, Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO), and ZIF-8(Zn).<sup>[153]</sup> The authors discovered that it is crucial to minimize the water content present during the synthesis to avoid the formation of an aldol-condensation product of Cyrene. Bhindi et al. highlighted the benefits of bio-derived Cyrene as well as  $\gamma$ -valerolactone for the preparation of coatings of HKUST-1(Cu), ZIF-8(Zn), and ZIF-67(Co).<sup>[154]</sup> The authors showed that their synthetic route yields higher porosity as well as enabled enhanced control over the phase formation. These pioneer studies show that it is possible to find bio-based dipolar aprotic solvent alternatives for the widely used *N,N*-dimethylformamide.

## 3.2. Room-Temperature Synthesis

### 3.2.1. Metal-Organic Frameworks

The terminology of room-temperature synthesis can encompass several methods, for clarity those methods that do not involve

strong external forces (such as ultrasonication, mechanical) are discussed in this section, focusing on different aspects and approaches adopted (Figure 5).

In an early study in 2008, Tranchemontagne et al. demonstrated a facile route to prepare a range of well-known structures, namely MOF-5(Zn), MOF-74(Zn), MOF-177(Zn), and MOF-199(Cu), at room-temperature by avoiding the use of nitrate salts, that are not desirable for larger scale synthesis.<sup>[155]</sup> The addition of a mild base, triethylamine, to the reaction mixture facilitated deprotonation of the respective ligands, while metal acetates served as the source for cations. The use of a base (diethylamine) instead of polar *N,N*-dimethylformamide was useful in preparing HKUST-1(Cu) at room-temperature by stirring copper nitrate and trimesic acid in a solvent mixture of water and ethanol.<sup>[44]</sup> The presence of the base altered the speed of crystallization and precluded the formation of unwanted side products. It is worth noting, that early examples of preparing metal-organic frameworks based on carboxylic acid linkers used slow diffusion of an organic base and a template, e.g., toluene as a template, or addition of a secondary species, such as hydrogen peroxide, at room-temperature into a solution of metal salt and linker.<sup>[156–158]</sup>

Majano and Pérez-Ramírez further improved the synthesis of HKUST-1(Cu) using Cu(OH)<sub>2</sub> as the metal source and avoiding the use of a base.<sup>[159]</sup> The choice of the metal hydroxide facilitated self-assembly of the metal-organic framework within a few seconds in a water/ethanol solvent mixture. This rapid synthesis was ascribed to straightforward acid-base reaction between metal salt and the carboxylic acid linker that led to formation of only water as the byproduct. Huo et al. also observed that the nucleation is strongly influenced by the selection of the metal salt.<sup>[160]</sup> Comparing acetate and nitrate salts of Cu(II), the rate of reaction, when carried out in water, was seen to be different and had a significant bearing on the morphology of the resulting nanoparticles. This was attributed to the pre-formed paddlewheel dimers in the case of Cu(OAc)<sub>2</sub>, whereas the reaction containing nitrates required longer crystallization times. The space-time yield (STY) of this protocol using Cu(OAc)<sub>2</sub> was calculated to be >2000 kg m<sup>-3</sup> day<sup>-1</sup>, which was slightly improved on the reaction based on Cu(OH)<sub>2</sub> (1842 kg m<sup>-3</sup> day<sup>-1</sup>) in the previous study. The pH of the reaction is also critical to obtain the desired crystalline structure,

as noted in a study by Siddiqui et al., where a slight alteration led to formation of either HKUST-1(Cu), at pH of 0.7-1.6 or a related MOF [Cu(BTC)·3H<sub>2</sub>O] at pH of 2.2-3.2 (BTC – benzene-1,3,5-tricarboxylate).<sup>[161]</sup>

Carboxylic acid linkers for preparing metal-organic frameworks usually have lower solubilities in water, for instance, the most employed ligand terephthalic acid has a solubility of only 0.017 g L<sup>-1</sup> at 298 K. To facilitate the synthesis of MOFs based on such linkers in water at room-temperature, Sánchez-Sánchez et al. proposed an approach of employing salts of the linkers.<sup>[19]</sup> By using disodium terephthalate obtained from a pre-synthesis step, MIL-53(Al) was prepared at room-temperature using water as the sole solvent. This was a significant improvement to the conventional protocol at the time that involved heating at >200 °C in *N,N*-dimethylformamide as the solvent. Instead of a separate step, the metal-organic framework could also be prepared in the same pot by adding stoichiometric amounts of sodium hydroxide. The latter approach was shown to be applicable for preparing a few other metal-organic frameworks—MOF-74(Zn), derivatives of MIL-53 (MIL-53-NH<sub>2</sub>(Al); MIL-53-NO<sub>2</sub>(Al)) and MOF-5(Zn). Kathalikkattil et al. reported the synthesis of ZnGlu at room-temperature within 5 min, using a similar one-pot approach of adding NaOH.<sup>[162]</sup> Dizaji et al. employed the approach of using NaOH to control the pH during the room-temperature formation of protein@Fe-fumarate composite nanoparticles.<sup>[163]</sup>

A comprehensive study focused on preparing MOF-74-M (CPO-27-M; M = Mg<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>) using only water as the solvent, with addition of NaOH was reported by Garzón-Tovar et al.<sup>[164]</sup> By optimizing parameters of pH, concentration and reaction time, the STY for preparing CPO-27-Zn was estimated to be as high as 18720 kg m<sup>-3</sup> day<sup>-1</sup>. As an outlier, the Cu(II) variant could not be prepared by the same method, which was attributed to the higher tendency of Cu(II) ions to form Cu(OH)<sub>2</sub> at pH = 7 rather than react with the linker. A pathway to resolve this was subsequently proposed by constant agitation between Cu(OAc)<sub>2</sub> and dhtp (2,5-dihydroxyterephthalic acid) in methanol for 20 h at room-temperature to form pure CPO-27-Cu.<sup>[165]</sup> The use of NaOH to facilitate the preparation of MOF-74-M (M = Co, Mg, Ni, Zn) was also reported by Vornholt et al. in a temperature window from 78 °C to -78 °C.<sup>[166]</sup> The effect of the base was more pronounced for forming MOF-74(Zn), when MeOH was used as the solvent, where a competing phase formed in its absence.

Formation of Zr(IV) (and Hf(IV)) based metal-organic frameworks is seen to be highly sensitive to the synthesis conditions and the metal clusters function as the building units in the growth of these stable structures.<sup>[167]</sup> Thus, unlike some of the other metal-organic frameworks, synthesis at room-temperature is more complex. DeStefano et al. proposed a two-step process of pre-fabricating the individual building unit intermediate followed by reacting it with the ligand to prepare UiO-66 series.<sup>[168]</sup> While the metal cluster was obtained by heating at 130 °C, the second reaction of synthesizing the metal-organic frameworks was carried out at 25 °C for 18 h. This method was also used to allow the preparation of its derivatives (UiO-66-NH<sub>2</sub>(Zr), UiO-66-NO<sub>2</sub>(Zr), UiO-66-OH(Zr)). In a follow-up study by the same group with slight modification, another example was reported for preparing Zr<sub>6</sub>-based NU-901 which is built from the tetratopic linker 1,3,5,8-(*p*-benzoate)pyrene.<sup>[169]</sup> In

a similar vein, Dai et al. reported the room-temperature synthesis of MOF-808(Zr), using prefabricated Zr<sub>6</sub> oxoclusters, with modulation of particle sizes based on the concentration of the reaction.<sup>[170]</sup> Also, high STY values (2516 kg m<sup>-3</sup> day<sup>-1</sup>) were estimated for the metal-organic frameworks with the smallest particle sizes. It is worth noting that initial studies of the possibility of room-temperature synthesis of UiO-66(Zr) and Zr-muconate, were based on using zirconium methacrylate oxocluster as the reagent.<sup>[171]</sup> Extending this approach, hafnium-based MOFs—UiO-66(Hf)-X (X = -COOH, -NO<sub>2</sub>, -NH<sub>2</sub>, -Br and -(OH)<sub>2</sub>), could also be prepared at room temperature by pre-fabricating the Hf-clusters.<sup>[172]</sup>

To move away from using *N,N*-dimethylformamide for preparing such metal-organic frameworks at room-temperature, Pakamòre et al. formulated a two-step synthesis of first preparing the sodium salt of the carboxylic acid, and subsequently mixing it with the Zr(IV) salt (zirconyl chloride octahydrate) and letting it react under stirring.<sup>[173]</sup> By this approach, UiO-66-NH<sub>2</sub>(Zr) could be formed in the presence of acetic acid as the modulator, within 1 h and cleaner conversion over 24 h. Huelsenbeck et al. extended this reaction to report the formation of UiO-66(Zr), ZIF-L(Zn), and HKUST-1(Cu).<sup>[174]</sup> It was found that by controlling the pH and concentration of the reaction, metal-organic frameworks with high STY values can be prepared. Chen et al. further showed that two other metal-organic frameworks in the UiO-66 series [UiO-66-F<sub>4</sub>(Zr) and UiO-66-(COOH)<sub>2</sub>(Zr)] could be formed in water using zirconium(IV) oxynitrate (ZrO(NO<sub>3</sub>)<sub>2</sub>) as the metal source with trifluoroacetic acid (TFA) or acetic acid (AA) as the modulators.<sup>[175]</sup> D'Amato et al. reported an alternate synthesis method for derivatives of UiO-66 series, including UiO-66-F<sub>4</sub>(Zr) using the same metal salt precursor and avoiding the use of TFA.<sup>[176]</sup> The reaction involved milling the reactants, with AA as the modulator, and incubating the slurry either at room-temperature or at 120°C. Water-based syntheses at room-temperature was also possible using acetylacetonate (acac) salts as demonstrated by Avci-Camur et al.<sup>[177]</sup> Employing Zr(acac)<sub>4</sub>, UiO-66-NH<sub>2</sub>(Zr), UiO-66-(OH)<sub>2</sub>(Zr) and Zr-fumarate were synthesized. This methodology was also tested in preparing a well-known metal-organic framework—MIL88A(Fe), using Fe(acac)<sub>3</sub> as the metal precursor. Dai et al. optimized the one-step synthesis for a range of MOFs based on M<sub>6</sub>-oxoclusters (M = Zr, Hf, Ce).<sup>[178]</sup> The STY for MOF-801(Zr) prepared by this route was estimated to be 168 kg m<sup>-3</sup> day<sup>-1</sup>. Likewise, a few studies have demonstrated the room-temperature synthesis of Ce(IV)-MOFs.<sup>[179-181]</sup>

MIL-100(Fe) is one of the more prominent Fe(III)-based metal-organic frameworks in the MIL-series, which bears high porosity and has a Fe-trinuclear secondary building unit. The conventional synthesis relied upon heating the precursors at elevated temperatures in the presence of an acid, such as HF.<sup>[182]</sup> Jeremias et al. observed that the formation of the secondary building units could be influenced by the addition of HNO<sub>3</sub> to a solvent mixture of dimethyl sulfoxide/water for preparing the metal-organic framework in HF-free reaction under reflux conditions.<sup>[183]</sup> Recently, Christodoulou et al. also demonstrated the HF-free hydrothermal synthesis.<sup>[184]</sup> Subsequently, Yuan et al. found that a room-temperature synthesis was possible by addition of benzoquinone to the reaction mixture in water, although isolation of the final product required several purification steps.<sup>[185]</sup> As an

alternate route to perform the synthesis at room-temperature, Guesh et al. developed a protocol that started the reaction from Fe(II) sources and letting it slowly oxidize during the reaction to form a cleaner product with high yield.<sup>[186]</sup> Subsequently, Zheng et al. proposed a variant of this approach of synthesizing monoliths of MIL-100(Fe) using a sol-gel method.<sup>[187]</sup>

It is worth mentioning that room-temperature synthesis has been successfully realized in the preparation of cationic MOFs, a subclass of ionic-MOFs, which bear residual, mobile ions. Kang et al. showed that Ag-TPPE (TPPE—1,1,2,2-tetrakis(4-pyridylphenyl)ethylene) could be prepared in high yields (92%) by mixing the metal salt and linker and stirring it for 3 h.<sup>[188]</sup> The use of sonochemical approach to prepare Ag-TPPE could help accelerate the process with the formation of the product within 1 h.

