Bachelor's thesis

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Is sustainable production of the MOFs MIL-101 and MOF-5 possible without reducing the hydrogen storage capacity of the material?

Bachelor's thesis in Natural Science with Teacher Education
Supervisor: Daniel Ali

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ABSTRACT

Metal organic frameworks (MOFs) are some of the most promising porous materials for hydrogen storage, two of the most promising being MIL-101 and MOF-5. The conventional syntheses of the two MOFs involves highly toxic solvents, and they are both time and energy consuming, as they require heating at high temperatures over a longer period of time. Different modifications can be done to the syntheses to make them more sustainable, however, some of these might reduce the hydrogen storing capacity (HSC) of the MOF. This thesis investigates whether a sustainable synthesis of MOF-5 and MIL-101 is feasible without reducing their HSC. MIL-101 can be synthesized by microwave-assisted synthesis, which is a time and energy efficient synthesis showing promising results at lab-scale with maintained surface area and therefore also most likely maintained HSC. As for MOF-5, the time and energy efficient sonochemical synthesis is the most promising, as this has a maintained surface area and therefore also most likely maintained HSC. However, this method shows a poor yield, which decreases the sustainability of the synthesis. Extracting the linker 1,4-benzenedicarboxylic acid (BDC) from PET-bottles is another way of increasing the sustainability of the syntheses of both MIL-101 and MOF-5.

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1 INTRODUCTION

Energy consumption has risen eight times over the past century, and by 2040, it is expected to increase by a further 56% [1]. In the transport sector, the main energy source today is fossil fuel, which generates massive amounts of greenhouse gases, predominantly CO_2. To meet this large energy demand in the future without a massive CO_2 emission, there is need for a new, clean renewable energy material to replace fossil fuels [2]. One of the materials that has potential to become this main energy source is hydrogen, which has an energy content of 33.3 kWh kg^{-1}, which is greater than both that of methane (13.9 kWh kg^{-1}) and of gasoline (12.4 kWh kg^{-1}) [3]. Other advantages with developing a hydrogen-based energy economy are zero CO_2 emission and the potential renewable nature of hydrogen production [4].

One of the main challenges with implementing hydrogen as the main fuel in transport technology is safe, economical, spaciously favorable and efficient storage [5]. The United States Department of Energy (DOE) has made both gravimetric and volumetric storage capacity guidelines that hydrogen storage in vehicles must meet by 2025 [6]. The targets set by DOE are 5.5 wt % (percentage mass H_2 of total mass) and 40 gL^{-1} (mass H_2 per volume of storing unit) at the temperature range 233-333 K and pressures up to 100 bar [2]. As hydrogen is a very light gas, with a molecular weight of only 2.016 $gmol^{-1}$ [7], the gas has to be stored in a very lightweight material to meet the percentage per total mass target. Many different methods of storing hydrogen are under consideration and development, and they include high-pressure gas, liquid hydrogen, complex hydrides, chemical hydrogen storage, carbon nanotubes and adsorption on porous materials [2, 5, 8].

One of the storage methods that has the best prospects of meeting the DOE targets is hydrogen adsorption on porous materials, one of them being adsorption on metal-organic frameworks (MOFs) [1, 3, 8]. MOFs are a rapidly growing group of crystalline compounds consisting of metal ions linked to organic ligands [9]. They are lightweight, have a massive surface area of up to 10 000 m^2g^{-1}, and are easily modified – making them interesting for hydrogen storage. There are many different MOFs with promising hydrogen storage abilities, two of the most researched being MOF-5 and MIL-101 [8]. However, for MOFs used for hydrogen storage to be a good and environmentally friendly choice, the synthesis and production of MOFs must also be sustainable. In the current production of MOFs, many hazardous and non-renewable solvents are used, the energy consumption is high, and the processes produces large amounts of dangerous waste [10]. Over the past years, vast research has been done in order to make the

synthesis of MOFs more environmentally friendly, sustainable, and safe [9]. This Bachelor's project will specifically focus on sustainable synthesis of MOFs used for hydrogen storage. The research question for the thesis is:

