



**University of
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**Synthesis of MOFs for Carbon Capture
Application**

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Abstract

The work in this thesis focuses on the synthesis of metal organic frameworks (MOFs) both in batch and continuous work. Improvements are made in both, compared to the previous research. Furthermore, post-modification experiments are conducted to advance the characteristics of end product. Also, their application as solid sorbents in carbon capture is investigated.

In Chapter 1, the background of greenhouse gas emissions is reviewed and discussed, followed by the development of carbon capture technologies and different adsorbents used in post-combustion carbon capture. An introduction to metal organic frameworks is then presented, including a literature review of the research to date, and various synthesis methods including batch and continuous routes. The last part of this chapter presents a literature review on how pre-synthetic design and post-synthetic modification synthesis of MOFs can be achieved. The theories and introductions of the characterization techniques used in this thesis are discussed in detail in Chapter 2.

Chapter 3 discusses a new batch method for the efficient synthesis of micro-sized HKUST-1 with high yield (84%) under mild conditions. Different activation methods are conducted in the washing process. Both ethanol and methanol are tested to remove the impurities in pores of the samples. Finally, the optimal sample of HKUST-1 achieved is shown to produce a relatively high surface area ($1615 \text{ m}^2/\text{g}$) with a CO_2 adsorption of 8.1% (measured by TGA at 1 atm and 27°C). A step increase in the surface area is made by immersing the powders into a solution consisting of NaCl, water and methanol.

Nano scale HKUST-1 is synthesized by adding trimethylamine (TEA) solution with the organic ligand precursor. The reaction rate is accelerated with this case because TEA solution is able to deprotonate the trimesic acid (the organic ligand). The method for nano scale HKUST-1 synthesis is the focus of Chapter 4.

Chapter 5 reports the continuous synthesis process of HKUST-1 and ZIF-8. This work builds on previous work at Nottingham. A counter-current Nozzle reactor is used in this work. The products were compared with commercial equivalents. Post-synthetic modification of HKUST-1 was made to improve the

hydrophobicity of HKUST-1 to extend its resilience to breakdown in the presence of moisture.

In Chapter 6, a hybrid material $\text{TiO}_2\text{@ZIF-8}$ is synthesized using the same reactor. Different reactor configurations were also used to generate a range of different products that are then compared.

To conclude, a summary of the work conducted in this thesis is presented in Chapter 7, followed by a discussion on potential future work.

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Achievements

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List of Abbreviations

BET	Brunauer–Emmett–Teller
CFD	Computational Fluid Dynamics
cm	Centimeter
FP7	Seventh Framework Programme
FT-IR	Fourier transform-Infrared Spectrum
Gr	Grashof number
LAI	Light adsorption imaging
mm	Millimeter
mmol	Milli mole
MOF	Metal-organic framework
nm	Nanometer
NP	Nanoparticles
P_c	The critical pressure
PVA	Polyvinyl alcohols
Re	Reynolds number
SBU	Secondary building unit
SChEME	School of Chemical, Environmental and Mining Engineering
S_cW	Supercritical water
scWHS	Supercritical water hydrothermal synthesis
SEM	Scanning electron microsocpy

T _c	The critical temperature
TGA	Thermogravimetric analysis
UV	Ultraviolet
μm	Micrometer
XRD	X-ray diffraction
ZIF	Zeolitic imidazolate framework

List of Symbols

%	percent
°	degree
Å	angstroms
S	second
θ	incident angle
λ	wavelength
<	less than
>	more than
h	hour

Chapter 1 Background

1.1 Carbon Capture

Carbon dioxide, as one kind of greenhouse gases, has a significant effect on the global climate. The motivation of this work is to mitigate the carbon dioxide emissions in the atmosphere. In this section, the current status of the climate change and the carbon capture technology development are reviewed.

1.1.1 Effects of Carbon Dioxide on Climate Change

Greenhouse gases are able to trap heat in the atmosphere, which makes the surface of the earth become warmer and consequently contributes to climate change [1, 2]. Carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and fluorinated gases are the main greenhouse gases that cause global warming [3, 4]. The Intergovernmental Panel on Climate Change (IPCC) recently estimated the global greenhouse gas

emissions in 2014 as illustrated in Figure 1.1. According to this inventories, carbon dioxide contributed the most and is therefore regarded as the main promoter for climate change [5]. Among this, 65% of the CO₂ was from fossil fuels used in industrial processes, 11% was caused by forestry and other land use through growth of trees and increase in soil carbon [6]. Unfortunately, greenhouse gas levels rise year by year and broke the alarming red line in 2013.

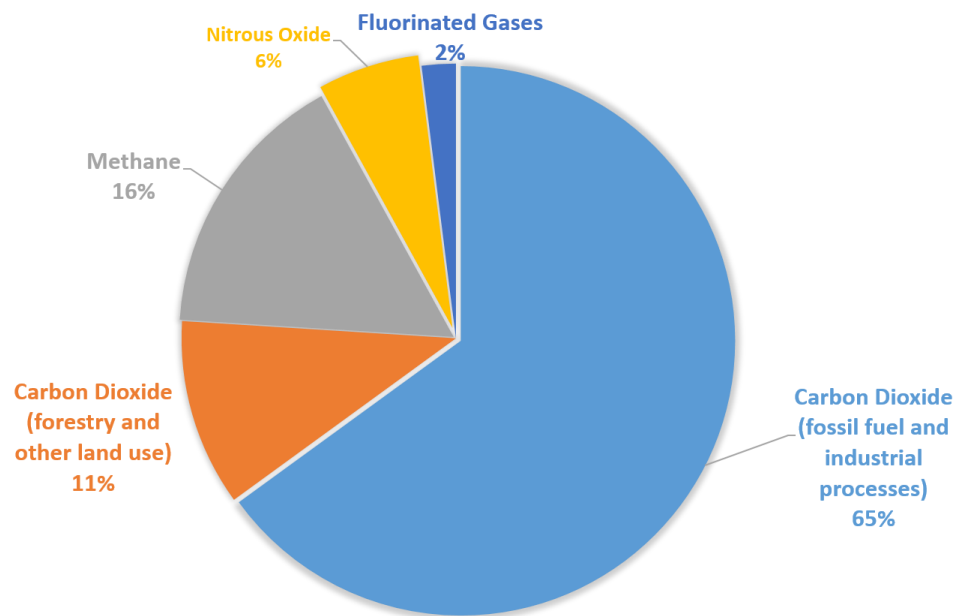


Figure 1. 1 Global greenhouse gases emission percentage in 2014 (Data is collected from IPCC [6])

In May 2013, CO₂ concentrations in the atmosphere reached the critical value of 400 ppm for the first time in human

civilization. The yearly average of CO₂ concentration exceeded 400 ppm in 2015. This become worse in September 2016 when the CO₂ level exceeded 400 ppm even at the annual minimum [7]. This event potentially implies that the CO₂ concentration will never fall down below 400 ppm in our lifetime. The curve in Figure 1.2 depicts the increasing trend of CO₂ concentration from 2005 to 2018. Clearly, it can be seen that CO₂ level is growing every year. This alarming trend has forced all countries to take serious measures to reduce CO₂ emissions [8].

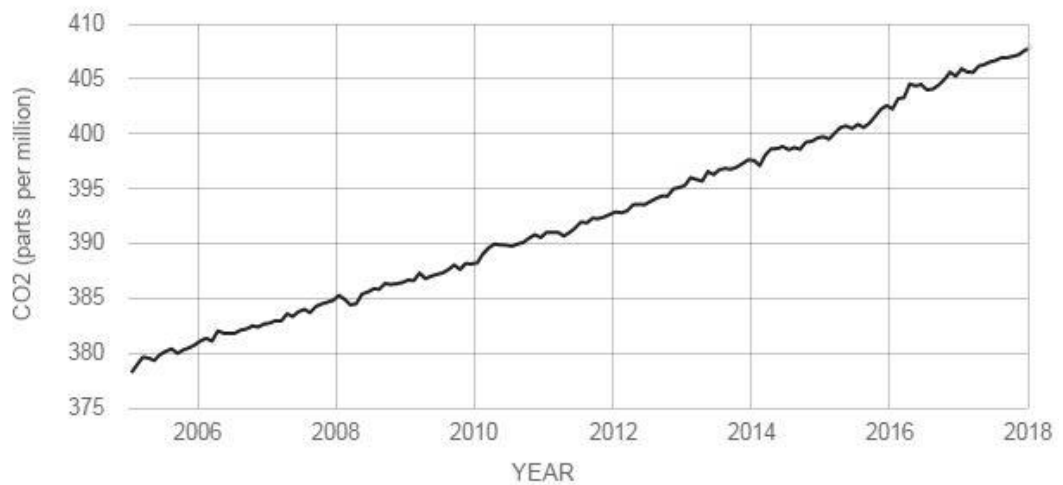


Figure 1. 2 CO₂ concentration in atmosphere from 2005 to present [9]

As mentioned above, most CO₂ emissions are produced from fossil fuel used in industrial processes. However, currently over 85% of global energy demand relies on the burning of fossil fuels

[10], and fossil fuels will possibly remain as the dominant source of primary energy demand for the next few decades [11, 12]. As a result, industrialized countries have been forced to reduce the greenhouse gas emission according to the Kyoto Protocol [13]. Thus, effective approaches to mitigate CO₂ emissions from industries are urgently required.

One of the most promising techniques is carbon capture and storage (CCS) [14]. According to the estimation of the Intergovernmental Panel on Climate Change (IPCC), 80-90% of CO₂ emissions released into the atmosphere could be reduced via the use of a modern conventional power plant equipped with carbon capture and storage technology [15].

1.1.2 Technologies for CO₂ Capture and Storage

Carbon capture and storage (CCS) is the process for CO₂ capture, transportation and storage [14, 16]. Based on the general process for the combustion of fossil fuels, there are three major methods used for CO₂ separation and capture: pre-combustion capture, oxy-fuel combustion and post-combustion capture [15, 17]. The pre-combustion capture and oxy-fuel combustion methods may incur substantial costs due to

necessary modifications to the existing plant [18] such as the capital cost involved in setting up the facilities for H_2 separation from CO_2 (in pre-combustion capture) and O_2 separation from air (in oxy-fuel combustion), as shown in Figure 1.3. As the post-combustion capture method can deal with the outlet gas directly released from the original plant, it is considered to be the most marketable technology [19, 20]

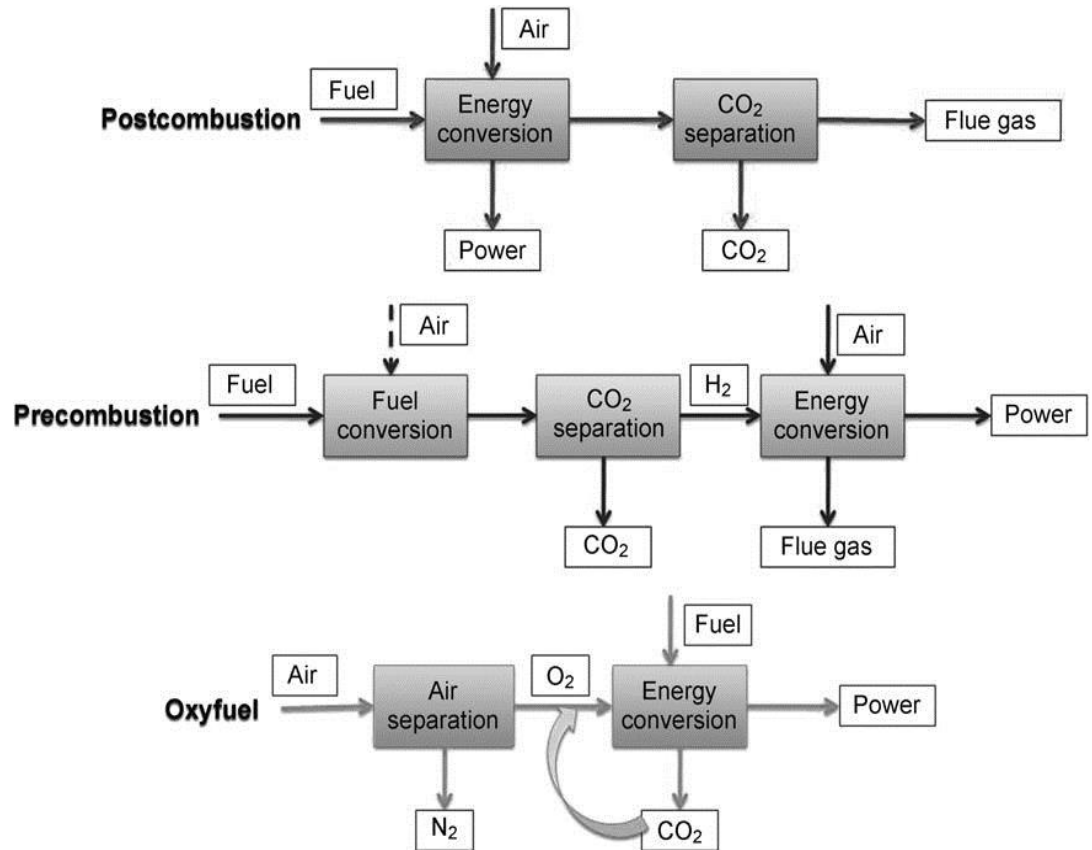


Figure 1. 3 Post-, pre- and oxyfuel combustion processes [21]

The post-combustion CO₂ capture is usually achieved by chemisorption or physisorption [22]. Amine scrubbing is one of the chemisorption processes in which the alkanolamines like monoethanolamine (MEA) solution is used as an absorbent [23, 24]. The CO₂ combines with the amine group in the absorbent and generates carbamate or bicarbonate [25, 26]. The remaining gas will flow through the absorption tower, and the diluted absorbent needs to be regenerated for reuse [25]. Such methods are also known as 'wet-scrubbing' technology which has been adopted in industries for more than 50 years with the primary alkanolamine MEA being the most dominant absorbent [25].

A recent analysis stated that the minimum thermodynamic energy penalty to capture 90% of CO₂ from the flue gas of a conventional power plant (assuming 12-15% CO₂ is contained in the flue gas at 40 °C) is 3.5% [27]. However, by contrast, current carbon capture systems using amine scrubbers present 25-40% energy penalty to achieve 90% CO₂ capture during the regeneration process on plant operation [28]. Obviously, the existing technology is energy intensive and not economical for reducing CO₂ emissions. In addition to the high energy/heat requirements, amine based absorption also present other

disadvantages: (i) extra corrosion control for the installation needed, (ii) loss of activity of the solvents caused by mixing of by-products, such as SO_x and NO_x . As a result, the power/energy requirement would increase while the efficiency declines [29].

A wide variety of the other materials can be employed in CO_2 adsorption technology e.g. solid adsorbents [30] have been considered as a promising method for carbon capture [27]. The main advantage of solid adsorbents is the lower energy consumption in the regeneration process achieved by thermal or pressure adjustment [31].

Carbon storage is also an important part in the CCS technology after CO_2 gas is captured. In this process, CO_2 is placed into a subsurface formations in order to achieve a safely and permanently storage way.

1.1.3 Materials for Adsorption based Carbon Capture

Songolzadeh et al. [31] discussed several significant factors for the adsorption process in their review: (i) the regeneration procedure, (ii) robustness of the adsorbent, (iii) selectivity for CO_2 , (iv) capacity of the adsorbent and (v) stability of the material after several adsorption/desorption cycles [31].

There are many different porous materials including natural, synthetic, organic, inorganic, crystalline and amorphous substrates [32]. Whilst many types exist, the most commonly used materials are inorganic and the carbon-based types of solid porous material in industry [33]. In this section, recent developments in CO₂ capture and separations using zeolites, activated carbon, amine functionalized adsorbents and metal organic frameworks (MOFs) are reviewed.

1.3.1.1 Zeolites

Zeolites are aluminosilicate minerals composing of alumina (AlO₄) and silica (SiO₄), which are highly ordered porous crystals [34]. The presence of aluminum in the structure forms a negative charge which can be compensated for by other cations such as alkali or alkaline-earth metals. Thus, zeolites are solids often containing the elements of aluminum, oxygen, silicon, sodium, potassium and magnesium with water molecules trapped in between them [35]. These alkali cations are able to attract CO₂ (acid gas) [36]. Therefore, a low silicon to aluminum ratios in the zeolites is ideal for the application in carbon capture [37].

It was reported that zeolites are hydrophilic materials so they are likely to be more sensitive to water than acid gases [37], and the water molecules will be favorably adsorbed to the alkali cation, leading to a large reduction in CO₂ adsorption capacity [38]. As a result, with zeolites used in the adsorption, the impurities such as SO_x, NO_x, and H₂O present in the flue gas are required to be removed. Zeolites perform better CO₂ adsorption under mild conditions (0-100 °C, 0.1-1 bar CO₂) than at elevated temperatures and humid environments. The amounts of CO₂ uptake ranges from 0.004 to 0.216 g CO₂/g zeolite at mild operating conditions [36].

The mechanism of CO₂ adsorption by zeolites is generally classified as physical adsorption, or physisorption, but several studies have revealed that chemisorption, or chemical adsorption also takes place in the process [39]. CO₂ is irreversibly adsorbed on the zeolite surface, forming carbonates and carboxylates. The chemisorbed CO₂ is not able to be released from zeolites via a pressure swing desorption process [40]. Thermal regeneration reduces capacity and the adsorption capacity reduces in a range of 0.007 to 0.022 g CO₂/g zeolite [41, 42] However, complete regeneration can be achieved by temperature swing, which

requires a highly elevated temperature around 350 °C [36]. Pressure swing adsorption (PSA) and thermal-swing adsorption (TSA) are two methods used for the regeneration when the adsorbent is saturated [43].

In conclusion, zeolites are useful due to the high CO₂ capacity at mild conditions which meet the requirements for post combustion. However, the adsorption efficiency can be adversely affected by the presence of NO_x, SO_x, and H₂O. In addition, the complete adsorbent recovery requires intensive energy consumption due to the chemisorption.

1.3.1.2 Activated Carbons

Activated carbons are carbonaceous and highly porous adsorbents with a low material costs [37]. This is because they can be produced from a wide variety of cheap resources such as coals, wood, industrial byproducts, etc.[44]. The large range of raw sources will lead to significant differences in the textural properties (e.g. pore distribution, pore size), resulting in different performances between activated carbons as the adsorbents.

Similar to zeolites, activated carbons can be tremendous sensitive to H₂O. It was reported that a bamboo activated carbon

went through a 75% reduction in capacity when exposed to a humid atmosphere [36]. Moreover, NO_x and SO_x impurities in the gas flow will compete with CO_2 gas for the adsorption sites. Therefore, pretreatment is required to remove these gas impurities.

The optimal CO_2 adsorption temperature for activated carbon is from 25 to 75 °C and like most other adsorbents, the ability of CO_2 adsorption decreases with an increase in temperature [45]. Activated carbons can reach equilibrium within a few minutes. In comparison with zeolites, activated carbons present a slightly lower ability to adsorb CO_2 at moderate conditions (0.1-1 bar CO_2 and 25-75 °C), which is around 0.003-0.154 g CO_2 /g activated carbon [36]. However, when the pressure increases the adsorption efficiency of activated carbons becomes higher than that of zeolites. Sircar et al. [46] has reported that under 10 bar CO_2 partial pressure and ambient temperature, activated carbon PX21 showed a capacity of 0.44 g CO_2 /g adsorbent, whereas zeolite 5A only demonstrated half of this capacity. Another study investigated activated carbon G-32H and zeolite 4A and 13X, discovering that activated carbon had a lower CO_2 capacity when the CO_2 pressure was below 1.7 bar, but a superior capacity was

recorded with CO₂ pressure above 1.7 bar [47]. The noticeable increase in CO₂ capacity under raised pressure implies that activated carbons are more suitable for pre-combustion capture than post-combustion system [48]. According to Kikkinides et. al. [49], activated carbons have a lower heat of adsorption compared to zeolites. Thus, regeneration process could be easily achieved by a pressure swing technology rather than temperature swing, indicating that lower energy and less time would be consumed [37].

In summary, activated carbons can be made from cheap resources and the regeneration costs are lower than zeolites. However, pretreatment of the gas stream from industries is necessary when employing either material as an adsorbent for CO₂ capture. In addition, the improved CO₂ adsorption performance of activated carbons in the elevated pressure suggests that they are more appropriate for pre-combustion utilization.

1.3.1.3 Amine Functionalized Adsorbents

Amine functionalized adsorbents refer to materials comprising of silicas as support with amine immobilized on it [50].

Poly(ethyeneimine) (PEI) is the most common used amine addition due to its high amine content (33% nitrogen by weight) [36]. The operating temperature for these adsorbents is around 50 to 75 °C. Amine contained adsorbents are easily decomposed at temperature around 100 °C [51]. Also, NO_x and SO_x impurities must be removed because they would irreversibly react with amines [52].

There is no need to remove water from the flue gas when using amine based adsorbents, which is a big difference to other adsorbents [53]. Furthermore, the presence of water can even enhance the adsorption efficiency because of the formation of bicarbonate [54]. It has been shown that a molar ratio of 1:1 for CO₂ to H₂O is the optimal adsorption condition [36]. Yue et al. [55] evaluated CO₂ adsorption capacity of SBA-15 silica immobilized by TEPA and DEA in a humid atmosphere and found a 20% increase in CO₂ adsorption. Additionally, the silica support can also significantly influence adsorption efficiency. Ordered silica frameworks are more superior to amorphous silica supports with regards to an even pore size distribution. Consequently, the amine can be uniformly impregnated into the pores [55].

Another distinction with the previously mentioned adsorbents is that the adsorption abilities of amine adsorbents are not affected by the pressure of CO₂ gas [56]. This means amine functionalized adsorbents are applicable for post-combustion system. The CO₂ capacities at 25-75 °C and 0.05-1 bar can be between 0.089 to 0.22 g CO₂/adsorbent [36, 50, 57].

To conclude, amine adsorbents possess the advantages of: (i) minimal impact from CO₂ pressure, (ii) perform even better in humid environments, (iii) have a relatively high CO₂ capacity while the disadvantages are: (i) easy to be destroyed at elevated temperature (>100 °C), (ii) desorption requires intensive energy input and time is needed via the temperature swing process because of the chemisorption kinetics, (iii) 4-9% capacity loss can occur after regeneration [44].

1.3.1.4 Metal Organic Frameworks (MOFs)

Metal organic frameworks (MOFs), as a new class of porous solid material, have shown great potential in the area of CO₂ capture [32]. The high surface area of MOFs is a significant property that can result in high CO₂ uptake capacity [58]. Temperature and pressure can both affect CO₂ storage capacity

measurements. The relationship between surface area and CO₂ capacity was first systematically analyzed by Yaghi et al. [32]. Nine MOFs were selected in the publication for comparison (listed in Figure 1.4 and Table 1.1) [59]. Generally, MOFs possessing higher CO₂ uptake capacity have higher surface areas. However, although the surface area of MOF-505 is nearly twice as high as that of MOF-74, 1,547 m² g⁻¹ and 816 m² g⁻¹, respectively, the CO₂ adsorption of MOF-74 is slightly higher than that of MOF-505 (Figure 1.4). This can be explained by the influence of the adsorbent-adsorbate interactions which would ultimately affect CO₂ capacity in MOF materials [58].

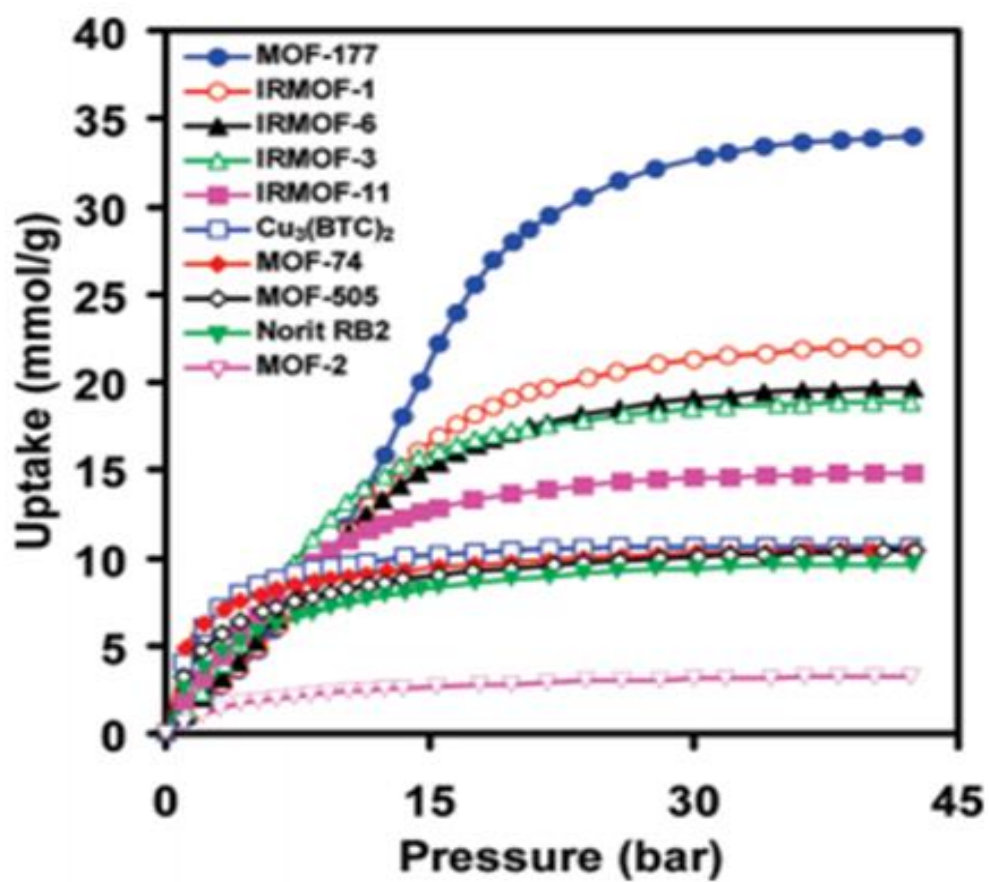


Figure 1. 4 Comparisons of CO₂ capacities for several MOFs up to 42 bars [59]

Table 1. 1 Comparison of CO₂ capacities for several MOFs at 35 bar and 298 K [58]

Chemical Formula	Common Name	BET Surface Area (m ² /g)
Zn ₂ (BDC) ₂	MOF-2	345
Cu ₂ (BPTC)	MOF-505	1,547
Zn ₂ (DOBDC)	Zn-MOF-74	816
Cu ₃ (BTC) ₂	HKUST-1	1,781
Zn ₄ O(HPDC) ₃	IRMOF-11	2,096
Zn ₄ O(NH ₂ BDC) ₃	IRMOF-3	2,160
Zn ₄ O(C ₂ H ₄ BDC) ₃	IRMOF-6	2,516
Zn ₄ O(BDC) ₃	IRMOF-1	2,833
Zn ₄ O(BTB) ₃	MOF-177	4,508

MOF-177 shows the best performance in CO₂ storage capacity when the pressure goes higher than 15 bar (Figure 1.4). The capacity of each material increases as pressure rises. However, for the purpose of dealing with CO₂ from flue gas at ambient pressures is more relevant.

Among these high surface area materials, HKUST-1 [Cu₃(BTC)₂(H₂O)·XH₂O (BTC=1,3,5-benzentricarboxylate)] is the

first MOF that was manufactured on an industrial scale, and it has been commercialized under the name of Basolite® C300 by BASF. [60]. HKUST-1 shows relatively high gas adsorption due to a partial positive charge present on the metals and the van der Waals surface interactions [61]. The CO₂ uptake amount at 0.9 bar and 295 K is 4.5 mmol g⁻¹ (19.9%) [33, 62].

Although the CO₂ capacity of MOF materials is a significant indicator of potential for CO₂ removal, the high gas selectivity is also of paramount importance to capture CO₂ in the flue gases. It is pointed out that being exposed to mixtures of different gases under various conditions, the capacities of MOFs would be reduced drastically in some cases [63]. Therefore, studies on selective adsorption are of fundamental importance. In the majority of reports, single-component isotherms and the IAST (Ideal Adsorbed Solution Theory) are used to measure the selectivity factor of a material. Although the calculation cannot be totally accurate as the theory does not take every experimental variable into consideration, the calculated result is valuable as a reference [64].

In accordance with recent research, MOF materials have shown great potential to separate CO₂ over other gases (such as H₂, N₂, O₂, and CH₄) [65, 66] Usually there are two main mechanisms involved in gas adsorptive separation of rigid MOFs, namely size/shape exclusion, and adsorbate-adsorbent interactions [33].

The CO₂ molecule has smaller kinetic diameter (3.3 Å) compared to most gases (except H₂, He, NO, H₂O, and NH₃) [67]. The comparison results are listed in Table 1.2. Efficient separation can be achieved by control of the pore size so that it lies between the kinetic diameters of CO₂ and other gases [68]. One example is Er₂(PDA)₃, which contains effective pore window size of 3.4 Å. This material almost cannot adsorb N₂ or Ar but shows a considerable adsorption of CO₂ [69].

