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# Abstract

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# 3.Exploring the impact of synthesis and defects on adsorption measurements

## 3.1. Introduction

Ideality is a rarely encountered phenomenon in nature. In fact, experience has shown that deliberate and concerted efforts must be made in order to obtain states of matter that have all the properties described by an “ideal state”. Often the divergence from ideality is small and can be approximated away, as is the case when assuming the ideal gas behaviour of noble gasses or ascribing the thermal radiation emitted by an object to a black-body spectrum. It is, however, in non-ideality where the fascinating complexity of the world asserts itself and where advances in our understanding can be found.

When considering crystals, the ideal description of an infinite periodic repetition of building blocks in three dimensional space is not applicable in the real world. From the necessary existence of crystal boundaries to the possible presence of other structural irregularities, these so called crystal “defects” can have varying effects on the bulk properties of the material. The presence of the defects is not necessarily a fault as they often impart the material with beneficial characteristics on multiple length scales. Crystal grain size and presence of additives such as carbon and nickel can completely change the hardness, ductility, tensile strength and corrosion resistance of steel.<sup>(1)</sup> An understanding of the interplay of defects in the lattices of alloys is an art in itself. Various other forms of disorder can introduce completely new behaviours altogether. The insertion of foreign elements into the crystal structure of semiconductor materials such as silicon can alter its electronic properties and is responsible for the ubiquitousness of computing devices based on the transistor.<sup>(2)</sup> This application of defects can be said to have ushered in the modern digital age, just as the creation of steel led to the industrial revolution. Other such emergent properties exist such as high temperature superconductivity,<sup>(3)</sup> or thermoelectric behaviour<sup>(4)</sup> which are influenced by defect-related spin effects or defect-mediated charge transfer. As such, the kind of heterogeneity afforded by defects is a key attribute in condensed matter physics and is a target for material design. The scientific foray in the control, either through generation or by inhibition of defects can be termed “defect engineering” and is another degree of freedom for material science.

As porous coordination polymers (PCPs) and their subclasses metal organic frameworks (MOFs) and covalent organic frameworks (COFs) became prominent topics of study in the field of porous materials the presence and desirability of defects in their ordered crystal structures has been put into question. Investigation of the propensity of these compounds to form defects has suggested potential benefits in the fields of catalysis,<sup>(5)</sup> gas storage and separation,<sup>(6–8)</sup> and has even alluded to applications in sensing and optoelectronics.<sup>(9)</sup> Furthermore, MOFs such as UiO-66 and similar oxo-Zr coordination

### 3. Exploring the impact of synthesis and defects on adsorption measurements

compounds have been shown to have intrinsically defective structures, where clustering and correlation of defects<sup>(10)</sup> is in fact energetically favoured. The engineering of defects in PCPs is currently the focus of many initiatives as it is seen as a highly desirable method of tuning their properties through judicious design .<sup>(11-13)</sup>

From the point of view of describing adsorption in such materials, the presence of defects introduces a conundrum. If a MOF can be defective, and is often intrinsically so, a slight change in synthesis conditions can introduce a large variability in its properties, and obtaining a “reference” isotherm may be a challenge. A large scale meta analysis of the correlation between material structure and its adsorption performance cannot be achieved unless the contribution of defects is assessed for each material.

In this chapter we explore the kind of changes in adsorption behaviour introduced through defect engineering with the high throughput processing tools presented in [chapter 1](#). First, the range of crystal defects that can be found in MOFs is presented. A summary of the known methods for controlling defects in such materials is discussed, as well as the known impact on different properties. Particular focus is placed on the zirconium variant of UiO-66, due to its aforementioned remarkable stability to the presence of defects. An alternative approach to defect generation in this MOF is explored, through induced leaching of linkers in a solvent solution of monotopic acids which have been shown to induce defect formation when present during synthesis. The influence on defect type and preponderence of the acid, its concentration and the solvent itself is investigated, through the changes in adsorption behaviour.