> ***Is sustainable production of the MOFs MIL-101 and MOF-5 possible without reducing the hydrogen storage capacity of the material?***

2 THEORY

2.1 STRUCTURE AND SYNTHESIS OF MOFS

A metal-organic framework (MOF) is a porous crystalline structure consisting of positively charged metals/clusters strongly linked by covalent bonds to anionic organic ligands (linkers), which together form a defined porous framework [11]. Traditionally, single metal ions were linked to organic ligands, whereas later years have found linking small inorganic polynuclear clusters known as secondary building units (SBUs) to organic ligands advantageous, as the SBUs help the MOF retain its porosity after removal of guest molecules [11]. The SBUs function as directional and stable building units, enabling the development of highly porous MOFs with a large surface area [12]. Many different organic ligands are used as linkers, carboxylate ligands and nitrogen-containing ligands being the most used [11]. These are the preferred type of organic ligands, as they make it possible to control the crystal growth of the MOF by slowly deprotonating the ligands under special conditions, usually the presence of a basic solvent [11, 13]. By changing the linkers, the cluster/metal ions, and the synthesis conditions, the framework topology, surface area and pore size can be altered [14]. Since the first MOF was discussed in 1965 [15], more than 100,000 unique MOFs with different areas of application has been synthesized by changing the different building blocks [9]. With machine learning, more than 900,000 MOFs have been predicted including the 100,000 which already have been made [16].

Conventionally, MOFs have been prepared via a solvothermal synthesis, where the SBUs and the organic ligands are dissolved in an organic basic solvent under high temperature and pressure to form MOF crystals [9]. Commonly used solvents are dimethylformamide (DMF), diethylene formamide (DEF) dimethyl sulfoxide (DMSO), methanol and acetonitrile [9, 11, 13]. The reaction time is long, ranging from a few hours to several days [9]. Over the last years, research has been done to find new, more sustainable forms of synthesis [9, 10]. These new forms of synthesis can be divided into two main categories: solvent-free and solvent-based synthesis [9]. For solvent-free synthesis, mechanochemical synthesis shows the best synthesis results, whilst for solvent-based synthesis solvothermal synthesis using microwaves or ultrasonic radiation, and synthesis using water, supercritical fluids, or ionic liquids are the most promising [9, 13, 17].

The large surface area of MOFs is one of the main contributors to their many different applications. The surface area can be calculated using either the Langmuir equation or the BET

equation [14]. As the Langmuir equation only takes monolayered adsorption into account, are the Langmuir specific surface areas normally considerably larger than the specific surface area calculated by the BET equation for the same material, which utilizes multilayer adsorption [14]. It is therefore important to only compare surface areas if they are calculated using the same equation.

2.2 HYDROGEN STORAGE

When hydrogen is stored in materials, it is stored by either chemisorption or physisorption [5]. In chemisorption-based materials, the hydrogen is adsorbed by chemical bonds that are formed between the adsorbate (hydrogen) and the adsorbent (material), and for the hydrogen to be released, energy must be applied [14]. In physisorption-based materials, hydrogen is adsorbed to the material only by intermolecular van der Waals forces [14]. MOFs belong to the latter category, where hydrogen is stored in the porous material by adsorbing on the surface of the pores within the MOF [5]. This is a reversible process, as no activation energy is needed to release the hydrogen [14]. Most physisorption-based materials have a good hydrogen storage capacity (HSC) at low temperature (77 K) and high pressure (100 bar), whereas the HSC is highly reduced at realistic temperature and pressure (298 K and 1 bar) [14].