Table 1. 2 Kinetic Diameters for Several Gases

Gas	He	NH	H₂O	H₂	NO	CO₂
Molecule	3					
Kinetic	2.60	2.6	2.65	2.89	3.17	3.30
Diameter (Å)	0					
Gas	Ar	O₂	N₂	CO	CH₄	
Molecule						
Kinetic	3.40	3.4	3.64	3.76	3.80	
Diameter (Å)	6					

Apart from the pore size of the adsorbent, the nature of the adsorbate-surface interaction is also a determining factor that plays a role in the adsorptive separations of guest gases [70]. For example, CO₂ possesses a higher quadrupole moment than other gases (e.g. N₂, H₂, and CH₄) thus endowing CO₂ with stronger adsorbate-adsorbent interactions which, in most cases, leads to a higher selective uptake of CO₂ over other gases [71]. A strategy of pre-designing ligands or post-synthetically modifying MOFs in order to tune these interactions has been broadly explored [33]. Long and co-workers compared MOF-253

[Al(OH)(bpydc), bpydc=2,2'-bipyridine-5,5'-dicarboxylate] and MOF-253·0.97Cu(BF₄)₂ with regards to the adsorption selectivity of CO₂ over N₂. They found that after inserting metal ions the selectivity is significantly enhanced from 2.8 to 12 [72].

There are also opportunities to combine the effect of size dependence with adsorbate-adsorbent interactions [73]. This cooperative effect is usually evident in dynamic MOFs, where the pore size changes reversibly resulting from different adsorbate-surface interactions. This restricts some molecules from entering [74]. MIL-53 (M(OH)(bdc), M = Al or Cr) is an example of this type of selective adsorption. Huxford et al. demonstrated the different adsorption curves for CO₂ and CH₄ by MIL-53 [75]. It can be easily seen that CO₂ uptake was significantly higher than that of CH₄ when the pressure was increased. This can be explained by a "breathing" mechanism where the strong interaction of CO₂ molecules with the framework causes pore shrinkage and reopening at high pressure, while CH₄ cannot cause this structural change [76]. When the gas is a mixture of CO₂ and CH₄, the mechanism works in a similar way to pure CO₂ [77] but the extent of the "breathing" decreases when CH₄ content increased, and the selectivity of CO₂ decreases with

increasing pressure. Therefore, to achieve an effective selective adsorption, a pressure swing adsorption (PSA) strategy is probably feasible with MIL-53(Al) [78].

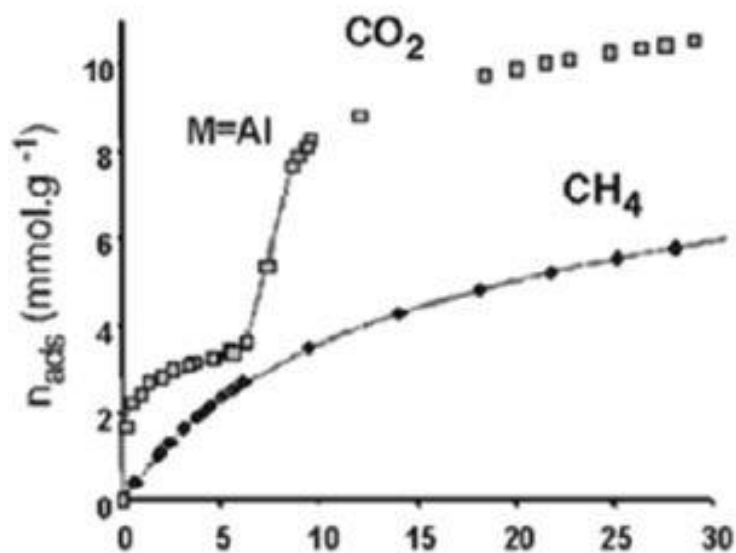


Figure 1. 5 Adsorption isotherms of CO₂ and CH₄ on MIL-53 at 304K [33]

Zeolitic imidazolate frameworks (ZIFs) consisting of M-Im-M bridges (where M is Zn, Co and Im stands for imidazolate linker) have recently emerged as a novel subclass of MOFs[79]. These materials are similar to traditional zeolites, where M ions mimic the role of silicon and the Im anions play the role of the oxygen in zeolite frameworks. The angle of the bridge between M-Im-M is around 145°, which is similar to the Si-O-Si bridges found in

zeolites as shown in Figure 1.6 [80]. The series of ZIFs is a highly useful type among MOFs due to its high chemical and thermal stability. In particular, ZIF-8 (2-Methylimidazole zinc salt) is one of the most extensively studied ZIF materials because of its potential use for gas storage and separations [81]. ZIF-8 possesses large surface areas but small apertures (11.6 and 3.4 Å in diameter respectively, shown in Figure 1.7). Theoretically, molecules with sizes bigger than 3.4 Å are not allowed to pass through the framework. However, it is experimentally observed that methane (3.8 Å) and nitrogen (3.6 Å) are adsorbed. This unexpected adsorption phenomenon is possibly ascribed to the structural flexibility of ZIF-8 [82]. Fairen et al. [83] utilized grand canonical Monte Carlo simulations (GCMC) to explore the flexibility in ZIF-8 and demonstrated that ZIF-8 structure changes in the same way during gas adsorption and at a very high pressure (i.e., 1.47 GPa). This behaviour can be explained by a swing effect in the imidazolate linkers. A strategy to control this effect is changing the functional group on the imidazolate linker which can contribute to tuning the opening of smaller windows [83]. A post synthetic modification method to enhance

the CO₂ adsorption and CO₂/N₂ selectivity for ZIF-8 will be discussed in Section 1.3.2.

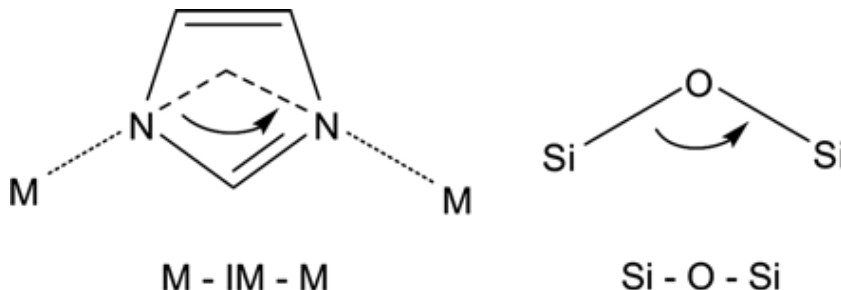


Figure 1. 6 M-Im-M and Si-O-Si bridge [84]

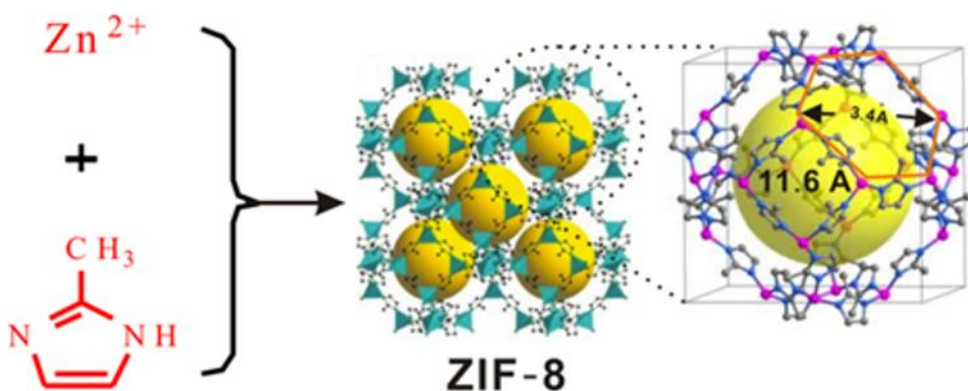


Figure 1. 7Figure 1.7 ZIF-8 framework [85]

1.2 Metal Organic Frameworks Synthesis

MOFs are hybrid materials combining organic ligands and metal ions or metal-containing clusters. Compared to traditional porous solid materials (such as zeolites and activated carbon) MOFs possess, by far, the highest surface areas per gram (around 6000

m²/g), known to date [58]. Furthermore, MOFs also have a higher degree of designability and adjustability in their structures and functions. Single X-ray diffraction can be used to determine the structure of MOFs because of their crystalline nature. Relationships can also be found between their structures and resulting properties and this information can be used to facilitate the development and design of MOFs for specific applications [86].

1.2.1 The Synthesis of MOFs

MOFs are generally synthesized by the coordination of metal ions or clusters with organic ligands. A base solution is usually added to accelerate the deprotonation of the organic ligands and increase its solubility, to form a more homogeneous nucleation environment [87]. MOFs are usually synthesized using batch solvothermal reactions, but this method requires a long reaction time, sometimes up to several days [10]. It is also hard to control crystal growth; a range of crystal sizes are often formed by batch synthesis [60]. The key strategy to overcome these drawbacks is to reduce the reaction time. A number of novel

synthesis approaches have been reported, such as microwaves [88-90], ultrasound [91-93] and mechanochemical [94-96].

However, batch processing of MOFs is not easily scaled-up due to equipment limitations. To achieve the goal of high-throughput, a few novel approaches associated with continuous reaction process have been reported recently. Gimeno-Fabra et al. [60] synthesized MOFs using a continuous-flow method which induces crystallization by rapidly mixing a stream of dissolved reagents with a pre-heated water flow. Characterisation of the products (TGA, XRD, SEM and BET) showed that HKUST-1 ($(\text{Cu}_3(\text{BTC})_2 \cdot 3\text{H}_2\text{O})$, BTC = benzene-1,3,5-tricarboxylate) had been produced in seconds rather than minutes or hours. The analysis results show that the properties of the product compare well with materials synthesized by batch reaction confirming that this continuous synthesis approach is suitable for MOF production, and should be applied in a wide range of MOFs [60]. Kim et al. [97] designed a continuous-flow microreactor-assisted (CFMA) solution process to synthesis MOF materials and utilized Cu-BTC complex as a candidate to investigate the effects of $\text{Cu}(\text{NO}_3)_2$ solutions and temperature on morphology and particle size. The result showed products synthesized in ethanol have more

uniformly shaped particles of smaller sizes (~ 150 nm) than those synthesized in water; increasing temperature leads to larger Cu-BTC crystals and smaller surface areas. The particle size and the crystal phase of these materials could therefore be adjusted by changing the relative ratios of water and ethanol solvents in the $\text{Cu}(\text{NO}_3)_2$ solution used as a precursor. By this method the Cu-BTC powder was obtained at a rate of 2.04 g h^{-1} via this single channel CFMA system. Higher production rates could be achieved by scaling up the current system using a multichannel reactor [97].

1.2.2 Hydrothermal and Solvothermal Synthesis

Hydrothermal synthesis were defined by Ballman and Laudise in 1963 [98]: Hydrothermal synthesis is reaction process proceeding under the elevated temperature and pressure, where aqueous solvents are used to dissolve chemicals which are of low solubility when in standard conditions [99]. High temperature refers to a temperature above the boiling point of the solvent and where elevated pressure is required [100].

When the temperature and pressure of water exceed its critical point ($T_c=374^\circ\text{C}$ and $P_c=22.1\text{MPa}$), it becomes a supercritical

solvent condition. The properties of supercritical water will be introduced in Section 1.2.2.1.

There have been increasing amount of publications around the hydrothermal process to synthesize nanoscale materials in the past three decades. Using water as a solvent means that the process can be termed as sustainable or green technology. A broad range of nanometer materials has been generated including sulfides (Liu et al., 2001), metal oxides [101], metals [102], metal organic frameworks [60] and carbonates [103, 104].

The synthesis is known as solvothermal instead of hydrothermal when non-aqueous solvents including methanol and ethanol are involved [105].

1.2.1.1 Supercritical Water

Supercritical water is employed in the continuous work when synthesizing titanium dioxide (TiO_2) in Chapter 6. Water is a good solvent for ionic salts, but is not able to dissolve non-polar compounds in normal conditions, since water is a polar molecule [106].

Interestingly, the properties of water can be changed when it is heated under a high pressure and the temperature exceeding its

critical point ($T_c=374^{\circ}\text{C}$ and $P_c=22.1\text{MPa}$). Figure 1.8 shows the phase change of water with regards to the temperature and pressure.

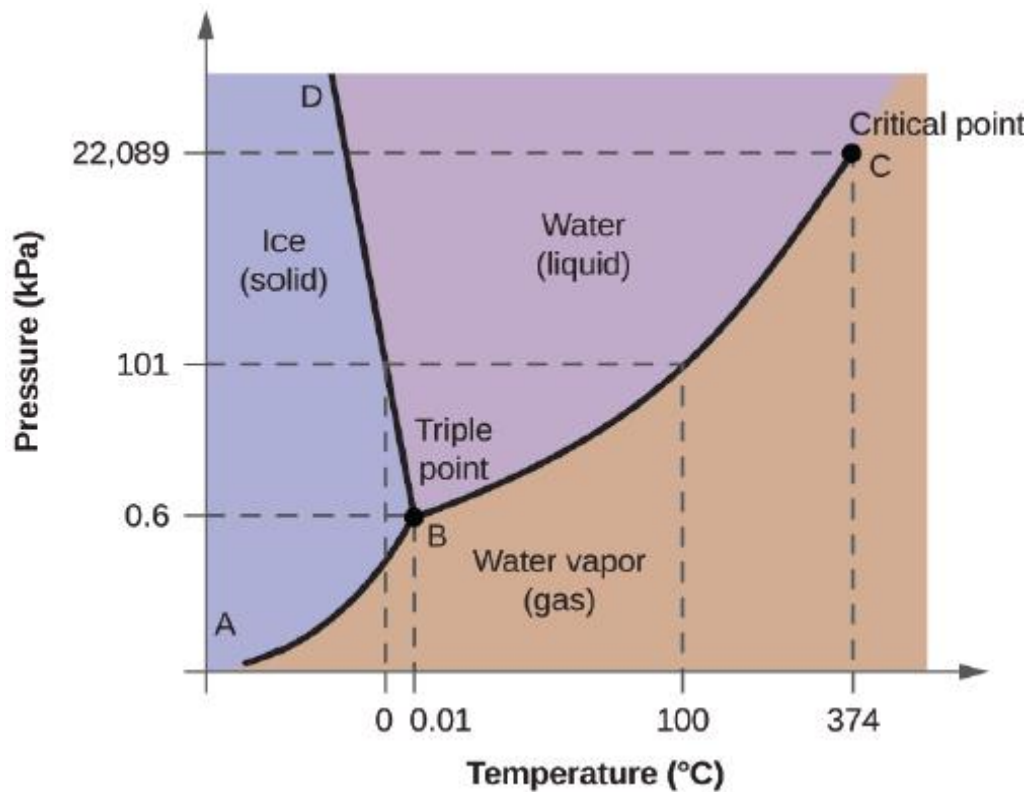


Figure 1. 8 Phase diagram of water.

The hydrogen bonds existing between water molecules begin to break down as it reaches its critical point [107]. The dielectric constant of water decreases and the dissociation constant increases, which indicates that water molecules are transformed to hydrogen and hydroxyl ions [99]. Water presents various

properties at and above the critical point, which is referred to as supercritical water (ScW). The surface tension reduces dramatically and the water can diffuse like a gas [108]. In addition, the density drops radically compared with ambient conditions. Figure 1.9 shows the changes of density, ionic product and dielectric constant for water with the increase of temperature in a constant high pressure of 24 MPa.

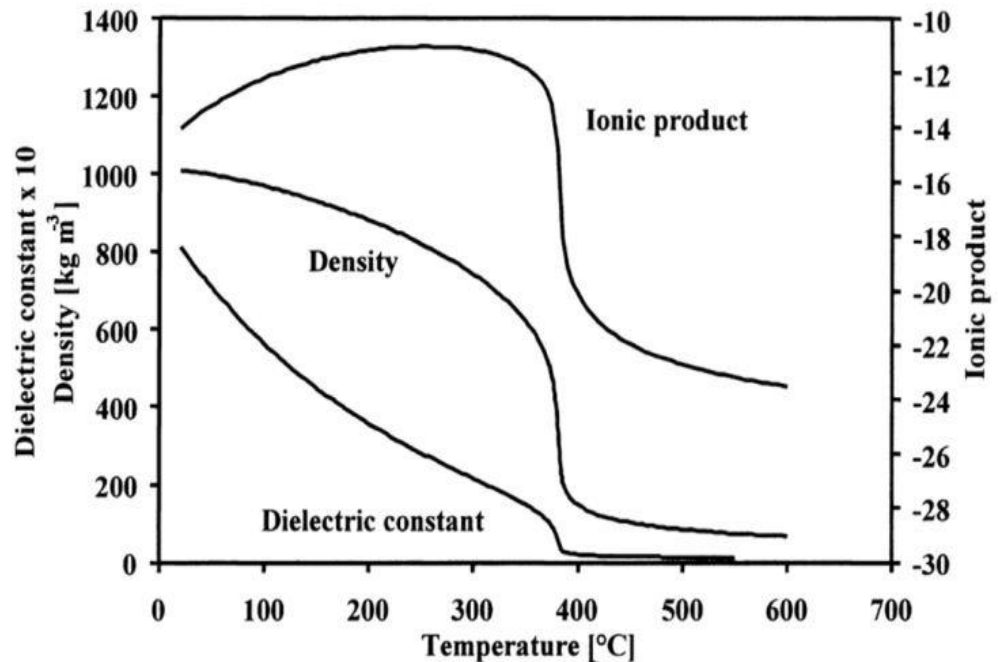


Figure 1. 9 Changes of density, ionic product and dielectric constant of water with temperature changes in a pressurized condition of 24 MPa [109].

ScW is different from water at ambient conditions because it can dissolve nonpolar molecules. However, the temperature and

pressure above critical point is not always a necessary condition in all hydrothermal processes. Sub-critical or near critical water (with temperature ranging from 100 °C to 374 °C under pressure) can be used as a solvent [110].

1.3 Hydrothermal Synthesis systems

Both batch and continuous synthesis system are discussed in this section.

1.3.1 Batch Synthesis System in this Project

Batch syntheses for MOFs were investigated in this project, which will be discussed in detail in Chapter 3. The main experimental instruments involved here include a heating jacket, reflux condenser, centrifuge and oven.

Figure 1.10 shows the main rig used in synthesis process. The temperature of the heating jacket and the temperature of the chemicals can be both measured by the thermocouple in the heating jacket. The magnetic stirrer can be put in the round-bottom flask, and the agitation speed of the stirrer can be altered to up to 900 rpm. The temperature and the agitation speed are displayed on the electronic display.



Figure 1. 10 A lab photo of the batch synthesis process

The activation process was also performed by heating via the heating jacket, while a condenser was connected to the round-bottom flask. The condenser was supplied with cooling water. Figure 1.11 shows the flow direction of the cooling water. Usually, the water flows counter current in order to achieve a high efficient heat exchange [111].

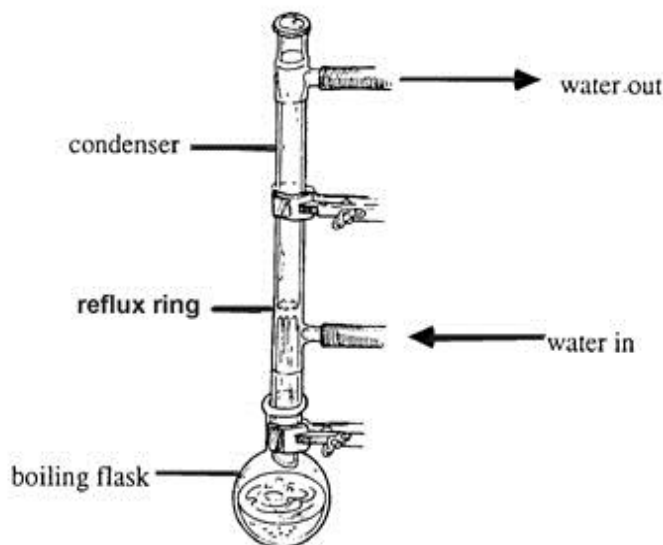


Figure 1. 11 A diagram for water flow in the condenser

The condensed steam drops down back to the flask. The agitation speed and the temperature is controlled during each experiment. The details would be shown in Chapter 3.

1.3.2 Continuous Flow Synthesis

Continuous flow reactors have several advantages over batch reactors, and this is discussed in Section 1.2.1. However, the development of continuous-flow reactors have been impeded by blockages occurring inside the pipelines and reactors.

Researchers at the University of Nottingham started to investigate continuous hydrothermal synthesis from the late

1990s to early 2000s. This research group used a T-piece reactor and synthesized zirconium oxides [112] and ferrites [113]. Nevertheless, problems with chemical blockage still took place, which resulted in inconsistent products being produced. As a result, the experiments had to be shut off for safety reasons. To address this problem, the fluid dynamics and mixing mechanism inside the T-piece reactor were investigated by Blood et al [114] at The University of Nottingham. They employed a method to mimic the density and viscosity of the precursor feeds, but of ambient pressure and temperature. This method was called light adsorption imaging (LAI). A dye was added in the metal salt stream, which allowed image analysis techniques to determine the locations of static zones and discover whether the mixing was poor. According to their work on different rates, the main conclusion was that regardless of flow rates or orientations the mixing situation created an undesirable mixing environment and thus blockages of particles would occur, which explained experimental findings.

The group at Nottingham [115] also employed LAI and CFD analysis with experimental data to simulate an improved substitute reactor. The researchers published an article in 2006

to show a new reactor design. A novel reactor was presented in the paper whereby particle build-up and blockages were avoided. In this design, the natural convection forces in the system were developed to create and promote eddying around the mixing point. This new reactor was patented as the Counter-Current Nozzle Reactor [115]. A schematic to describe the flow arrangements is shown in Figure 1.12. This reactor is used extensively in Chapter 5 and 6. A photograph of the counter-current reactor system taken from the lab in Nottingham is shown in Figure 1.13.

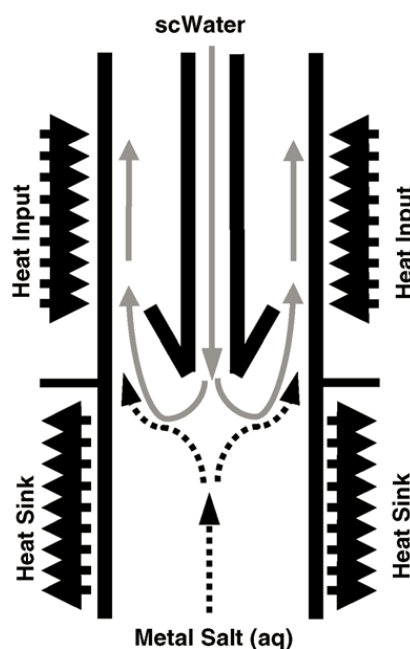


Figure 1. 12 A schematic of the Counter-Current Nozzle reactor, designed at The University of Nottingham [115]

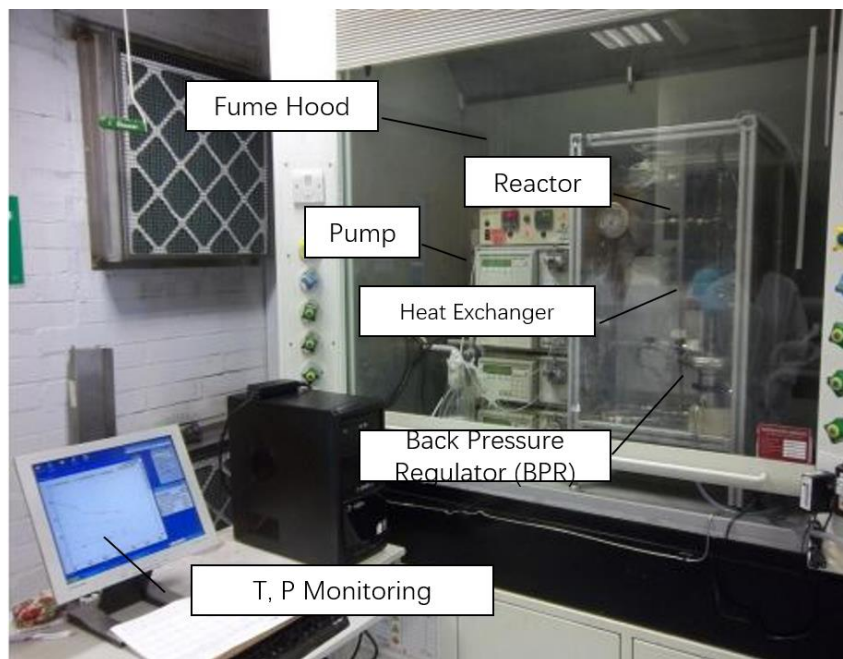


Figure 1. 13 A photograph of the counter-current rig in the lab in Nottingham

1.3.2.1 Reactor Engineering for the Supercritical Water Synthesis System

This section will discuss the impact of reactor geometry on hydrothermal synthesis.

The flow diagram for the supercritical water hydrothermal synthesis (scWHS) is given in Figure 1.14. The reactor was previously designed as a T-piece which caused poor product reproducibility due to particle accumulation and blockage in the

reactor and at the inlets. Consequently, frequent cleaning had to be conducted between runs.

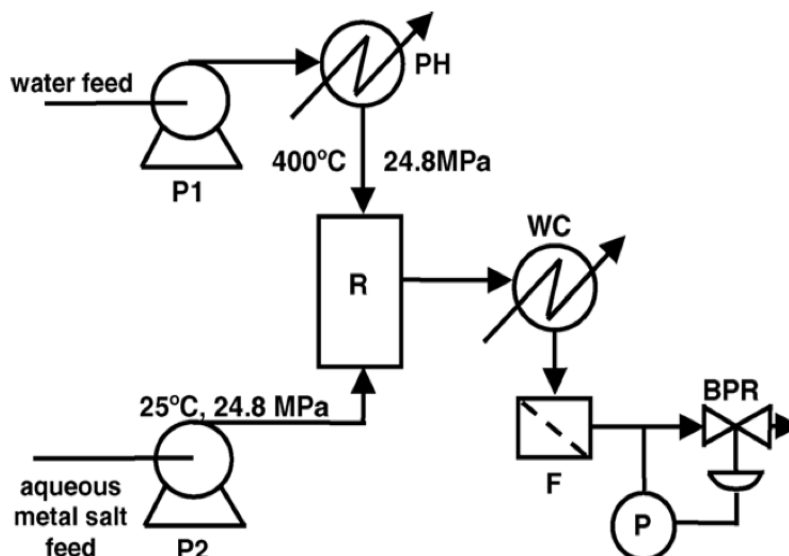


Figure 1. 14 Flowsheet of scWHS for the experiments in Nottingham [107]

P1 and P2: Gilson HPLC Pumps, PH: preheater, R: continuous reactor, WC: water cooling, F: Filter, BPR: Tescom back pressure regulator, P: pressure transducer.

To investigate the inner mechanism of the reactor, two modelling techniques (LAI and CFD) were employed to explore the T piece reactor. The efficiency of the reactor at a variety of flowrates and reactor/inlet orientations were examined by LAI modeling. Interestingly, it was found that the flow regime within

the reactor is different from that of conventional reactors. The Reynolds numbers (Re) for both streams calculated were extremely low (148 for the ScW inlet, and 20 for the metal salt inlet). This means that each feed stream was highly laminar. However, the fluid phenomenon observed from LAI and CFD techniques did not agree with this. On the contrary, unexpected extremely turbulent mixing occurred when two fluids meet in the reactor. It was explained that the driving force for the turbulent flow mixing came from the buoyancy forces, rather than the inertial forces from the process pumps. The densities of two feeds are significantly different: density for supercritical water is 371 kg/m^3 , metal salt density is around 998 kg/m^3 . This has led to a strong convection when they mixed. According to the dimensional analysis such as Grashof number ($Gr=9.5 \times 10^9$) and Reynolds number (Re), the natural forces induced by the interaction of two feeds are able to produce turbulent flow [114]. As a result, T-piece reactor shows a poor efficiency in such supercritical water hydrothermal synthesis [116]. The new reactor is specifically designed to: (i) improve the mixing efficiency, (ii) handle the product accumulation situation and (iii) deliver an enhanced heat transfer profile.

i) Design Criteria

The key factor to optimize the reactor was to study the density difference of two feed fluids. These criteria listed below should be satisfied:

- (i) Uniform mixing and instant mixing of two precursors;
- (ii) Short residence time and narrow residence time distribution;
- (iii) Low temperature for the metal salt stream before it flows into the reactor and rapid heating in the reactor, for the purpose of avoiding precipitation in the pipes prior to the reactor;
- (iv) Strong downstream flow to keep particles from being accumulated in the reactor.

These requirements contributed to the design of a new reactor: referred to hereafter as the Nozzle reactor [117] (Figure 1.13). This reactor is a pipe-in-pipe construction with the supercritical water flowing downstream through the internal pipe (1/8 inch outer diameter) and out the end to meet the upward stream aqueous metal salt which flows through the outer pipe (3/8 inch

outer diameter). The resultant products are carried out from the side arm of the reactor.

In order to study the inner mechanism of the reactor, LAI and CFD modelling were employed and the details have been illustrated in the following section.

ii) LAI and CFD modelling

Figure 1.15 (a) shows the steady state concentration map and Figure 1.15 (b) shows the fluid velocity in the reactor calculated by FLUENT [114]. It can be concluded that this reactor uses the density difference between two fluids. An instant mix and reaction takes place as the two reactants meet. The turbulent eddies then flow downwards out of the reactor. No chemical accumulation occurs within the reactor inlets, and no recirculation occurs which can cause 'stagnant zones' [114]. These two problems were the main issues that adversely affected the product reproducibility in T piece design [107].