Should I mention DEFNET?

maybe put in overall intro?

## 3.2. The defective nature of MOFs

### 3.2.1. Types of crystal defects and their analogues in MOFs

From a crystallographic point of view, defects can be described as features which suspend the order of components in an ideally regular lattice. The building blocks in the case of MOFs can be either individual atoms, molecules or other higher order structural building units (SBUs). Any change with leads to local breaking of symmetry with respect to the original structure can be viewed as a defect.

With respect to dimensionality, defects can be described as point defects, line defects (such as edge dislocations), plane defects (such as grain boundaries or stacking faults) and bulk defects (macroscopic voids, phase coexistence). When it comes to point defects, we can broadly refer to several types: **substitutional defects**, where an existing building unit is replaced or transformed into another, **inclusion** or **interstitial defects**, where a foreign component or building block is included in the framework and **vacancy defects** where one of the lattice sites is unoccupied. In the context of MOFs, the same general categories of defects apply. However, due to the higher degrees of freedom available in these compounds, a greater variety of potential crystal defects can exist.

**Vacancy** defects are encountered through missing linker and missing cluster defects. These analogues of Schottky defects arise from the removal of one or several topological

### 3. Exploring the impact of synthesis and defects on adsorption measurements

nodes or vertices. In most cases, the charge neutrality of the framework is maintained through coordination of available counterions or solvent molecules through changes in the oxidation state of the metal atoms may also occur.

**Substitution** point defects are also highly common in MOFs, as the usual requirement for framework connectivity is the existence of “click groups” on metal nodes and linkers. Any piece which fulfils the connection and size requirements may be used, a property which has been exploited through the topological approach to creating new MOFs.<sup>(14–16)</sup> It also allows for MOFs in which nodes or vertices are partly replaced with analogues to be created. This strategy has been successfully employed to create mixed-linker or mixed-metal structures.<sup>(17,18)</sup> It should be noted that if the distribution of the substitutions takes a homogenous pattern throughout the lattice, the structure no longer falls under the definition of a defect.

A special case of substitutional defects which are present in MOFs are mixed valence defects. When metals with multiple stable oxidation states, such as Cu (I-II), Fe (II-III) etc. are part of the framework, a change in their oxidation state can occur. This has been shown to be an integral part of copper paddlewheel and iron trimesate containing MOFs<sup>(19)</sup> and can even be seen with the naked eye, as such defects have been shown to give HKUST-1 its common blue colour.<sup>(20)</sup>

**Inclusion**-type point defects are loosely applied to MOFs. As the definition describes an interstitial defect to be an atom occupying an usually vacant space, all foreign bodies occupying the available porosity of the MOF, including aforementioned counterions and solvents could be considered as defects in the traditional crystallographic sense. Introduction of nanoparticles such as metals or metal oxides inside the pores has also been studied, with beneficial effects in catalytical applications.<sup>(21)</sup>

A common feature of structured high porosity compounds is interpenetration. While not a defect in the classical sense, it has important effects on their properties.<sup>(22)</sup> With a large enough pore size, a secondary lattice can form in the pore voids of the primary one. This imposes a limit on the common design strategy of isoreticular synthesis, but can introduce new features such as better adsorption through confinement, increase in active site count and even flexibility.

Finally, the surface of the MOF can also be regarded as a boundary or plane defect. The nature of the surface plays a role in intra-particle interactions, important when considering the agglomeration behaviour or inclusion of crystals in a membrane.<sup>(23)</sup> The surface properties are also crucial in MOF films,<sup>(24,25)</sup> where the layers are better defined by interfacial characteristics than through bulk properties. Crystal size effects can also be through of as a consequence of surface characteristics, more specifically, of surface-to-volume ratio. When considering soft materials,<sup>(26,27)</sup> it has been shown that their flexible behaviour is highly influenced by the entropy barriers introduced by the surface.