HSC can be calculated and defined in two different ways, either by mass H_2 per liter MOF (gL^{-1}) or by weight percentage H_2 (wt %). Weight percentage is calculated by this equation [1]:

$$\text{wt \%} = \frac{(\text{mass } H_2)}{(\text{mass MOF } + \text{ mass } H_2)} \cdot 100\% \quad (1)$$

There are different factors affecting the HSC of a MOF, most prominent being surface area, pore size and volume, heat of adsorption (ΔH_{ads}), pressure, and temperature [11, 14, 18]. Research show that at low temperatures (77 K), the HSC is mostly affected by the heat of adsorption at low pressures (below 30 bar), by the surface area at intermediate pressures (30-100 bar) and by free volume at high pressures (above 100 bar) [3, 11]. To increase the HSC at higher temperatures, the attraction between the adsorbate and the MOF must be increased. To maximize this attraction, the ideal pore size, which is approximately the same size as the diameter of the hydrogen molecule (1.2 Å) [19], should be obtained [3, 14]. Small pore sizes increase the Van der Waals forces on the hydrogen molecule, which further increases the HSC [3]. This happens independent of pressure [3].

2.3 PROMISING MOFS FOR HYDROGEN STORAGE

Machine learning technology predicts that there are around 8,000 different MOFs that can be used for hydrogen storage, and many of these have already been studied [11, 16]. Two of the most promising MOFs for hydrogen storage are MOF-5 and MIL-101, as their small pores and large surface areas lead to increased van der Waals interactions between the pore walls and the hydrogen molecules [8, 11, 14, 20].

2.3.1 MOF-5

MOF-5 (IRMOF-1) was the first MOF suggested having hydrogen storage abilities back in 2003 [3, 11, 14]. MOF-5 consists of cationic, octahedral OZn_4 SBUs linked to anionic 1,4-benzenedicarboxylic acid (BDC) linkers in a cubic framework structure, which means that MOF-5 also is known as $Zn_4O(BDC)_3$ [11]. The structures of the linker BDC, the SBU OZn_4 and the entire MOF-5 can be seen in figure 1. In 2003, it was reported to have an HSC of 4.5 wt % H_2 at 77 K and 1 bar [14], and since then different modifications have been done to increase the HSC [1, 8]. MOF-5 is conventionally synthesized by a solvothermal reaction with BDC and Zn-salt in a DMF solvent, with a reaction temperature of 333 K and a reaction time of 72 hours [3, 9, 14]. The product typically has a Langmuir surface area of 3205 m^2g^{-1} and a pore size of 11 Å [21].

2.3.2 MIL-101

MIL-101 is recognized as one of the benchmark MOFs for hydrogen storage, and it has a recorded HSC of 6.1 wt % H_2 at 77 K and 80 bar [3, 14, 22]. MIL-101 consists of cationic, trigonal prism-structured Cr_3OF SBUs linked to anionic BDC ($Cr_3OF(BDC)_3$), resulting in both a hexagonal and pentagonal framework, with pore sizes of 29 Å and 34 Å respectively [21, 23]. The structures of the linker BDC, the SBU Cr_3OF and the entire MIL-101 can be seen in figure 1. Typically, MIL-101 is prepared by a solvothermal reaction, mixing hydrated chromium nitrate with BDC in hydrogen fluoride (HF) dissolved in water as a solvent [20]. The synthesis is carried out between 473-793 K with a reaction time of 8-20 hours [20]. During the synthesis, the product is washed with ethanol and DEF [22]. The finished product has a typical pore volume of 2.3 cm^3g^{-1}, and a BET surface area of 4100 m^2g^{-1} [9, 24].