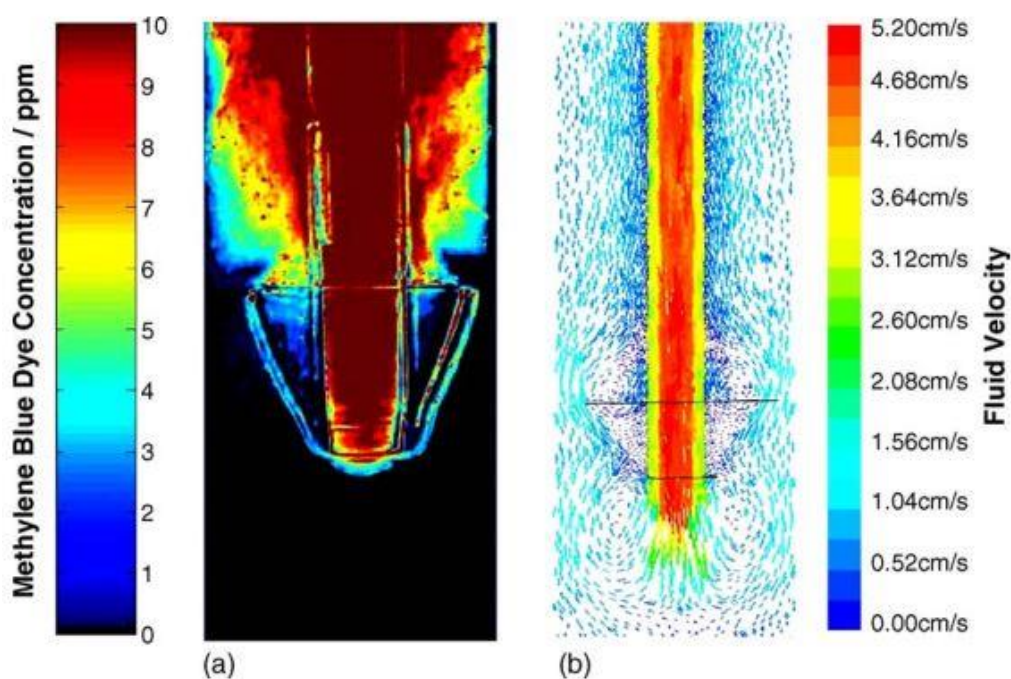


Figure 1. 15 (a) steady state LAI concentration map of then Nozzle Reactor (b) steady state CFD calculated using FLUENT. The flow rates for supercritical water and metal salt are 10 ml min⁻¹ and 5 ml min⁻¹, respectively.

Heating/cooling across the flow system can be adjusted, as it is shown in Figure 1.14. The metal salt stream is normally kept under 50 °C before it comes into contact with the supercritical water in the reactor. In this case precipitation is avoided prior to the reactor. This can efficiently solve the precipitation problem commonly observed in earlier ScWHS reactor systems [118]. For the earlier reactors, the big difference of the density between two reactants resulted in the supercritical water flowing upwards and

come into contact with the metal salt stream. This would induce the precipitation of metal salt in the inlet and lower the hydrothermal synthesis yields. The consequence of sample precipitation and reactor blockage can be severe in some experiments and thus mid-experiment shut-downs have to be implemented. In a previous study, an attempt has been made where cooling jackets were attached on the metal salt stream pipe, while only few improvement with regards to the blockage was achieved[118].

On the contrary, no premixing occurs in the Nozzle Reactor, since mixing only occurs at the tip of the inner pipe. An 'Idealisation' rating system was used to evaluate various reactors using LAI method, which has been described in the earlier article [107]. The lower rating number represents greater mixing efficiency. The result of the rating system is a single number (0-1, 0 meaning ideal, 1 meaning non-ideal). There are 74 previous reactors with different geometries simulated including T-pieces, Y-piece, +piece and x piece. The lowest rating number obtained was 0.15. While for the Nozzle Reactor the calculated value is 0.05 much lower than other reactors [114, 115].

To summarize, the Nozzle Reactor was able to perform well under supercritical water hydrothermal conditions. Several different products were produced using the reactor and the details are shown in the next section.

iii) Particle Synthesis and Characterisation

To assess the Nozzle Reactor in the actual experiment, it was constructed in a high-pressure rig. Figure 1.16 depicts the construction of the fittings in the nozzle reactor. The materials and size employed for the tubes, as well as the heater have been labeled in the diagram. A cone section (a Swagelok ferrule) was added to the end of the inner pipe in the initial design. The aim of installing this part is to maximize the mixing effect, since the cone section plays a role in dissipating the heated water as a spinning disc. However, the cone was not used in later publications because it largely reduces the available flow area.

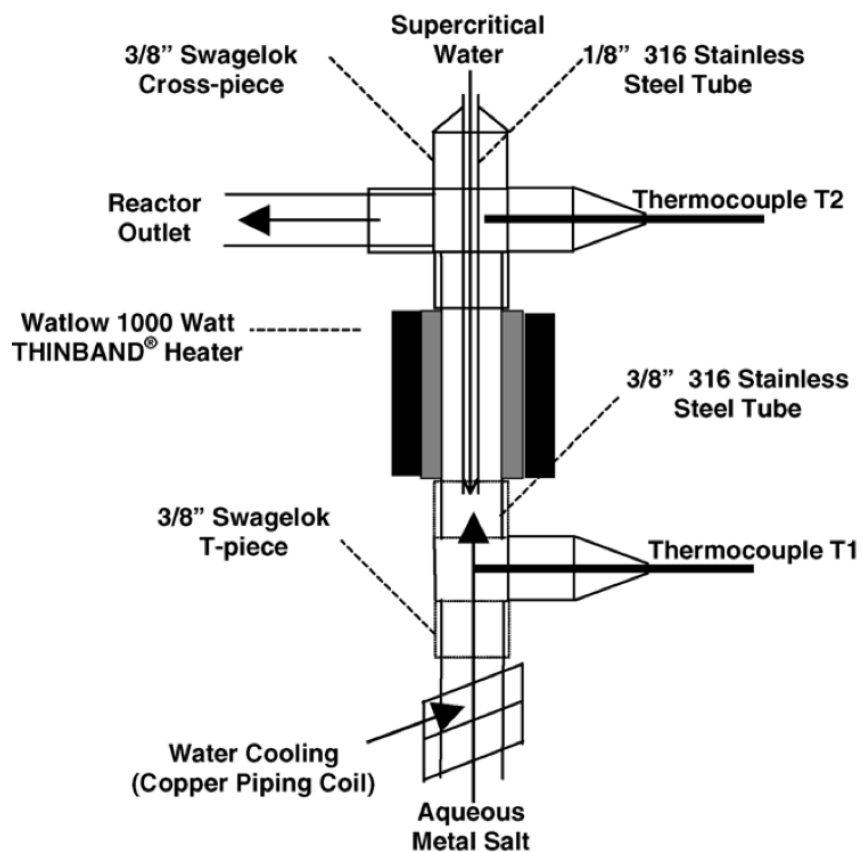


Figure 1. 16 The Nozzle Reactor fitted in a high-pressure rig
[115] (*" represents inch unit*)

A variety of materials have been produced using this reactor.
 Table 1.3 below lists their particle sizes.

Table 1. 3 Particle sizes of metal oxides synthesized by scWHS Nozzle Reactor [107]

Metal oxides	S_{BET} (m^2g^{-1})	Particle diameter (nm)	Reference
TiO ₂ (anatase)	110	13	[119]
CeO ₂	90	9	[112]
ZrO ₂	195	6	[120]
ZnO	17	64	[121]
CuO/CuO ₂ /Cu	15	50	[107]
CuO/ZnO	55	15	[107]
Ag	60	9	[102]

Reproducibility Assessment

The process of producing CeO₂ was used to assess the reproducibility of this reactor. The testing procedures and conditions used are as follows [112]:

- (i) 0.2 M Cerium ammonium nitrate flowed upwards at a rate of 5 mL min⁻¹.

- (ii) Supercritical water flowed downwards at a rate of 10 mL min⁻¹.
- (iii) The temperature of supercritical water was set as 410 °C.
- (iv) The system pressure was set at 24.8 MPa.
- (v) Cooling jackets were mounted on the reactor outlet and metal salt inlet.

Five prolonged runs (up to 9 h) were carried out [112]. Among these runs only minimal particle accumulation occurred, and no blockages were observed. During the test, the pressure was kept constant. The temperature profile can be obtained from data recordings of two thermocouples T1 and T2 (labelled in Figure 1.16). Thermocouple T1 was inserted 2 cm away from upstream of the reactor in the metal salt inlet. The temperature remained steady at about 24°C, suggesting the metal salt stream remained “cold” before it met the supercritical water. This can minimize the precipitation phenomenon of metal oxides before the reactor. In addition, thermocouple T2 was situated 4cm away from the outlet of the reactor, which recorded the temperature of resultant product flowing out from the reactor. According to the recorded data, the temperature remained at around 370 °C in steady state.

This also proved that the mixing occurred in a short time and the heat transfer was fast.

The collected fluids were then dried in an oven to obtain CeO_2 powders. BET surface areas were measured and the results are shown in Figure 1.17.

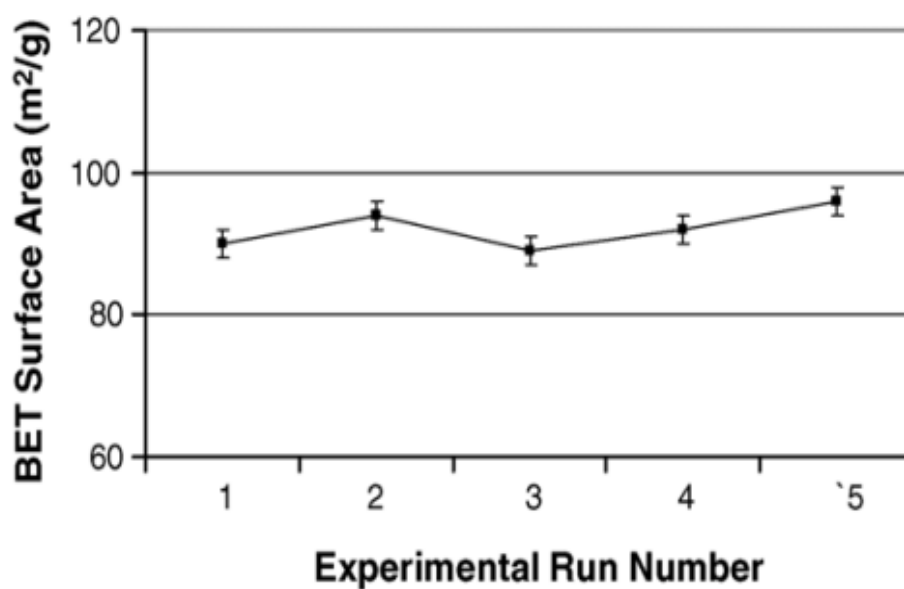


Figure 1. 17 BET surface area analysis for five CeO_2 products [112].

The surface areas for the five groups of CeO_2 products were in the range between 85 and 95 m^2g^{-1} , indicating outstanding product reproducibility compared to the samples synthesized by

previous T-piece reactor, which had a fluctuate in surface area from 52 to 104 m²g⁻¹ [112, 118].

iv) Continuous Hydrothermal Synthesis Scale Up

In order to apply this reactor system at industrial scale, Lester et al. built several pilot scale system before building a full scale plant. Meanwhile, the products generated from the scaled-up system did show significant differences with those produced from lab scale rig. Furthermore, the scaled up process needed to show economical feasibility if it was to be widely adopted by industry. A pilot scale reactor system was built in 2007 and it belongs to Promethean Particles Ltd. This is a spin-out company funded by Seventh Framework Programme (FP7).

A photo of this pilot system is shown in Figure 1.18. The maximum flowrate of this system was designed to be 60 litres/hr with a pipe-in-pipe piece. The outer diameter of the outer pipe is 1½" (3.81 cm) with a wall thickness of ¼" (0.635 cm), and the outer diameter of the internal pipe measures at ½" with a wall thickness of 0.083" (0.211 cm).



Figure 1. 18 The pilot scale reactor system in Promethean Particles Ltd.

1.4 MOFs Designs and Modifications

As stated before, a material's pore size and shape are of vital importance in terms of selective adsorption. MOFs have a higher degree of designability and tunability than other porous materials [33]. The general methods applied to tune their pore size and shape are pre-synthesis design and post-synthetic modifications. Additionally, the effect of humidity on CO₂ adsorption and selective adsorption is a significant consideration for the

application of MOFs in flue gas streams; the flue gas from power plants usually contain 5-7% water by volume [122]. MOFs such as MOF-5 and HKUST-1 are highly sensitive to water whereby their structures break down in a water existing environment and thus lose the ability to adsorb CO_2 [123]. Therefore, water stability of MOFs is a necessary property in real industrial applications, and water stability of MOF materials can also be improved by post synthetic modification [124].

1.4.1 Pre-Synthetic Design

The desired pore size of a MOF can be achieved by selecting or controlling the length of its ligand. In general, shorter ligands create MOFs with smaller 'windows' with narrow or open channels. Longer ligands lead to larger pores and larger volumes [125, 126]. However, if the length of the ligand is increased too far then interpenetration of the framework can occur which can reduce the pore volume and total surface area [127, 128].

A typical material with a short ligand is $\text{M}(\text{HCO}_2)_2$ ($\text{M}=\text{Mg}$, Mn , Co , or Ni), which offers a remarkable degree of selective adsorption of CO_2 over CH_4 at 195 K [129]. It is observed that there is nearly no adsorption of CH_4 . In this case the short linker

COO⁻ connects metal atoms and form a structure that has large cavities connected by small channels. The ZIF family also uses short ligands (imidazole rings). Some studies on ZIF membranes show promising results for CO₂ capture potential [130]. Materials possessing this type of structure generally have a high potential in selective adsorption. For this reason big cavities in the material can be used to provide a high adsorption capacity and whilst small neck increases the selectivity [131]. In contrast, MOFs with longer ligands have a reduced pore volume because bigger cavities are prevented from forming due to the interpenetration of the structure. As a result of this, this type of MOF is inferior in gas storage. However, they do show some advantages in selective adsorption and separation due to the decreased pore size [132]. Notable examples are Zn(adc)(bpee)_{0.5} and PCN-17(M) (M=Yb, Dy, Y, or Er) reported by Chen and co-workers [128]. Both of these two examples exhibited high selective adsorption toward H₂ over N₂ and CO.

1.4.2 Post-Synthetic Modification

Post-synthetic modification (PSM) can be regarded as an effective way to tune the properties of the pores. It has been

shown that additional ligands can be post-synthetically introduced into a MOF structure [133]. Suh and co-workers explored a typical example $\text{Zn}_2(\text{tcpbda})(\text{H}_2\text{O})_2$ (SNU-30, $\text{H}_4\text{tcpbda}=\text{N},\text{N},\text{N}',\text{N}'$ -tetrakis (4-carboxyphenyl) biphenyl-4,4'-diamine), which was first synthesized and then combined with 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (bpta) to produce $\text{Zn}_2(\text{tcpbda})(\text{bpta})$ (SNU-31) [134]. The inserted bpta ligands are coordinated to Zn(II) by substituting the H_2O molecules of SNU-30. The bpta ligands divide the original large channels. The modified MOF excludes N_2 , H_2 , O_2 , and CH_4 while still allowing CO_2 to enter. The reason of this behaviour is thought to be ascribed to the higher quadrupole moment of CO_2 .

PSMs have been widely applied in MOFs to obtain targeted properties. As mentioned previously, water stability is of significant importance in the removal of CO_2 in flue gas. The first industrial-scale manufactured MOF HKUST-1 [135], although possessing a high CO_2 uptake capacity, is not stable under hydrothermal conditions [60]. A strategy of introducing graphite oxide to this MOF has been reported to improve its hydrothermal stability [136]. Additionally, the surface area of the modified material has a 50% increase compared to the original HKUST-1

(from $841 \text{ m}^2 \text{ g}^{-1}$ to $1257 \text{ m}^2 \text{ g}^{-1}$) when graphite oxide content is 8.7 wt% in the composite. The hydrothermal treatment experiment was carried out in an autoclave heated to 393 K and kept for 12 h. XRD, TG, DTG and BET were used to evaluate the composites incorporated with different amount of graphite oxide and compared the results with pure HKUST-1. The experimental results indicated that HKUST-1 modified with graphite oxide in a proper range of quantity (8.7-27.2 wt%) can effectively improve the hydrothermal stability. This improvement is probably attributed to the creation of a more hydrophobic environment around the metal centers due to the existence of a carbonaceous component from graphite oxide. A higher content of graphite oxide leads to distortion of the structure in the parent MOF whereby water molecules can easily attack the framework.

Apart from incorporating another composite to modulate the hydrophobicity, reducing or blocking the material's contact with water molecules is another operational strategy [137]. Zhang *et al.* explored a facile and general method for coating MOFs with PDMS (polydimethylsiloxane) using a thermal vapor deposition technique [124]. Three water sensitive MOFs were selected (MOF-5, HKUST-1, and $[\text{Zn}(\text{bdc})(\text{ted})_{0.5}]\cdot 2\text{DMF}\cdot 0.2\text{H}_2\text{O}$) with

various SBUs (secondary building units). SBUs are molecular complexes and cluster entities in which ligand coordination modes and metal coordination environments can be utilized in the transformation of these fragments into extended porous networks using polytopic linkers. All of these three materials underwent a PDMS coating process. They were heated in a sealed glass container with the existence of PDMS stamp under 235 °C. Silicone molecules were generated from degradation of PDMS and deposited on the surface of the MOFs as a thin layer. The coated products showed significantly increased water stability. Furthermore, subsequent XRD and N₂ adsorption experiments respectively revealed that the original crystalline structure and the porosity (as well as the surface area) of the studied MOFs was retained. The retention of these properties are highly important to real applications e.g. gas storage and gas separation.

Unlike HKUST-1, ZIF-8 has a remarkable water stability but a relatively low CO₂ adsorption capacity. Using a post-synthetic modification strategy, Xian *et al.* prepared a novel material based on parent ZIF-8 material [122]. The original pure ZIF-8 was added into 30% ethylenediamine solution, and then treated at a high temperature (416 K for 1 h and 381 K for 6 h) in a stainless-

steel autoclave. PXRD results indicated that the modified ZIF-8 retained its crystallinity and FTIR spectra showed that N-H groups were present on the surface of the modified sample. More notably, the modified sample was found to have 39% higher surface area than the original one, which would greatly increase the CO₂ uptake capacity. Furthermore, CO₂/N₂ selectivity was predicted by using single-component isotherms and IAST. It was reported that at a low pressure range, especially at 0.1 and 0.5 bar, the modified ZIF-8 possessed a CO₂/N₂ selectivity nearly two times greater than that of the original ZIF-8 at the condition of 298 K and equimolar of CO₂ and N₂.

Chapter 2 Characterisation

Techniques

2.1 Powder X-ray Diffraction (XRD)

Powder X-ray diffraction instrument is often used to discover the crystal structure and ordering of crystalline materials, such as the space between lattice planes and the crystalline content. Each structure or crystal can be determined by comparing with library database because different materials possess various diffraction patterns [138].

Crystals are solid materials with atoms arranged in a regular long-range order [139], while amorphous solids comprise of atoms that are not ordered in any form of lattice pattern. The difference has been depicted in Figure 2.1. The XRD analysis cannot elucidate the nature of amorphous materials [140].

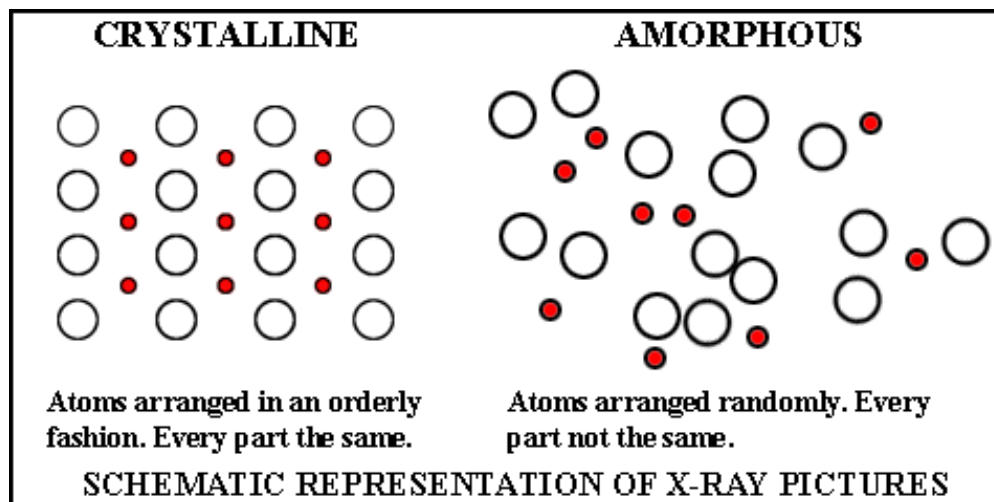


Figure 2. 1 Atoms arrangements of crystalline and amorphous

X-rays are a form of electromagnetic radiation with a wavelength (λ) ranging from 0.2 to 10 nm, which is at atomic level and much smaller than that of visible light. Therefore, X-rays possess higher energy that can penetrate deeper into matter [141]. X-ray scattering technique has the great advantage compared to the other analytical techniques due to its non-destructive nature.

2.1.1 Fundamental Principles of XRD

The fundamental principles of XRD are as follows: monochromatic X-rays are generated in a cathode tube. Copper K alpha beam is usually used as the diffractometer to produce X-ray beams, since it is more intense compared to K beta [142].

As shown in Figure 2.2, the X-ray beam of known wavelength (λ) impinges on the atoms in crystal with an incident angle θ and be scattered at every different direction. A detector recording the intensity is rotated around the sample (Figure 2.3).

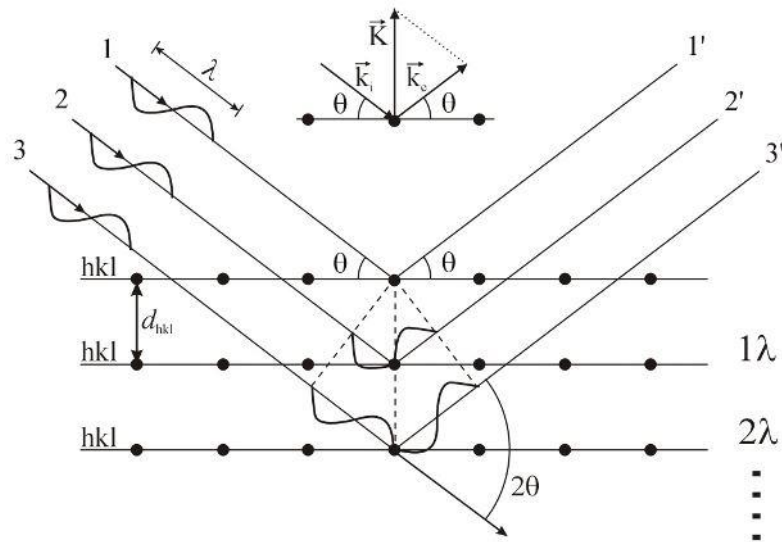


Figure 2. 2 Diffraction from a set of planes

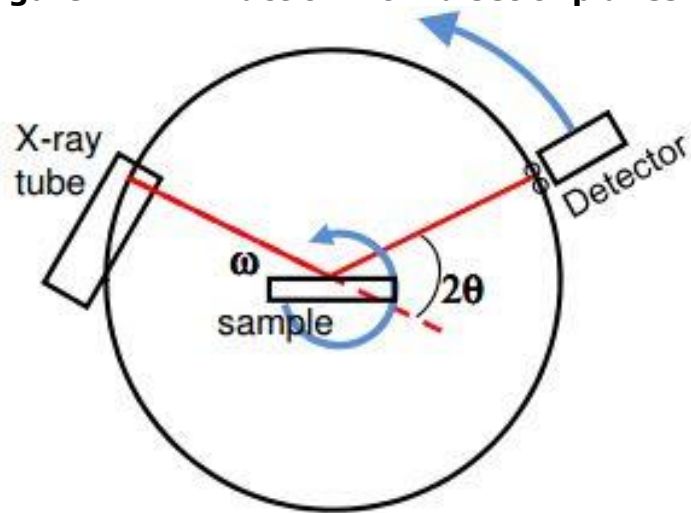


Figure 2. 3 Detector moved around the sample

A diagram with the angle 2θ as x axis and the intensity as y axis can be obtained according to the data recorded from the detector. Figure 2.4 shows an example of the XRD pattern for HKUST-1.

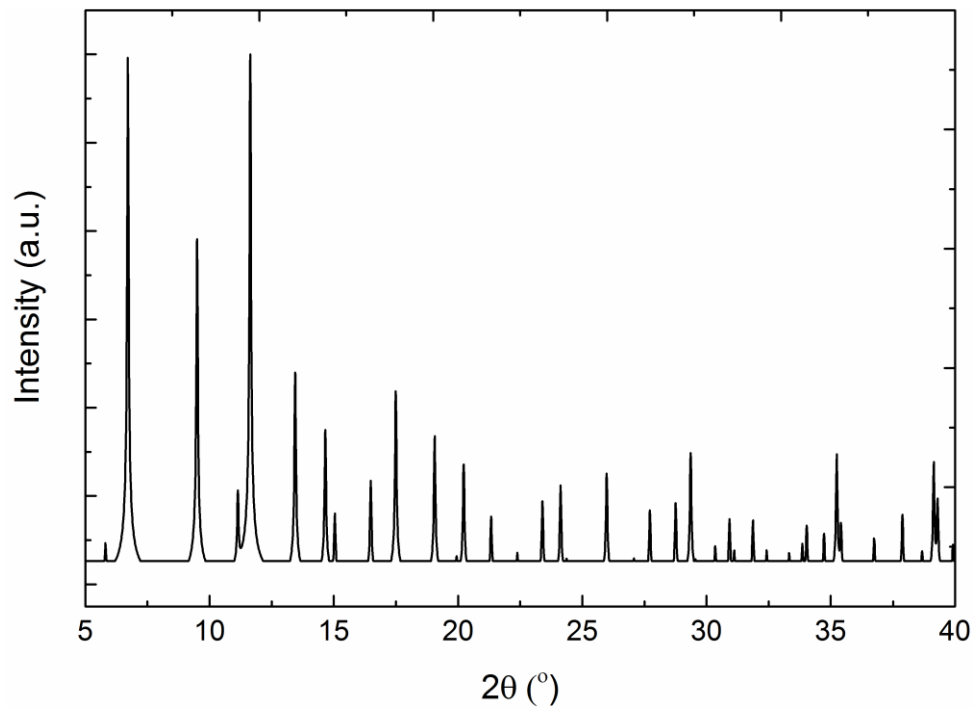


Figure 2. 4 XRD pattern for HKUST-1

The XRD patterns can reveal qualitative and quantitative information about the crystal materials.

2.1.2 Qualitative Analysis from XRD Patterns

(i) By matching the peaks obtained from XRD instrument with the reference patterns, the composition of the unknown materials can be determined

(ii) For a mixture, the peaks in the XRD pattern are a sum of the patterns diffracted from all phases;

(iii) The shape of the peaks indicate crystalline materials with smaller size (Figure 2.5) and materials with microstrain and other defects in the structure have broader peaks [143].

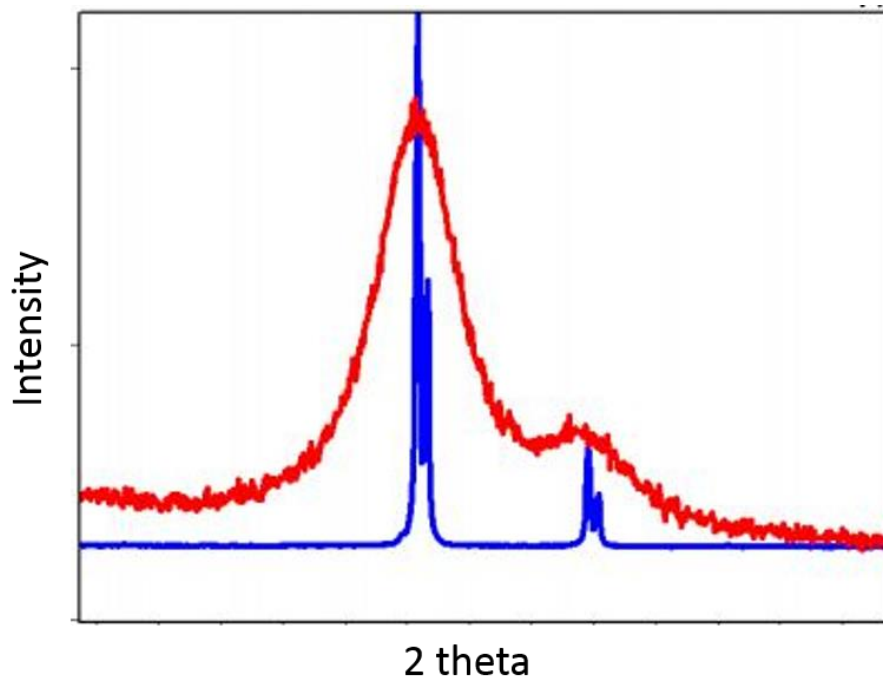


Figure 2. 5 XRD pattern for bulk ceria (blue) and nanosized ceria (red)

For an unknown material, the peaks detected can be compared with that from “library” and match to find the chemicals.

2.1.3 Quantitative Analysis from XRD Patterns

In 1913, Sir W.H. Bragg and his son Sir W.L. Bragg discovered that intense peaks were produced by X-rays reflected off crystals [144], and they proposed the Bragg`s Law to describe the relationship between the X-ray wavelength (λ), the spacing between diffracting planes (d), and the incident angle (θ):

$$\lambda = 2d_{hkl} \sin\theta$$

A number of factors that cause the changes of the interatomic distances including temperature, substitutional doping, stress etc. will lead to a difference in the peak positions.