### 3.2.2. Zeolitic Imidazolate Frameworks

An initial method for preparing ZIF-8(Zn) at room-temperature was proposed by Cravillon et al. by stirring zinc nitrate and 2-methyl imidazole in methanol.<sup>[189]</sup> The presence of higher amounts of linker was suggested to obtain a narrow distribution of particle sizes, as the excess ligand would function as a capping agent on the edge of the crystallites. Venna et al. observed that this synthesis reaction followed Avrami kinetics,<sup>[190]</sup> where an initial nucleation occurred (<10 min), followed by rapid crystallization with the formation of a metastable phase.<sup>[191]</sup> After ≈60 min the rate of crystallization was seen to be stagnant over 24 h with greater homogeneity. Each step also corresponded to the change in pH of the solution, as well as gradual changes in the morphology and size of the particles. The effect of pH was seen to have a greater influence when zinc carbonate was used as the metal ion source.<sup>[192]</sup> The basic pH, promoted by the counterion, was suggested to form hydroxyl species, which in effect led to formation of ZnO particles together with ZIF-8(Zn). However, longer reaction time led to completion of the reaction in favor of ZIF-8(Zn), and such a coexistence of ZnO was not observed when zinc nitrate, zinc sulfate or zinc chloride were used. Another facet of the synthesis is the solvent that was seen to have a pronounced effect on the reaction rate and the quality of the product. Comparing the synthesis in a series of alcoholic solvents, acetone, *N,N*-dimethylformamide, and water, Bustamante et al. observed that the solvent functioned as a structure directing agent, and the deprotonation of the linker was strongly dependent on the hydrogen bond donating ability of the solvent.<sup>[193]</sup> While water did not lead to formation the desired product, no solid could be isolated in the reaction mixture having *N,N*-dimethylformamide.

Control over crystal size and shape of framework solids is of high importance, especially in specific applications. In this regard, different strategies have been proposed in the literature. By adding 1% solution of poly(diallyldimethylammonium chloride) to a similar reaction scheme as above, Nune et al. observed selective formation of hexagonal nanocrystals.<sup>[194]</sup> The average particle diameter was reported to be  $57 \pm 7$  nm with a thickness of 42 nm. Interestingly, upon using different polymers or their mixtures, such as poly(allylamine hydrochloride) (PAH), poly(ethyleneimine) (PEI), (poly(diallyldimethylammonium chloride) or polyvinyl pyrrolidone (PVP) did not result in the formation of hexagon shaped crystallites. It is worth noting that

ZIF-7(Zn) nanoparticles could be prepared at room-temperature around PEI, where the colloidal solution was used as a precursor to form oriented films on membranes.<sup>[195]</sup> Unlike employing an organic polymer, Cravillon et al. showed control over the morphology of the resulting particles using an auxiliary linker in the reaction pot.<sup>[196]</sup> Screening a range of modulators with varying chemical characteristics, e.g., formic acid, *n*-butylamine or 1-methylimidazole, a control over particle sizes ranging from 10 nm to 1  $\mu$ m was achieved. It was further suggested that the linker exchange reactions from the intermediate step are driven by the concentration of the bidentate ligand and the  $pK_a$  of the modulator.

As in the syntheses of carboxylic acid-based metal-organic frameworks, the use of a base to promote linker deprotonation and consequently facilitate the formation of zeolitic imidazolate frameworks has been demonstrated successfully. Using triethylamine (TEA) in a slow diffusion method at room-temperature, Morris et al. reported the preparation of ZIF-90(Zn) crystals.<sup>[197]</sup> Gross et al. further explored this procedure, by preparing ZIF-8(Zn) and cobalt-based ZIF-67(Co) in an aqueous solution containing TEA at room-temperature in less than 10 min.<sup>[198]</sup> Nordin et al. noted that the concentration of TEA relative to the total molar concentration of the reactants, has a strong correlation to the particle sizes in the case of ZIF-8(Zn).<sup>[199]</sup> Duan et al. reported the formation of meso-/macropores when a much higher concentration of an organic base, such as diethanolamine, *N,N,N,N*-tetramethylethylenediamine, *N,N*-dimethylbutylamine or *N,N*-dimethylethanamine were used in the preparation of ZIF-8(Zn), ZIF-67(Co) or ZIF-90(Zn).<sup>[200]</sup> The functioning of the excess base as a structure directing agent was proposed as a pathway to result in the formation of defective crystallites of ZIFs.

### 3.2.3. Covalent Organic Frameworks

An approach to prepare 2D covalent organic framework films at room-temperature was proposed in compounds containing boronic ester linkages by Medina et al.<sup>[201]</sup> The reaction promoted by vapor-assisted formation was based on previous approaches for preparing covalent organic framework powders facilitated by steam at higher temperatures.<sup>[202]</sup> The covalent organic framework films were synthesized by dropping a solution of the reactants diboronic acids and hexahydroxytriphenylene (HHTP) in polar organic solvents onto a glass substrate. This setup was then placed in a desiccator containing another vessel with mesitylene and dioxane. The slow diffusion over 72 h led to conversion into uniform covalent organic framework films, which was demonstrated for two covalent organic frameworks (BDT-COF, COF-5) with different boronic acid precursors. Room-temperature batch synthesis of 2D COFs was further explored by Peng et al.<sup>[203]</sup> Using a solution-suspension approach, COF-LZU1 was prepared by forming a solution of the reactants, i.e., 1,3,5-triformylbenzene (TFB) and *p*-phenylenediamine (PDA), in dioxane. Upon addition of acetic acid to this solution, the precipitation commenced which led to the formation of the desired product after 3 d. This approach was also demonstrated to prepare two other COFs, namely, NUS-14 and NUS-15. The synthesis of COF-LZU1 was also tested in a continuous flow reactor, where the STY was reported as  $703 \text{ kg m}^{-3} \text{ d}^{-1}$ . Using acetic acid as the catalyst

at room-temperature, Wang et al. developed the method for preparing cyclodextrin (CD) COFs, namely,  $\beta$ -CD COF and  $\gamma$ -CD COF.<sup>[204]</sup> The products were obtained by reacting functionalized CD precursors with terephthaldehyde (TPA) in a solvent mixture of water and ethanol (1:1, v/v) at room temperature over 48 h.

Synthesis in water is of high relevance for the practical application of any material. In this regard, recent studies have focused on developing methods to prepare covalent organic frameworks in aqueous medium. Franco et al. developed a “biomimetic” approach wherein stable covalent organic framework colloidal particles could be formed in water.<sup>[205]</sup> The colloids were formed as micellar structures by employing surfactants—CTAB (hexadecyltrimethylammonium bromide) and SDS (sodium dodecyl sulfate). The synthesis was optimized for an imine-based COF-TAPB-BTCA-COF (TAPB—1,3,5-tris(4-aminophenyl)benzene, BTCA—1,3,5-triformylbenzene), by mixing the micellar solutions of individual reactants and allowing the mixture to react for 72 h. Using ethanol, the stable aggregates were broken into floccules. This method was also demonstrated for preparation of another imine-COF—Tz-COF (prepared from BTCA and 2,4,6-tris(4-aminophenyl)—1,3,5-triazine), and MIL-100(Fe) which typically requires harsh synthesis conditions. Later, He et al. reported the formation of imine COFs from water at room-temperature in presence of acetic acid, without using surfactants to prepare TPB-DVA-COF.<sup>[206]</sup> The authors observed that the morphology and growth of the structures were influenced by the presence and amount of a cosolvent such as acetonitrile, methyl acetate, ethyl acetate, and *n*-butanol. Likewise, the order of adding acetic acid and the method of mixing (standing or under stirring) was seen to alter the size of the particles and their crystallinity.

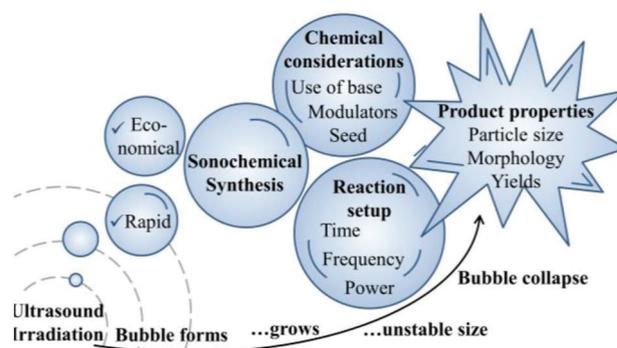
Another pathway to access imine-based COFs at room-temperature was investigated by Zhu et al.<sup>[207]</sup> Instead of employing acetic acid or a surfactant in the previous examples, the use of transition metal nitrates catalyzed the reaction without requiring any additional heating. Several COFs could be obtained using this approach, and Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O outperformed other metal nitrates, with target products synthesized in 10 min. Room-temperature synthesis has also been realized for the formation of imine-COF composites with metal nanoparticles. Using citrate-stabilized Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Lin et al. were able to form a composite, with the COF grown from TAPB and TPA.<sup>[208]</sup> The reaction was achieved within 5 min in the presence of DMSO as the solvent, with a high yield of COF loading in the composite ( $\approx$ 54%).

### 3.3. Sonochemistry

Sonochemical syntheses of reticular materials are rapid, economical, and offer a good control over various aspects of the reaction set-up and thus, the resulting materials properties (Figure 6).

#### 3.3.1. Metal-Organic Frameworks

An early example of preparing MOFs using ultrasonication was reported by Qiu et al. to synthesize Zn<sub>3</sub>(BTC)<sub>2</sub>·12H<sub>2</sub>O.<sup>[209]</sup> Sonication at a frequency of 40 kHz at power 60 W, increasing yields



**Figure 6.** The various aspects of sonochemical synthesis of reticular frameworks.

were observed with increasing reaction time from 10 to 90 min. Similarly, the particle sizes were also seen to increase from 50 to 100 nm at 5–10 min to 700–900 nm when the reaction was carried out for 90 min. In a similar vein, Son et al. optimized the synthesis of MOF-5(Zn) using sonochemical process.<sup>[210]</sup> Testing the reaction in NMP solvent, in a sonicator delivering power of 200 W at a frequency of 20 kHz, the optimal reaction conditions were found to be either 30% or 50% power and sonication of 10 min. Longer durations in either case were found to have poorer crystal qualities and lower pore surface areas. Related to MOF-5(Zn), the synthesis of [Zn(BDC)(H<sub>2</sub>O)] could be achieved using ultrasonic irradiation for 10–90 min at 40 kHz on a sonicator delivering power of 60 W.<sup>[211]</sup> Likewise, another well-studied MOF, HKUST-1(Cu), could also be prepared using ultrasonication in 5–60 min in a solvent mixture of *N,N*-dimethylformamide, EtOH, and water.<sup>[212]</sup> The yields were found to rise from 62.6% at 5 min to  $\approx$ 85% at 60 min. When the reaction was extended to 90 min, both the crystal structure and morphologies were found to be severely affected, reiterating that longer sonication is detrimental to the stability of coordination networks. This observation was reinforced in a detailed study by Armstrong et al., where they found that such a detrimental effect was more pronounced at lower concentrations of the reactants.<sup>[213]</sup> For higher concentration reactions, crystal growth took place by the solid-on-solid model. Similarly, sonochemical synthesis has found success in preparing a range of other metal-organic frameworks, including those based on lanthanides,<sup>[214]</sup> other transition metals,<sup>[215,216]</sup> p-block metals,<sup>[217]</sup> or MOF composites<sup>[218]</sup> by optimizing the power, time, and solvents. Ultrasonication can also be used to transform coordination polymer structures quickly, as in the case of the transformation of MOF STAM-1 into a new coordination polymer STAM-2.<sup>[219]</sup>

In a comparative study between ultrasonication, microwave and conventional heating, using MIL-53(Fe) as the model compound, it was found that sonochemical reaction could deliver clean products in shortest time with smallest particle sizes.<sup>[220]</sup> The rapid synthesis for both ultrasonication and microwave-assisted heating was attributed to physical processes of formation of hot spots rather than any chemical effects. Further studies by Gordon et al. on calculating the energy consumption during the reaction between different processes also validated that both sonochemical and microwave-assisted methods were significantly more efficient over conventional heating to prepare

MIL-53(Fe).<sup>[221]</sup> It was estimated to prepare MIL-53(Fe), while conventional heating required 3900 and 67 000 kJ of energy for nucleation and crystallization respectively. The corresponding values for microwave and sonochemical routes were 54 and 3240 kJ, and 540 and 756 kJ respectively. Sonochemical synthesis in NMP was also found to deliver fast products ( $\approx 30$  min), smaller particle sizes (5–20  $\mu\text{m}$ ) with high pore surface areas over microwave-assisted and conventional heating in the case of MOF-177(Zn).<sup>[222]</sup>

MOF-74 represents one of the most studied compounds in literature and controlling its physical features such as particle sizes and morphology is of topical interest. Yang et al. tested its sonochemical synthesis using MOF-74(Mg) as the model compound.<sup>[45]</sup> Unlike previous reports, the desired product did not form by mixing the reactants only in either *N,N*-dimethylformamide, *N,N*-diethylformamide, or ethanol. However, using optimal amounts of an organic base, namely TEA, to deprotonate the ligand, delivered the target MOF with homogeneous morphology and particle sizes within 1 h. Another approach to facilitate reactions and control morphologies and particle sizes has been the use of modulators that are typically monocarboxylate salts. To promote the synthesis using ultrasonic irradiation of a Zn-based MOF built from two ligands—[Zn(NH<sub>2</sub>-bdc)(4,4'-bpy)], Wiwasuku et al. explored the effectiveness of using sodium acetate as a modulator.<sup>[223]</sup> Sonication for 60 min in a reaction containing 0.5 mmol of sodium acetate yielded 82% of MOF formation with homogeneous, octahedral shaped crystallites. Decreasing the concentration of the modulator lowered the yields, while higher amounts led to aggregation of particles.