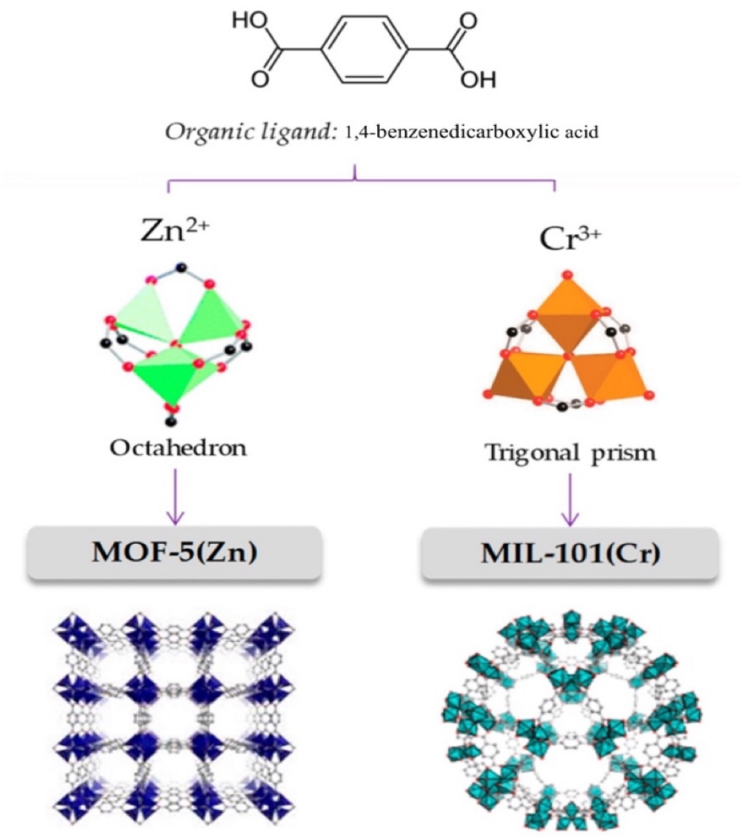

Figure 1: Framework topology, structure of SBUs and structure of the organic linker BDC of MOF-5 and MIL-101. Adapted from *Metal-Organic frameworks in Green Analytical Chemistry* by Rocío-Bautista, 2019 [21].

2.4 Green and sustainable synthesis

In 1998, 12 principles of green chemistry and sustainable production were introduced to the world by Warner and Anastas [25]. By following the principles, a more sustainable synthesis process can be obtained. The 12 principles are; 1. *Prevention of waste*, 2. *Atom economy*, 3. *Less hazardous chemical synthesis*, 4. *Design safer chemicals*, 5. *Safer solvents and auxiliaries*, 6. *Design for energy efficiency*, 7. *Use of renewable feedstock*, 8. *Reduce derivatives*, 9. *Catalysis*, 10. *Design for degradation*, 11. *Real-time analysis for pollution prevention* and 12. *Inherently safer chemistry for accident prevention* [25]. Principles 8, 9 11 and 12 do not focus on synthesis, and they are therefore outside the scope of this thesis. For simplicity, principle 1 is combined with principle 2 and principles 4 and 10 are combined with principle 3, as they mostly cover the same topics. Therefore, the principles that will be the focus of this bachelor's thesis are principles 2, 3, 5, 6 and 7, as they focus on sustainable synthesis. The 2nd principle, *atom economy*, advocates for maximizing of product, that is as high a yield as possible. The 3rd principle, *less hazardous chemical synthesis*, wants to minimize use of toxic and hazardous chemicals used in and produced from synthesis for both environment and human

health. The 5th principle, *safer solvents and auxiliaries*, searches for use of as few solvents and as non-toxic solvents as possible. The 6th principle, *design for energy efficiency*, wants to minimize energy consumption during synthesis, where ideally, synthesis should be carried out at 298 K and 1 bar. The 7th principle, *use of renewable feedstock* focuses on the fact that raw materials should be renewable when technically and economically viable.

3 DISCUSSION

Over the past decades, different ways of making the synthesis of MOFs more sustainable have been studied. Different approaches have been tried, varying from different reaction conditions, different heating methods, with and without solvent, and use of renewable linkers. This discussion will first present how the conventional syntheses of MOF-5 and MIL-101 fails to meet the principles of green chemistry, followed by a presentation of different techniques that improve the sustainability of the two syntheses, and how these alterations affect the HSC of the MOF.

By conventional synthesis, neither the production of MOF-5 nor of MIL-101 follows the 12 principles of green chemistry [25]. The solvothermal synthesis of MOF-5 uses DMF as a solvent, which is toxic, non-renewable, and expensive, and ideally should be replaced for a more sustainable synthesis to be obtained [9, 14]. Furthermore, the synthesis process takes 72 hours and involves heating at 333 K, which is both energy and time-consuming. For the process to become more sustainable, shorter reaction time and room temperature are preferred [25]. Similarly, the solvothermal synthesis of MIL-101 uses HF dissolved in water as a solvent. HF is a toxic solvent, as it is highly irritating for the skin and can be fatal if swallowed [26]. Moreover, the synthesis has a reaction time of 8-20 hours and takes place at temperatures up to 793 K, which results in a time and energy-consuming process. In order to make the synthesis of MOF-5 and MIL-101 more sustainable, different alterations can be done to the syntheses of the two MOFs. However, these alterations often impact both the surface area, pore volume, and structure of the MOFs, which further can impact the HSC of the synthesized material.