#### 3.2.2. Consequences of defects

The introduction of defects in the regular crystal lattice of metal organic frameworks can have a dramatic impact on their properties. In general, the following may occur:

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defect  
types

### 3. Exploring the impact of synthesis and defects on adsorption measurements

- the porosity of the structured is altered, increasing in the case of vacancy defects and decreasing when bulky substitutions or inclusions are made;
- interactions with adsorbed molecules change, through the different pore environment encountered or through the generation of coordinatively unsaturated sites (CUS);
- the stability of the resulting structure is lower than that of the parent MOF, influencing bulk mechanical and thermal properties.
- electronic properties can be changed which may affect the optical electric or magnetic behaviour of the material.

From a purely geometric point of view, the introduction of missing linker or missing cluster defects leads to more voids in the structure, increasing its porosity. The better developed pore network has a large impact on the transport properties of the compound, leading to increased diffusion rates. It often results in a larger specific surface area and pore volume and thus useful for applications such as gas storage which depend only on the available surface or capacity.

The inclusion of defects also changes the landscape of the pore walls leading to different interactions with adsorbed molecules. Charge balancing counterions, molecules capping defect sites or functionalizations of substituted linkers or CUS can change the chemistry of the pore, with specific interactions towards certain adsorbates.<sup>(28)</sup> For example, adsorption of water on oxo-Zr MOFs, has been seen to be dominated by the percentage of defects. The pore filling step can shift from high partial pressure ( $0.6 p/p_0$ ) to much lower pressures as seen in UiO-66<sup>(7)</sup> and MOF-801.<sup>(6)</sup> Defect site adsorbed molecules can also lead to cooperative phenomena, such as the beneficial effect of defect-adsorbed water on the catalysis of Fischer esterification.<sup>(5)</sup> or the CO<sub>2</sub> capture on amine-grafted metal centers.<sup>(29)</sup> Another example can be seen in MOFs containing Fe trimers, such as MIL-127(Fe) or MIL-100(Fe) where heating or acid treatment can induce a reduction of one of the iron atoms to two, generating additional Lewis sites<sup>(19)</sup> or providing CUS for cooperative binding of carbon monoxide through a spin transition mechanism.<sup>(30)</sup>

Of course, defects are also problematic. Most metal organic frameworks synthesised to date suffer from poor stability. Even if the stability of the component parts is not an issue, the framework may not have enough structural stability to be able to sustain itself when fully evacuated. The activation process itself can lead to framework collapse, due to the forces encountered in guest removal, necessitating complex activation processes, such as supercritical drying or preliminary solvent exchange. After activation, the metal-ligand bond is susceptible to attack by adsorbed species. Here, defects in the framework have been shown to play a major role in its stability (or lack thereof).<sup>(31)</sup> Copper paddlewheel containing structures are particularly vulnerable to such attack.<sup>(32)</sup>

Finally, several completely different phenomena may emerge through the introduction of defects. Optical properties such as colour centers and induced luminescence,<sup>(20)</sup> changes in thermal conductivity or induced magnetic properties such as ferromagnetism<sup>(33)</sup> have been shown to be a consequence of the presence of defects.

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### 3. Exploring the impact of synthesis and defects on adsorption measurements

#### 3.2.3. Defect engineering of MOFs

Since defects introduce another degree of freedom for controlling the properties of metal organic frameworks, the study of their formation can lead to new methods of tuning a material towards a desired application. There are two major pathways of introducing defects, through control of the structure during synthesis or through post-synthetic methods.

For defect generation during synthesis, the so called “solid solution” approach is to mix several types of building blocks together, be it multiple linkers or metallic nodes. Mixing functionalised versions of linkers leads to the creation of partly-substituted MOFs. Mixed valency frameworks can also be synthesised through this method, as can be seen in the replacement of up to 32% of the linker in the framework in the ruthenium HKUST-1 analogue with a defect-generating linker.<sup>(34)</sup> The commonly used method of improving crystallinity and particle size of modulator-assisted synthesis<sup>(35)</sup> has been shown by Shearer et al. to be a reliable method of introducing defects.<sup>(36)</sup> The modulators act as capping agents and occupy metal coordination sites.