Interpenetrated structures have attracted attention for several niche applications and forming them cleanly requires controlled synthetic attempts. To prepare such a framework using sonochemical route, Kim et al. studied the formation of a copper-based MOF having a catenated structure, namely, Cu-TATB (known as PCN-6, where TATB = 4,4',4''-s-triazine-2,4,6-triyltribenzoate).<sup>[224]</sup> In the literature a non-catenated version, PCN-6' has also been reported. Interestingly, by tuning the power of ultrasonic irradiation, either of those two metal-organic frameworks could be formed for the same reaction time with 60% (300 W) power delivering PCN-6, whereas 30% power yielded PCN-6'. The effectiveness of this approach was also tested on synthesizing IRMOF-9(Zn) and IRMOF-10(Zn), which have the same precursors but the former having a catenated framework. Previous attempts at synthesis relied on controlling the concentration, with a higher concentration of reactants leading to interpenetration. However, in the case of sonochemical synthesis, the same amount of reactants delivered different products, depending on the ultrasonic power. Sonochemical synthesis has recently been applied to form stable Zr(IV)-based metal-organic frameworks, namely, MOF-525(Zr) and MOF-545(Zr) in 2.5 and 0.5 h respectively. Both the syntheses used modulators, with benzoic acid for MOF-525 whereas trifluoroacetic acid for MOF-545.<sup>[225]</sup> As both the MOFs started from the same metal ion and linker, different levels of power from an equipment delivering 500 W (20 kHz) and different time were required to be screened to identify the conditions for cleaner conversions in either case.

### 3.3.2. Zeolitic Imidazolate Frameworks

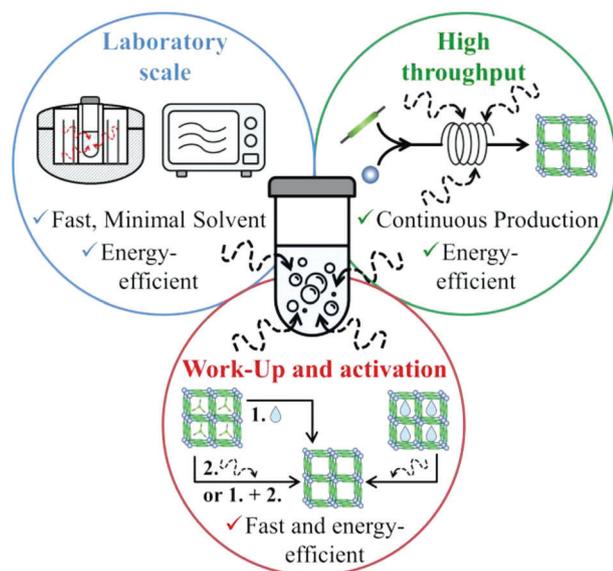
Initial attempt to prepare zeolitic imidazolate frameworks using sonochemical synthesis was reported by Seoane et al.<sup>[226]</sup> Testing the formation of ZIF-7(Zn), ZIF-8(Zn), ZIF-11(Zn), and ZIF-20(Zn) at a frequency of 47 kHz, the effect of temperature and time were examined not only in terms of synthesis conditions but also for obtaining narrower particle size distributions. Broadly, complete conversions were noted in a time interval of 6–9 h and lower temperatures (45–60 °C) compared to conventional synthesis. Building on these results, Cho et al. investigated larger-scale sonochemical synthesis (1 liter) of ZIF-8.<sup>[227]</sup> Initially, the process was optimized at a power of 500 W and frequency of 20 kHz, by controlling the pH using either or a combination of an organic base—TEA, and sodium hydroxide (NaOH). It was observed that the pH and reaction time had a strong influence on the yields. Based on the smaller scale screening, larger batch synthesis was found to deliver the highest yield and useful physical properties for a synthesis time of 2 h using both the bases.

Ultrasonication has also been found to assist the modulation of bulk properties during crystallization. Amali et al. prepared ZIF-8(Zn) as a sacrificial agent for obtaining porous carbons for electrochemical applications.<sup>[228]</sup> By sonicating the precursors (zinc nitrate and 2-methylimidazole), the obtained ZIF-8(Zn) had the presence of both micro- and meso-/macro-pores, which was not observed upon a forming the product without sonication. Unlike examining the synthesis in organic solvents, Nalesso et al. recently explored the effect of various parameters, namely, frequency, power, and time, on the formation of ZIF-8(Zn) from water.<sup>[229]</sup> It was noted that both sonication and agitation reactions had similar effects on the crystallinity and particle sizes compared with mixing without any external forces. For synthesis involving ultrasonication, slightly lower BET surface areas were observed which was attributed to competing processes of micromixing and shockwaves. The latter was proposed to cause structural damage and longer times of sonication might increase it further.

### 3.3.3. Covalent Organic Frameworks

Yang et al. reported an early example of using sonochemical synthesis for preparing two boroxine-based COFs, namely, COF-1 and COF-5.<sup>[230]</sup> To optimize the synthesis, parameters such as mole ratio, time, and power were employed and surface area measurements were made for each phase. COF-1 required 100% sonication power and a reaction time of 1 h, while COF-5 could be prepared at much lower power (50%). Apart from a significant improvement in terms of reaction time, 3 d by conventional solvothermal reaction, the materials obtained from sonochemical synthesis were reported to have slightly improved physical properties. Yoo et al. further extended this pathway to prepare a core-shell composite of growing COF-5 over a CNT (carbon nanotube) matrix. The obtained material which was prepared by sonicating the COF precursors in the presence of CNTs for 2 h, was found to yield uniform growth of COF-5.<sup>[231]</sup>

The use of sound energy in preparing imine-bonded COFs was explored by Zhao et al. The reaction was optimized using a



**Figure 7.** Overview of the advantages of microwave-assisted synthesis for reticular materials at laboratory scale, their opportunities with respect to high throughput set-ups as well as for work-up and activation of materials.

known COF, namely, TAPB-DMTA COF (TAPB stands for 1,3,5-tris(4-aminophenyl)benzene; DMTA—2,5-dimethoxybenzene-1,4-dicarboxaldehyde), as a model compound.<sup>[232]</sup> The synthesis was found to work in aqueous conditions and target materials were formed in as little as 5 min. The yields were found to increase with time, with both yield and physical characteristics remaining largely unaltered after 60 min of reaction. The COF could also be formed in the presence of varying concentrations of acetic acid. Six other reported COFs and two new COFs (sonoCOF-8 and sonoCOF-9) were prepared under the optimized reaction parameters. The same group further reported high-throughput synthesis. Using 11 amine and 11 aldehyde precursors, the synthesis resulted in 18 new COF products having either 1D or 2D structures.<sup>[233]</sup>

### 3.4. Microwave-Assisted Synthesis of Reticular Frameworks

The unique ability to selectively heat individual starting materials, thereby improving the yield of the final product while having enhanced control over the reaction pathway and significantly reducing the required energy, shows that microwave-assisted syntheses are a great option for green and sustainable syntheses. **Figure 7** gives an overview of the promising possibilities at the laboratory scale, the options for high-throughput settings and hitherto unconventional possibilities for their use for the work-up and activation of reticular materials.

#### 3.4.1. Metal-Organic Frameworks

Compared to other reticular materials, the synthesis of metal-organic frameworks using microwave heating is more frequently reported and has been more extensively investigated. The earliest publications (in early 2000s) on microwave synthesis of metal-

organic frameworks MIL-100(Cr),<sup>[234]</sup> IRMOF-1(Zn), IRMOF-2(Zn), and IRMOF-3(Zn) focused on the extraordinary rapidity of reactions compared to conventional solvothermal synthesis from 4 d to 4 h for MIL-100(Cr) and in as little as 25 s for the IRMOFs, and demonstrated control of crystal sizes on the micron to sub-micron scale achieved by varying reactant concentration.<sup>[235]</sup> However, a major drawback from these procedures is the use of toxic substances, i.e., hydrofluoric acid for MIL-100(Cr) and *N,N*-diethylformamide for the IRMOFs. Nevertheless, since this seminal work, substantial progress has been made towards improving sustainability using microwave heating to prepare metal-organic frameworks by considering aspects from green chemistry, the circular economy model, and applying process intensification principles. These aspects include using greener/waste-derived reactants and less solvent, reducing reaction times and energy consumption, and exploiting microwave heating in purification and activation steps.

**Using Greener/Waste-Derived Reactants:** Several microwave syntheses of MOFs in greener/benign solvents, such as water and alcohol, have been established. Using identical ethanol/water reaction mixtures and by varying the temperature and time, Seo et al. reported the syntheses of three Cu-MOFs such as HKUST-1(Cu).<sup>[236]</sup> Working in fully aqueous-based synthesis, Chalati et al. obtained MIL-88A(Fe) and Márquez et al. produced nanosized MIL-100(Al, Cr, Fe).<sup>[237]</sup> After systematic synthesis optimization, Márquez et al. developed a phase pure synthesis of MIL-100(Al) under strong acidic conditions (4 M HNO<sub>3</sub>, pH 0.7, at 210 °C for 30 min with a heating ramp of 10 min) but avoiding the use of hydrofluoric acid, which represents a less hazardous alternative pathway to MIL-100(Cr).<sup>[237]</sup> Also, Thomas-Hillman et al. accomplished an aqueous-based synthesis of MFM-300(Al) which is also known as NOTT-300(Al) without the utilization of the corrosive additive (piperazine C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>) in considerably less time (10 min compared to 3 d for the conventionally heated solvothermal route), and improved yield (83 instead of 75%), greater uniformity in particle size and morphology, and with significantly enhanced gas uptake capacities (26%, 70%, and 90% greater for CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub> respectively).<sup>[238]</sup> Lin et al. successfully prepared two isostructural MOFs using ionic liquids which are considered as green and safe solvents and heat incredibly rapidly in an applied microwave field.<sup>[140]</sup> Compared to the conventionally heated ionothermal synthesis, their microwave route gave a similar yield purer in phase and produced materials with higher crystallinity, but in only 50 min at 200 °C rather than 3 d at 180 °C.