One way to reduce both reaction time and temperature is by using ultrasonic waves [9]. MOF-5 has successfully been synthesized using this technique, called sonochemistry [27] . The technique uses ultrasonic waves that create high local temperatures and pressures within liquids (~5000 K and 1000 bar) [9]. In this synthesis of MOF-5, 1-methyl-2-pyrrolidone (NMP) is used as solvent [27]. This is a cheaper alternative to DMF, but also this categorized as toxic [28], making the synthesis non-sustainable according to the 5th green chemistry principle (*safer solvents and auxiliaries*). The synthesis is carried out at 423 K, and the total reaction time is reduced from 72 hours to 30 minutes [14, 27]. This leads to a significantly lower energy consumption, which is an important part of the 6th green chemistry principle (*design for energy efficiency)*. The product showed promising high-quality crystals comparable to the crystals obtained from conventional synthesis, and the achieved Langmuir surface area was 3208 m^2g^{-1}

[9]. This is almost identical to the Langmuir surface area achieved from conventional synthesis of MOF-5 (3205 m^2g^{-1}), and although not measured, it is expected that the MOF-5 from ultrasonic synthesis has comparable HSC to that of conventional MOF-5 at 77 K and intermediate pressures (30-100 bar). This is due to the HSC being mostly affected by surface area at these conditions [3]. However, MOFs produced from ultrasonic synthesis has been registered to have a lower product yield than that of conventional synthesis, affecting the atom economy of the synthesis, which is the 2nd green chemistry principle. Furthermore, this makes this a less attractive synthesis method for upscaled production of MOF-5 [29]. Therefore, one must consider whether energy and time efficiency or atom economy is more important for the sustainability. At the same time, the use of a toxic solvent reduces the allover sustainability of the synthesis.

Another way to make a solvothermal synthesis more sustainable is by using a microwave-assisted synthesis, a method by which MIL-101 has been successfully synthesized [9]. In this type of synthesis, electromagnetic microwaves interacts with polar dipoles in a solution, creating thermal energy [29]. The synthesis uses water and ethanol as a solvent, which is both cheaper and less hazardous compared to the conventional solvent HF. This makes for a more sustainable production following the 5th principle of green chemistry (*safer solvents and auxiliaries*). The reaction time was reduced from up to 20 hours down to 40 minutes, and the reaction temperature was reduced from 793 K to 483 K [17]. This results in both a time and energy saving process, which follows the 6th principle of green chemistry (*design for energy efficiency)*. The synthesized crystals show promising characteristics with a BET surface area of 3900 m^2g^{-1}, pore sizes of 13.0 Å and 18.2 Å and a pore volume of 2.3 cm^3g^{-1} [17]. Both BET surface area and pore volume are comparable to the characteristics achieved from conventional synthesis of 4100 m^2g^{-1} and 2.3 cm^3g^{-1} respectively. The pore sizes are smaller compared to the conventional pore sizes of 29 Å and 34 Å, however as both surface area and pore volume are almost the same, the HSC at 77 K and pressures 30-100 bar is expected to be almost maintained. Additionally, at ambient temperature (298 K) and intermediate pressures, the HSC is expected to be higher, as the HSC increases with reduced pore size. Thus far, microwave-assisted synthesis has only been done in laboratory scale [29]. Microwaves have a relatively small penetration depth, making it difficult to use this method efficiently in upscale production [29], which makes it less feasible for this method of synthesis to be used for creating MOFs for hydrogen storage in vehicles. Nevertheless, for other structures of MOFs (e.g. UIO-66), research has been done to upscale a microwave-assisted synthesis using a tubular reactor with

small diameters [29]. This has shown promising results, and it is possible to believe that MIL-101 can be produced using this method, making microwave-assisted synthesis of MIL-101 a sustainable synthesis with possibility for upscaling.