Post-synthetic methods are also widely employed for defect generation. Through acid treatment of the previously mentioned MIL-100(Fe), cleavage of one of the Fe–O bonds can be induced, with a protonation of the carboxylic linker and the generation of a CUS.<sup>(37)</sup> Thermal treatment can achieve the same results, with weakly coordinated molecules removed to expose metal CUS or even *in situ* linker decomposition.<sup>(38)</sup> Ligand exchange has also been shown to be achievable post-synthetically,<sup>(39)</sup> through the replacement of existing linkers, capping agents or even induce structural “healing”.

#### 3.2.4. The propensity of UiO-66(Zr) for defect generation

The UiO-66(Zr) MOF and its derivatives are well known due to their thermal and chemical stability.<sup>(40)</sup> It is composed of  $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$  clusters (seen in Figure 3.1a) which are connected with benzene dicarboxilate (BDC) linkers to form a face-centered cubic framework. Due to its exceptional stability among MOFs, it has been the focus of many studies, where it has shown promise<sup>(41)</sup> in use for gas adsorption and catalytic applications.

It has been used for a support for nanoparticles, such as palladium<sup>(42)</sup> or platinum.<sup>(43)</sup>

However, UiO-66 is particularly adept in its ability to support vacancy defects. Due to the stability of the Zr-O bond, and the high linker to metal ratio, the UiO family of MOFs can tolerate a high defectivity in their structure, which manifests through either missing linker (Figure 3.1b) or missing cluster (Figure 3.1c) defects. Ever since the discovery of a number of defects in the pristine material through neutron powder diffraction methods<sup>(44)</sup> and the theoretical basis laid down by Cliffe et al. for the existence of correlated defective nanodomains where the existence of a vacancy induces defect formation in neighbouring sites , this MOF became a prototypical framework for the study of defects. The modulated synthesis approach, initially used as a means of creating novel topologies and controlling crystal size<sup>(45)</sup> has been remarkably successful in obtaining defective versions of UiO-66(Zr).<sup>(36)</sup> Post-synthetic methods such as ligand

### 3. Exploring the impact of synthesis and defects on adsorption measurements

exchange,<sup>(39)</sup> temperature-induced dehydroxilation of the zirconium cluster<sup>(46)</sup> and thermal removal of one of the linkers in a mixed-linker variant<sup>(17)</sup> have been similarly adept in obtaining defective structures.

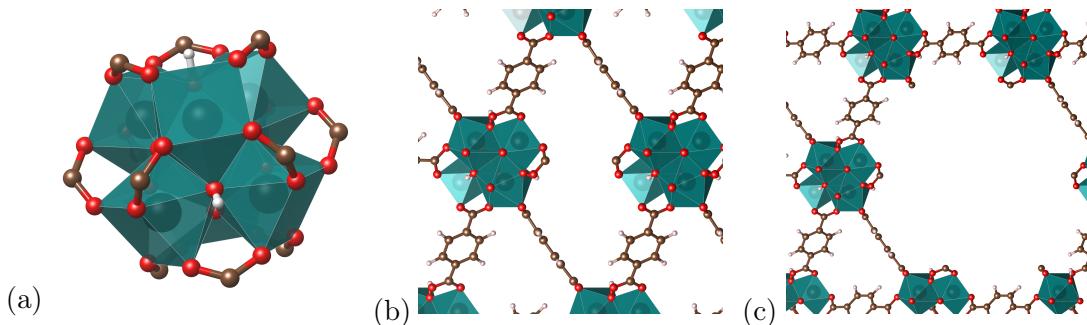


Figure 3.1.: (a) The 12-coordinated Zr cluster in UiO-66(Zr) which connects with benzene dicarboxilate (BDC) linkers. Two prototypical defect types are shown (b) a missing linker defect and (c) a missing cluster defect. Zirconium octahedra are represented in turquoise, oxygen in red, carbon in brown and hydrogen in white.