The crystal size x also can be evaluated from XRD analysis by Scherrer equation, which is named after Paul Scherrer [145, 146].

$$x = \frac{K\lambda}{\beta * \cos \theta}$$

where: K is a dimensionless shape factor, usually taken as 0.9,

λ is the X-ray wavelength,

θ is the incident angle of the X-ray,

β is the full width at half maximum of the intensity (FWHM).

Figure 2.6 depicted how to find FWHM.

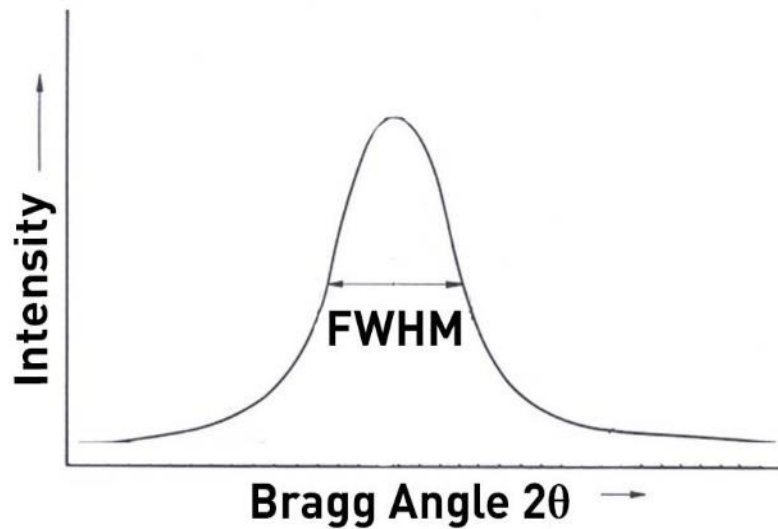


Figure 2. 6 FWHM in a XRD pattern diagram

The accuracy to calculate the grain size is affected by the uncertainties of peak positions and its FWHM value. Regarding the operating process, by decreasing the step size or conducting careful subtraction of the instrumental broadening the accuracy is able to be improved. While some errors also can be caused from the goniometer, which is an instrument set in the XRD equipment to measure angle. The accuracy of the goniometer is $\pm 0.005^\circ$.

The accuracy for an XRD pattern can be considered as a high quality pattern if the difference between measured and theoretical peak positions ($\Delta 2\theta$) is not bigger than $\pm 0.04^\circ$.

2.1.4 Experimental XRD Analysis

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 A25 diffractometer operated at 40 kV and 35 mA between $5^\circ 2\theta$ and $70^\circ 2\theta$ with a Cu K α radiation. The scan speed was 1s/step and the step size was 0.02° .

2.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX/EDS)

A scanning electron microscope is widely used to observe the morphology of materials with magnifications between 100 and 100,000 times [147]. High-resolution and 3D images can be obtained by SEM. This technique was developed in the 1950s by Professor Charles Oatley's group [148].

2.2.1 Fundamental Principles of SEM

An electron beam is emitted from the electron gun. The electron beam interacts with atoms at different depth of the sample, a variety of signals can be produced by the interactions. The detector collects these signals and converts them to a visual image. The schematic of a typical SEM arrangement is displayed in Figure 2.7.

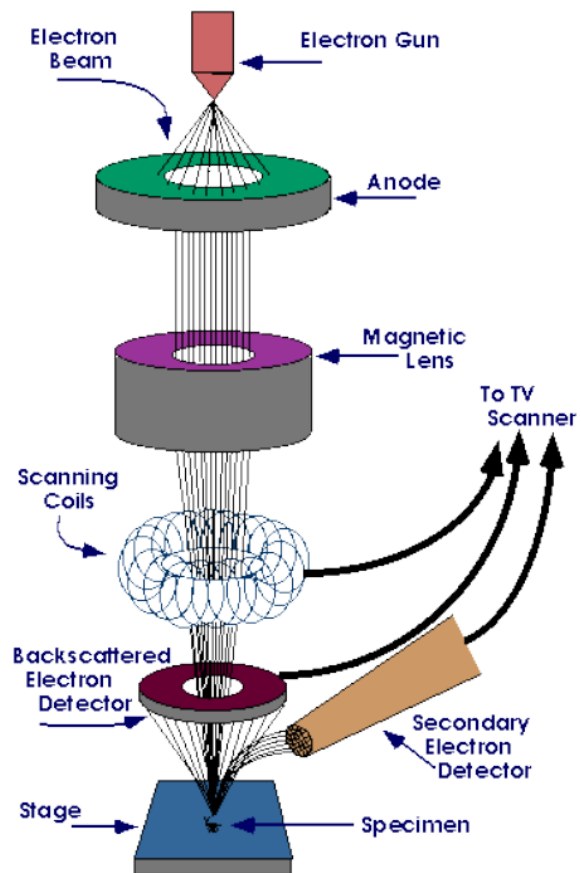


Figure 2. 7 Schematic diagram of SEM including important components in the instrument [149]

The various signals mentioned above mainly includes secondary electrons (SE), back scattered electrons (BSE), X-rays, etc.. Figure 2.8 shows the mechanisms of these three emissions.

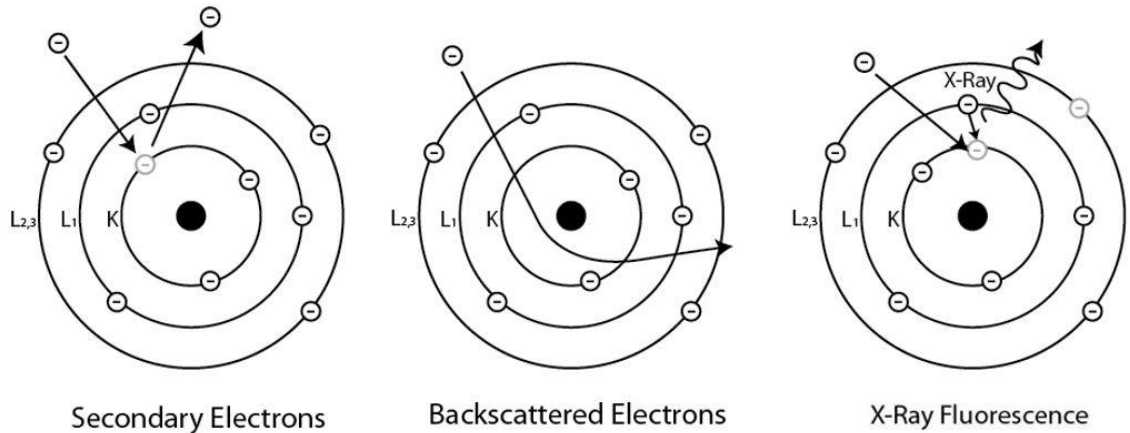


Figure 2. 8 Electron emission mechanisms

The signals obtained by the scatter from collisions between incident electron beam and the electrons in the k-orbital of the sample atoms are called secondary electrons (SE) emissions [150]. The high resolution images of the sample can be obtained by secondary electron imaging (SEI), where the resolution can reach 1 nm [151], and SE is usually used to observe the surface topology of the sample.

Backscattered electrons (BSEs) are elastically scattered from the sample. The scattering efficiency is relevant with the atomic

number of the sample. With a greater atomic number (Z) more backscattered electrons can be obtained and collected by the detector. Because signals are scattered from deeper locations in the specimen, a lower resolution image (than that of SE) will be obtained from the BSE signal. However, the BSE signal possess a higher energy compared to SE, and can deliver information about the elements distribution in the specimen [152].

X-ray signals are produced when the inner shell electrons of an atom are replaced by the outer-shell electrons when the electron beam collides the specimen, as shown in Figure 2.8. These signals can be used to evaluate the abundance of an element (or elements) in the sample [149].

2.2.2 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDX) system is attached kit to an SEM or TEM (Transmission Electron Microscopy, will be introduced later in this chapter). This technique is often used in elemental analysis and the signals collected here are X-ray signals. SEM or TEM coupled with EDX can be a powerful method for sample surface quantitative analysis, although EDX analysis is not suitable for light elements such as H, He and Li [153]. The

accuracy shows different for various elements. Elemental standards can be used in order to improve the accuracy of the results. However, lines overlap sometimes increases the errors and prevents quantification. In addition, uniform samples achieve a better accuracy than non-uniform samples; light elements are harder to quantify as mentioned above. In order to obtain a higher accuracy, background (also called as matrix corrections) should be done. If the operations are correctly conducted, the errors can maintain as small as 1~2% percent in the total composition in some cases [154].

2.2.3 Sample preparation

The samples for SEM are attached to a carbon tape, and the carbon tape stuck to a specimen holder. The size of the samples are supposed to be within the size range that would fit on the specimen stage inside the instrument chamber. For the nonconductive materials, coating performance is necessary to make their surface electrically conductive.

In this work, the SEM was a ZEISS Sigma VP operating at a voltage of 15 or 20kV, with a gold coating system made by LEICA EM SCD 500.

2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a technique used to measure the weight change of samples whilst temperature is increased or decreased. The temperature range of a typical TGA instrument is around 25 to 1000 °C. A variety of gas atmospheres including N₂, CO₂ and air can be introduced to the samples. Normally, the sample weight ranges from 1 mg to 150 mg, although most MOFs use sample weights of around 10 mg.

For thermogravimetric analysis, samples can be either in the form of powders or small lumps in order to keep a uniform temperature for the sample, and also, to make sure that the sample temperature is as close to the set gas temperature as possible. The accuracy of the weight change is ± 0.01 mg. All the experiments involving TGA in this project were repeated conducting by at least three times and the average value was calculated as the effective value. TGA can be applied to analyze different parameters: (i) water content or the residuals in the material, (ii) quantitative gas adsorption analysis, (iii) the evaporation rates as a function of temperature, etc..

In this work NETZSCH TG instrument was used to discover the thermal stability and compositions of the samples.

2.4 Fourier Transform Infrared

Spectroscopy (FTIR)

Fourier transform infrared spectroscopy utilizes infrared (IR) radiation to study the fundamental vibrations and associated rotational-vibrational structure present in a molecule. This technique can be used to identify chemical bonding and molecular structure.

FTIR can simultaneously collect raw data over a wide spectral range, and Fourier transform methodology is used to determine the signals. Distinct peaks corresponding to the stretching or bonding of chemical bonds can therefore be identified.

In this project, FTIR was applied to detect whether DDSA has been incorporated into HKUST-1. This was possible because DDSA contains carbon-carbon double bond.

2.5 Ultraviolet-Visible Spectroscopy (UV-Visible)

Ultraviolet-visible spectroscopy (UV-Vis) is a characterization technique for liquid or solid samples. This technique is used for quantitative and qualitative analysis of different substances. In this project, a solid state reflectance spectroscopy Cary 300 Bio was used to measure solid samples. Light in the visible and adjacent (near-UV and near-infrared) ranges irradiates the sample, the extra light at wavelengths that cannot be absorbed by the sample is reflected and detected. The machine then reads out the absorbed wavelength across the spectrum.

Before running the samples, zero and baseline correction should be operated, which is done by blocking the light using a black board. It is aimed to eliminate the interferences from the air and the instrument itself. BaSO₄ has been taken as the reference material to reflect off the light, due to its dense property. It can reflect light efficiently up to 98%. In this case, almost all the light the machine fires at the sample should be reflected back from BaSO₄, except from those captured by the

instrument/atmosphere. Therefore, the background effects can be determined and subtracted from later readings.

The relationship between absorbance and transmittance is explained as the following diagram. Absorbance and transmittance are negatively correlated: i.e. if all the light is absorbed, the transmittance percent is zero, while the absorption is infinite (i.e. 100%).

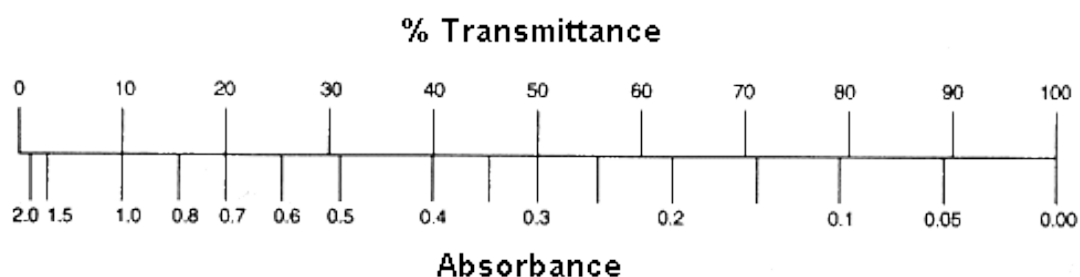


Figure 2. 9 The relationship between transmittance and absorbance.

For solids the transmittance can be calculated using the following

$$T = I_0/I = e^{(-\sigma/N)}$$

Where, I = Transmitted radiation, I₀ = Incident Radiation, σ =Cross Section, N=(number) density.

2.6 Brunauer–Emmett–Teller (BET) Analysis

Brunauer–Emmett–Teller (BET) technique is used to explore the physical adsorption of gas molecules on a solid surface and measure the specific surface area of materials. The BET theory was first published by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938 in the Journal of the American Chemical Society [155]. This theory is applied to multilayer adsorption, which is an extension of the Langmuir theory (applied for monolayer molecular adsorption). To properly use the BET theory the following hypotheses should be satisfied:

- i) Physical adsorption takes place for the gas molecules on a solid in layers infinitely;
- ii) Gas molecules only interact with adjacent layers;
- iii) The Langmuir theory can be applied to each layer.

The BET equation is:

$$\frac{1}{v \left[\left(\frac{p_0}{p} \right) - 1 \right]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c}$$

where p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed

gas quantity (for example, in volume units), and v_m is the monolayer adsorbed gas quantity, c is the BET constant.

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right),$$

where E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction. A straight line with $1/v[(p_0/p-1)]$ and (p/p_0) can be drawn and is called a BET plot (Figure 2.10). This linear relationship is only maintained in the range of $0.05 < p/p_0 < 0.35$. The value of the slope A and the y-intercept can be used to calculate the monolayer adsorbed gas quantity v_m and the BET constant c by using the following equations:

$$v_m = \frac{1}{A + I}$$

$$c = 1 + \frac{A}{I}.$$

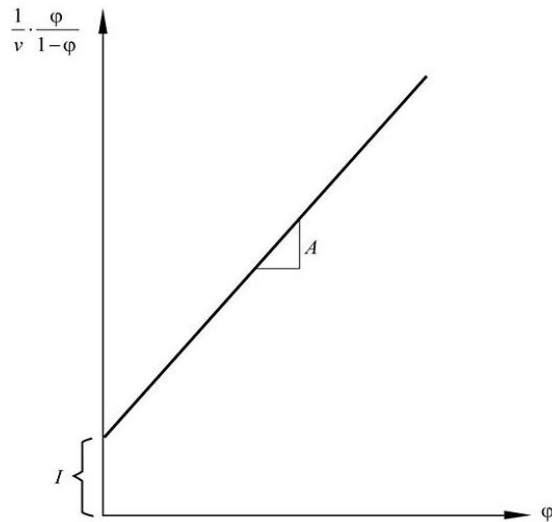


Figure 2.10 BET plot

Thus, the total surface area S_{total} and the specific surface area S_{BET} are calculated by the following equations:

$$S_{\text{total}} = \frac{(v_m N s)}{V},$$

$$S_{\text{BET}} = \frac{S_{\text{total}}}{a},$$

where N is Avogadro's number, s is the adsorption cross section of the adsorbing species, V is the molar volume of the adsorbate gas, and a is the mass of the solid sample or adsorbent.

Micromeritics ASAP 2020 equipment was used in this project to measure the specific surface area of the samples. Before each

analysis, degassing process is necessary in order to remove water in the sample. Nitrogen is the most used gaseous adsorbate that does not chemically react with material surfaces to quantify specific surface area, and also employed here. Therefore, a typical BET analysis is usually conducted at the boiling temperature of N_2 (77 K). All the experiments involving BET in this project were repeated conducting by at least three times and the average value was calculated as the effective value.

Chapter 3 Screening of HKUST-1 synthesized in batch and post treatment of the products

3.1 Aims and Objectives

This chapter describes a new hydrothermal batch method for the efficient synthesis of HKUST-1 at high yield and under low temperature and pressure conditions to avoid harsh operating conditions such as high pressure. Different synthesis and activation conditions were tested in order to understand their influence on properties of the synthesis of HKUST-1 under atmospheric pressure.

A simple post modification of the pristine HKUST-1 materials was made to enlarge the surface area, and subsequent CO₂ uptake capacity.

In addition, powdered samples were pressed into pellets for further application.

3.2 Introduction

3.2.1 Historic Methods for HKUST-1 Synthesis

HKUST-1 ($\text{Cu}_3(\text{BTC})_2$) is one of the most widely studied MOFs owing to its high surface area and large pore volume. It was first reported by Chui [156] in 1999. This Cu-based material consists of copper nodes and organic ligand benzene-1,3,5-tricarboxylate (BTC), each copper is coordinated with four oxygen atoms and water molecules [156]. This framework contains a bimodal pore size distribution, the larger cage with 9 Å in diameter and the smaller pore with 3.5 Å in diameter [157, 158]. Compared with traditional porous solid materials (such as zeolites and activated carbon), MOFs possess (by far) the highest surface areas known to date [159]. Furthermore, the structures and pore sizes of MOF materials are relatively easier to be tuned for the specific application [160]. In recent years, MOFS have been found to show great potential in the area of CO_2 capture [161]. MOFs are hybrid materials combining organic ligands and metal ions or metal-contained clusters.

In the past few years, various synthesis strategies were reported, such as microwave assisted synthesis [162, 163],

ultrasonic synthesis [158, 164], mechanochemical synthesis [165] and conventional hydro/solvothermal synthesis. Except the conventional method, the other methods involved the use of specific instruments, but for the conventional method, high pressure [166] or long reaction time (from days to weeks [160]) is often required as elevated temperature and pressure provide thermodynamic conditions favorable the formation of MOF in shorter time [167], considerably less severe operating conditions for the synthesis of HKUST-1 in a few minutes still require operating pressure of 100 bar [168]. However, high pressures even in the autoclave are always associated with safety issues and high costs. The BET surface area reported in literature ranges from 400-1800 m²/g, while most in the range of 700-1000 m²/g [169-172]. Table 3.1 shows the previous reported hydrothermal method for the synthesis of HKU

Table 3. 1 A summary for hydrothermal methods for HKUST-1 synthesis

Year	Container	Time (h)	Temp.* (°C)	Solvents	Yield (%)	S_{Langmuir} (m ² /g)	S_{BET} (m ² /g)	Ref.†
1999	Autoclave	12	180	EtOH/H ₂ O	60	917.6	692.2	[156]
2012	Autoclave	18	110	EtOH/H ₂ O	N/A	N/A	1055	[169]
2015	Atmosphere	12	80	DMF	92	N/A	1387	[173]
2015	Autoclave	24	120	EtOH/H ₂ O	N/A	N/A	1140	[174]
2015	Autoclave	24	100	EtOH	89.4	N/A	1507	[175]
2017	Capped vials	5	60	EtOH	41.6	2100	N/A	[176]
2017	Capped vials	5	79	DMF	55	1200	N/A	[176]

*Temp is the abbreviation of temperature; †Ref is the abbreviation of Reference

In the past three years, Khoshhal et al. [173] produced HKUST-1 under the atmospheric pressure with DMF as the solvent. Al-Janabi et al. reported an optimised procedure to synthesize HKUST-1, which lead to production of HKUST-1 with a yield of 89.4% and a BET surface area of 1507 m²/g [175]. However, the MOF was prepared in a sealed autoclave at 100°C therefore a high pressure would be unavoidable and the preparation process required 24 hours to complete. Most recently, Colin et al. also adopted hydrothermal methods to produce HKUST- 1 with a high surface area [176]. However, the yield was rather low especially when only using ethanol as the solvent. In summary, most recent methods adopted by other researchers in the synthesis of HKUST-1 normally involved in a high pressure, and either the yield or the surface area of the products is low. Few methods were under atmospheric pressure but not yielding a product with high surface areas. Therefore, there is a need to develop new method for the preparation of MOFs at much milder preparation conditions with high surface area and high yield, which can be used for CO₂ adsorption with a high uptake capacity.

In this work, a novel and highly efficient solvothermal method was developed for the synthesis of HKUST-1 under atmosphere

pressure and low temperature. Each MOF was characterized to optimize conditions for the synthesis of HKUST-1. The HKUST-1 was also tested in terms of its potential in CO₂ adsorption.

3.2.2 Commercial HKUST-1

Currently HKUST-1 products can be bought from Sigma-Aldrich, which is a distributor of MOFs provided by BASF with the products named after Basolite®. The BASF company produced this HKUST-1 MOF by using electrochemical synthesis and this technology has been first patented in 2005 [177]. This is also the first time that using electrochemical routes to synthesize MOFs. The process details are described below [178]:

The anodes are 5 mm thick bulk copper plates, placed in an electrochemical cell with the organic linker: 1,3,5-benzenetricarboxylic acid as the cathode dissolved in methanol solution. Figure 3.1 is a photo for the laboratory scale synthesis. The voltage used is between the range from 12 to 19 V and the current adopted is 1.3 A. During a period of 150 minutes a greenish blue precipitate was observed to be generated in the cell. These products were afterwards separated by a filter and

dried at 120 °C overnight. Consequently, pure HKUST-1 powder was obtained.



Figure 3. 1 A photo for the electrochemical cell setup being under operation for HKUST-1 preparation [178]

The surface areas of Cu-MOF products were measured as 1649 m² g⁻¹ and achieved 1820 m² g⁻¹ after activating at 250 °C. The products turned dark blue after the high temperature treatment. The topology and size distribution can be observed via scanning electronic microscopy (SEM) as shown in Figure 3.2. The shape of

the particles exhibited is octahedron and the size distributes from 0.5 to 5 μm .

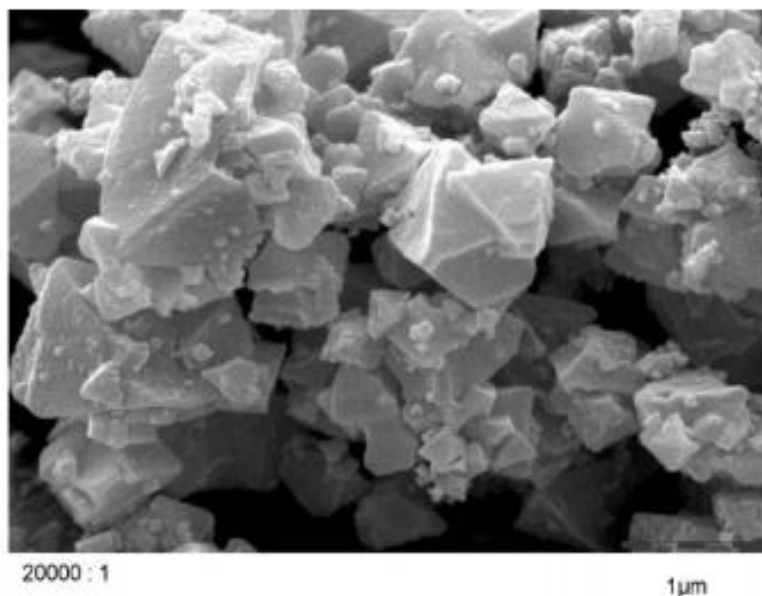


Figure 3. 2 An SEM image for the lab scale electrochemical synthesis Cu-MOF (scale bar: 1 μm) [178]

3.2.3 Chemical Treatment to Enhance the CO₂

Adsorption of MOFs

CO₂ reduction is becoming a highly focused topic all around the world, since it is closely related to the world's climate change [27]. In the recent studies, MOFs are known as having great potential in CO₂ capture, mainly because of their high surface area. Furthermore, several researchers have demonstrated that by doping alkali-metal ions (Li, Na, K, Be, Mg, Ca, Sc and Ti) into

MOFs structures can efficiently improve H₂ adsorption [179-183], CH₄ uptake [184] and CO₂ adsorption [185].

Based on the previous experimental and theoretical investigations, Yang et al.[186] considered that alkali metal ions can facilitate the CO₂ uptake ability. They used different concentrations of lithium naphthalenide (Li⁺C₁₀H₈) to dope Li⁺ into HKUST-1 frameworks. According to their explanations in the publication, the strong nucleophilicity property of lithium naphthalenide [182] enables the electron to transfer from the naphthalenide radical anion to the rehydrated Cu²⁺ sites [187]. In this way, Li⁺ ions were also successfully added into the frameworks.

Before testing the CO₂ adsorption enhancement effect of the Li⁺ doped HKUST-1, the group first investigated the impact of Li content on the BET surface areas of the products. Four products with various concentrations of Li⁺ were tested and compared with the pristine HKUST-1 (with no Li added). The results have listed in Table 3.2. It can be obviously concluded that the surface area decreased dramatically with the increase of Li/Cu ratio (Li content increase).

Table 3. 2 Impact of Li content in the Li@Cu₃(BTC)₂ product on BET SSA[186]

Li@Cu₃(BTC)₂	Li/Cu (mol mol⁻¹)	BET SSA (m² g⁻¹)
1	0	1587
2	73.9	65
3	16.0	173
4	0.12	634
5	0.07	795

To facilitate the analysis, powder X-ray diffraction patterns of these samples are presented in Figure 3.3. The patterns of the products with Li/Cu=16 and 73.9 show significant differences with the other three patterns. New peaks at $2\theta=32^\circ$ appeared, suggesting the MOF frameworks have been destroyed when excess Li⁺ was introduced. On the other hand, the XRD patterns with Li/Cu=0.12 and 0.07 match well with the untreated product. In a conclusion, Li content should be controlled in a proper range

to avoid the destruction of framework. Yang et al.[186] gave the following explanations for these results:

- (i) When Li^+ content remains at a low range, stable lithium alkoxide species would be formed by the reaction between H_2O in the Cu^{2+} sites and the lithium naphthalenide complex[188, 189].
- (ii) If the content of Li^+ is high, the excess lithium naphthalenide can probably turn Cu^{2+} to Cu^+ or substitute Cu^{2+} sites owing to its high nucleophilicity. Thus, the sample framework collapse and directly influence the surface area. Furthermore, the gas adsorption ability is also inhibited.

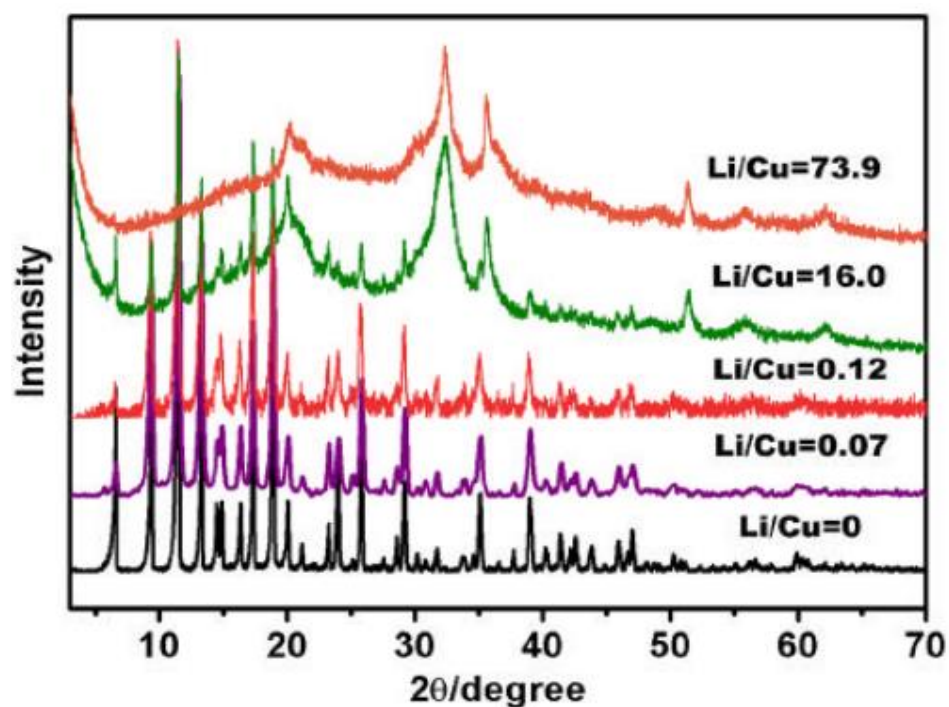


Figure 3. 3 PXRD patterns for the unmodified HKUST-1 and products doped with different amounts of Li^+ ions[186]

The gas adsorption measurements were conducted by using a Hiden Isochema Intelligent Gravimetric Analyzer (IGA-003) at 298 K and 18 bar. The CO_2 uptake amount of the Lithium doped sample with a Li/Cu ratio equal to 0.07 is 469 mg g^{-1} , much higher than that of unmodified sample (295 mg g^{-1}).

Llewellyn et al.[190] also reported a chemical treatment method to increase the CO_2 capacity of MOF MIL-101: first treated by ethanol solution and followed by NH_4F solution. In 2014, Yan et al [191] illustrated a simple method to improve CO_2

uptake of HKUST-1. They first prepared HKUST-1 based on previously reported method[156] and the unmodified sample is referred to as M0. Different solvents and inorganic salts including water, ethanol and NH_4Cl are used to treat M0 at room temperature or at 65 °C. Table 3.3 summarize the nomenclature of different samples.