The 6th principle of green chemistry says that a sustainable production should, if possible, be carried out at room temperature (298 K) and 1 bar. MOF-5 has been successfully synthesized at these conditions, using DMF as a solvent and with the addition of triethylamine (TEA) during synthesis [30]. The synthesis is carried out at room temperature, and has a reaction time of 41 hours, before being dried at 423 K for 12 hours. This leads to the reaction conditions during the synthesis being sustainable, whilst the latter part of the synthesis process requires heating at 423 K for 12 hours, which is not sustainable according to the 6th green chemistry principle. The total synthesis time is 53 hours, which is considerably higher than most of the other synthesis methods. Another factor impacting the actual sustainability of the reaction is the use of DMF as a solvent and TEA as an additional chemical required during synthesis. DMF is as previously mentioned a toxic solvent, and with the addition of TEA the synthesis uses both toxic solvents and more solvents/chemicals than the conventional synthesis. Consequently, the process does not follow the 5th principle of green chemistry *(safer solvents and auxiliaries).* Moreover, the produced material has a Langmuir surface area of 784 m^2g^{-1}, which is considerably lower than that of conventionally synthesized MOF-5 (3205 m^2g^{-1}), most likely leading to a lower HSC at 77 K and intermediate pressures (30-100 bar) [30].

Another method used to make the synthesis of MOFs more sustainable is a solvent-free synthesis, namely a mechanochemical synthesis. This is a method where the reagents are grinded using a mortar to produce solid-solid reactions [9]. MIL-101 has been successfully synthesized using this method combined with heating at 493 K for 4 hours [24]. As this is a solvent-free synthesis, both green chemistry principle 3 and 5 (*less hazardous chemical synthesis* and *safer solvents and auxiliaries* respectively) are met. This leads to both a safer and more economical synthesis. Both reaction time and temperature are reduced from conventional synthesis, and consequently also meeting the 6th green chemistry principle (*design for energy efficiency)*. The produced MOF has a BET surface area of 2764 m^2g^{-1}, which is considerably lower than that of conventional MIL-101 (4100 m^2g^{-1}) [9]. The registered pore volume was 1.7 cm^3g^{-1} and the pore sizes were 15 Å and 20 Å, also these lower than that of conventional MIL-101 (2.3 cm^3g^{-1}, 29 Å and 34 Å respectively) [24]. This is arguably one of the most sustainable synthesis methods of MIL-101, but as both surface area, pore size and pore volume are noticeably reduced, the HSC, although not measured, is expected to be considerably lower

than that of conventional MIL-101. As a side note, this is an upscalable synthesis method, as it only involves solid-state reactions [29], making it an interesting area for mass production of MOFs for hydrogen storage in vehicles, if the quality of the product could be improved.

Another way of increasing the sustainability of synthesis is by following the 7th principle of green chemistry (*use of renewable feedstock)*. Both MOF-5 and MIL-101 includes the organic linker BDC, which is a chemical compound with many different areas of use, as it is a precursor in polyethylene terephthalate (PET) [31]. Commercially, PET is used in the production of plastic bottles, as well as audio and video tape, X-ray films and other forms of plastic products [31]. Annually, 24 million tons of PET is produced, resulting in massive amounts of waste [31]. In 2016, a group of researchers developed a method of extracting BDC from PET-bottles, which further was used to produce MIL-101 [31]. The synthesis was a combination of ultrasonic and conventional solvothermal synthesis, and it was carried out at a temperature of 483 K and had a total reaction time of 9 hours. De-ionized water was used as a solvent in combination with formic acid, and it was washed using DMF. The finished product had a BET surface area of 3233 m^2g^{-1} and a pore volume of 1.3 cm^3g^{-1} [31]. Measurements show a hydrogen uptake of 2.1 wt % H_2 at 77 K and 1 bar, which is lower than that of conventionally synthesized MIL-101 (6.1 wt % H_2, 77 k and 80 bar). This is an expected result, as the surface area is considerably lower than that of conventional MIL-101 (4100 m^2g^{-1}). However, as the two HSC are measured at different pressures (1 bar vs 80 bar), the actual difference is expected to be smaller, as higher pressure equals higher hydrogen uptake. The synthesis has only been carried out in lab scale thus far, but it is possible to believe that it can be carried out in a big commercial production scale in the future [31]. Along with MIL-101, MOF-5 uses BDC as a linker, consequently making synthesis using BDC from PET-bottles a possibility, but this is yet to be done [31].