In addition to modifying reaction procedures toward using greener solvents, microwave-assisted methods have also been established that use and produce greener reactants. Researchers focused on using greener metal salt precursors such as oxide and hydroxide,<sup>[239]</sup> as well as renewable or waste-derived organic linkers which is advantageous from both an economic and waste remediation perspective.<sup>[240]</sup> For example, Dreischarf et al. successfully synthesized CAU-28(Zr) at 80 °C in only 1 h using a renewable linker (2,5-furandicarboxylic acid, C<sub>6</sub>H<sub>4</sub>O<sub>5</sub>) which can be obtained from biomass by sugar oxidation.<sup>[133]</sup> Further key examples are syntheses of metal-organic frameworks whereby the commercial linker terephthalic acid (C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>) is replaced with waste-sourced poly(ethylene terephthalate) (PET). Manju et al. reported a stepwise procedure involving initial depolymerization of PET (by microwave heating), subsequent isolation of terephthalic

acid and finally the material synthesis.<sup>[241]</sup> In contrast, Deleu et al. demonstrated the successful synthesis of three MOFs using waste-derived PET, namely MIL-53(Al), MIL-47(V), MIL-88B(Fe), in a one-step one-pot method.<sup>[242]</sup> A drawback of such a one-step one-pot method is that it is not easily transferable to a range of metal salt precursors: while the optimal metal salt precursor for MIL-53(Al) was  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$  gave no product and  $\text{Al}(\text{NO}_3)_3$  resulted in unsafe pressure build-up.<sup>[242]</sup>

Few reports go further and demonstrate highly rapid procedures using minimal or no solvent. Tannert et al. developed an innovative microwave-assisted dry gel conversion (MW-DGC) method for MIL-100(Fe), UiO-66(Zr), MIL-140A(Zr), and Al-fumarate using low quantities of solvent (<10 mL) in 3 h or less with microwave powers ranging from 600 to 800 W.<sup>[243]</sup> However, this method has a couple of disadvantages: it requires grinding the metal salts and linker prior to microwave heating and solvent-intensive washing/soaking steps afterward, and in some cases, the syntheses required the addition of modulators or an ionic liquid to facilitate the formation of a dry-gel, or slightly poorer crystallinity and porosity were obtained.<sup>[243]</sup>

Lanchas et al. reported the solvent-free preparation of three metal-organic frameworks, namely MIL-100(Fe), MOF-199(Cu) and MBioF, using a domestic kitchen microwave oven operating at 210–700 W and up to 20 min.<sup>[83]</sup> Lanchas et al.<sup>[83]</sup> and Kudelin<sup>[244]</sup> noted that mixing of the solids prior to heating and melting of at least one of the solid reagents during heating are crucial for successful syntheses. Although these reactions yielded up to 83%, 97%, and 91% for MIL-100(Fe), MOF-199(Cu), and MBioF(Co), respectively, the same final materials obtained using a conventionally heated oven (for 10 to 48 h) showed improved crystallinity and much higher apparent BET surface areas (1713 c.f. 1130  $\text{m}^2 \text{g}^{-1}$  for MOF-199(Cu), 2492 c.f. 849  $\text{m}^2 \text{g}^{-1}$  for MIL-100(Fe) prepared from  $\text{FeCl}_3$  and 260 c.f. 415  $\text{m}^2 \text{g}^{-1}$  for MBioF(Co)). However, the apparent BET surface areas of MIL-100(Fe) could be enhanced (from 23 to 1245  $\text{m}^2 \text{g}^{-1}$ ) by addition of NaOH powder to the microwave reaction.<sup>[83]</sup> Building on this, Lanchas et al. synthesized further metal-organic frameworks using microwave heating, but similar to their previous work these had substantially lower porosity (reduced by ca. 30–50%). Nevertheless, an interesting aspect of the solvent-free route was that the MOFs contained random meso/macropores, which the authors ascribe to the evaporation of water during synthesis.<sup>[175]</sup>

**Reducing Reaction Times and Energy Consumption:** Since the pioneering work in the early 2000s,<sup>[234,235]</sup> microwave heating has repeatedly been shown to facilitate a steady reduction in reaction time (from the order of days to seconds) and subsequently a decrease in the energy consumption.<sup>[80]</sup>

Arenas-Vivo et al. reported a systematic study on the effect of time, temperature, concentration, solvent (water, ethanol, and *N,N*-dimethylformamide), and presence of HCl modulator on the microwave-assisted synthesis of three different metal-organic frameworks based on 2-aminoterephthalic acid ( $\text{C}_8\text{H}_7\text{NO}_4$ ), namely MIL-53-NH<sub>2</sub>(Fe), MIL-101-NH<sub>2</sub>(Fe) and MIL-88B-NH<sub>2</sub>(Fe).<sup>[245]</sup> Reactions were completed in 5 min and pure phases of MIL-53-NH<sub>2</sub> and MIL-101-NH<sub>2</sub> were obtained in water whereas ethanol gave phase pure MIL-88B-NH<sub>2</sub>.

Additionally, Moosavi et al. used machine learning to identify key experimental variables from analyzing successful, partially successful, and failed syntheses; this information was then

used to propose the most diverse set of reaction conditions for optimizing the synthesis of HKUST-1(Cu) using a microwave-based high-throughput robotic platform.<sup>[246]</sup> Employing the same microwave-based high-throughput robotic platform, Domingues et al. used genetic algorithms to systematically improve the synthesis conditions of Al-PMOF which is based on meso-tetra(4-carboxyphenyl)porphine ( $\text{C}_{48}\text{H}_{30}\text{N}_4\text{O}_8$ ).<sup>[247]</sup> Interestingly this study identified concentration and solvent as having the greatest influence on crystallinity while yield is affected most by solvent type.

Since 2018, further efforts have also been made to scale-up microwave-assisted synthesis of metal-organic frameworks using green reaction conditions. This includes larger batch syntheses such as 1 gram-scale synthesis of MOF-303(Al) in deionized water in 5 min,<sup>[22]</sup> and the production of HKUST-1(Cu) in ethanol using a combination of continuous flow oscillatory baffled reactors and microwave heating technologies.<sup>[248]</sup> The latter example is important since it considers the amount of microwave energy absorbed by the reaction mixture and the effect of mixing, both of which are crucial for scale-up of metal-organic framework synthesis beyond the laboratory in an efficient and sustainable way.

**Exploiting Microwave Heating in Activation Steps:** In addition to synthesis, microwave heating has also been used to purify and/or activate metal-organic frameworks since this offers reduced time and, therefore, energy consumption post-synthesis. In 2021 Woodliffe et al. reviewed how microwave heating has been used to remove coordinating and pore-filling solvent, modulators, and to empty the pores of metal-organic frameworks prior to gas sorption.<sup>[54]</sup> However, further research is required to evaluate the generality of microwave-assisted purification and/or activation, particularly for those metal-organic frameworks more prone to structural collapse.

### 3.4.2. Zeolitic Imidazole Frameworks

Microwave heating has also been extensively used to prepare a wide range of zeolitic imidazolate frameworks with most reporting reduced reaction times (many h to min) and the ability to prepare sub-micron-sized crystals.<sup>[249]</sup> So far, most comparative studies of synthesis routes and efforts to develop green and sustainable methods have been performed using ZIF-8(Zn).<sup>[250]</sup> In the following, the optimization of synthesis will be discussed with respect to using greener/waste-derived reactants and reducing solvent and/or solvent-free microwave syntheses.

**Using Greener Reactants:** Microwave-based methods for preparing zeolitic imidazolate frameworks typically involve pre-mixing the metal salt(s) and linker(s) in the reaction solvent for a predetermined amount of time (min to h and sometimes using ultrasound) before placing in a microwave reactor to affect crystallization.<sup>[249]</sup> However, most procedures use toxic solvents such as *N,N*-dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ ). Recently, a life cycle assessment of various ZIF-8(Zn) synthesis methods conducted by Xia et al. revealed that the main environmental burden arises from the solvent (especially for washing steps) and can be lessened by substituting with methanol or water.<sup>[251]</sup> Interestingly, the study showed only minor differences in environmental impact between synthesis routes, though the environmental burden of microwave-assisted route is marginally less than the analogous

conventionally heated solvothermal method.<sup>[251]</sup> Only a few reports demonstrate syntheses of zeolitic imidazolate frameworks in alcohol solvents,<sup>[84,250,252]</sup> and to the best of our knowledge, only one report utilizes aqueous conditions. This may be attributed to the fact that zeolitic imidazolate frameworks can easily be prepared at room-temperature in aqueous conditions. Bao et al. investigated the influence of the linker to metal ion molar ratio and variation in metal salt anion (nitrate/acetate) on the crystallinity and morphology of ZIF-8(Zn) in aqueous systems using microwave heating.<sup>[253]</sup> A molar ratio of 5:1 showed poor crystallinity with a roughened morphology, whereas increasing the molar ratio to 10:1 and above gave ZIF-8(Zn) with improved crystallinity and a homogenous hexagonal morphology. Replacement of acetate for nitrate required molar ratios above 20:1, which the authors ascribe to differences in pH value.<sup>[253]</sup> ZIF-67(Co) can also be prepared through the same synthetic strategy.<sup>[253]</sup>

Yang and Lu successfully prepared ZIF-8(Zn) using ionic liquids as solvent.<sup>[254]</sup> Compared to ethanol and distilled water, acetone was the most effective at removing the ionic liquid. However, the apparent BET surface area of ZIF-8(Zn) obtained through the microwave-assisted and the conventional ionothermal syntheses ( $471 \text{ m}^2 \text{ g}^{-1}$  and  $341 \text{ m}^2 \text{ g}^{-1}$ , respectively), is lower than for ZIF-8 synthesized at room-temperature under aqueous conditions ( $1079 \text{ m}^2 \text{ g}^{-1}$ ).<sup>[255]</sup>

Inspired by the room-temperature<sup>[256,257]</sup> and mechanochemical<sup>[258]</sup> syntheses of ZIF-8 from ZnO, which requires 6–24 h reaction times, Bazzi et al. developed two 30 min routes using microwave and ultrasound.<sup>[259]</sup> However, in all cases, the final reaction products contained a mixture of ZnO starting material as well as ZIF-8(Zn) owing to incomplete conversion. Although greater conversion was achieved using ultrasound compared to microwave heating, reactions performed in water using ultrasound gave an unwanted side product,  $\text{Zn}(\text{OH})_2$ .<sup>[259]</sup> More complete conversion may be possible by altering the pH of the reaction mixtures, e.g., by addition of acid or base.

**Reducing Solvent and/or Solvent-Free Microwave Syntheses:** To date, two microwave-assisted solvent-free methods are reported and only for ZIF-67(Co). In 2014, Lanchas et al. reported this along with the metal-organic frameworks MIL-100(Fe), MOF-199(Cu), and MBioF(Co).<sup>[83]</sup> Unlike the metal-organic frameworks, ZIF-67(Co) did not exhibit lower but comparable apparent BET surface areas compared to conventional syntheses ( $1851 \text{ c.f. } 1799 \text{ m}^2 \text{ g}^{-1}$  for 10–48 h conventional and 6 min microwave syntheses, respectively).<sup>[83]</sup> Also, Zhang et al. developed a solvent-free preparation of ZIF-67(Co).<sup>[260]</sup> Their method consists of three steps: grinding of the precursors by hand, heating the resulting powder in a domestic kitchen microwave oven 5 min at 900 W, and finally, washing the solid products thrice with methanol. The resulting ZIF-67(Co) exhibited rhombic dodecahedral morphology and an apparent BET surface area of  $1120 \text{ m}^2 \text{ g}^{-1}$ . Although attempted, the procedure could not be transferred to ZIF-8(Zn).<sup>[260]</sup>

### 3.4.3. Covalent Organic Frameworks

To date, covalent organic frameworks are mainly prepared using solvothermal synthesis, but also more and more syntheses using

microwave heating are being published.<sup>[261,262]</sup> These will be discussed with respect to using greener solvents, reducing reaction times and energy consumption, and exploiting microwave heating in purification and activation steps.

**Using Greener Solvents:** As with zeolitic imidazolate frameworks, most covalent organic frameworks are synthesized in organic solvents, including *N,N*-dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ ), mesitylene ( $\text{C}_9\text{H}_{12}$ ), trifluoromethanesulfonic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ), 1,2-dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ ), and 1,4-dioxane ( $\text{C}_4\text{H}_8\text{O}_2$ ). However, there are limited reports of covalent organic frameworks synthesized using greener solvents such as water and alcohol.

Hou et al. reported the aqueous synthesis of an oxygen-rich covalent carbon nitride (CNO).<sup>[263]</sup> This involved heating a mixture of HKUST-1(Cu) and urea ( $\text{CH}_4\text{N}_2\text{O}$ ) in distilled water using a domestic kitchen microwave oven, operating at 700 W for 6 min. This was followed by washing with an excess of sulfuric acid (0.5 M) and excess distilled water. In this procedure, HKUST-1(Cu) promotes a reaction between trimesate ( $\text{C}_9\text{H}_3\text{O}_6$ ) and urea ( $\text{CH}_4\text{N}_2\text{O}$ ) resulting in the formation of CNO, an oxygen-rich  $\text{C}_2\text{N}$  material. Although the authors remark on the greenness of this route,<sup>[263]</sup> the use of expensive HKUST-1(Cu) is undesirable from a sustainability aspect, as is the production of a copper-rich waste stream.