Table 3. 3 Nomenclature and description of different samples

MOF samples	Solvent Treated	Temperature (°C)
M0	-	-
M0/N-E-W	Water+Ethanol+ NH_4Cl	65
M0/E-W	Water + Ethanol	65
M0/W	Water	65
M0/E	Ethanol	65
M0/N-E	Ethanol + NH_4Cl	65
M0/N-E-RT	Ethanol + NH_4Cl	Room T
M0/E-RT	Ethanol	Room T

All of these samples were examined by using powder x-ray diffraction to determine if the framework structures were adversely affected. Figure 3.4 shows the XRD patterns of the unmodified HKUST-1 and solvent treated (at 65°C) HKUST-1. It can be seen from the patterns that the structure of the sample treated by pure water was destroyed, while the other samples remain structure integrity after different chemical treatment. It is also inferred by Yan et al.[191] that the existence of ethanol in water can prevent the structure of M0 being destroyed.

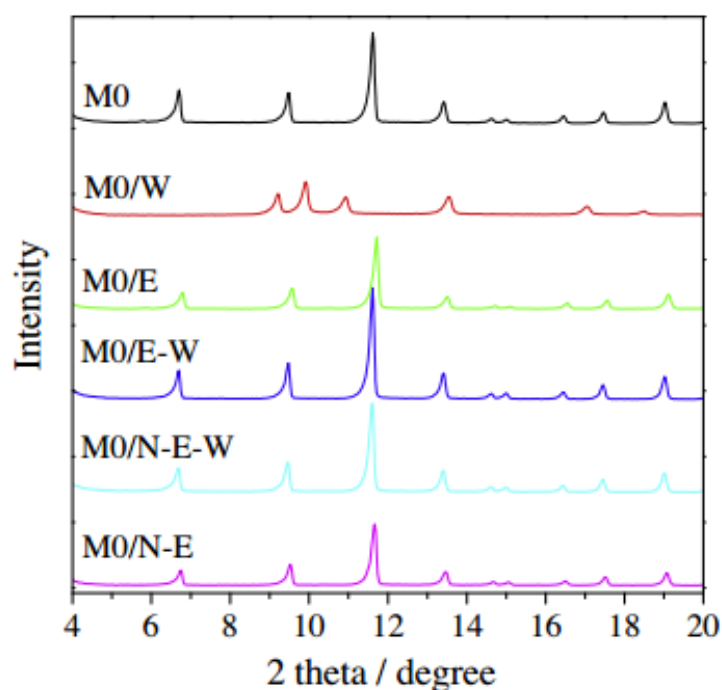


Figure 3. 4 A comparison of XRD patterns between unmodified HKUST-1 and solvent treated HKUST-1 [191]

Figure 3.5 shows the SEM images of untreated HKUST-1 and chemical treated sample. The morphologies have no changes compared with the original sample. Therefore, combined the results from XRD patterns, the conclusion can be drawn that treating HKUST-1 by ethanol containing solvents the product exhibits little or no change in the crystal structure, as well as the morphology.

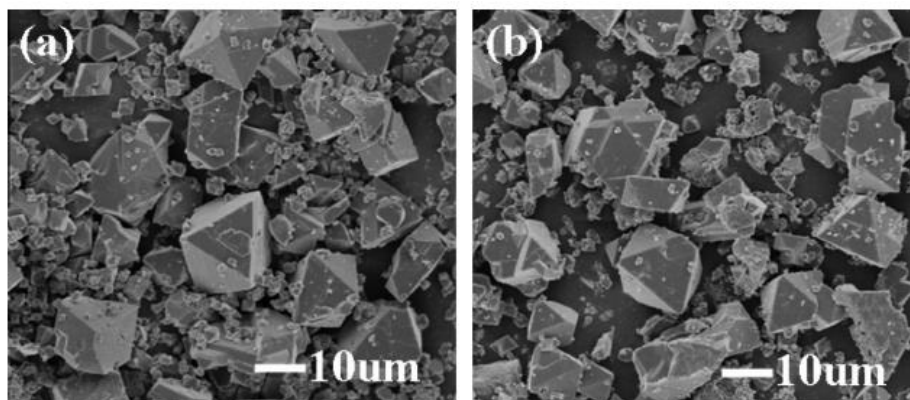


Figure 3. 5 SEM images of (a) M0 and (b) M0/N-E [191]

The CO₂ adsorption capacity of different samples at 0°C and 1 atm are listed in Table 3.4. It can be clearly seen that the CO₂ uptake ability of HKUST-1 greatly improved after treated by NH₄⁺.

Table 3. 4 The amount of CO₂ adsorbed by different samples (0°C, 1 atm)

MOF samples	CO₂ uptake amount mmol g⁻¹
M0	7.23
M0/N-E-W	10.58
M0/E-W	9.68
M0/W	2.52
M0/E	9.43
M0/N-E	11.64
M0/N-E-RT	10.67
M0/E-RT	9.30

The infrared spectrum (IR) experiments were conducted on samples M0, M0/E, M0/N-E and M0/N-E-W before and after degassing at 180°C. The results have shown in Figure 3.6. The peaks appearing with the wavenumber around 1676 cm⁻¹ can be attributed to DMF. Obviously this peak becomes much weak after degassing at 180°C. Nevertheless, the peak still can be observed (Figure 3.7 B). This illustrates that DMF molecules are not removed completely by thermal treatment alone. However, it is clear that after chemical soaking this band disappears, indicating DMF has now been totally removed. According to Yan et al.[191], NH₄⁺ reacted with unreacted 1,3,5-tricarboxylate acid, but NH₄ band is not present in the IR spectra, meaning NH₄⁺ has also removed by washing process.

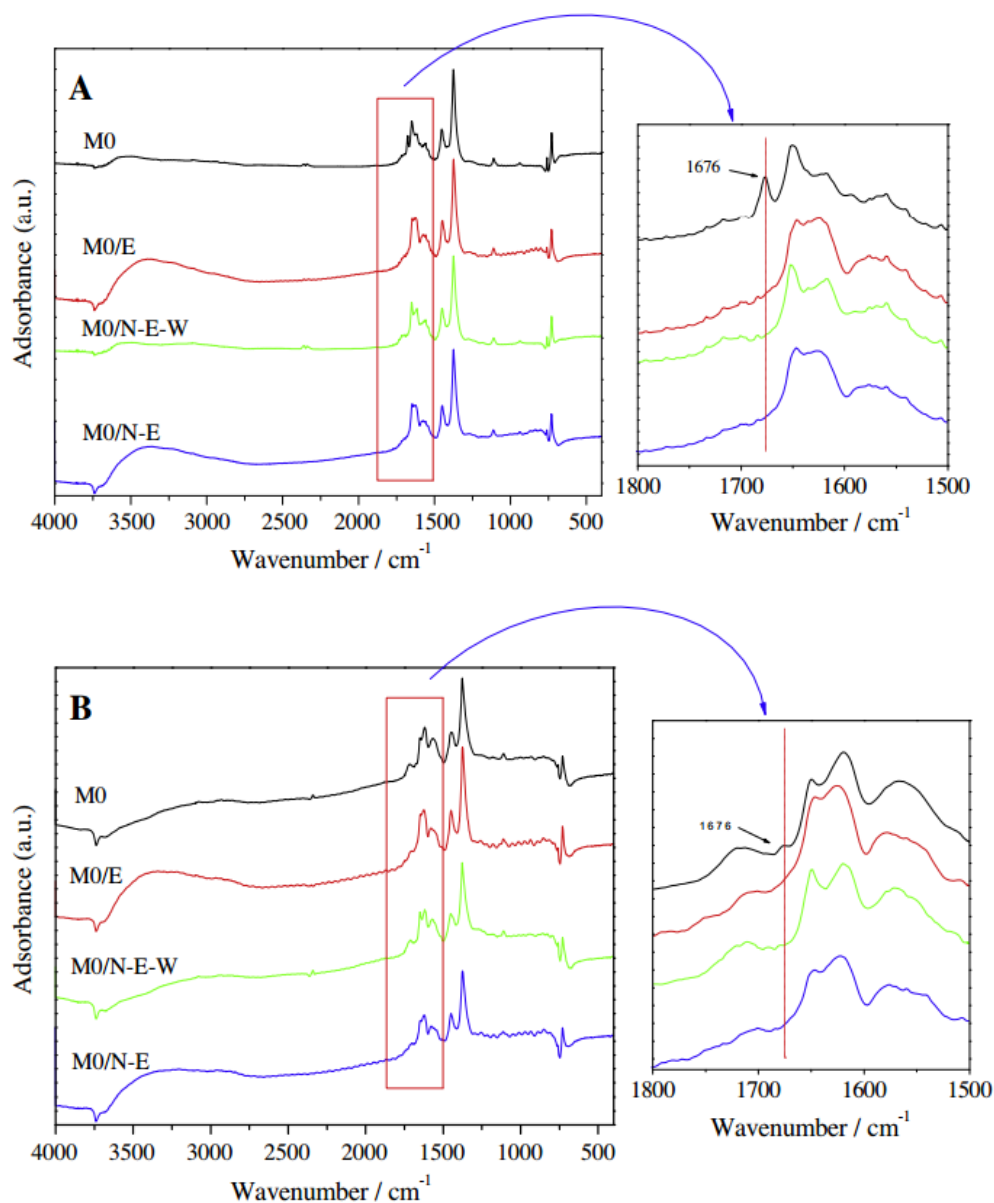


Figure 3. 6 IR spectra results of unmodified sample and chemical treated samples. (A) Before degassing (B) After degassed at 180°C under a reduced pressure.

In my work, an attempt was made to enhance the CO₂ uptake of HKUST-1 via soaking the sample in NaCl solution. The aim initially was to dope Na⁺ in the structure, but the examination

techniques including EDX-SEM, TGA did not give any evidence of the presence of Na. However, an enhancement of CO₂ adsorption still occurred after the post treatment. The details will be discussed in Section 3.4

3.2.4 Shaping of Metal-Organic Frameworks

When considering how to employ metal organic frameworks in industrial scale applications, shaping and formulation of the powders into a macroscopic body becomes quite necessary [192-196]. The form of the adsorbent plays an important role in determining the overall performance [197, 198]. In order to minimize the effects of pore diffusion, smaller particle size is required; while for the purpose of reducing the pressure drop through the reactor, bigger particle size is preferred [199]. Thus, a compromise between these two respects should be made [200].

Several techniques can be used to shape MOFs, such as pressing, granulation, extrusion and pressing etc. The bodies can be normally shaped as tablet, pellets, monoliths and spheres [201-204]. Figure 3.7 shows various shaped bodies. In addition, to successfully apply the shaped materials in industry, the properties of mechanical strength, chemical stability, surface

areas and dense packing inside the column is also important [205-208].

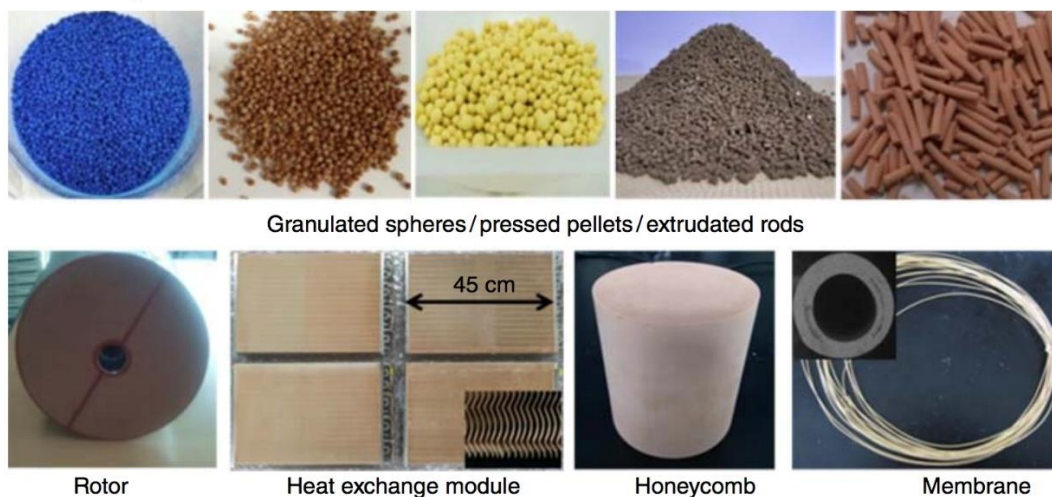


Figure 3. 7 Various shaped bulk MOFs with different forming methods [200]

3.2.4.1 Granulation

Granulation, also named as spheroidizing, is a process to shape the samples via the powder agglomeration effect. This technique is similar with the formation of a snowball. Figure 3.8 has illustrated the formation process. The binder here was used to intensify the strength of the granules to avoid structure collapse after thermal treatment. Different binders are required for each type of materials. For example, inorganic materials normally require inorganic binders because a majority of inorganic materials will be calcined at a high temperature. Silica sols and

alumina are usually applied as inorganic binders [209]. Conversely, for Metal Organic Frameworks plasticizers or organic binders are more appropriate, since thermal treatment with high temperature will be avoided due to the organic ligand contained in the MOFs. Therefore, binders such as polyethylene oxide, polyethylene glycol, polyvinyl alcohol, or cellulose can be used as the additives to the organic materials [78, 210-212].

The advantages of using granulation technique are: (i) shaped products can be generated continuously so that the quality is relatively constant. (ii) inexpensive and simple methods, although the shape and size are irregular compared with the other shaping techniques. The binding force is mainly provided by the liquid bridges between particles and capillarity [213-215]. The granulation process includes the following key stages [216]:

- (i) Wetting and nucleation
- (ii) Consolidation
- (iii) Attrition and breakage

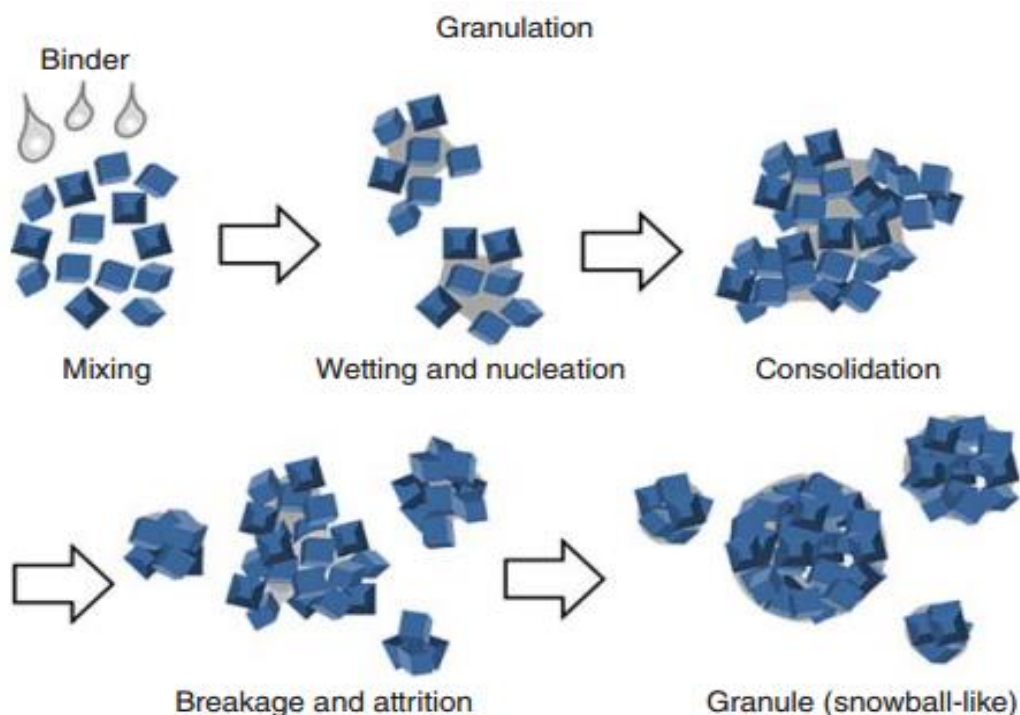


Figure 3. 8 The flow diagram of granulation process [200]

Cameron et al [214] produced HKUST-1 spheres by wet granulation method. Firstly the powder was mixed with a polymer binder, and then the mixture was shaped by a homemade granulator. Sequentially, ethanol was added periodically to wet this mixture for powder agglomeration. As a result, the HKUST-1 granules with sizes ranging from 1 mm to 3 mm were generated. The surface area of this material only has a small reduction of less than 4%. Figure 3.9 presents the size and morphology of the sphere-like granules.

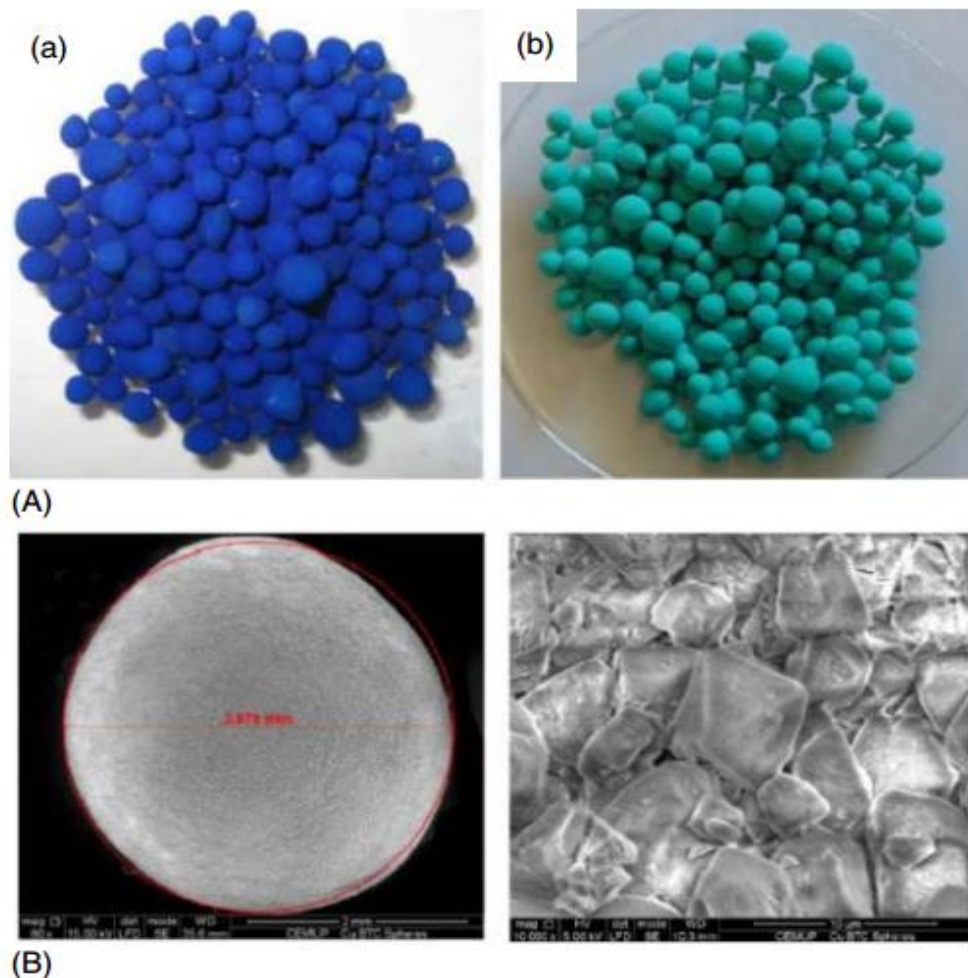


Figure 3. 9 Photographs (A) and SEM images (B) images of HKUST-1 granules: (a) Dehydrated HKUST-1 and (b) after air exposure (hydrated form) [214].

3.2.4.2 Extrusion

Extrusion is a process where powder state materials are pushed through a confined space or a die and form the products called extrudates [217, 218]. Figure 3.10 illustrates the extrusion process. Ramirez and coworkers [219] first shaped HKUST-1 (Cu-

BTC) extrudates at mm-scale. They synthesized HKUST-1 with a surface area of $1750 \text{ m}^2\text{g}^{-1}$. A Caleva Mini Screw Extruder with a die of 2 mm diameter was utilized to obtain shaped HKUST-1 bodies. 20 wt% kaolinite was added as the binder and their testing result shows that the binder additive did not destroy the crystallinity, but led to the huge reduction of surface area to $900 \text{ m}^2\text{g}^{-1}$.

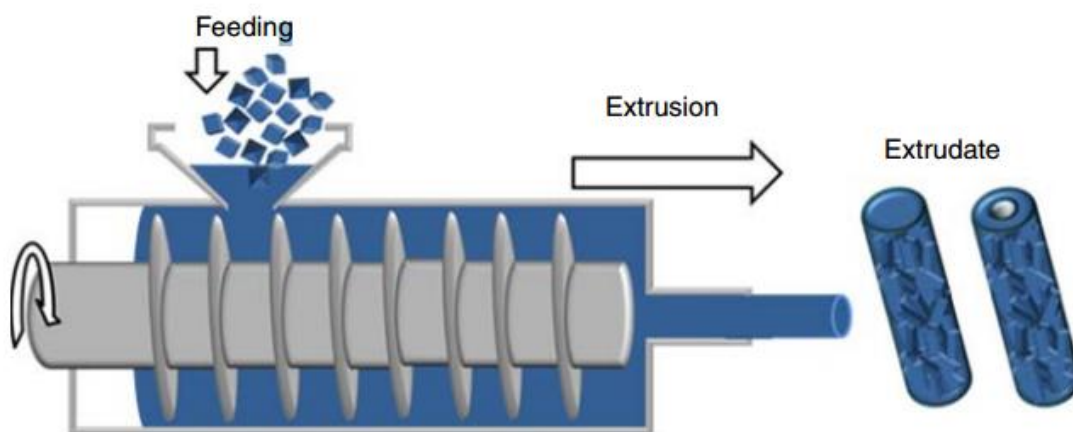


Figure 3. 10 Extrusion process and the resultant extrudates.

3.2.4.3 Pressing

The shape of the bodies generated by pressing is relatively regular compared to the other shaping techniques. This method is widely applied in industrial usages, for the reason that it is suitable for mass production. Figure 3.11 demonstrates the procedure of pressing the fluffy powders into a pellet. Usually,

proper amount of powders are filled in a metallic mold and then the upper punch is pressed by extra force to compact the powders. The achieved product possesses a much higher density with the pristine powder materials. It is important to evaluate the surface area and adsorption capacity after compaction for MOFs [220].

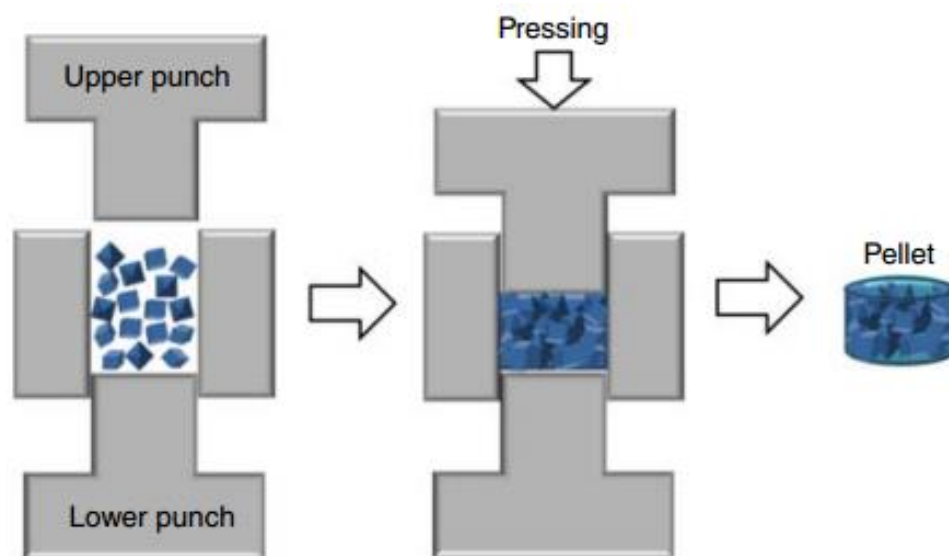


Figure 3. 11 Schematic diagram for the pressing technique for shaping MOFs.

By using this processing method to shape MOFs, binders usually are not normally added. Several researchers manufactured binder-free but still robust pellets [221-223]. Tagliabue et al. [221] produced CPO-27(Ni) pellets without any binders in a form of hard disk. When the pristine powder

materials were compacted under 0.1 GPa pressure, the colour of powder did not change and remained in the original yellow. However, when the pressing pressure increased to 1 GPa, the colour changed obviously from yellow to dark brown. This observation indicated deep modifications in the CPO-27 crystal structure. The researchers found a dramatic decrease in the crystallinity after pressing at 1 GPa, which was probably occurred by the breakdown of the MOF structure [221]. Another research group pressed the commercialized HKUST-1 offered by BASF into pellets and examined the adsorption capacity. The result shown a capacity decrease of 21% occurring in the HKUST-1 pellets occurred due to the pressing process.

More recently, Bazer-Bachi et al. shaped three MOFs which are ZIF-8, HKUST-1, and SIM-1 also by the pressing technique. This research group added an organic binder of cellulose ester, K15M in the process, and different pressures were utilized. Figure 3.12 shows the testing results for these three materials after pressing. All of these materials were found to be partly amorphization [224]. Interestingly, they discovered the acid-base properties of ZIF-8 were not influenced when its textural and structural properties have been modified. Thus, the catalytic activity of ZIF-

8 was maintained similarly. This can be attributed to the defects effect facilitating the catalytic activity.

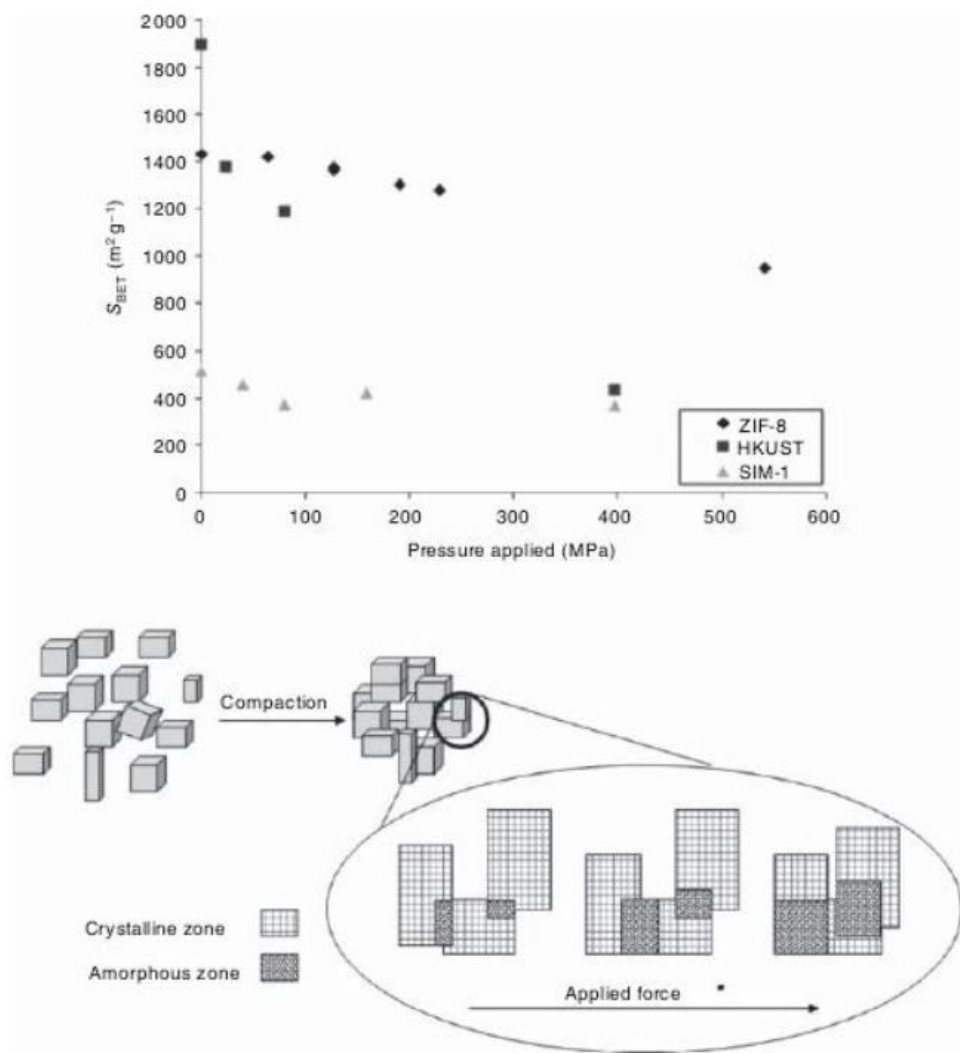


Figure 3. 12 The changes of BET surface area of samples after pressed by different pressures and a graphic illustration for the effect of applied force on the crystal structure [224].

A pressing method was chosen in this work to shape HKUST-1, since the technique is the simplest and the surface area will not

decrease significantly when applying the proper range of pressures.

3.3 Experiment A: HKUST-1 synthesized at mild conditions

3.3.1 Materials and Preparation Method

All chemicals used in this work were purchased from Sigma Aldrich and used without further purification. In a typical synthesis process, copper nitrate trihydrate (98%) and benzene-1,3,5-tricarboxylic acid (95%) solution was mixed and heated to 50 °C for 3 hours. After being cooled down to room temperature, it was placed in a dryer at 120°C for 12 hours. The collected pristine HKUST-1 was then activated by methanol or ethanol. Finally, the product was centrifuged and dried at 120 °C overnight. It should be noticed that methanol is classified as danger in the material safety data sheet, it can be fatal or cause blindness if swallowed. Eye, skin, respiratory tract irritation and even central nervous system depression is possible to be caused. Therefore, it is of significantly important to wear PPE (personal protective equipment) during using methanol. In this study, different preparation conditions were tested to identify the

optimal product. Table 3.5 lists the denominations for different products.