In these vacancy defects, the metal sites are almost always capped, with monoacids such as formate and acetate, water, hydroxil groups or other counterions being able to assume the role of capping agent. It has been shown by Thornton et al. that the influence of these defects on the adsorption properties depend not only on their position, but also on these capping agents.<sup>(47)</sup>

The presence of vacancy defects and more recently, the interplay between the two<sup>(48)</sup>

## 3.3. Materials and methods

### 3.3.1. Materials

The UiO-66(Zr) MOF used in this study was synthesised according to the procedure described in section B.4. This particular method was chosen to ensure that a structure with a minimal number of intrinsic defects would be obtained.

The material was then gestated in a solvent solution of modulator through.

To generate a comprehensive map of all of the potential influence of different variables on defect

### 3.3.2. Methods for quantifying defects

- X-ray diffraction - TGA -

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### **3.4. Results and discussion**

### **3.5. Conclusion**

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# A. Common characterisation techniques

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## A.1. Thermogravimetry

Thermogravimetry (TGA) is a standard laboratory technique where the weight of a sample is monitored while ambient temperature is controlled. Changes in sample mass can be correlated to physical events, such as adsorption, desorption, sample decomposition or oxidation, depending on temperature and its rate of change.

TGA experiments are carried out on approximately 15 mg of sample with a TA Instruments Q500 up to 800 °C. The sample is placed on a platinum crucible and sealed in a temperature controlled oven, under gas flow of  $40 \text{ cm}^3 \text{ min}^{-1}$ . Experiments can use a blanket of either air or argon. The temperature ramp can be specified directly and should be chosen to ensure that the sample is in equilibrium with the oven temperature and no thermal conductivity effects come into play. Alternatively, a dynamic “Hi-Res” mode can be used which allows for automatic cessation of heating rate while the sample undergoes mass loss.

The main purpose of thermogravimetry as used in this thesis is the determination of sample decomposition temperature, to ensure that thermal activation prior to adsorption is complete and that all guest molecules have been removed without loss of structure. To this end, experiments are performed under an inert atmosphere (argon), and the sample activation temperature is chosen as 50 °C to 100 °C lower than the sample decomposition temperature.

## A.2. Bulk density determination

Bulk density is a useful metric for the industrial use of adsorbent materials, as their volume plays a critical role in equipment sizing.

Bulk density is determined by weighing 1.5 ml empty glass vessels and settling the MOFs inside. Powder materials are then added in small increments and settled through vibration between each addition. The full vessel is finally weighed, which allowed the bulk density to be determined. The same cell is used in all experiments, with cleaning through sonication between each experiment.

## A. Common characterisation techniques

### A.3. Skeletal density determination

True density or skeletal density is determined through gas pycnometry in a Microtrac-BEL BELSORP-max apparatus. Helium is chosen as the fluid of choice as it is assumed to be non-adsorbing.

The volume of a glass sample cell ( $V_c$ ) is precisely measured through dosing of the reference volume with helium up to ( $p_1$ ), then opening the valve connecting the two and allowing the gas to expand up to ( $p_2$ ). Afterwards approximately 50 mg of sample are weighed and inserted in a glass sample cell. After sample activation using the supplied electric heater to ensure no solvent residue is left in the pores, the same procedure is repeated to determine the volume of the cell and the adsorbent. With the volume of the sample determined, the density can be calculated by.

$$V_s = V_c + \frac{V_r}{1 - \frac{p_1}{p_2}} \quad (\text{A.1})$$

### A.4. Nitrogen physisorption at 77 K

Nitrogen adsorption experiments are carried out on a Micromeritics Triflex apparatus. Approximately 60 mg of sample are used for each measurement. Empty glass cells are weighed and filled with the samples, which are then activated in a Micromeritics Smart VacPrep up to their respective activation temperature under vacuum and then back-filled with an inert atmosphere. After sample activation, the cells are re-weighed to determine the precise sample mass. The cells are covered with a porous mantle which allows for a constant temperature gradient during measurement by wicking liquid nitrogen around the cell. Finally, the cells are immersed in a liquid nitrogen bath and the adsorption isotherm is recorded using the volumetric method. A separate cell is used to condense the adsorptive throughout the measurement for accurate determination of its saturation pressure.