Ashraf et al. demonstrated the successful synthesis of a novel crystalline anionic Ge-COF-1 in methanol in the presence of lithium methoxide using microwave irradiation at  $180^\circ\text{C}$  for 6 h, with stirring.<sup>[264]</sup> There are two more examples of microwave-assisted COF syntheses in ethanol and water. In 2017, Das et al. reported the preparation of a viologen-based covalent organic gel framework (viologen is the 4,4'-bipyridinium ion) using the Zincke reaction.<sup>[265]</sup> A self-standing non-porous crystalline covalent organic gel framework was obtained in ethanol:water (1:1, v:v) using microwave heating, which was unobtainable using the conventionally heated solvothermal route. The second example named PV-COF, also a viologen-based framework synthesized via a Zincke reaction, was reported by Skorjanc in 2020.<sup>[266]</sup> A typical synthesis involved reaction between an amino derivative of porphyrin and Zincke salt (1:2 molar ratio) in a 4:1 mixture of water:ethanol under microwave heating at  $90^\circ\text{C}$  for 2 h.

Two COFs, namely  $\text{COF}_{\text{BTC}}\text{-Fe}$ <sup>[267]</sup> and  $\text{COP}_{\text{BTC}}\text{-Mn}$ ,<sup>[268]</sup> have been prepared in ethylene and with 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) which acts as a catalyst.<sup>[262]</sup> The synthesis of  $\text{COF}_{\text{BTC}}\text{-Fe}$  involves heating the reagents in ethylene glycol at  $180^\circ\text{C}$  for 10 min, whereas  $\text{COP}_{\text{BTC}}\text{-Mn}$  is synthesized at  $150^\circ\text{C}$  in 20 min.

By evaluation of the reaction conditions described in this section above, it is likely that the limited examples of covalent organic framework synthesis in water and alcohols are a consequence of poor solubility of aromatic monomers from which they are typically prepared.

Covalent triazine frameworks, which are a subtype of covalent organic frameworks and are constructed from nitrile-containing monomers, are typically synthesized under ionothermal conditions using molten  $\text{ZnCl}_2$ , which serves as both solvent and a Lewis acid catalyst. Zhang et al. were the first to demonstrate the successful preparation of CTF-1, using microwave-assisted ionothermal synthesis whereby microwave heating is used in place of conventional heating, as these typically require long reaction times of 20–40 h.<sup>[269]</sup> The microwave-assisted

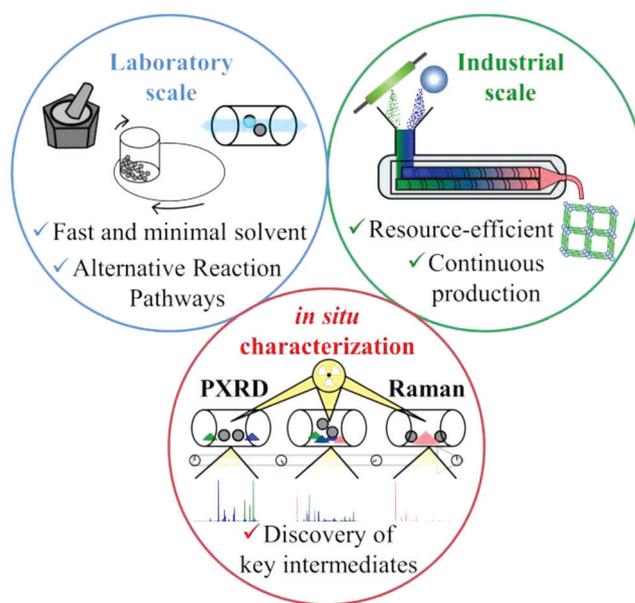
ionothermal synthesis at 280 W, involving cyclotrimerization of 1,4-dicyanobenzene ( $C_6H_4(CN)_2$ ) in molten  $ZnCl_2$ , yielded amorphous CTF-1 with an apparent BET surface area of  $1526\text{ m}^2\text{ g}^{-1}$  after 30 min, while the highest surface area of  $2390\text{ m}^2\text{ g}^{-1}$  was achieved after 60 min.<sup>[269]</sup> Since this work, other groups have also reported the microwave-assisted ionothermal synthesis of amorphous CTF-1 with modifications to reaction time and power (varying between 1.5 h and 6 min and 120–700 W)<sup>[270–272]</sup> or by performing the reaction in a mixture of  $ZnCl_2$  and  $FeCl_3 \cdot 6H_2O$  in ethanol for 60 min at 350 W, followed by washing in aqueous hydrochloric acid to afford a series of CTF( $Fe_2O_3$ ) composites.<sup>[273,274]</sup>

Microwave-assisted ionothermal synthesis has also been used to prepare crystalline polyimide nanosheets, namely CTF-PI.<sup>[275]</sup> This involves reaction between melamine and pyromellitic dianhydride in 3 min at 600 W. The reaction product is then washed with diluted HCl/*N,N*-dimethylformamide/methanol several times to afford the CTF-PI product in 95% yield (based on melamine). This microwave-based procedure offers substantial time reduction compared with the conventionally heated solvent-free synthesis (without  $ZnCl_2$ ) requiring 4 h.<sup>[276]</sup>

Disadvantages of the microwave-assisted ionothermal route include high synthesis temperatures ( $>400\text{ }^\circ\text{C}$ , as  $ZnCl_2$  must be molten) and extensive washing steps required to purify the reaction products. To overcome these issues, Ren et al. developed a milder microwave-based procedure for the synthesis of a range of CTFs using a Brønsted acid catalyst, trifluoromethanesulfonic acid (TFMS).<sup>[277]</sup> Reaction mixtures were heated dynamically at max. 300 W and  $110\text{ }^\circ\text{C}$  in a CEM Discover SP microwave reactor. The much lower temperature employed in TFMS-catalyzed reactions avoids undesired decomposition and side reactions, such as C–H bond cleavage and carbonization.

**Reducing Reaction Times and Energy Consumption:** The earliest report on microwave-assisted covalent organic framework synthesis by Campbell et al. in 2019 highlighted the unprecedented rapidity of microwave-based reactions compared to conventional solvothermal routes (d to min).<sup>[278]</sup> Since then, most microwave-assisted procedures for covalent organic framework synthesis have continued to emphasize the substantial reduction in time.<sup>[262]</sup> In particular, the preparation of CTF-1 using microwave heating has seen marked reductions in time (from 40 h<sup>[279]</sup> to 30 s<sup>[280]</sup>) and, consequently, energy consumption compared with the traditional conventionally heated (ionothermal) route.

**Exploiting Microwave Heating in Activation Steps:** Recently, Woodliffe et al. reviewed the application of microwave heating in the purification of covalent organic frameworks.<sup>[54]</sup> In 2009, Campbell et al. were the first to involve heating microwave-synthesized COF-5 in 30 mL of dried acetone for 20 min at  $55\text{ }^\circ\text{C}$  and 200 W followed by filtration and activation under vacuum.<sup>[278]</sup> A marked increase in the apparent BET surface area of COF-5 from  $901\text{ m}^2\text{ g}^{-1}$  (as synthesized) to  $1467\text{ m}^2\text{ g}^{-1}$  (after first extraction) and  $2019\text{ m}^2\text{ g}^{-1}$  (after second extraction) was observed. In the same article, the authors also reported a similar purification procedure for COF-102; heating the microwave-synthesized material in 30 mL of dried tetrahydrofuran to  $65\text{ }^\circ\text{C}$  for 20 min at 200 W. The purification of COF-5 using microwave heating was further evaluated by Ritchie et al. in 2010.<sup>[281]</sup> A range of purification procedures were investigated including mi-



**Figure 8.** Overview of the advantages of mechanochemistry for reticular materials at laboratory and industrial scale as well as their characterization during synthesis in situ.

crowave heating in dry acetone, rinsing with acetone at room-temperature, and simply drying in a desiccator. The apparent BET surface areas were  $2335$ ,  $1927$ , and  $1404\text{ m}^2\text{ g}^{-1}$  for microwave, acetone washing, and desiccator methods, respectively. While these few examples show microwave heating to be advantageous in the purification of covalent organic frameworks, further research is required to demonstrate the applicability of this purification route across a wider range of materials—especially those prone to pore collapse.

### 3.5. Mechanochemistry for Reticular Materials

Mechanochemical syntheses are a potent methodology for the efficient and green production of chemicals, which also encompasses reticular materials.<sup>[282]</sup> Advantages range from atom-economical synthesis, resource-efficient (including solvent-free) treatments in the laboratory and industrial scale, control and monitoring of the process with direct and fast ex situ as well as in situ characterization, making a strong case for mechanosynthesis to be more commonplace for the synthesis of reticular materials (Figure 8).

#### 3.5.1. Metal-Organic Frameworks and Zeolitic Imidazolate Frameworks

In 2006, Pichon et al. were the first to report the successful synthesis of a porous metal-organic framework  $Cu(INA)_2$  (INA = isonicotinate), prepared by a solvent-free method using a ball mill.<sup>[283]</sup> The reactants, hydrated copper acetate, and isonicotinic acid, were ground for the short reaction time of 10 min at 25 Hz in a mixer mill, using a flask and a singular ball made of stainless steel. With the advantage of hindsight, an important detail is the

presence of small amounts of water, as the used copper reagent is hydrated. Indeed, many reactions reportedly benefit from the addition of min amounts of liquid, resulting in so-called liquid-assisted grinding. The liquid/solid ratio for liquid-assisted grinding reactions is typically around 0.1–1  $\mu\text{L mg}^{-1}$ , and this ratio (referred to as  $\eta$ ) has been shown to be an significant reaction parameter.<sup>[284]</sup>

Another important boon of mechanochemistry and its implied lifting of the solubility restriction for employable reagents is the use of metal oxides and hydroxides as metal sources. Most notably zinc oxide (ZnO) has been used to produce a variety of compounds with distinct framework topologies. A great example for the phase selectivity is contributed by Beldon et al. using reagents ZnO and imidazole (Im).<sup>[285]</sup> Milling of these compounds neat (without additives) results in a mixture of substrates and  $\text{Zn(Im)}_2$  (znc topology). Liquid-assisted grinding using ethanol results in phase-pure  $\text{Zn(Im)}_2$ , whereas using *N,N*-dimethylformamide leads to ZIF-4(Zn) (cag topology). Further adaptations can be achieved by adding salts in sub-stoichiometric quantities in ion-assisted grinding, which can be combined to ion-liquid-assisted grinding, improving yields and reducing reaction rates.<sup>[286]</sup>

Equipped with the knowledge that ZnO is a suitable starting reagent, Julien et al. proved that MOF-74(Zn), with its distinct honeycomb structure (hcb topology), can be produced by liquid-assisted grinding using ZnO, 2,5-dihydroxyterephthalic acid, and water or *N,N*-dimethylformamide as additive.<sup>[287]</sup> Using in situ PXRD, the authors elucidated a multistep mechanism going through dense intermediates, the nature of which depends on the used liquid. Further exploring the possibilities of these insights into the formation of MOF-74, Ayoub et al. showed that the isolated intermediates can be used as precursors to allow the formation of bimetallic MOF-74 with ratios  $M1/M2 = 1$  with high accuracy, using various combinations of Zn, Mg, Co, Ni, and Cu.<sup>[288]</sup>

A similar approach of using intermediates is required when targeting several metal-organic framework structures with metal clusters as nodes in their framework, which have so far not been obtained directly from simple starting materials. These include two of the most famous materials MOF-5(Zn)<sup>[289]</sup> and UiO-66(Zr)<sup>[290,291]</sup> amongst others. In order to produce these compounds with appreciably high crystallinity, precursors containing the correct clusters, i.e.,  $[\text{Zn}_4\text{O}]^{6+}$  and  $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ , should be used in the mechanochemical reaction.

### 3.5.2. Covalent Organic Frameworks

Mechanochemical means can also be used in the production of covalent-organic frameworks. In a similar manner to metal-organic frameworks, reagents are ground or milled together, in dry or (ion-)liquid-assisted grinding approaches. This was for example realized by Biswal et al., using 1,3,5-triformylphloroglucinol and aromatic diamines resulting in the same products obtained from solution-based syntheses.<sup>[292]</sup> The common advantages of avoided solvent-waste, shorter reaction times, and syntheses without additional heating source were reported also for these materials. An observed drawback of mechanochemistry in this case was comparatively lowered crystallinity and concomitant available surface area as found by gas

physisorption. In a follow-up study, the same group showed the possibility of further improving these physical properties by a post-synthetic heat-treatment.<sup>[293]</sup> Additionally, they were able to demonstrate the possibility for translating these syntheses to an extrusion technique enabling continuous production as well as shaping of the material.