Table 3. 5 List of HKUST-1 samples and corresponding preparation conditions

Sample	Reaction	Oven	Activation	Dry
ID	Condition	condition	Condition	condition
T1-N	3h, 50 °C		No activation	12h, 120 °C
T1-E1	3h, 50 °C		3h, ethanol	12h, 120 °C
T2-E1	9h, 50 °C		3h, ethanol	12h, 120 °C
T1-E1-2	3h, 50 °C	12h, 120 °C	3h, ethanol	12h, 180 °C
T1-M1	3h, 50 °C		3h, methanol	12h, 120 °C
T1-M2	3h, 50 °C		3h, methanol twice	12h, 120 °C

3.3.2 Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 A25 diffractometer operated at 40 kV and 35 mA between $5^{\circ}2\theta$ and $40^{\circ}2\theta$ with a Cu K α radiation. The scan speed was 1s/step and the step size was 0.02° [223] Thermal stability test was performed on a thermogravimetric analysis instrument (NETZSCH STA49 F3) under high-purity nitrogen (99.999%) flow atmosphere, following the method described elsewhere [225]. Approximately 10 mg sample was heated from 30 to 900 °C with a heating rate of 10k/min. The morphology of materials was observed using a scanning electron microscopy (SEM ZEISS Sigma VP) operated at 20kV. Nitrogen adsorption experiments were performed using a Micromeritics Tristar 3020 instrument operated at 77k. Before each test, the sample was degassed at 150 °C for 12 hours to remove water.

3.3.3 CO₂ adsorption-desorption test

The CO₂ uptake capacity was examined using the NETZSCH TG instrument at 1 bar. In a typical test, the temperature was initially increased to 150 °C under N₂ atmosphere (99.999%) and then decreased to 27 °C for 30 min. The gas flow was switched

to pure CO₂ for 30mins after temperature was stable. CO₂ cyclic adsorption-desorption uptake test was performed to evaluate the stability of HKUST-1. In this cyclic test, N₂ gas was used to squeeze out the adsorbed CO₂ in the sample at the same temperature. The adsorption and desorption processes were repeated for 10 times continuously. The N₂ gas flow rate was set at 100 mL/min and CO₂ at 133 mL/min. Blank group was done for every test to eliminate the influence of buoyancy.

A CO₂ isothermal adsorption test was carried out using a Micromeritics ASAP 2020 instrument at 27 °C for 12 h.

3.3.4 Results & Discussions

3.3.4.1 Crystal Structure Characterization

It can be seen from Figure 3.13 that the main X-ray diffraction peaks for each sample matched well with the patterns obtained from simulation based on single crystal data, as well as those reported in the literatures [226]. The sharp peaks for all samples suggest they possess a high degree of crystallinity [226].

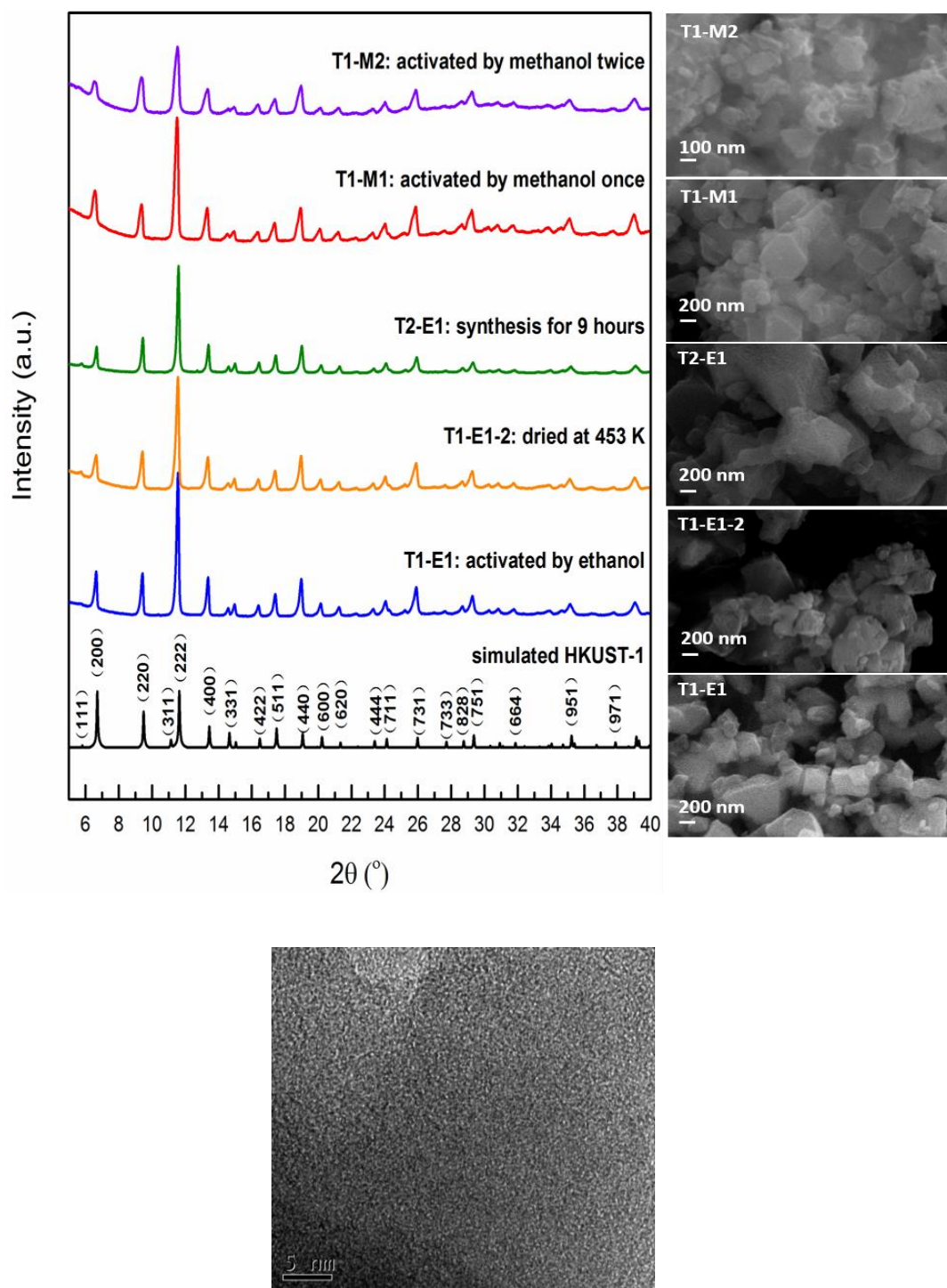


Figure 3. 13 Top: XRD patterns of the samples synthesized under different reaction conditions. Insets show the corresponding SEM images; bottom: TEM image for T1-M1

The colour of as-synthesized HKUST-1 powder is light blue, but after activation by ethanol or methanol it turns in dark blue. This colour change of the sample is consistent with those reported in the literature [175]. According to Yan [227], this change implies that the co-ordination number of copper decreased from six to four. The activation process elutes the coordinated solvent or water with copper sites.

There is a small difference observed from the comparison with simulated patterns. The intensity ratios of (331) to (420) plane, and (200) to (220) plane are both notably higher for the simulated patterns, which also can be understood as dehydrated samples. This phenomenon is in agreement with that reported by Klaus et al. [166]. This difference is difficult to be avoided because HKUST-1 will rapidly adsorb water during the preparation process of doing XRD test. Ajay et al.[228] stated that the marked reduction of peak intensities of (111) and (200) is related to the FCC crystal structure loss on account of hydration of HKUST-1.

From the SEM images, no significant differences in terms of morphology were observed among these activated samples. Their

crystal sizes are all in the range from 100 to 500 nm. The SEM image of T1-M2 clearly shows crystal surface defects and smaller sizes compared with T1-M1, meaning the second washing process has significant influences on the structure of HKUST-1 and damage takes place on the surface. This damage also influences the sample's surface area and also CO₂ capacity. The TEM image further proves the porosity of produced sample.

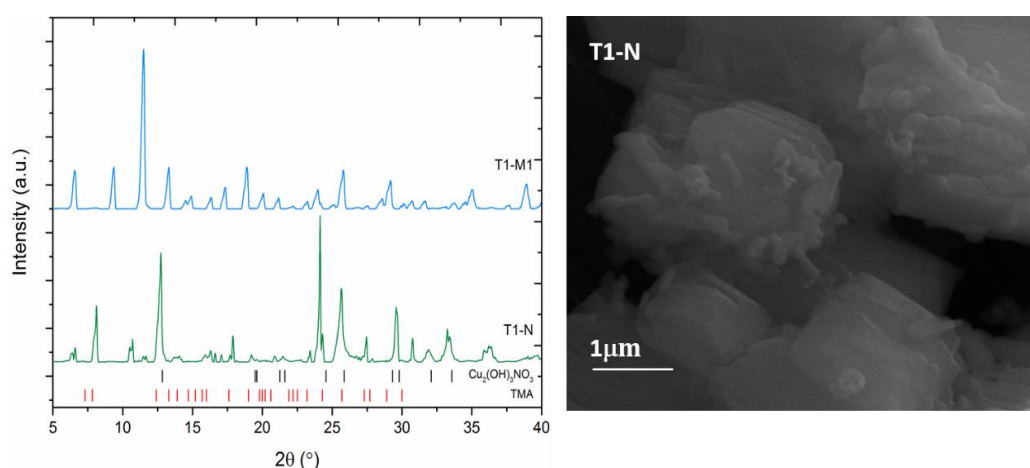


Figure 3. 14 Comparison of non-activated sample and one-time methanol activated sample

The XRD pattern for the sample without activation (T1-N) is significantly different from the activated samples. T1-M1 was taken as the typical sample to make the comparison with T1-N. As it is shown in Figure 3.14 there are three main different peaks on $2\theta = 7.9^\circ$, 10.7° , 12.7° . The unreacted copper nitrate and trimesic acid may remain in the samples. In addition, the

diffraction data of simulated $\text{Cu}_2(\text{OH})_3\text{NO}_3$ indicates it is present in the sample. It is also reported [229] that the copper based precursors include $\text{Cu}_2(\text{OH})_3\text{NO}_3$. However, after taking these impurities into consideration the pattern of T1-N is still not consistent with that of HKUST-1. This result suggests that new crystalline complex are formed via chemical bindings. The activation process breaks these bindings and then the XRD shows pure phase HKUST-1. Moreover, the pH value of T1-M1 solution is measured as 0.68, and 7.22 for T1-M2 solution. These solutions were collected from the upper layers after centrifugation for each sample. The pH value's huge change indicates that the first time activation has cleaned up the sample.

3.3.4.2 Thermogravimetric Analysis

Figure 3.15 presents the weight loss of samples when the temperature was raised from room temperature to 600 °C at a heating rate of 10 °C per minute in nitrogen atmosphere. The shapes of the TGA curves are all similar to those reported for HKUST-1 crystals [160, 230].

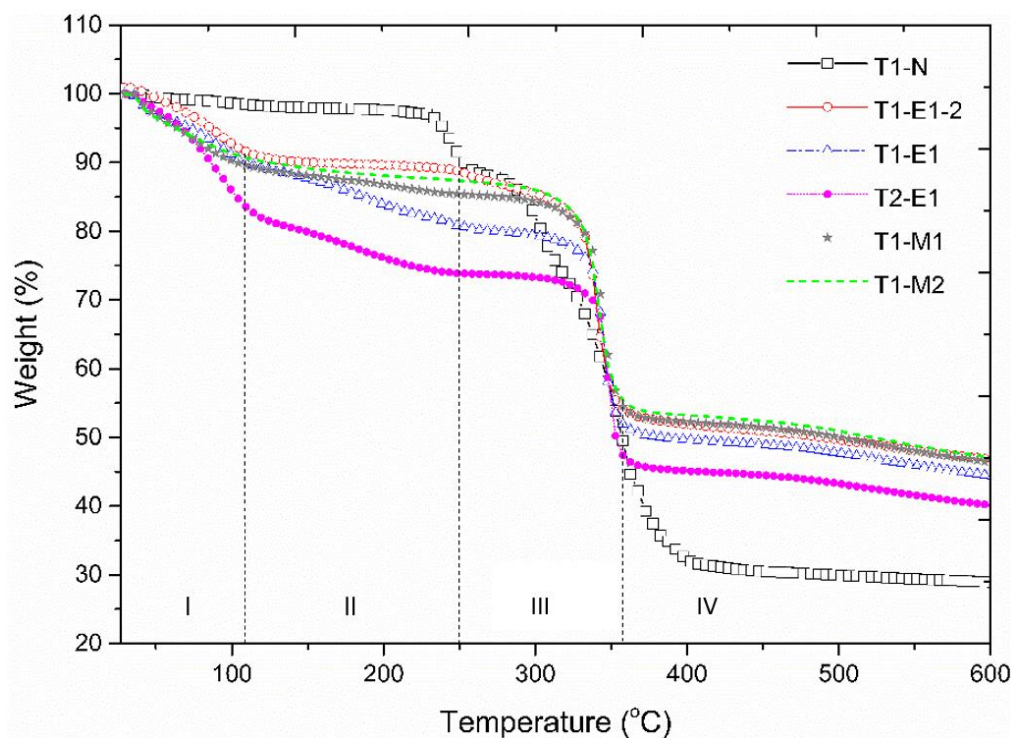


Figure 3. 15 Thermogravimetric analysis of various samples

The first mass loss stage between 30 and 110 °C can be ascribed to the evaporation of physically adsorbed water. When exposed in the air environment, HKUST-1 can instantaneously adsorb water into the pores and occupy the 96 j position [156, 166].

The two products activated by ethanol (T1-E1, T2-E1) have an obvious weight loss in step (II) between 110 and 250 °C, which indicates the release of water chemically bonded on copper atoms, and solvent physically adsorbed molecules in internal

pores [166]. This is consistent with what Witri et al. [170] reported. The coordination bonds between water and copper requires the higher temperature (150 ~ 300 °C) to break, which is higher than that of physically adsorbed water molecules.

It is obvious that the products activated by methanol show a small loss at this stage, and the product without activation (T1-N) exhibits a plateau at the temperature range from 30 to 230 °C. This indicates that no solvent molecules are physically adsorbed in the pore interior. This can be explained by the non-porous structure of T1-N, which can be clearly analyzed from N₂ adsorption experiment in the next part. Hence, it is speculated that the guest molecules released in stage II are formed during the ethanol activation process. It should be noticed that the sample with ethanol activation but underwent 180 °C drying (T1-E1-2) displays no obvious mass drop, which suggests that the higher drying temperature can eliminate the guest molecules, but on the other hand it might lead to the formation of more defects in the framework.

All activated products only lost small amount of weights in stage III and then their frameworks began to breakdown when

temperature was raised to above 320 °C (stage IV) due to the damage of the relatively weak coordination bond between copper and the ligands [231, 232], whereas for the sample without washing and activation, the collapse covers a broader region as a result of the residuals such as unreacted chemicals mixed in the product. Powder XRD pattern showed the compositions after being heated to 600 °C, which are Cu, Cu₂O and CuO. It can therefore be concluded that the sample activated by methanol contains much less impurities than those washed by ethanol, and methanol is a better activation agent than ethanol. Methanol is able to remove the guest molecules inside the pore system with a higher efficiency than ethanol resulting from its smaller molecular size.

3.3.4.3 Textural properties

N₂ adsorption-desorption isotherms at 77 K are shown in Figure 3.16. The non-activated sample exhibits a plateau with almost zero N₂ adsorption, indicating its non-porous structure. Similar shapes of the isotherm curves are revealed by sample T1-M1, T2-E1, T1-E1 and T1-E1-2. Their adsorption equilibriums are all quickly reached in the low relative pressure region, and there are no hysteresis loops shown in the high relative pressure. This

shape indicates they belong to an isotherm of type I according to the IUPAC (International Centre for Theoretical and Applied Chemistry) classification [172, 233]. Samples with Type I isotherm are of microporous (<2nm) structure [165].

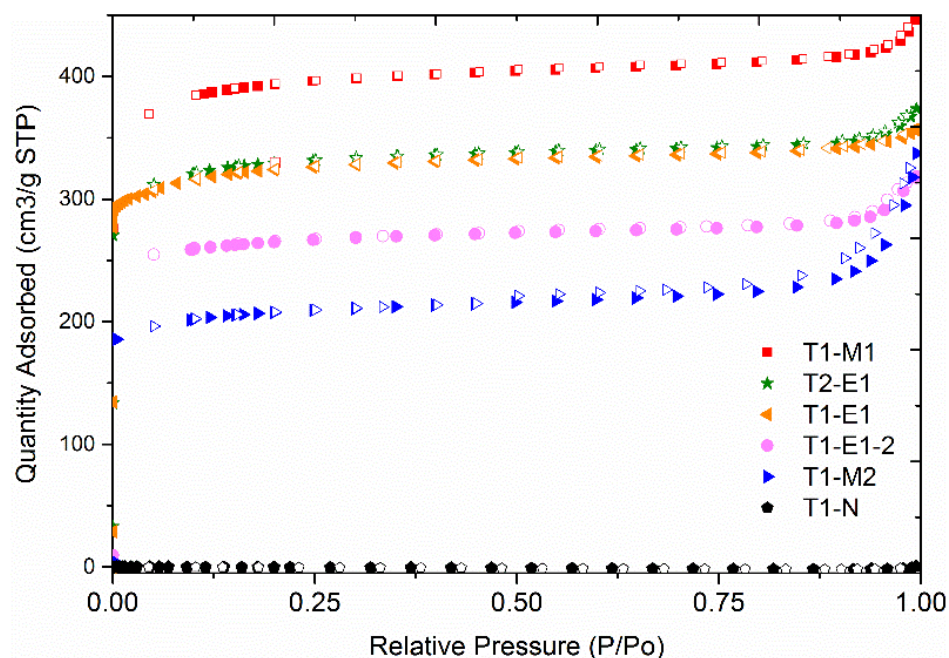


Figure 3. 16 N₂ adsorption-desorption isotherms for different samples

Results of BET surface area and porosity properties are listed in Table 3.6. The sample activated by methanol once possesses the highest BET surface area of 1616.1 m²/g. Its total pore volume and micropore volume are determined to be 0.69 cm³/g and 0.61 cm³/g, respectively. These values are relatively high compared with the reported results [233]. The high gas uptake capacity

states that the guest molecules in the pore interior are absent after activation process [234] which is also in consistent with TGA results. The surface area of T1-E1 and T2-E1 is very similar, so as the pore volume. Therefore, it is speculated that mixing time does not have significant influence on the textural properties of the sample prepared and three hours' mixing is adequate. While T1-E1-2 is of a much lower surface area, which is attributed to the drying process. The BET surface area of T1-M2 is about half of the T1-M1. It is seen from Figure 3.16, T1-M2 presents a hysteresis loop at high relative pressures, which is attributed to the stack of the particles or capillary condensation occurring in mesopores (2-50nm) [235]. The mesopores are inferred to be formed in the second washing process and meanwhile the micropore structure is broken down, to some extent. The BET and porosity results suggest that methanol is a better activation agent than ethanol to purify the sample, since the size of methanol molecules is smaller so that it is easier to get exchanged of the guest molecules in the pores. In addition, it is optimal to wash once to achieve a high surface area and avoid damaging the micropore structure.

Table 3. 6 Textural properties of different HKUST-1s*

Sample	S_{BET}	S_{Langmuir}	V_p	V_m
ID	(m^2/g)	(m^2/g)	(cm^3/g)	(cm^3/g)
T1-N	0	0	-	-
T1-E1	1268.3	1475.2	0.55	0.51
T1-E1-2	1051.5	1208.0	0.49	0.41
T2-E1	1273.6	1501.0	0.58	0.51
T1-M1	1615.1	1805.5	0.69	0.61
T1-M2	801.4	971.8	0.52	0.31

* V_p : total pore volume at 0.99 p/p_0 , V_m : micropore volume by t-plot analysis.

3.3.4.4 CO₂ adsorption and structure stability

The high surface area of MOFs is a significant feature that can result in a high CO₂ uptake capacity [159]. In addition, HKUST-1 contains unsaturated metal sites (also known as open metal sites) that have relatively strong affinity to CO₂ [10, 236]. Therefore, it is worth studying the CO₂ adsorption performance by HKUST-1.

The CO₂ adsorption was carried out using a TGA under atmospheric pressure. Different temperatures were tested to investigate temperature influence on CO₂ uptake. Figure 3.17 shows the amount of CO₂ adsorbed on the sample T1-M1 at 27, 50, 70, 90 and 110 °C. It was found that CO₂ uptake was 8.08% (calculated by the weight gain from the sample), which is relatively high compared with data reported by others [237, 238]. Figure 3.18 illustrates relationship between MOF textural properties and CO₂ uptake. It is clear that textural property has a strong influence on CO₂ uptake. T1-M1 possesses the highest CO₂ uptake capacity (8.08% or 1.84 mmol/g) among these five samples, which has the highest V_m, V_p as well as surface area.

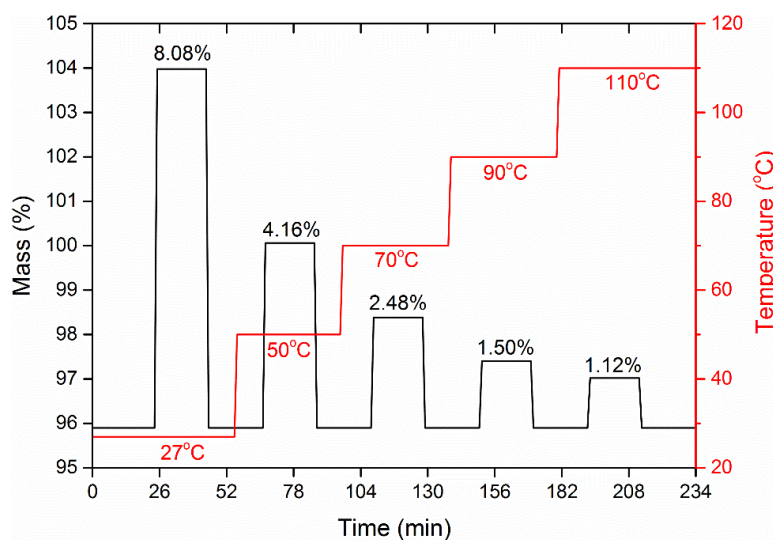


Figure 3. 17 CO₂ uptake at different temperatures

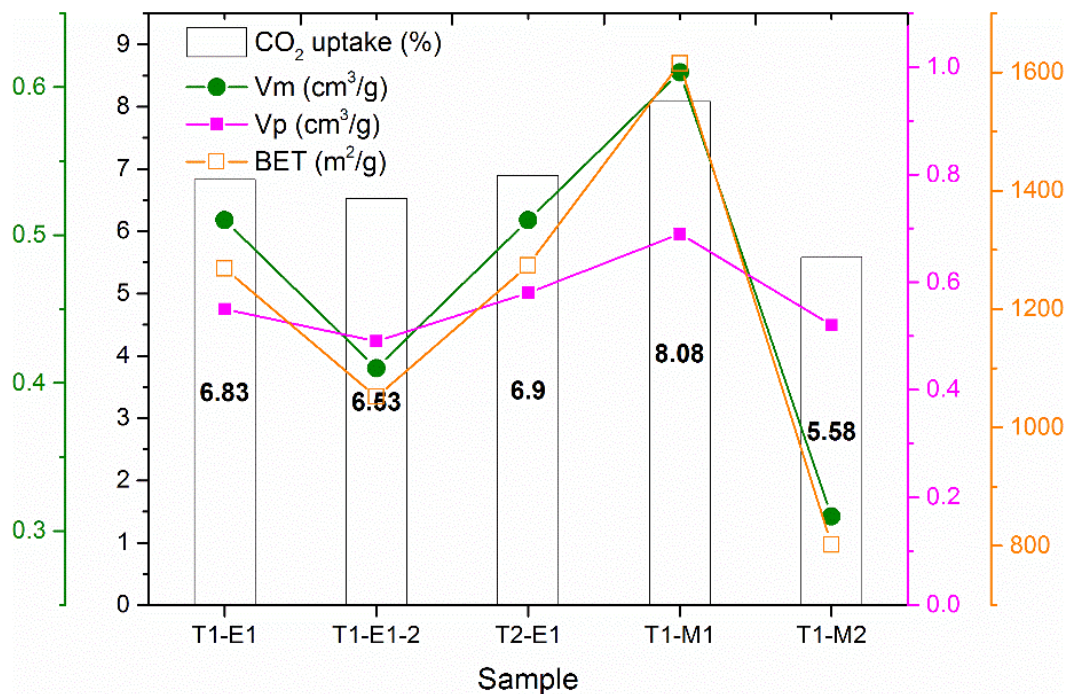


Figure 3. 18 Relationship between CO₂ capacity and total pore volume, micropore volume and BET surface area

The CO₂ adsorption isotherm curve for the sample with the highest surface area (T1-M1) is shown in Figure 3.19. The measurement condition was at 27 °C and ambient pressure in order to match the post-combustion CO₂ capture application environment, since the partial pressure of CO₂ in the flue gas is often around or lower than 1 bar [10, 239]. The result is in agreement with what was reported by others [240], which shows that under 1 bar the product is able to adsorb 4.2 mmol/g (equals to 18.5%). This value is much higher than what was obtained using TGA. This is believed to be due to the sample

being degassed in advance which released more sites for CO₂ uptake.

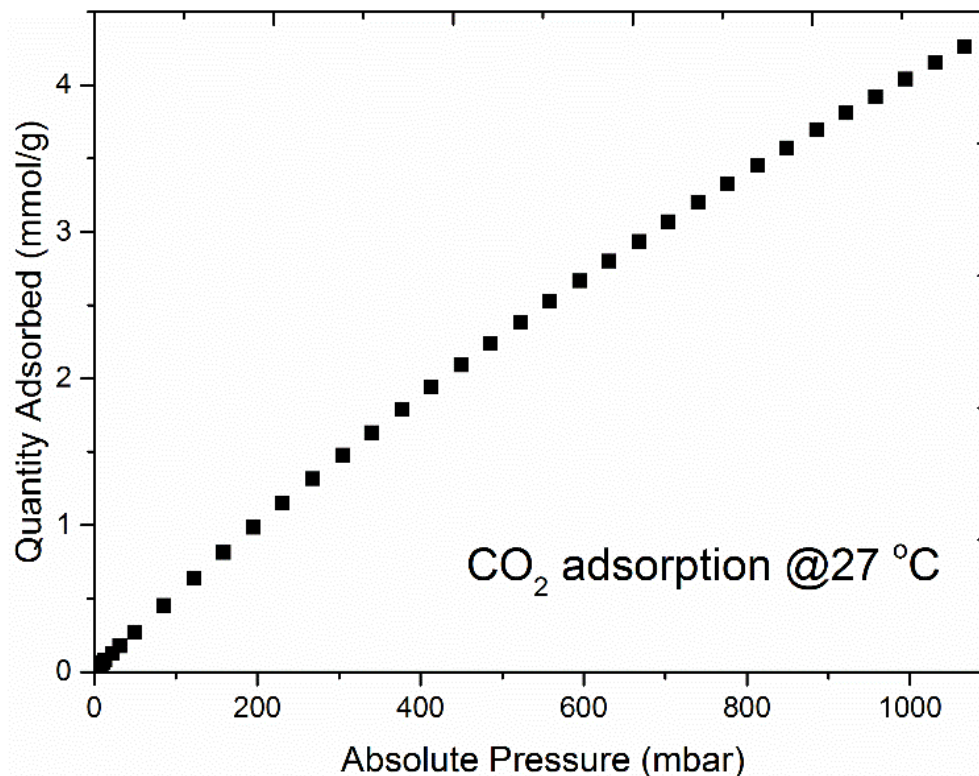


Figure 3. 19 CO₂ isotherm curve at ambient temperature

In 2016 Meng et al. [241] concluded that at atmospheric temperature and pressure, the CO₂ uptake capacity of HKUST-1 synthesized from different researchers varies from 2.9 to 5.1 mmol/g. To evaluate CO₂ adsorption performance of our HKUST-1, comparisons with reported data is illustrated in Table 3.7.

Table 3. 7 CO₂ adsorption capacities by various MOFs

MOF Name	Adsorption capacity (mmol/g)	Adsorption condition	Reference
HKUST-1	1.82	30 °C, 10bar	[233]
HKUST-1	3.27	25 °C, 1bar	[241]
HKUST-1	4.20	27 °C, 1bar	This study
HKUST-1	4.5	22 °C, 0.9bar	[62]
MIL- 101(Cr)	1.17	30 °C, 10bar	[233]
ZIF-8	0.76	25 °C,, 1bar	[242]
UIO- 66(Zr)	2.7	25 °C,, 2bar	[240]

Compared with the other widely studied MOFs as shown in Table 3.7, the HKUST-1 prepared in this study shows a higher adsorption ability under similar adsorption conditions. This is due to unsaturated metal centers providing a stronger physisorption of the CO₂ [10, 239]. It can also be concluded that HKUST-1 prepared in this study is promising for CO₂ adsorption application.