As mentioned, there are many ways to make the syntheses of MOF-5 and MIL-101 more sustainable. Arguably the most sustainable synthesis route is the mechanochemical synthesis, as it is completely solvent free. This method has not been carried out for MOF-5 yet, but has delivered promising results for MIL-101. However, this method leads to a considerably lower surface area of MIL-101 and will consequently most likely lead to a lower HSC. The method that maintains the surface area and therefore the HSC of MIL-101 the most is microwave-assisted synthesis. By using this method, it is possible to sustainably synthesize MIL-101 without affecting the HSC at lab-scale. As for MOF-5, the sonochemical synthesis is the most sustainable method out of the discussed methods, as it reduces both the reaction time and temperature, whilst maintaining the surface area and therefore most likely the HSC. However,

the yield of the sonochemical synthesis is considerably lower, which makes this a less attractive synthesis route as yield affects the atom economy and thus also the sustainability. If the yield of the production could be improved, this could be both a sustainable and economically favorable method of synthesizing MOF-5 without reducing HSC. Finally, a way to make both the synthesis of MOF-5 and MIL-101 more sustainable is by using BDC produced from PET-bottles. If the production of BDC from PET could be commercialized, this could be a way of improving the sustainability of the suggested syntheses, as well as a way of improving the sustainability of the conventional syntheses of the MOFs, which for MOF-5 already is carried out commercially [13].

4 CONCLUSION

Hydrogen is a promising energy carrier, and it can lead to reduced CO_2 emission and a more sustainable energy usage in the world. MOFs are some of the most promising materials for storing hydrogen, and sustainable synthesis of MOFs is desirable for a green and environmentally friendly hydrogen economy. There are different possible sustainable alterations to the conventional synthesis of MOFs, but these alterations can lead to lower surface area and pore volume, and consequently lead to a lower hydrogen storage capacity (HSC).

The most promising sustainable method of synthesizing MIL-101 without reducing the HSC is microwave-assisted synthesis. This method shows no large reduction in surface area, and thereby keeping the HSC the same as for conventionally synthesized MIL-101. A drawback to this method is that it is difficult to upscale, however using different reactor setups may still make this a good option, although this is not tried out yet. As for MOF-5, the most sustainable synthesis is a sonochemical synthesis, which shows promising results with approximately maintained surface area, and therefore also most likely maintained HSC. However, the synthesis has a poor yield, which reduces the sustainability. If the yield could be improved with further research, this could be both a time and energy efficient method, resulting in a sustainable synthesis with good HSC.

Plastic from PET-bottles is a global area of concern, and sustainable synthesis of MIL-101 and MOF-5 can be a small part of the solution of how to reduce plastic waste. By extracting BDC from PET-bottles, plastic waste is reduced whilst MIL-101 and MOF-5 can be synthesized with a sustainable linker. Combining this linker with either a mechanochemical, microwave-assisted or sonochemical synthesis, can lead to a green and sustainable production of MOFs. As reducing the CO_2 emission in the world by providing an effective hydrogen economy combined with reduced waste from PET-bottles is desirable, this is definitely an area that deserves more research in the future.

Finally, as for the question whether a sustainable synthesis of MOFs that reach the DOE targets is possible, no conclusion can be made yet, as this is heavily reliant on whether such a MOF is even possible to make. If a MOF that reach the target can be synthesized, it is possible to believe that different sustainable improvements can be done to the synthesis, as the result from this thesis shows that a more sustainable synthesis almost without reduction in HSC is possible.