### 3.5.3. Boron Imidazolate Frameworks

The intrinsic advantages of mechanochemical methods for the synthesis of reticular materials are also neatly highlighted in a class of compounds called boron imidazolate frameworks. These framework materials are commonly prepared from pre-formed boron-imidazolate complexes, cross-linked with another metal cation, often lithium or copper.<sup>[294]</sup> The synthesis of boron imidazolate frameworks is performed in a two-step process, first forming a boron imidazolate complex which is subsequently cross-linked with another type of metal cation to form the 3D connected framework material. The second, framework building step was the target of a recent study investigating the possibility for mechanochemical syntheses. Using a ball milling protocol analogous to above-described methods for metal-organic frameworks and zeolitic imidazolate frameworks, Lennox et al. were successful in preparing boron imidazolate frameworks compounds based on lithium, copper, and also the previously unreported silver.<sup>[295]</sup> All reactions were performed without the use of solvent and with easy to use solid reactants LiCl, CuCl, and  $\text{AgNO}_3$ , in a liquid-assisted grinding or ionic-liquid-assisted grinding protocol to drive the reactions to completion in mere 60 min. Additionally, these reactions can also be performed using LiOH or  $\text{Cu}_2\text{O}$ , providing alternative reagents. Once more, the facile and fast mechanochemical methodology to obtain boron imidazolate frameworks may be considered preferable to conventional solution synthesis, yielding products which even outperform conventionally obtained products in accessible surface area and framework stability.

### 3.5.4. Characterization of Mechanochemically Obtained Compounds

As alluded to earlier, mechanochemical synthesis has potential advantages regarding monitoring of the process and the characterization of the chemicals throughout the treatment.<sup>[296,297]</sup> The mechanisms of formation of solids from solution-based methods are often difficult (although not impossible) to ascertain due to a lack of, or the complexity of, suitable in situ techniques, while ex situ measurements commonly require work-up procedures that are time- and resource-consuming and may even alter the nature of the compound of interest. A typical ball mill-based mechanochemistry reaction can be stopped at any time and samples are often directly suitable for common-place characterization methods for solids, such as powder diffraction (PXRD), Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy or scanning electron microscopy (SEM). Even more importantly, the simple design of vibrator ball mills, in combination with a relative freedom in choosing the appropriate milling materials, has allowed the design of in situ characterization setups, most notably powder X-ray diffraction and Raman spectroscopy.<sup>[298]</sup>

Studying solid-to-solid phase transformations from crystalline precursors to porous framework materials *in situ* can help to elucidate the formation mechanism and reveal potentially important reaction intermediates. Such measurements have been performed utilizing high energy X-rays accessible at synchrotron facilities, combined with the use of milling flasks fashioned from organic polymers like PMMA (poly(methylmethacrylate)), with much higher transparency to X-rays compared to more durable materials like stainless steel or ceramics. This setup allowed in-depth analysis and insights into the mechanosynthetic formation of MOF-74(Zn), ZIF-8(Zn), and others.<sup>[287,297,299]</sup> Besides information about crystallographic phases using PXRD, molecular interactions have also been probed employing *in situ* using Raman spectroscopy.<sup>[300]</sup> In contrast to X-rays, even laboratory spectrometers are capable of delivering processable information from ball mills. Both methods, PXRD and Raman spectroscopy, can even be combined into a dual-characterization setup.<sup>[301]</sup>

### 3.5.5. Industrial Scale Mechanochemistry

In addition to established mechanochemical synthesis protocols, Martinez et al. provided an important perspective on combining mechanochemistry with additional means of inducing chemical reaction, such as thermal or electrical energy.<sup>[302]</sup> Applying heat and mechanical stress and friction at the same time is already common practice in extrusion processes. These are of special interest for the implication of mechanochemical syntheses to industrial scales.<sup>[303]</sup> Reactions carried out in the typically used twin-screw extrusion method still follow the principles of mechanochemistry, although adaptations to protocols developed for benchtop ball mill devices have to be made. With this in mind, the James group and the spin-off company MOF Technologies Ltd. have developed robust methodologies for the production of several porous materials,<sup>[304]</sup> based on their early success with HKUST-1(Cu), ZIF-8(Zn), and Al(fumarate)(OH).<sup>[305]</sup>

Similarly, the Užarevič group showed the translatability of a ball milling protocol into extrusion-based procedures for several Zr-based metal-organic frameworks.<sup>[291]</sup> These reactions are still carried out without solvents and produce metal-organic frameworks in good crystallinity and surface areas competitive with conventionally synthesized compounds. During the reaction, the mixtures are allowed to pass through zones of variable temperature to ensure complete conversion to the desired product. Important advantages of extrusion are its continuous operation compared to the batch process in ball mills, as well as the widespread use of extrusion technology in the chemical industry, allowing tapping into a well-founded base of knowledge around its usage and adaptability to different types of materials.

### 3.6. Solvent-Free Synthesis of Materials

A principal focus area in current chemistry is to address the presence of solvents in almost every step of a chemical reaction and also work-up and purification steps. The associated economic and ecological impact of the production of the solvent itself as well as its safe recycling or disposal is of interest for both academia as well as industry. Besides mechanochemistry (using 0.2–2  $\mu\text{L}$

$\text{mg}^{-1}$ ), a couple of other solvent-free protocols have been used to successfully obtain reticular materials.

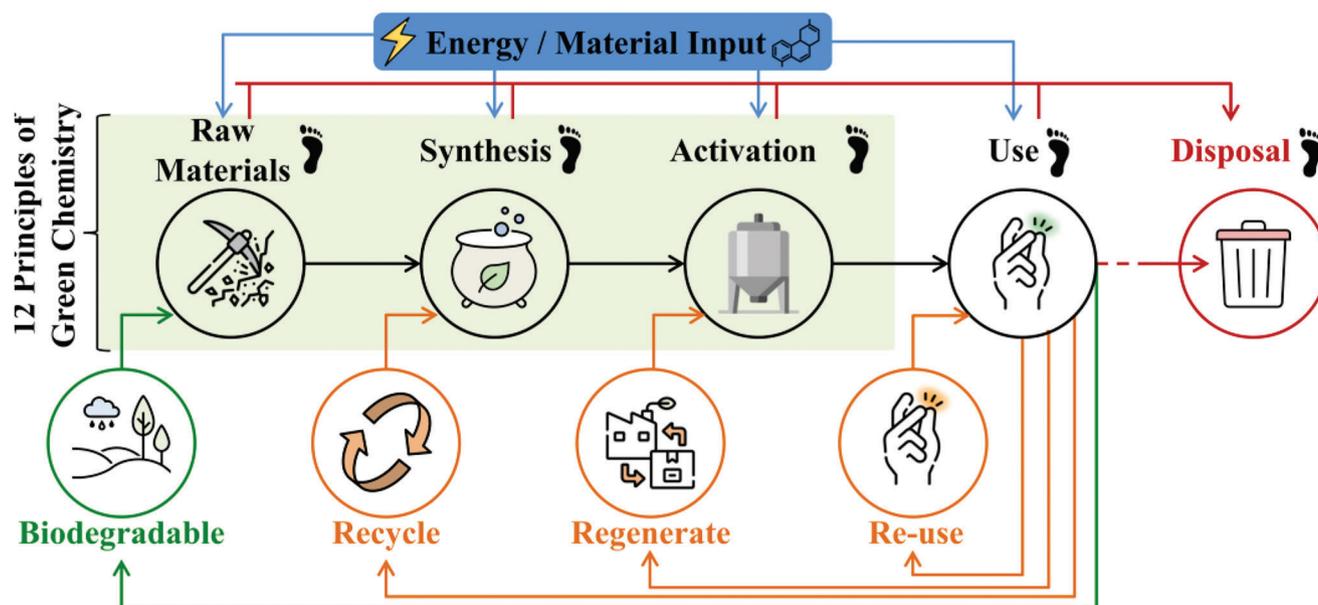
Direct thermal treatment of solid mixtures in the absence of solvents has been shown to be a viable alternative to common solvothermal synthesis in several cases. Typically, the reagents are mixed, sometimes by grinding manually or in a mill, and then heated in a sealed vessel. Metal-organic frameworks based on different metals and ligands have been prepared in this way, such as iron imidazole<sup>[306]</sup> (ZIF-8(Zn) analog) or different aluminum trimesates.<sup>[307]</sup> A notable difference, in addition to the avoidance of a solvent, is in the efficiency. For example, Gu et al. report a possible 100-fold increase in yield per batch when comparing the two methods in their synthesis of the UiO-66(Zr).<sup>[308]</sup> Similarly beneficial is the possibility to avoid harmful reagents such as HF in the synthesis of Cr-based MIL-53, MIL-88B,<sup>[309]</sup> or MIL-100.<sup>[310]</sup>

Another technique called accelerated aging<sup>[311,312]</sup> relies on the diffusion of adequate reagent molecules in a static solid mixture using humidity and catalytic amounts of inorganic salts. Although there is only a limited number of studies using this method, the mild conditions and minimal requirements regarding synthesis equipment render it an attractive alternative.

In these solid-state syntheses, mixing of the starting materials may be performed to ensure homogeneity. However, keeping in mind that mechanical forces themselves may induce reactions, tests, and characterizations should be performed prior to further treatments,<sup>[313]</sup> such as heating at elevated temperatures or exposure to humid air, to assess any potential chemical changes.

## 4. Importance of Life Cycle Assessment for Reticular Materials

Despite recent achievements in the green synthesis of reticular materials, their environmental sustainability remains a challenge still to be unlocked, as relevant life cycle stages such as use/maintenance, disposal, and end-of-life have not yet been addressed adequately. To get the bigger picture of their environmental sustainability, more efforts should be made to understand and assess the complete life cycle that are key aspects for industrial applications (Figure 9). This should include considering where the raw materials come from, how the material is synthesized and purified (with respect to their energy efficiency), used, and disposed. Moreover, taking into account the Earth's finite resources our linear "take-make-waste" system should be shifted toward a "Circular Economy" that eliminates waste ending in incinerators, landfills, or waterbodies, re-circulates products/materials, and regenerates nature (highlighted by the orange and green loops in Figure 8). To circulate reticular materials at the highest value and to retain the value invested during their synthesis (materials, time, and energy), they should be kept in use as long as possible and when they cannot be used any longer, they should be assessed against the "Resource Hierarchy,"<sup>[314]</sup> i.e., the raw materials should be extracted to enable a subsequent synthetic cycle (reuse > regenerate > recycle > biodegrade). If they are based on biological materials such as cellulose, the materials can re-enter the biological cycle again via composting or anaerobic digestion. In the following section, different aspects considering a life cycle thinking, including i) the choice of raw material, ii) their reuse, iii) their regeneration, iv) their recycling, v) their biodegradation,



**Figure 9.** Overview of an ideal “Circular Economy” for reticular materials that covers their full life cycle from the choice of raw material, synthesis and purification to their use and final disposal highlighting the importance by introducing additional loops (orange and green) to their life cycle, namely their reuse, their regeneration, their recycling, their biodegradation. The conventionally considered life cycle stages encompass energy and material inputs, and result in a given footprint due to emissions to air, land or water.

and vi) their disposal, will be highlighted and vii) examples as well as viii) recommendations of full life cycles will be discussed.

#### 4.1. The Choice of Raw Material

When designing a novel material, the selection of the raw material should clearly avoid toxic and scarce materials, such as the elements cobalt, nickel, or vanadium, which not only raise environmental sustainability concerns but also present serious supply chain security issues as recently highlighted by the EU Critical Raw Materials Act.<sup>[315]</sup> The scarcity of these critical raw materials (CRMs) is expected to be exacerbated in the near future as the global energy demand is estimated to increase by 27% from 2017 to 2040.<sup>[28]</sup> Recently, another even more sustainable approach has been highlighted by El-Sayed et al.: the utilization of battery waste, wastewater, used polyethylene terephthalate or polylactic acid, as efficient node- and linker-precursors for the production of new metal-organic frameworks.<sup>[240]</sup> This strategy reduces the use of virgin raw materials, lowers waste-generation, and potentially limits CO<sub>2</sub> emissions. Next to this, reticular materials solely based on readily available metals, or renewable and biodegradable materials represent a promising area of research to be further developed.