Since structural stability of the adsorbent is significant during CO₂ adsorption, CO₂ cyclic adsorption-desorption test of T1-M1 was conducted and the results are shown in Figure 3.20. The amount of CO₂ adsorbed by the MOF of each cycle is almost the same, suggesting that with N₂ feeding CO₂ is almost completely outgassed and the product can be regenerated to adsorb CO₂ repeatedly, and the product maintains its structural integrity after several cycles, which suggests that the product is able to be re-used without losing its CO₂ uptake capacity. The reversible adsorption also demonstrates that the interaction between metal and CO₂ involves no chemical bonding [236].

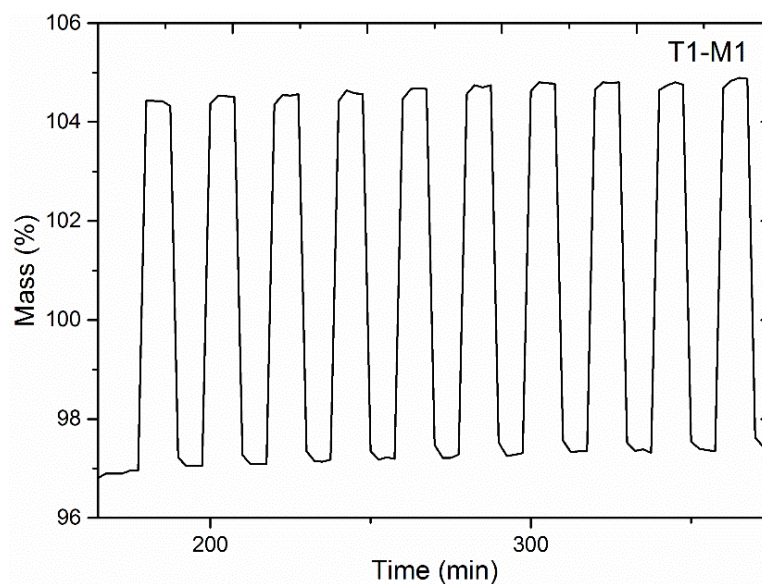


Figure 3. 20 CO₂ cyclic adsorption for the optimal sample T1-M1

3.3.5 Conclusions

By Experimental A, it is confirmed that this new approach can be used for the rapid synthesis of HKUST-1 MOFs with a comparable high surface area ($1615 \text{ m}^2/\text{g}$) as those MOFs prepared under harsh operating conditions. The new approach can be carried out safely under ambient pressure and mild temperature with a high yield of MOFs of 84%. In addition, the CO_2 adsorption tests showed that the HKUST-1 prepared in this study had a good CO_2 uptake capacity of $4.2 \text{ mmol CO}_2/\text{g}$.

3.4 Experiment B: Surface area enhancement via post synthesis modification

3.4.1 Preparation of Materials

In this section, the pristine HKUST-1 product was obtained from Experimental A. Afterwards, the powder-state sample was divided into seven groups (0.5g for each) set in a sealed glass bottle for further chemical treatments. Different amounts of NaCl were dissolved in the mixed solutions of methanol and DI water

(methanol : DI water = 20: 10 mL). Water is used in order to dissolve NaCl solids. The molar ratios of NaCl to HKUST-1 is 0.05, 0.5, 1, 2, and 10, respectively. After the NaCl solids were fully dissolved, each salt solution was poured into the pre-prepared HKUST-1. Another two groups, as the control groups, were immersed respectively in pure methanol and mixture of 20 mL methanol and 10 mL water. Table 3.8 has listed the detailed amount of each group for a clear comparison. These seven samples were immersed for 24 h statically in room temperature, and then the MOFs were washed by 30 mL methanol via centrifuge. Finally, the samples were dried in an oven with a temperature of 120 °C for around 3 hours for further characterization and testing.

Table 3. 8 The preparation of different post-immersion groups.

ID	NaCl:HKUST-1	NaCl (g)	MeOH (mL)	H ₂ O (mL)
HKUST-1/Me	/	0	30	0
HKUST-1/Me/H ₂ O	/	0	20	10
Na1	0.05:1	0.0024	20	10
Na2	0.5:1	0.024	20	10
Na3	1:1	0.048	20	10
Na4	2:1	0.096	20	10
Na5	10:1	0.48	20	10

3.4.2 Characterization

Characterization techniques including SEM, TGA and XRD were employed to examine these samples, BET surface areas were also measured by using the same instrument and parameters described in Section 3.3.2.

3.4.3 CO₂ Adsorption Test

The CO₂ uptake capacity was examined using the NETZSCH TG instrument at 1 bar. The N₂ gas flow rate was set at 100 mL/min

and CO₂ at 133 mL/min. The method used is as follows: the temperature was initially increased to 150 °C under N₂ atmosphere (99.999%) and then decreased to 27 °C for 30 min. After temperature keeping stable the gas flow was switched to pure CO₂ for 30mins. The mass for each sample is between 10 and 30 mg. Blank group was done for every test to eliminate the influence of buoyancy.

3.4.4 Results & Discussions

3.4.4.1 Crystal Structure for the chemical treated samples

X-ray diffraction patterns were recorded for the samples after being immersed in various solvents and comparison was made with the pristine HKUST-1. The results are shown in Figure 3.21. The sample ID present in Figure 3.21 have been explained in Table 3.8. The patterns of solvent-treated samples (HKUST-1 Me/H₂O, HKUST-1/MeOH, Na1, Na2, Na3, Na4 and Na5) are in good agreement with the pristine HKUST-1, and also match well with those reported in the other literature [156, 243, 244]. The unchanged XRD patterns indicates that soaking HKUST-1 products in these solvents will not destroy the original crystal

structure. It was reported that the crystal structure collapsed when soaking HKUST-1 in pure water [191]. However, the present of methanol mixed with water protected the MOF structure, since the sample HKUST-1 Me/H₂O shows an unaffected pattern (Figure 3.21).

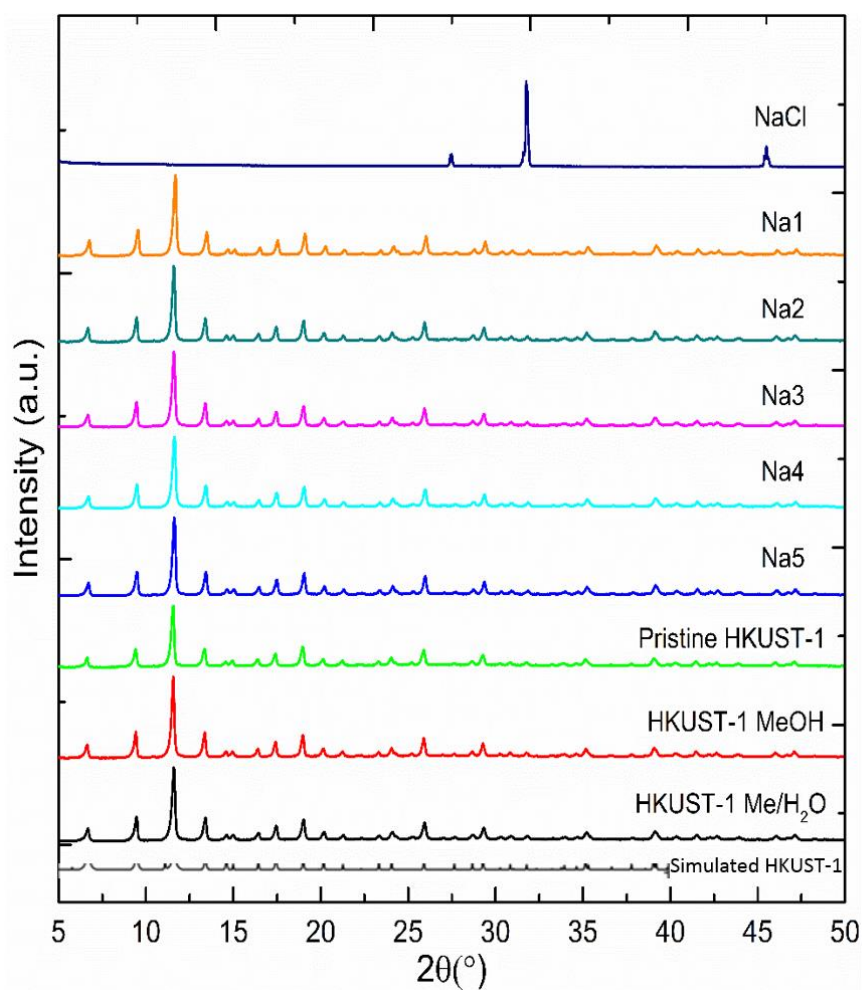


Figure 3. 21 XRD patterns for samples with and without post-immersion

To further verify that the structure retained its integrity, the morphology of each sample was observed using SEM. Figure 3.22 exhibits the topologies of the pristine HKUST-1, HKUST-1 soaked in pure methanol and in the mixture of methanol and water. Figure 3.23 displays the morphologies of solvent treated HKUST-1. The same scale bar was utilized for all of these images in order to provide a direct comparison. According to the EDX tests carried out simultaneously with SEM, sodium (Na) element was not detected in all treated HKUST-1 samples, which means NaCl has been washed out clearly in the washing process. Additionally, no big differences with regards to morphology were found in these images. Therefore, combined with the results from XRD, it can be concluded that the chemical treatment makes little or no change to the crystal structure and morphology of the pristine HKUST-1 sample.

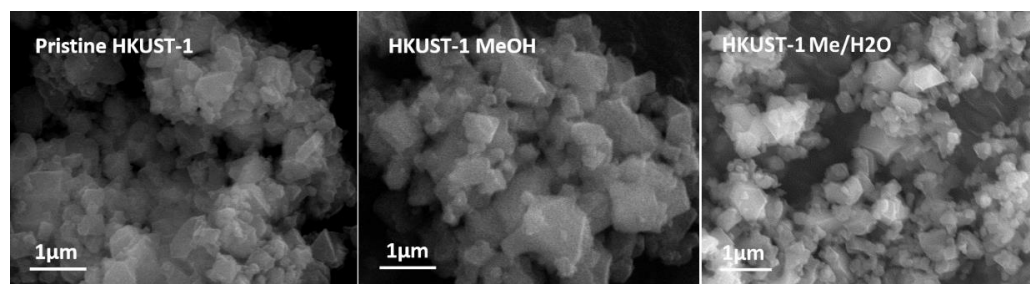


Figure 3. 22 SEM images for HKUST-1 with and without post-immersion.

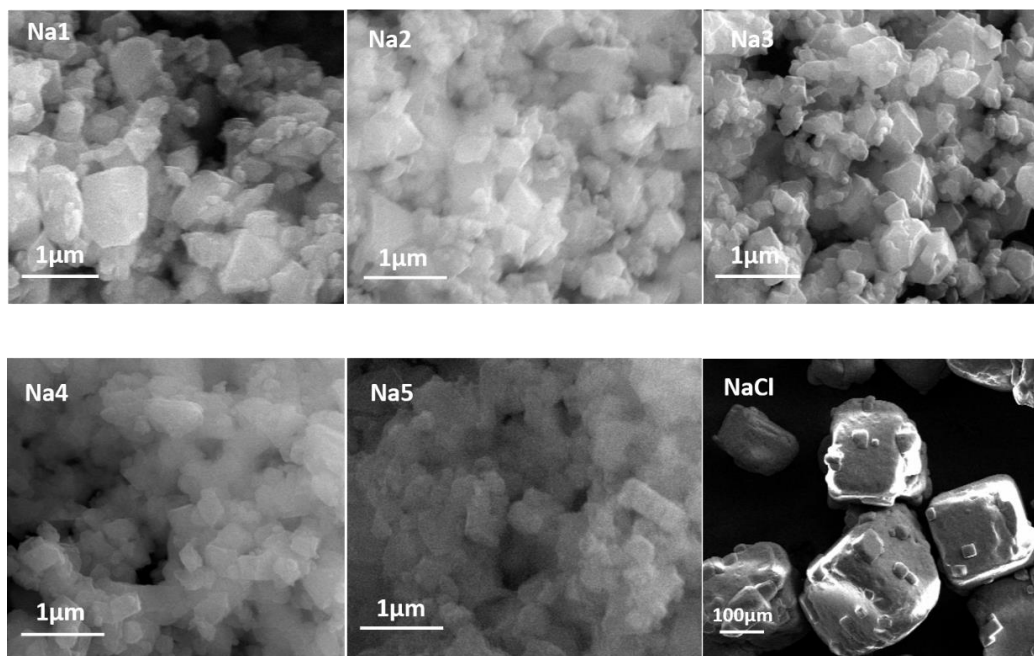


Figure 3. 23 SEM images for samples after NaCl solutions soaking.

3.4.4.2 Thermogravimetric Analysis

The thermogravimetric curves can reveal information about the composition of sample. Figure 3.24 has presented the sample mass changes with the increase of temperature from 27°C (room temperature) to 900 °C under a nitrogen atmosphere. The general shapes of all these samples are similar and are also in agreement with those reported previously. There are four main stages of mass loss for the pristine untreated HKUST-1 sample. The first weight loss is due to the removal of physically adsorbed water, occurring in the temperature range from 27 °C to 110 °C,

approximately. The second drop stage takes place between 110 °C and 250 °C, indicating the chemically adsorbed water and trapped inner impurities elimination. However, the chemical treated samples do not present this stage mass loss, which means the impurities have been washed out before the TGA test. NaCl decomposition curve is also present in Figure 3.24. The decomposition starts at around 800 °C, and there is no weight loss before this temperature. This trend matches well with that reported by Lin et al. [169]. By comparing the curve shape of NaCl and NaCl treated HKUST-1 samples, it is possible to conclude that NaCl is easy to remove in the later activation process. The different residual masses between different samples (around 1-8%) should be caused by the different impurities contents, as the weight loss shows various for each sample in the first weight loss stage.

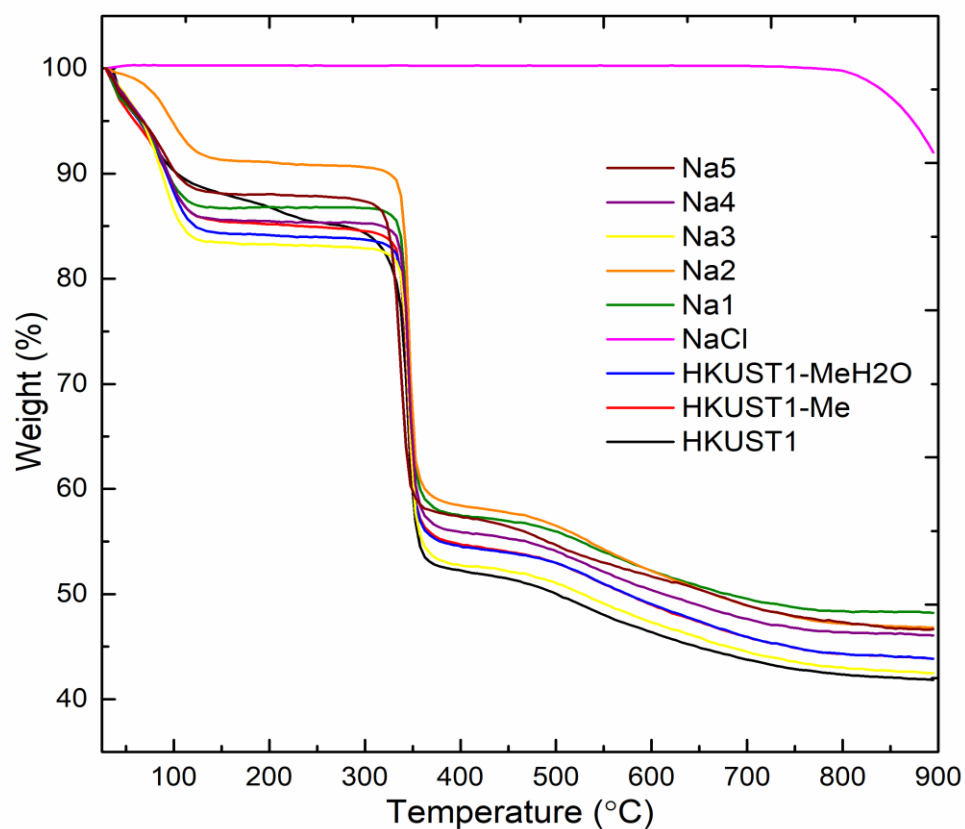


Figure 3. 24 Decomposition curves of different samples in nitrogen (1atm)

3.4.4.3 Textural properties and CO₂ adsorption capacities

After seeing the TGA results for the solvents treated samples, it is inferred that these samples probably possess higher surface area. Therefore, nitrogen adsorption experiments were carried out to measure their surface areas. The data has been recorded by Micromeritics Tristar 3020 instrument and the isotherm curves have been shown in Figure 3.25. The nitrogen adsorption quantity of pristine HKUST-1 is much lower than the others.

Sample Na2 (soaked in NaCl solution with the molar ratio of Na to HKUST-1 equal to 0.5) presents the highest adsorption capacity.

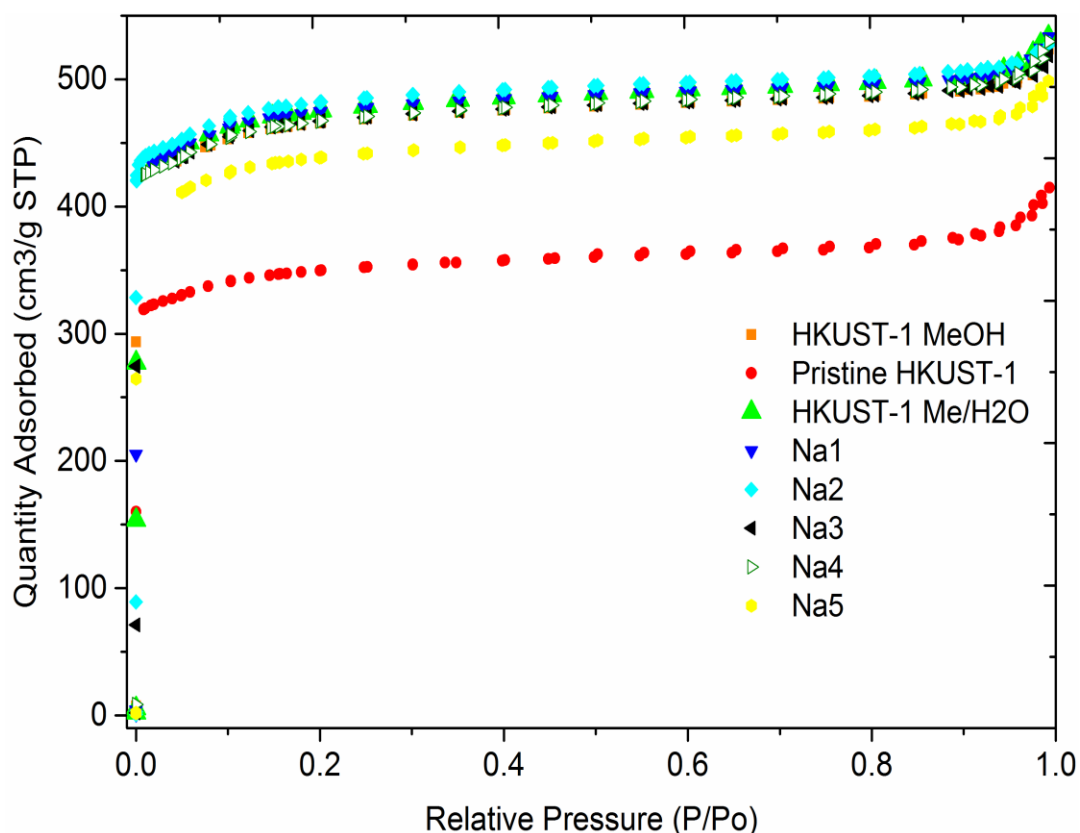


Figure 3. 25 BET results for the samples after post-immersion with various solvents.

Theoretically, the enlarged surface area leads to an improvement in carbon capture, since more 'spare' space is released from the inner pores. To confirm this theory, CO₂ uptake tests were carried out using a thermogravimetric analysis instrument (NETZSCH STA49 F3) at 1 atm and 27 °C. The results

have been listed in Table 3.9. Generally, in this case the CO₂ adsorption capacity increases with the increase of surface area. Sample Na2 possesses the highest CO₂ uptake ability, which is 15% higher than that of the pristine HKUST-1. The other chemical treated samples also have improvements. To be immersed in methanol or the mixture of methanol and water results in a similar CO₂ adsorption ability enhancement. According to the results in Table 3.9, the existence of sodium chloride in the solvent facilitate the removal of impurities.

It is worth noting that when the ratio of NaCl to HKUST-1 increases to 1:10, the surface area drops significantly. According to the information delivered from TGA result (Figure 3.24), the reason for the decrease is probably caused by the existence of NaCl impurities in the sample. The curve of Na5 exhibits a more serious decrease starting from the temperature around 800 °C, which is the decomposition temperature of NaCl. Although no sodium is detected using EDX, this might because of the very little NaCl content in sample Na5.

Table 3. 9 A summary of CO₂ capacity for the HKUST-1 immersed in different solvents

ID	BET Surface Area	CO ₂
	m ² g ⁻¹	%
Pristine HKUST-1	1615	8.08
HKUST-1/Me	1806	9.04
HKUST-1/Me/H ₂ O	1873	9.08
Na1	1906	9.25
Na2	1910	9.33
Na3	1819	9.26
Na4	1812	9.21
Na5	1702	8.80
NaCl	0.3	0.00

3.4.5 Conclusions

In experiment B, a simple post treatment method is developed to enhance the CO₂ adsorption of HKUST-1, which is immersing the powder state pristine HKUST-1 in a solvent mixed by NaCl, methanol and water. It is found that when the molar ratio of NaCl to HKUST-1 equals to 0.5, the sample after immersion has a best

performance in CO₂ uptake capacity. However, NaCl impurities would remain in the sample after washing if a high NaCl (e.g. NaCl: HKUST-1 = 10) amount was added. Thus, the surface area and CO₂ adsorption capacity will be reduced.

3.5 Experiment C: Pellet Pressing

3.5.1 Pellets preparation

The press technique was adopted to shape the powder HKUST-1 in our experiment (Figure 3.26). A hand press with model number KEQI 769YP-15A and a mould with inner diameter of 1 cm was utilized (Figure 3.27). The compaction procedures were as follows:

- (1) Weigh 0.5 g HKUST-1 powder and fill it in the mould;
- (2) Check the height of the oil is 2/3 of the oil tank, and the pressure relief valve is open;
- (3) Put the mould in the center of the work table of the hand press, screw down the screw rod;
- (4) Tighten the pressure relief valve clockwise;
- (5) Press down the pressure via the rotator on the top the rig to the desired pressure (1MPa-3MPa) and ensure the appropriate time (about 1 min in our experiment);

- (6) Release handle rotator counter-clockwise;
- (7) Remove the mould after loosening the relief valve and collect the pellet.

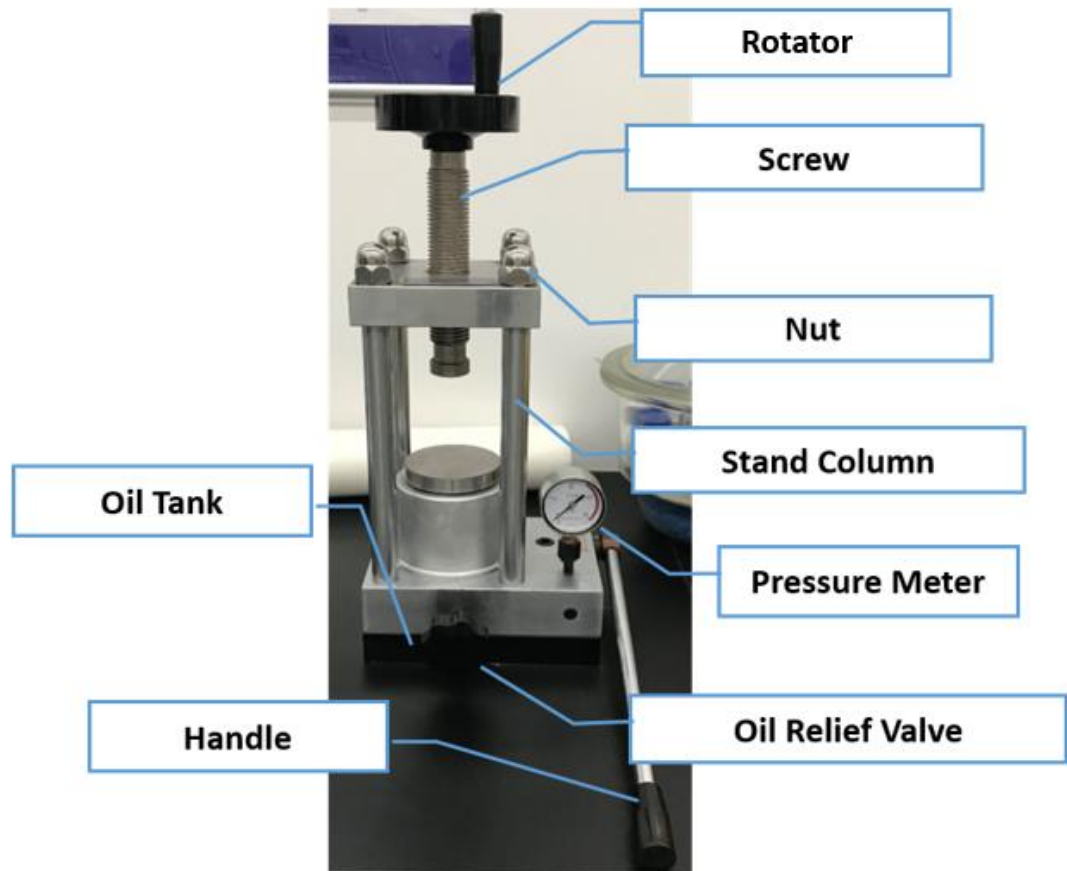


Figure 3. 26 A photograph of the hand press with components labelled

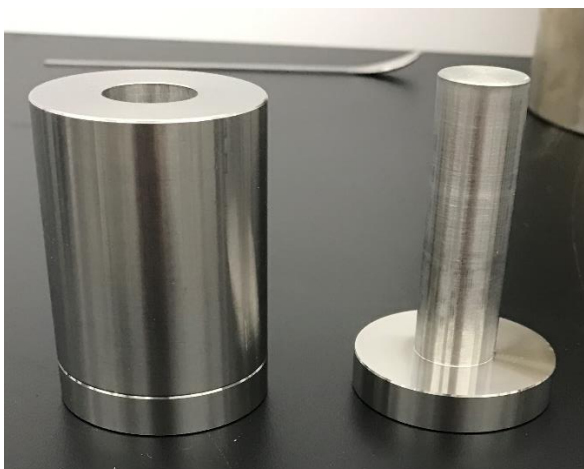


Figure 3. 27 Mould used in the press experiments

The obtained 1 cm diameter pellets were then crushed into small pieces by a lab spoon with proper force for the purpose of later characterization. Figure 3.28 is a photo of the crushed small pieces with treatment by different pressures.

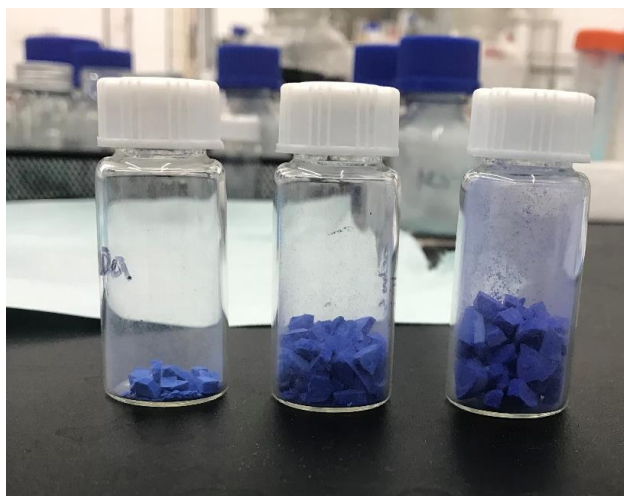


Figure 3. 28 Pellets pressed by pressure of 1MPa, 2MPa and 3MPa (from left to right) and crushed to granules.

In order to see if the structure and adsorption capacity were influenced by the shaping process, samples testing techniques including SEM, XRD, TGA and BET were used respectively. The parameters used when operating these techniques were as the same as those were mentioned in the above section.

3.5.2 Results & Discussions

The XRD patterns of pressed pellets are shown in Figure 3.28. The pattern of the three pressed samples, compared to the pristine HKUST-1, indicates that the structure was not destroyed by the pressure. This indicates that the pressure range in this experiment is reasonable. The SEM images in Figure 3.30 also give an evidence that no destruction occurs in the structure, since the morphology does not change significantly.