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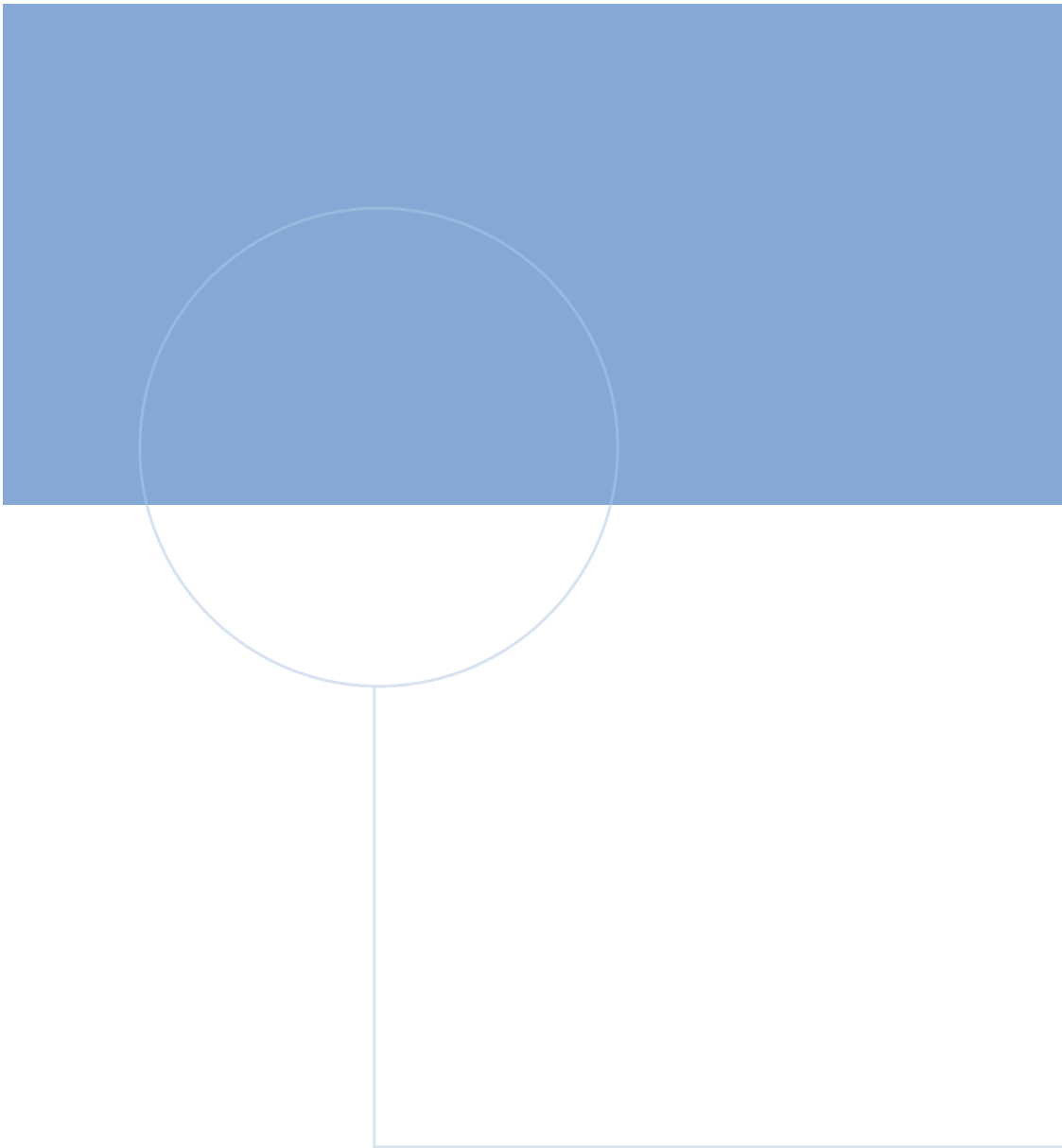

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