#### 4.2. Reusing Reticular Materials

The reuse strategy is strongly encouraged, and mainly relies on long operating lifespans of reticular materials over extended periods. The resilience of the coordination bonds formed between the individual building units as well as guest molecules

within the assembled frameworks, such as gases, antibiotics, biological compounds, dyes, or metal ions, can be exploited for customized applications. Therefore, reticular materials not only hold the great promise to outperform the long-term reusability of currently used materials in numerous applications, such as gas storage and separation, catalysis, or energy-related applications, but also allow for easier and fast regeneration, for instance by washing using energy-efficient ultrasound-assisted processes.<sup>[316]</sup> Maintaining capacities above 90% for more than five consecutive cycles in highly efficient adsorption of metals and dyes,<sup>[317,318]</sup> or when used as Brønsted–Lewis acidic catalyst clearly validates these assumptions.<sup>[319]</sup> The field of rechargeable batteries could also benefit from the stability merits of reticular materials.<sup>[320,321]</sup> When used as electrolyte additives of typical carbonate electrolytes, the metal-organic frameworks UiO-66(Zr), HKUST-1(Cu), or MIL-101-NH<sub>2</sub>(Al) can stabilize the solid electrolyte interface and prevent electrolyte decomposition to render reduced over-potentials and increasing operating lifespans by three-times.<sup>[322]</sup> Wei et al. found that owing to its porous characteristics HKUST-1(Cu) is able to buffer the volume expansion upon Li<sup>+</sup> insertion/extraction and alleviate mechanical stresses, producing lithium-ion battery anodes with no capacity fade at 3000 mA g<sup>-1</sup> for over 400 cycles.<sup>[323]</sup> In another example, Demir-Cakan et al. showed that the porosity of MIL-100(Cr) can act as nanostructured confined matrix physically encapsulating polysulfides (that contaminate the system and reduce stability) to render increased capacity retention over conventional Li–S batteries suffering from the “polysulfide shuttle” effect.<sup>[324]</sup> Other methods to extend Li–S battery lifespan include the chemical adsorption of negatively charged polysulfides at the Lewis acidic sites,<sup>[325]</sup> onto open metal sites,<sup>[326]</sup> or via the assistance of organic linkers,<sup>[327]</sup> or the use of metal-organic frameworks as separators

that transport  $\text{Li}^+$  while keeping soluble polysulfides at the cathode side (0.019% capacity decay per cycle over 1500 cycles).<sup>[328]</sup>

#### 4.3. Regenerating Reticular Materials

As their performance decays, reticular materials should be collected after use and then regenerated to regain pore accessibility and ensure efficiency for the subsequent use. To ease material recovery from diverse media, for instance, magnetically active materials are of great interest as they respond to external magnetic fields.<sup>[329]</sup> To regain the accessibility of the pores, a variety of techniques such as heat/vacuum, solvent-exchange, freeze-drying, and drying processes with supercritical  $\text{CO}_2$  have been explored, but also innovative methods such as microwave-assisted activation processes gain more and more attention.<sup>[54]</sup> For the recovery of photothermal effects, for example in  $\text{UiO-66-NH}_2(\text{Zr})$ , the irradiation with UV/Vis light ( $500 \text{ mW cm}^{-2}$ ) is a cheap and sustainable solvent removal approach.<sup>[330]</sup>

#### 4.4. Recycling Reticular Materials

Once a material cannot be regenerated anymore, it should undergo a recycling strategy for its reintroduction to the system. Even though thereby its embedded value is lost, waste can be avoided, and materials are kept in the economic cycle. Recycling involves the collection of waste and its re-synthesis into materials with the same or improved characteristics or a completely new material. With respect to the resynthesis of the same material, Chu et al. recently reported an environmentally friendly procedure to reversibly digest  $\text{UiO-66}(\text{Zr})$  using ammonium bicarbonate, and its successfully re-synthesis verified by an apparent BET surface area of  $1247 \text{ m}^2 \text{ g}^{-1}$  compared to the original value of  $1254 \text{ m}^2 \text{ g}^{-1}$ .<sup>[331]</sup> Industrially feasible and green processes for recycling  $\text{HKUST-1}(\text{Cu})$  involve a solvent-assisted reconstruction process achieving a 94% porosity recovery,<sup>[332]</sup> or the simpler ethanol/water-assisted ball-milling approach reconstructs the degraded material to 95% of the original surface area within 30 min.<sup>[333]</sup> Regarding the preparation of a new material based on recycling, metal-organic frameworks in particular have been used as precursors and self-sacrificing template materials for further multifunctional inorganic nanoparticles. Such bottom-up strategies mainly focused on Co-MOFs for the preparation of  $\text{Co}_3\text{O}_4$  nanoparticles for electrode materials,<sup>[334]</sup> high-performance electrocatalysts,<sup>[335]</sup> hybrid cobalt-carbon catalysts for hydrogen evolution reaction with improved stability,<sup>[336]</sup> or magnetic porous carbons.<sup>[337]</sup>

#### 4.5. Biodegradation of Reticular Materials

Biological materials can undergo conventional biodegradation processes, such as composting, or anaerobic digestion, decomposing into non-harmful by-products that could return to the biological cycle to feed the soil and grow biomass. As a result, reticular materials solely based on natural materials would not leave a permanent footprint.<sup>[17]</sup> In line with this idea, Smaldone et al. reported the preparation of metal-organic frameworks prepared entirely from edible products such as  $\gamma$ -cyclodextrin oligosaccharide

produced enzymatically from starch, KCl, and grain alcohol.<sup>[65]</sup> So far, this has mainly inspired research in the field of metal-organic frameworks with applications in biomedicine,<sup>[338]</sup> while other research directions are still poorly explored and should be investigated more in the future. Covalent organic frameworks have a great potential to develop biodegradable materials. For example, porphyrin-based covalent organic framework nanosheets can be slowly degraded into small molecules via metabolism under physiological environments, proving their in vivo biodegradation.<sup>[339]</sup> Besides, biodegradable covalent organic frameworks can be synthesized taking advantage of disulfide groups (a degradable functional group found in many organic polymers).<sup>[340,341]</sup>

#### 4.6. Disposal of Reticular Materials

The eventual damage to ecosystems and human health caused by reticular materials upon their disposal, should be minimized wherever possible. Ideally, the fate of reticular materials together with their resulting toxicity and biodistribution should be already considered during the design phase.<sup>[342]</sup> Especially when handled in powder form, and nano-scalar particle sizes, the materials' (usually) higher reactivity and enhanced ability to penetrate living tissues have to be considered. To facilitate their handling, they are therefore often incorporated into composites<sup>[343,344]</sup> including polymeric, metallic, or ceramic matrices in the form of films,<sup>[345]</sup> membranes,<sup>[346]</sup> hydrogel,<sup>[347]</sup> aerogels,<sup>[348]</sup> fibers,<sup>[349]</sup> beads<sup>[350]</sup> or monoliths.<sup>[351]</sup>

#### 4.7. First Examples of Life Cycle Assessment of Reticular Materials

Even though strategies aimed at extending the life cycle of reticular materials are implemented during the design phase, it is extremely complicated to quantify their environmental impact with the life cycle assessment methodology in a standardized fashion and apply ecodesign strategies (International Standards ISO 14040 and ISO 14044).<sup>[352–354]</sup> In this iterative process the environmental impacts of material synthesis, characterization, and application are analyzed, and finally, they are re-designed according to the resulting data. Such impact assessment studies can be performed only considering the synthesis step (cradle-to-gate perspective), the raw materials to disposal stages (cradle-to-grave perspective), or even considering the whole cycle including recycling (cradle-to-cradle perspective). Given its multi-output character, the results obtained quantify not solely the global warming potential (measured in equivalent  $\text{CO}_2$  emissions) but also additional categories such as fine particulate matter formation, ecotoxicity, eutrophication, water consumption, or acidification. Data from such studies could be used for cross-comparison with related (nano)particles and to determine the most environmentally sustainable reticular materials. As each synthetic step, i.e., material acquisition, synthesis, washing, purification, and activation, is evaluated, environmental hotspots can be identified so that synthetic set-ups can be optimized upon subsequent ecodesign.<sup>[355]</sup>

To date, the life cycle assessment considering the synthesis step of only a few reticular materials has been performed, including the well-known  $\text{MOF-74}(\text{Ni})$ ,  $\text{UiO-66-NH}_2(\text{Zr})$ ,  $\text{ZIF-8}(\text{Zn})$ ,

**Table 1.** Comparison of the life cycle assessment studies performed with reticular materials, and compared to inorganic TiO<sub>2</sub> nanoparticles, graphene oxide, and chitin nanoparticles. Abbreviations: global warming potential (GWP); *N,N*-dimethylformamide (DMF); methanol (MeOH).

Material	GWP (kg CO <sub>2</sub> equiv kg <sup>-1</sup> )	Comments	Refs.
MOF-74(Ni)	12.3–1136.2	Four solvent-based synthesis (conventional heating). Bench scale (1 kg production). 15 impact indicators.	[356]
UiO-66-NH <sub>2</sub> (Zr)	43.0 to 353.0	Three solvothermal and aqueous-based syntheses. Pilot scale. 7 impact indicators.	[357]
ZIF-8	86.6–1571.2	Five solvent-based synthesis (conventional heating). DMF/MeOH cause up to 85% of the overall impacts. Bench scale (1 kg production). 18 impact indicators.	[358]
Imine-based COF	48.9–61.5	Results reported for printed COFs. Monomer synthesis and solvent use are main drivers. Laboratory scale. 7 impact indicators.	[359]
TiO <sub>2</sub>	8.0/12.0–86.0	Continuous flow solvo/hydrothermal syntheses. Full scale plant (>1000 t year <sup>-1</sup> ). Cumulative energy demand.	[360]
Reduced graphene oxide	1060.0–2360.0	Hummer's synthesis with glucose and hydrazine. Bench scale (1 kg production). 16 impact indicators.	[361]
Chitin nanocrystals	543.5–906.8	Chitin nanocrystal isolated from crustacean shells. Bench scale (1 kg of treated biomass). 18 impact indicators.	[362]

and an imine-based COF. In **Table 1** their global warming potentials (typically based on 1 kg of materials as the functional unit) are summarized and compared to common synthetic routes to inorganic TiO<sub>2</sub> nanoparticles, reduced graphene oxide, and bio-based chitin nanocrystals.