### A.5. Vapour physisorption at 298 K

Vapour adsorption isotherms throughout this work are measured using a MicrotracBEL BELSORP-max apparatus in vapour mode. Glass cells are first weighed and then filled with about 50 mg of sample. The vials are then heated under vacuum up to the activation temperature of the material and re-weighed in order to measure the exact sample mass without adsorbed guests. The cells are then immersed in a mineral oil bath kept at 298 K. To ensure that the cold point of the system occurs in the material and to prevent condensation on cell walls, the reference volume, dead space and vapour source are temperature controlled through an insulated enclosure.

## **A.6. Gravimetric isotherms**

The gravimetric isotherms in this thesis are obtained using a commercial Rubotherm GmbH balance. Approximately 1 g of dried sample is used for these experiments. Samples are activated *in situ* by heating under vacuum. The gas is introduced using a step-by-step method, and equilibrium is assumed to have been reached when the variation of weight remained below 30 µg over a 15 min interval. The volume of the sample is determined from a blank experiment with helium as the non-adsorbing gas and used in combination with the gas density measured by the Rubotherm balance to compensate for buoyancy.

# B.Synthesis method of referenced materials

## B.1. Takeda 5A reference carbon

The Takeda 5A carbon was purchased directly from the Takeda corporation. The sample was activated at 250 °C under secondary vacuum (5 mbar) before any measurements.

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## B.2. MCM-41 controlled pore glass

MCM-41 (Mobil Composition of Matter No. 41) is a mesoporous silica ( $\text{SiO}_2$ ) material with a narrow pore distribution. First synthesised by the Mobil Oil Corporation, it is produced through templated synthesis using mycelle-forming surfactants. The material referenced in this thesis was purchased from Sigma-Aldrich. The activation procedure consists of heating at 250 °C under secondary vacuum (5 mbar).

## B.3. Zr fumarate MOF

The synthesis of the Zr fumarate was performed in Peter Behren's group in Hannover, through modulated synthesis. This MOF can only be synthesised through the addition of a modulator, in this case fumaric acid, to the ongoing reactor, as detailed in the original publication.<sup>(?)</sup>

The procedure goes as follows:  $\text{ZrCl}_4$  (0.517 mmol, 1 eq) and fumaric acid (1.550 mmol, 3 eq) are dissolved in 20 mL N,N-dimethylformamide (DMF) and placed in a 100 mL glass flask at room temperature. 20 equivalents of formic acid were added. The glass flasks were Teflon-capped and heated in an oven at 120 °C for 24 h. After cooling, the white precipitate was washed with 10 mL DMF and 10 mL ethanol, respectively. The washing process was carried out by centrifugation and redispersion of the white powder, which was then dried at room temperature over night

## B.4. UiO-66(Zr) for defect study

The UiO-66(Zr) sample preparation was adapted from Shearer et al. <sup>(?)</sup> as follows:  $\text{ZrCl}_4$  (1.55 g, 6.65 mmol), an excess of terephthalic acid (BDC) (1.68 g, 10.11 mmol), HCl 37 % solution (0.2 mL, 3.25 mmol) and N,N'-dimethylformamide (DMF) (200 mL, 2.58 mol) were added to a 250 mL pressure resistant Schott bottle. The mixture was stirred for 10 min, followed by incubation in a convection oven at 130 °C for 24 h. The resulting white precipitate was washed with fresh DMF (3× 50 mL) followed by ethanol (3× 50 mL) over the course of 48 h and dried at 60 °C. After drying, the sample was

### *B. Synthesis method of referenced materials*

activated on a vacuum oven by heating at 200 °C under vacuum for 12 h. The yield was 78 % white microcrystalline powder. Before the experiment, the sample was calcined at 200 °C under vacuum (5 mbar) to remove any residual solvents from the framework.