#### 4.7.1. MOF-74(Ni)

One of the earliest life cycle assessment studies by Grande et al. was directed at determining the impacts of four synthetic routes for MOF-74-Ni (also known as CPO-27-Ni). Covering different solvent compositions for synthesis (*N,N*-dimethylformamide/ethanol/ water/tetrahydrofuran) and cleaning procedures (methanol/water/tetrahydrofuran), global warm-

ing potential values ranging from 12.3 to 1136.2 kg CO<sub>2</sub> equiv kg<sup>-1</sup> were obtained. As the impacts were driven by the use of solvents, either during synthesis or during cleaning steps, the authors proposed diverse ecodesigned scenarios, and found that a fully aqueous synthesis could reduce the global warming potential by a factor of 92. Additional impact categories such as freshwater toxicity and resource depletion also benefit from avoiding the organic solvents *N,N*-dimethylformamide or tetrahydrofuran.<sup>[356]</sup>

#### 4.7.2. UiO-66-NH<sub>2</sub>(Zr)

Considering a hypothetical pilot-scale production, Luo et al. showed that the global warming potential of UiO-66-NH<sub>2</sub> synthesized by a conventional solvothermal method could be lowered from 353.0 to 43.0 kg CO<sub>2</sub> equiv kg<sup>-1</sup> moving into an aqueous solution-based production (overall environmental burdens are lowered by 91%). These improvements are driven by reduced organic solvent consumption, together with a two to three fold yield increase.<sup>[357]</sup>

#### 4.7.3. ZIF-8(Zn)

Nturos et al. reported the environmental impacts of five solvent-based synthetic routes (conventional heating) towards ZIF-8(Zn) revealing global warming potential values ranging from 86.6 to 1571.2 kg CO<sub>2</sub> equiv kg<sup>-1</sup>. The 18-fold difference observed is also reflected in additional impact categories such as ionizing radiation, fine particulate matter formation, ozone formation, acidification, eutrophication, ecotoxicity, human toxicity, land use, mineral resource scarcity, fossil resource scarcity, and water consumption. Syntheses relying on water and having yields above 68% provide the lower impacts, while using *N,N*-dimethylformamide or methanol increases the global warming potential dramatically reaching a share of up to 85% of the overall environmental impacts.<sup>[358]</sup> Xia et al. also compared the different production processes of ZIF-8(Zn) and their results confirm that using recyclable or biodegradable solvents substantially reduces the environmental footprint.<sup>[251]</sup>

#### 4.7.4. Imine-Based COF

Espada et al. focused on the printing of imine-based COFs synthesized upon a Schiff reaction between two trigonal building blocks in air at room-temperature. A global warming potential of 48.9–61.5 kg CO<sub>2</sub> equiv kg<sup>-1</sup> is reported depending on the printing method. Their results revealed that the monomer synthesis represents the largest contributor to the environmental impacts. Herein, halogenated emissions to air, palladium catalyst, and the large waste disposal (given the low yield for hydrazine synthesis) are the main cause. The solvent choice for the processing into complex geometries through printing technologies also is a remarkable contributor, where 3D inkjet printing yields 5–65% lower impacts when compared to surface printing.<sup>[359]</sup>

#### 4.7.5. *TiO<sub>2</sub> Nanoparticles, Reduced Graphene Oxide, and Chitin Nanocrystals*

Similar to the huge variation in observed global warming potentials for reticular materials (with a maximum range of 12.3 to 1136.2 kg CO<sub>2</sub> equiv kg<sup>-1</sup>), also the results of laboratory-scale nanoparticle syntheses deviate strongly. This reflects the uncertainty of results when it comes to analyzing processes that are not technologically mature. When compared to the mature continuous flow solvo-/ hydrothermal syntheses of TiO<sub>2</sub> nanoparticles relatively low values of only 8.0 to 86.0 kg CO<sub>2</sub> equiv kg<sup>-1</sup> were obtained.<sup>[360]</sup> In contrast to this, the synthesis of reduced graphene oxide (1060.0–2360 kg CO<sub>2</sub> equiv kg<sup>-1</sup>),<sup>[361]</sup> and the chitin nanocrystal isolation from crustacean shells (543.5–906.8 kg CO<sub>2</sub> equiv kg<sup>-1</sup>)<sup>[362]</sup> require much more energy and resource intensive processes than reticular materials.

Comparing the life cycle assessment studies of the different reticular materials, it becomes very evident, that altering the solvent used during synthesis or cleaning steps has the biggest impact on the resulting global warming potential and related impact categories. This highlights that the efforts to shift to fully aqueous syntheses have been very well invested and should even be intensified in the future. When comparing reticular materials syntheses to common synthetic routes of TiO<sub>2</sub> nanoparticles, reduced graphene oxide, and chitin nanoparticles, another aspect that plays a crucial role to lower the global warming potential becomes clear: the transition from laboratory scale to technologically mature industrial scale has a major impact on energetic and chemical efficiency and needs to be further optimized.

### 4.8. Challenges and Recommendations for Future Life Cycle Assessment

Although these life cycle assessment pioneer studies have opened the path towards environmental impact assessment of synthesis of reticular material, its accurate implementation into the reticular chemistry field is highly complex and still challenged by various aspects. To foster more life cycle assessment practitioners in the reticular materials field, these challenges will be accompanied by a series of recommendations in the following.

#### 4.8.1. *Lack of Guidelines*

First, the implementation of life cycle assessment in emerging materials still leaves room for interpretation on how data should be gathered and how it will be evaluated. For instance, the different life cycle impact assessment methods (ReCiPe 2016, CML, TRACI, CED...) categorize the results into diverse impact categories, which often, do not match. Setting unambiguous instructions for system boundary, functional unit, or impact category definition (such as those performed by Product Category Rules) are therefore required.

#### 4.8.2. *Selection of System Boundary*

The system boundary selection does not have a widely accepted scientific method,<sup>[363]</sup> i.e., considering only the synthesis step

(cradle-to-gate), the raw materials to disposal stages (cradle-to-grave), or even considering the whole cycle including recycling (cradle-to-cradle). Different selections may yield loss of relevant information and avoid environmental impact transference issues, but due to the lack of standardized databases for reticular materials or minimum information requirements, to date end-of-life issues, such as degradability or toxicity, still remain widely unknown.

#### 4.8.3. *Setting a Functional Unit*

The conventional mass allocation used so that the impacts are reported per kg of material makes sense when the functional properties are comparable.<sup>[362]</sup> If reticular materials are applied in energy storage applications as active materials, kg CO<sub>2</sub> equiv kWh<sup>-1</sup> may yield more meaningful results,<sup>[364]</sup> while kg CO<sub>2</sub> equiv mmol<sup>-1</sup> would be desirable for CO<sub>2</sub> uptake applications. Such room for interpretation makes a direct comparison cumbersome.

#### 4.8.4. *Creation of Midpoint or Endpoint Indicators*

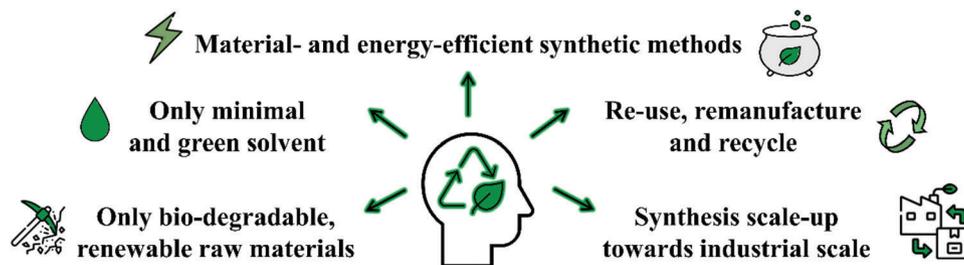
While midpoint indicators are defined close to emissions (categories such as global warming, and acidification, among others), for the endpoint type, emissions are aggregated to obtain variables of direct societal concern such as human health, natural environment, and natural resources. The complexity of the models needed to implement endpoint indicators, and the fact that data may be lost in the process, encourage the use of midpoint indicators.

#### 4.8.5. *Availability of Complex Precursors in Existing Databases*

The precursors used during syntheses are scarcely found in existing sources for life cycle assessment data, including theecoinvent database, the US Argonne National Laboratory Greenhouse gases, Regulated Emissions, and Energy use in Technologies Model (GREET), the Industrial Design & Engineering Materials Database (IDEMAT), the CPM LCA Database, or the openLCA Nexus database. This makes the allocation of all the inputs and outputs of the process difficult. Either a similar component appearing in the database is selected (which may lead to deviations in the results), or a specific process is simulated to obtain such precursors. In the latter, there is a risk of not obtaining comparable results due to the different scales used during manufacturing.

#### 4.8.6. *Implementation of Machine Learning*

The evolving character of reticular material syntheses, including novel precursors, linkers, structures, functionalization, or activation routes makes it virtually impossible to keep pace and quantify the impact for all the materials being reported. Hence, the implementation of machine learning together with life cycle assessment could help the future rational sustainable material design and discovery.<sup>[365]</sup>



**Figure 10.** Overview of some key learning points for more green and environmentally sustainable synthesis in emerging materials.

#### 4.8.7. Process Scalability

If material synthesis modeling is carried out at small scales (in the gram range), significant impact from energy and chemical use may arise.<sup>[366]</sup> Scaling-up optimizes the process (in terms of material and energy use) in such a way that a 6.5-fold reduction on the impacts could be achieved shifting the production from 10 g to 50 kg.<sup>[367]</sup> Therefore, the utilization of more industrial-scale processes such as continuous flow chemistry, solvo-/ hydrothermal, electrochemistry, microwave-assisted heating, or mechanochemistry syntheses is encouraged.<sup>[50,51]</sup>

#### 4.8.8. Considering the Reuse of Chemicals

Another aspect that should be given more attention is whether or not the used solvents are being reused. If so, the amount of solvent used has to be standardized, and a new process for solvent recirculation and concentration should be added.

### 5. Concluding Remarks and Future Outlook

This review has highlighted relevant strategies to boost the environmentally sustainable synthesis of reticular materials by systematically applying the 12 fundamental principles of Green Chemistry, optimizing the chosen synthetic methodology in the most energy-efficient way, and greater adoption of a life cycle thinking perspective (**Figure 10**). An important point to consider here is that sometimes the overall sustainability of a synthesis can be difficult to quantify. Applying all 12 principles to the same synthetic procedure might be impossible, and sometimes a trade-off between them might still yield an improvement to the sustainability of the overall process even if when one part of the process might seem, at first glance, less sustainable. To date, the syntheses of existing and novel metal-organic frameworks, zeolitic imidazolate frameworks, and covalent organic frameworks have been successfully improved, from a green and sustainability perspective, mainly by performing reactions in more environmentally friendly solvents, such as water or bio-derived Cyrene, and/or optimizing existing reaction conditions by working at room-temperature and/or by using energy-efficient methods, such as sonochemical-, microwave-assisted and mechanochemistry. Several multi-component hybrid/composite structures of reticular materials, such as MOF nanoshell structures,<sup>[368]</sup> MOF/COF-based hybrids,<sup>[369,370]</sup> yolk-shell nanocatalysts,<sup>[371]</sup> polyoxometalate/MOF composites,<sup>[372,373]</sup> as well as ZIF-<sup>[374]</sup> and COF-based

composites,<sup>[375]</sup> have been recently introduced as functional solids targeting a range of applications. It is worth recognizing the need to prepare such systems by a greener route moving forward. In addition to the tremendous efforts to make the synthesis greener, researchers are increasingly trying to understand the full life cycle of reticular materials, starting from their raw materials, to use/maintenance, reuse, regeneration, recycling, disposal, and end-of-life. Owing to the limitless creativity of researchers and the various opportunities given the unprecedented versatility of reticular materials, the number of innovative reports on i) the generation of waste-derived solvents and precursor materials, ii) the long-term reusability of customized reticular materials, iii) the effective regeneration of reticular materials by specialized synthetic set-ups, as well as iv) the reversible digestion and re-synthesis of reticular materials is constantly increasing. The pioneering studies in life cycle assessment of reticular materials have highlighted two key learning points: the solvent used as well as the process scale of a synthesis has the biggest impact on the resulting global warming product. Avoiding and replacing hazardous organic solvents with water can reduce the overall environmental impact significantly. Moreover, scaling-up and modifying laboratory scale synthesis to a technologically mature industrial scale can maximize the energetic and chemical efficiency.<sup>[376]</sup>

In this regard, it is worth mentioning some of the industrial production methods for reticular framework materials that have been employed by early and upcoming companies and start-ups. Among initial examples, BASF tested the electrosynthesis approach to prepare a range of Zn-based metal-organic frameworks—MOF-2, MOF-5, and IRMOF-8.<sup>[377]</sup> BASF also established the large-scale synthesis of Al-based metal-organic frameworks, such as MIL-53, MIL-96, MIL-100, and MIL-110 using water-based synthesis. Optimizing the synthesis of Al-fumarate could yield a high space-time yield of  $>3600 \text{ kg m}^{-3} \text{ day}^{-1}$ .<sup>[378]</sup> Nuada (previously MOF Technologies) built on the mechanochemical synthesis approach and were able to prepare several metal-organic frameworks using single-screw or twin-screw extrusion method.<sup>[304,305]</sup> Promethan particles have used the continuous flow solvo-/hydrothermal synthesis (CFHS/CFSS) approach, which has been shown to have rapid preparation for a range of metal-organic frameworks with high space-time yield values.<sup>[379]</sup> Another commercially available metal-organic framework—MIL-100(Fe) (sold under name KRICT F100), has been reported to be prepared by a HF-free, hydrothermal synthesis route.<sup>[380]</sup> With the development of more mature synthetic routes, covalent organic frameworks have recently started becoming available as a commercial product as well.<sup>[381]</sup> We believe that considering all the discussed aspects, we

can learn a lot from the past for the design and synthesis of novel reticular materials which have the enormous potential to replace current nonsustainable systems, thus allowing us to minimize our footprint on Earth and protect it for future generations.

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## Conflict of Interest

The authors declare no conflict of interest.

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covalent organic frameworks, Green chemistry, life cycle assessment, metal-organic frameworks, zeolitic imidazolate frameworks

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