## **B.5. UiO-66(Zr) for shaping study**

The scaled-up synthesis of UiO-66(Zr) was carried out in a 5 L glass reactor (Reactor Master, Syrris, equipped with a reflux condenser and a Teflon-lined mechanical stirrer) according to a previously reported method.<sup>(?)</sup> In short, 462 g (2.8 mol) of H<sub>2</sub>BDC (98%) was initially dissolved in 2.5 L of dimethyl formamide (DMF, 2.36 kg, 32.3 mol) at room temperature. Then, 896 g (2.8 mol) of ZrOCl<sub>2</sub> · 8H<sub>2</sub>O (98%) and 465 mL of 37% HCl (548 g, 15 mol) were added to the mixture. The molar ratio of the final ZrOCl<sub>2</sub> · 8H<sub>2</sub>O/H<sub>2</sub>BDC/DMF/HCl mixture was 1 : 1 : 11.6 : 5.4. The reaction mixture was vigorously stirred to obtain a homogeneous gel. The mixture was then heated to 423 K at a rate of 1 K min<sup>-1</sup> and maintained at this temperature for 6 h in the reactor without stirring, leading to a crystalline UiO-66(Zr) solid. The resulting product (510 g) was recovered from the slurry by filtration, redispersed in 7 L of DMF at 333 K for 6 h under stirring, and recovered by filtration. The same procedure was repeated twice, using methanol (MeOH) instead of DMF. The solid product was finally dried at 373 K overnight.

## **B.6. MIL-100(Fe) for shaping study**

The synthesis of the MOF for the shaping study was done at the KRICT institute using a previously published method.<sup>(?)</sup> To synthesise the MIL-100(Fe) material Fe(NO<sub>3</sub>)<sub>3</sub> was completely dissolved in water. Then, trimesic acid (BTC) was added to the solution; the resulting mixture was stirred at room temperature for 1 h. The final composition was Fe(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O : 0.67 BTC : n H<sub>2</sub>O (x = 55–280). The reactant mixture was heated at 433 K for 12 h using a Teflon-lined pressure vessel. The synthesized solid was filtered and washed with deionized (DI) water. Further washing was carried out with DI water and ethanol at 343 K for 3 h and purified with a 38 mM NH<sub>4</sub>F solution at 343 K for 3 h. The solid was finally dried overnight at less than 373 K in air.

## **B.7. MIL-127(Fe) for shaping study**

MIL-127(Fe) was synthesized by reaction of Fe(ClO<sub>4</sub>)<sub>3</sub> · 6 H<sub>2</sub>O (3.27 g, 9.2 mmol) and C<sub>16</sub>N<sub>2</sub>O<sub>8</sub>H<sub>6</sub> (3.3 g) in DMF (415 mL) and hydrofluoric acid (5 M, 2.7 mL) at 423 K in a Teflon flask. The obtained orange crystals were placed in DMF (100 mL) and stirred at ambient temperature for 5 h. The final product was kept at 375 K overnight. MIL-127(Fe) was synthesized by reaction of Fe(ClO<sub>4</sub>)<sub>3</sub> · 6 H<sub>2</sub>O (3.27 g, 9.2 mmol) and C<sub>16</sub>N<sub>2</sub>O<sub>8</sub>H<sub>6</sub> (3.3 g) in DMF (415 mL) and hydrofluoric acid (5 M, 2.7 mL) at 423 K in a Teflon flask.

*B. Synthesis method of referenced materials*

The obtained orange crystals were placed in DMF (100 mL) and stirred at ambient temperature for 5 h. The final product was kept at 375 K overnight.