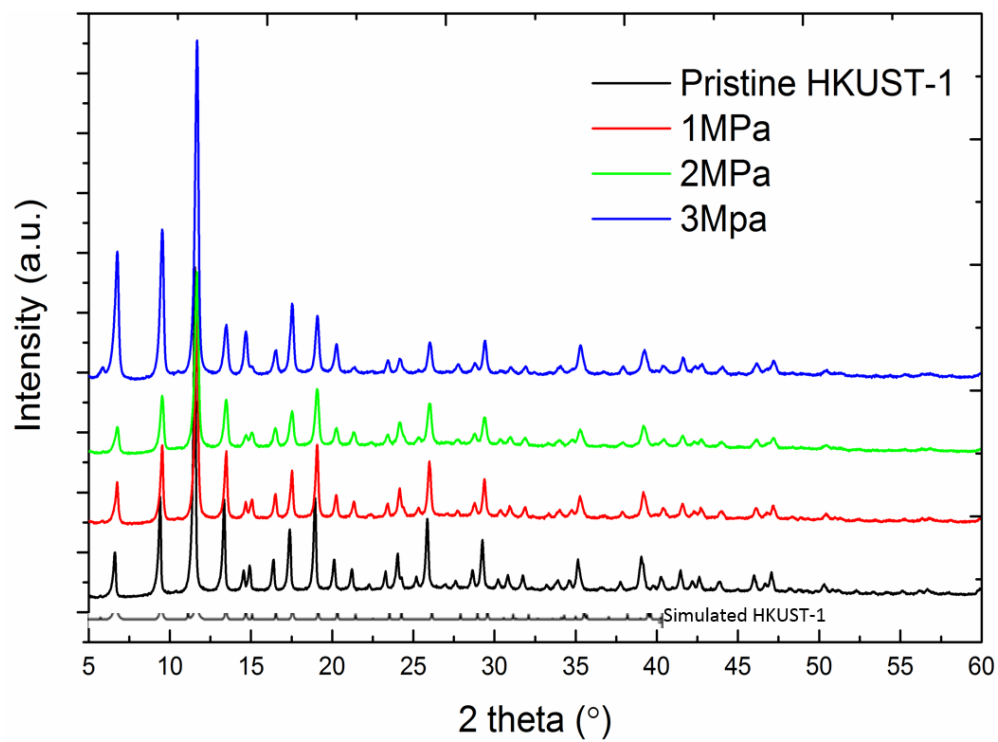


Figure 3. 29 Comparisons for the XRD patterns of HKUST-1 before and after press shaping.

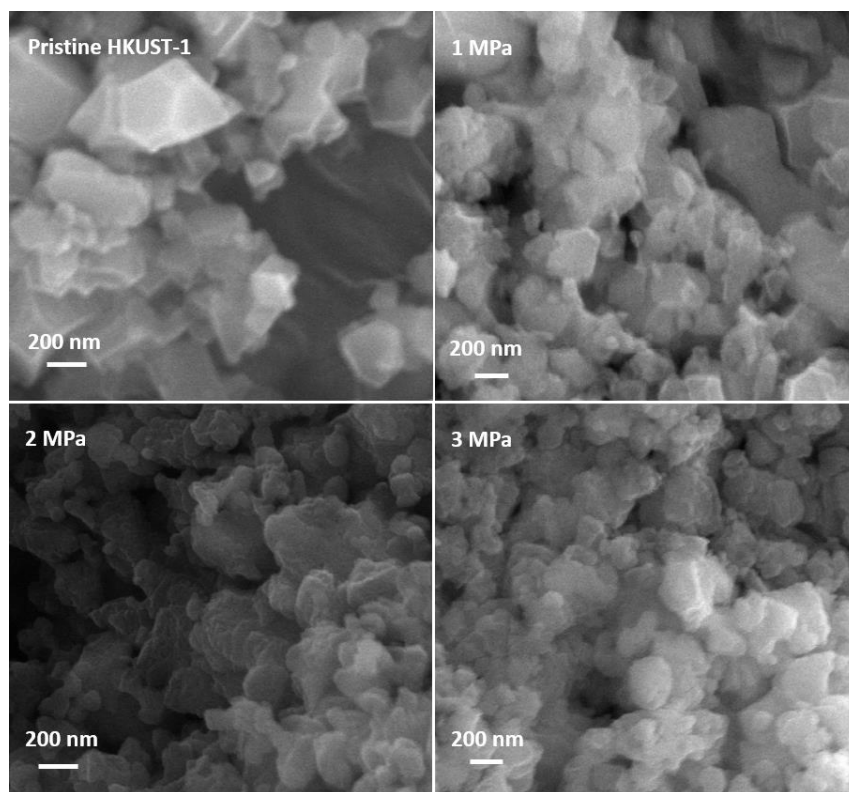


Figure 3.30 SEM images for the powder HKUST-1 (pristine HKUST-1) and shaped HKUST-1.

The surface area of these three samples were measured by Micrometrics Tristar 3020, and CO₂ uptake experiments were done by TGA at 1 atm 27 ° C. The results were depicted in Figure 3.31 and listed in Table 3.10. It can be easily seen that with the increase of the applied pressure on the sample, the BET surface area and the CO₂ adsorption ability decreases to some extent. However, the mechanical strength tests have not been done. Therefore, more work is needed in order to determine the

optimal pressing pressure of the sample for the industrial application.

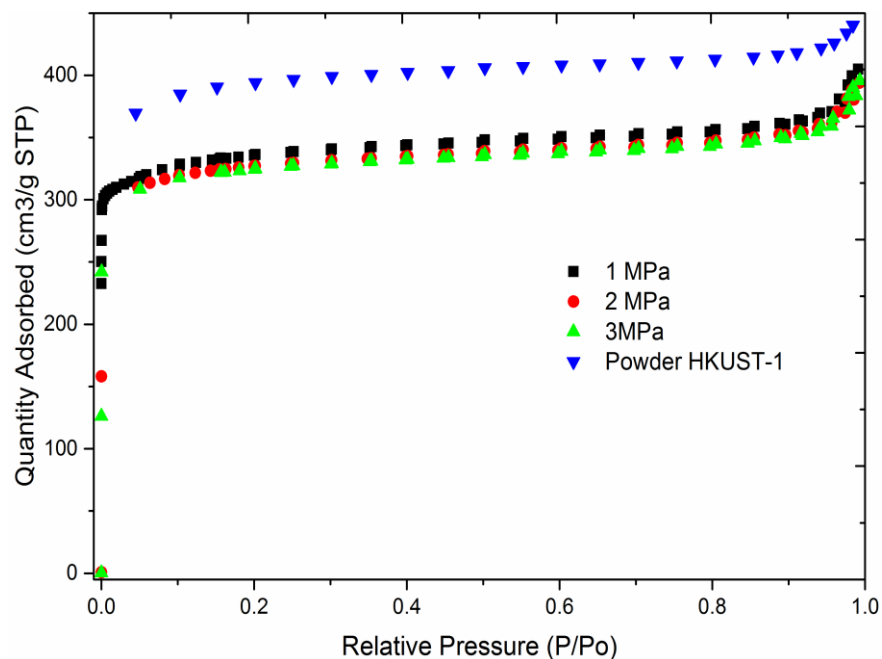


Figure 3. 31 N₂ adsorption isotherms for the powder HKUST-1 and shaped HKUST-1.

Table 3. 10 Surface area and CO₂ capture for HKUST-1 before and after pressing

ID	BET	CO ₂
	m ² g ⁻¹	%
Powder HKUST-1	1615	7.87
Pellet-1mpa	1324	7.42
Pellet-2mpa	1279	7.32
Pellet-3mpa	1178	7.05

3.6 Conclusions

To conclude, three experiments were carried out in Chapter 3. Firstly, HKUST-1 was synthesized using a new batch method under a mild synthesizing condition. A relatively high surface area ($1615 \text{ m}^2/\text{g}$) and a high CO_2 uptake capacity (8.08 % measured by TGA at 1 atm and 27°C) was achieved by the optimal sample. In the second part, based on this synthesized HKUST-1, a simple chemical soaking method was developed to enhance the surface area of the sample. Consequently, the surface area of HKUST-1 rose up to $1910 \text{ m}^2/\text{g}$ and the CO_2 uptake ability increased by 15%. In the third experiment, the powder-state HKUST-1 sample obtained in Experiment A was pressed to become a pellet shaped body for further application, without destroying the framework structure.

Chapter 4 Synthesis and Activation of Nanoscaled HKUST-1 in a batch reactor

4.1 Aims and Objectives

Batch experiments are described in this chapter. The experiments were carried out in order to optimise reaction conditions for continuous flow experiments described in subsequent chapters.

4.2 Introduction

4.2.1 Nanoscale Materials

Nanotechnology was first brought forward in 1959 by Richard Feynman in a talk titled "There`s Plenty of Room at the Bottom" [245], but actually nanoparticles (NPs) have been present for several million years [246].

The nanoscale materials refer to the substances those with the size between one to one hundred nanometers at least in one dimension [246]. The nanometer is a unit in length, which equals to 1×10^{-9} meter.

4.2.2 Advantages of Nanoscale Materials

The small scale of these nanomaterials can give rise to various properties with regards to the chemical and physical properties compared with the larger scaled chemicals: e.g. stronger strength and better chemical reactivity [247]. These phenomena are based on “quantum effect”, as well as the increased surface area[248]. Due to these improved characteristics a wide range of applications have been discovered, and which are listed in Figure 4.1.

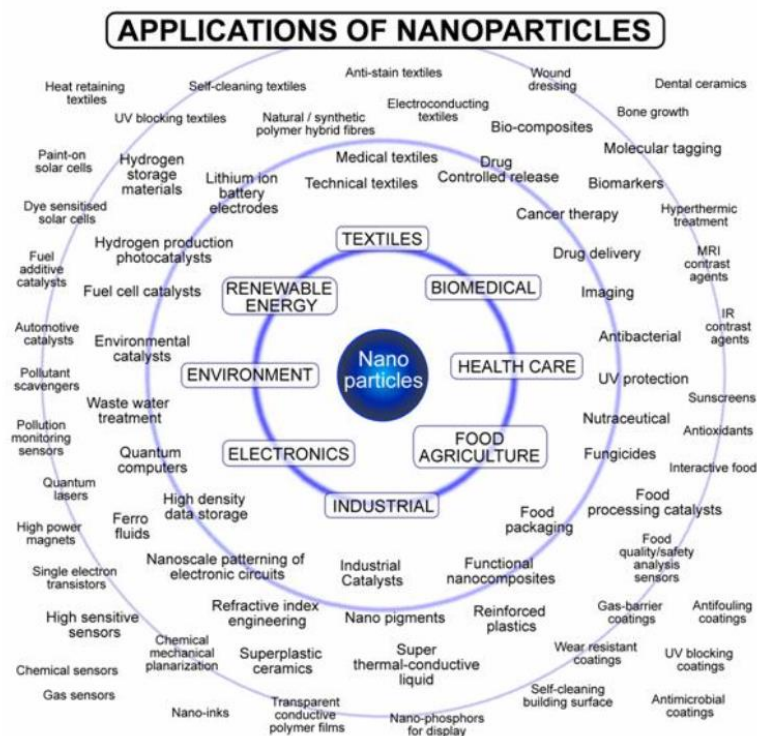


Figure 4. 1 A review figure for the applications of nanoparticles[249]

Another important advantage of nanoscale materials compared with the large scale particles is the reduced weight requirements, which means the loading weights can be lower if this kind of materials were employed in an industrial application. In addition, this will mean that the process costs can be reduced, and the device can be constructed smaller without affecting performance.

In this study, experiments were carried out to develop and optimize a new method for the preparation of HKUST-1 in a fast and efficient manner. Attempts were also made to control the MOFs in nanoscale with high surface area and high yield.

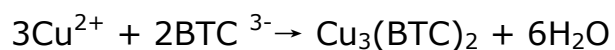
4.3 Experiment: Nano scaled HKUST-1 synthesized in batch

The synthesizing process for the materials produced in Chapter 3 required a drying process before activation, in order to obtain a high yield of HKUST-1. However, it is impossible to do this drying step separately during the continuous process. Therefore, it is needed to bring in some kind of chemical additives to speed up the nucleation rate. Triethylamine, a

commonly used weak base, was used here as the deprotonation agent to facilitate the synthesis.

4.3.1 Materials and Preparation

In this study, a new method was developed for the rapid preparation of porous HKUST-1. A mixture of copper nitrate trihydrate (Sigma Aldrich, 98%), trimesic acid (TMA) (Sigma Aldrich, 95%), and Triethylamine (TEA) (Sigma Aldrich, 99.8%, anhydrous), with a molar ratio of 3:2:6, was added into a solution, which consists of equal parts in volume of deionized water and ethanol (Sigma Aldrich, 99%). The ratio used was according to the stoichiometric ratio of these three chemicals in the reaction. The sample was heated under constant stirring to a pre-set temperature of 50°C, and then cooled down to room temperature using an ice bath to form pristine HKUST-1. Once the pristine HKUST-1 was prepared, the slurry activation/or powder activation was applied, which involves the use of either ethanol or methanol to wash the HKUST-1 to remove impurities trapped in the pore structure of the sample. The reaction equation between these two precursors is as follows:



Slurry activation refers to the way that HKUST-1 is already in a slurry state before activation (prior to centrifuge and supernatant liquid removal); powder activation refers that the HKUST-1 is in a powder state before activation (after the process of centrifuge and supernatant liquid removal, the slurry was dried in an oven at 80 °C overnight to obtain the completely dried powder).

Therefore, in this study three samples with different washing/activation methods were collected. Table 4.1 lists the activation conditions for different sample IDs present in the later descriptions. These synthesis and activation experiments were all performed in a reflux condenser. The amount of ethanol or methanol used was kept at the same level as 62.5 ml per gram of pristine HKUST-1.

Table 4. 1 Synthesis and activation conditions for HKUST-1 samples

Sample ID	Washing agent	Sample state before activation
A1-E1	Ethanol	Slurry
A1-M1	Methanol	Slurry
A1-PM1	Methanol	Powder

4.3.2 Characterization

Morphology and particle size of the synthesized HKUST-1 MOFs were analysed by using a Scanning Electron Microscope (SEM, ZEISS Sigma VP/Oxford Instruments). The structure of the solid phase and crystallinity were analysed by using a Powder X-ray diffraction (XRD) with a scanning rate of $0.02^{\circ}/\text{s}$ (2θ) using monochromatic $\text{CuK}\alpha$ radiation (Bruker D8 A25) at 40kV and 35mA. The surface area (Brunauer–Emmett–Teller, BET) and pore size of the HKUST-1 were measured using a Micromeritics Tristar 3020 Instrument following the method described elsewhere [250]. Thermal decomposition was studied using a thermogravimetric analyser (TGA, NETZSCH STA49 F3). Reaction temperature and sample weight were recorded at 10 s intervals and the samples were heated from 35 to 900 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2 atmosphere.

4.3.3 CO_2 adsorption-desorption test

CO_2 adsorption was conducted in a TGA system (NETZSCH STA49 F3) following procedures adopted by others [172]. Initial treatment of the activated sample was carried out in N_2 at 150 $^{\circ}\text{C}$ for 12 h. The adsorption was carried out using ultra purity CO_2

and N₂ (99.999%) gas. A gas mixture of 133 mL/min of CO₂ and 100 mL/min of N₂ were introduced into the sample chamber. Temperature and pressure of the adsorption chamber was maintained constant at 27 °C and 1 atm, respectively.

A CO₂ isotherm of the HKUST-1 MOFs at 27 °C was obtained using the Micromeritics ASAP 2020. The degas process of the activated sample was conducted at 150 °C for 12 h. The adsorption pressure varied from 2.7 mbar to 1100 mbar, as described elsewhere[251].

4.4 Results and Discussions

4.4.1 Crystal Structure Characterization

With the addition of triethylamine, the reaction became much more rapid, since it is believed that the alkaline TEA accelerates the deprotonation of H₃BTC to promote the nucleation of particles into nanoscale [252]. XRD analyses were conducted to show the crystalline phases of the HKUST-1. It can be seen from Figure 4.2 that the XRD patterns of three obtained samples match well with that of simulated one. The peaks of all three samples exhibit in a sharp style, which implies that they have

high degrees of crystallinity. There is an obvious difference in the intensity ratio of (200) to (220) between the ethanol activated sample and the methanol activated sample. The ratio in A1-E1 is much lower than that of A1-M1 and A1-PM1. According to Ajay et al.[228] the reduction of peak intensity of (200) plane is correlated with the FCC crystal structure loss, which is probably caused by the hydration of HKUST-1 sample.

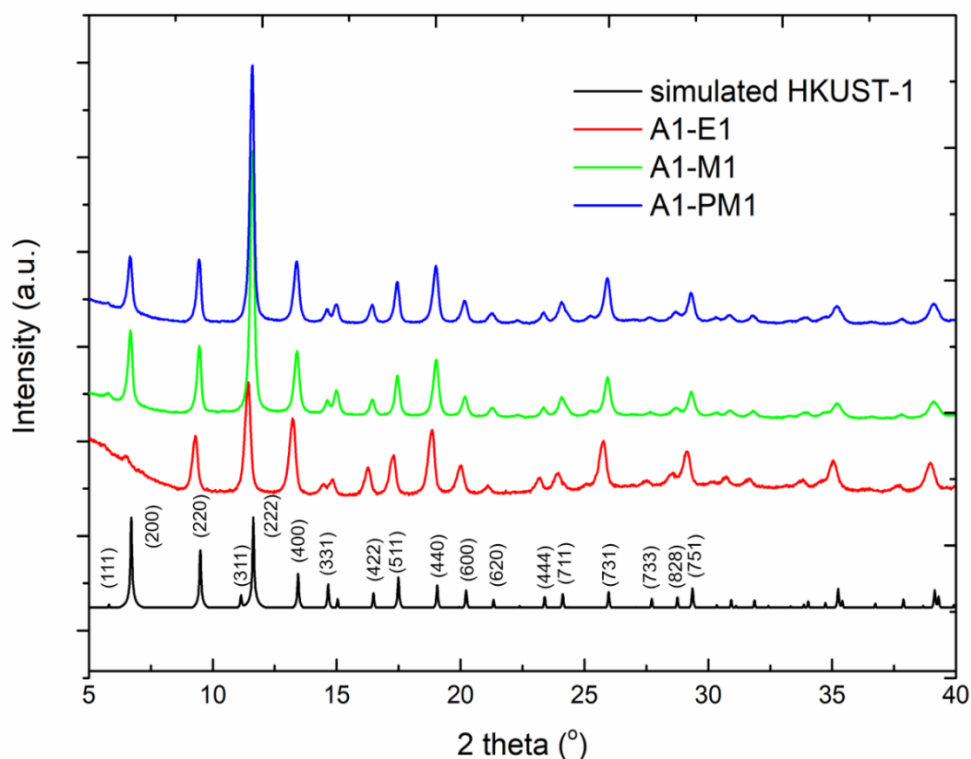


Figure 4. 2 Comparison of XRD patterns for the slurry/powder activated samples.

Figure 4.3 shows the SEM images for the samples. There is no significant difference in terms of morphology among these three samples. The crystal sizes are similar, within the range between 50 nm and 80 nm. This range indicates they are nanoscaled particles, which is significantly smaller than the products generated without TEA addition (100-500 nm) that are discussed in Chapter 3. The much smaller particle size gives the evidence that with TEA addition the nucleation rate is increased.

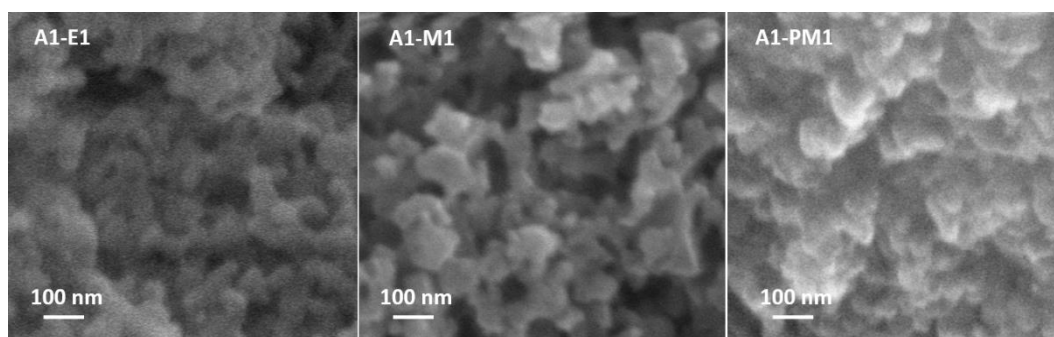


Figure 4. 3 SEM images for the slurry/powder activated samples.

4.4.2 Thermogravimetric Analysis

The decomposition performance was tested using a TGA. The relationship between the sample mass and the temperature has been presented in Figure 4.4. The shape of each curve is similar to those reported in the previous work [160, 230]. As it has been

discussed in Chapter 3, the mass loss curve of HKUST-1 can be divided into four stages:

- (i) physically adsorbed water evaporation;
- (ii) Chemically bonded water and impurities left in internal pores removal;
- (iii) Heat resistance;
- (iv) Structural breakdown.

The physically adsorbed water amount seems similar among all these three samples by comparing the first stage mass loss between the temperature of 27 °C and around 110 °C, but sample A1-E1 contains slightly more water according to the curves. The biggest difference is in the second weight loss stage with the temperature between 110 and about 210 °C. The decomposition curve of sample A1-PM1 exhibits almost a plateau within this temperature range, only a small amount reduction occurred. The weight of sample A1-M1 drops more than that of sample A1-PM1, meaning more impurities exist in the structure. Obviously, the weight of sample A1-E1 decreases drastically in this period.

Therefore, a conclusion can be made that the removal efficiency of powder activation by methanol is best among these three methods. The washing agent methanol is more optimal than ethanol in case of removing impurities inside the pores, which might because of the smaller molecule size of methanol. Furthermore, compare the result from XRD patterns (Figure 4.2), sample A1-E1 contains more chemically bonded water. Thus, it can be speculated that by ethanol washing these water molecules are hard to be removed.

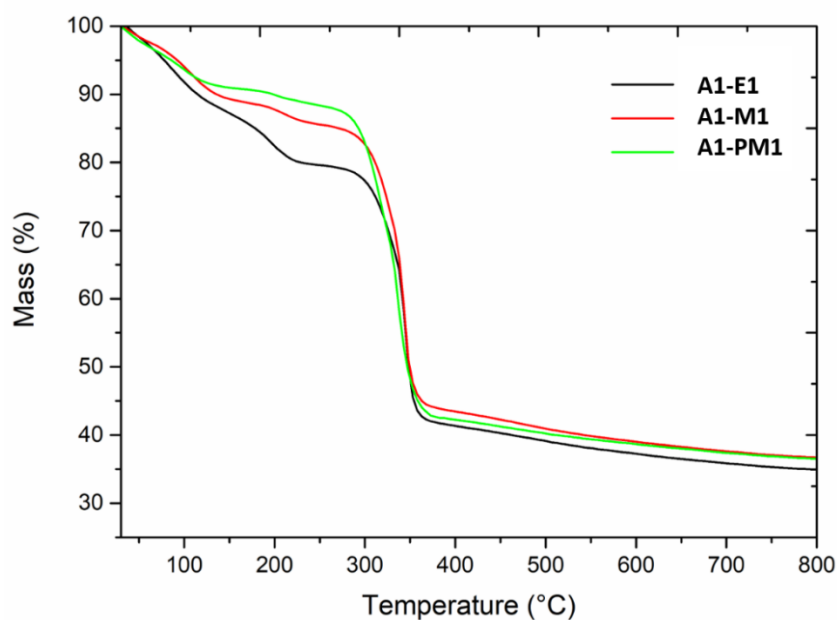


Figure 4. 4 Thermal decomposition curves for three samples

4.4.3 Surface area and CO₂ adsorption capacity

The nitrogen adsorption tests were carried out in Micromeritics Tristar 3020 instrument under the temperature of 77K. All the samples underwent the degassing process before analyses. Figure 4.5 illustrates the isotherm curves for samples with different activation processes. The sample activated by ethanol with slurry state (A1-E1) displays the lowest gas adsorption ability, but when the washing agent changes to methanol, the adsorbed gas amount increases considerably. The sample activated in the dried powder state presents the highest adsorption capacity.

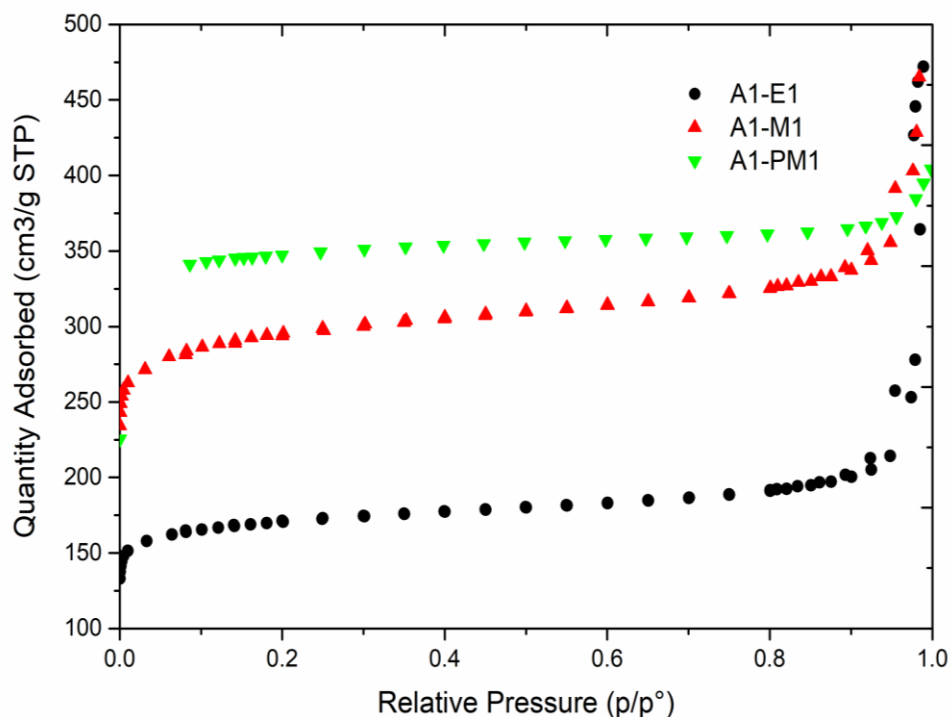


Figure 4. 5 Nitrogen adsorption isotherms at 77 K, using Tristar 3020.

In addition, CO₂ adsorption experiments were carried out using a TGA. The adsorption occurs at 27 °C and 1 atm. In order to give a clear comparison, Table 4.2 lists the BET surface area and CO₂ uptake ability. It can be clearly seen that the CO₂ adsorption capacity increases with increasing surface area.

This result is also in agreement with the result from TGA. For sample T1-PM1, as it has been discussed in Section 4.4.2 most impurities have been washed out in the activation process,

leading to more space inside the pores, thus a higher surface area.

However, the highest value of BET surface area among these three samples is 1338 m²/g, which is still lower than that of the product T1-M1 synthesized in Chapter 3. This might be attributed to the TEA addition in the preparation stage.

Therefore, further studies were conducted in order to obtain a higher surface area nano scaled HKUST-1 sample and the results have been published in 2018 [253]. In this work, the optimized sample achieved a BET surface area of 1524 m²/g after washed by methanol in the dry state for four times. Although the BET surface area increases significantly, the activation process becomes much more complicated and is not suitable for adaptation in a continuous rig. On the other hand, the use of processing, time and energy would add cost.

Table 4. 2 Surface area and CO₂ adsorption capacity for different samples

Sample ID	BET surface area (m ² /g)	CO ₂ adsorption capacity (wt%)
A1-E1	666	5.95
A1-M1	1147	6.40
A1-PM1	1338	7.27

- CO₂ uptake occurs at 1atm and 27 °C.

4.5 Conclusions

In summary, nanoscaled HKUST-1 product has been synthesized in a mild condition in this chapter. The average particle size is around 65nm, which is notably smaller than the product named T1-M1 mentioned in Chapter 3. This is mainly because adding trimethylamine as the base in the ligand solution to deprotonate the 1,3,5-benzen-tricarboxylate and increases the rate of nucleation. Three different methods were used to wash the pristine HKUST-1 sample in the activation process for the reason to eliminate the impurities. According to the test results (including TGA, XRD, BET and CO₂ adsorption test) the optimal method is using a methanol wash. A comparably high surface area of 1338 m²/g was achieved.

Chapter 5 Continuous Synthesis of MOFs for CO₂ Adsorption and Post-Modification of HKUST-1

5.1 Introduction

5.1.1 Literature review for continuous synthesized MOFs

In the last two chapters, the work was focused on batch synthesis. However, by using batch processing the production of MOFs is not easily scaled-up due to size limitations. To achieve the goal of high-throughput a few novel approaches associated with continuous reaction process have been described in recent years.

The Lester group in collaboration with Warwick University (Walton group) first published the method for continuous syntheses of HKUST-1 and CPO-27(Ni) in 2012 [60]. A high pressure (250 bar) and high temperature (100-400°C) system was used in the process. The downside would be the potential

increase in the cost and safety issue. Most recently, McKinstry et al. described a continuous process using a stirred tank reactor for the production of HKUST-1 using milder conditions (60°C) in 2017 [254]. However, the production yield was low, at 40% and only used ethanol as the solvent, with particle size not stated. Therefore, there is scope for a high yield continuous synthesis method with green solvent operating at mild conditions.

Herein, a novel method to synthesize nanoscale HKUST-1 with a high yield (64%) was presented via using the same reactor technology reported by Lester group [60] but with different synthesis conditions. ZIF-8 was also synthesized using the same rig in Nottingham, and further comparisons with the commercial product manufactured by BASF [255] were made to assess the quality of our products. The drive towards greener solvents specifically means avoiding using standard MOF solvents like DMF or THF [256]. Commercial ZIF-8 and HKUST-1 are both sold as around £30 per gram. While for our lab-scale continuous synthesis, the materials cost is around £0.9 per gram product. The energy consumption is roughly calculated as £0.08 per gram product. Therefore, our product shows potential for the future application.

5.1.2 Post Synthetic Modification of MOFs

Post synthetic modification (PSM) is regarded as an effective way to tune the properties of MOFs to obtain targeted application. It has been shown that additional ligands can be post synthetically introduced into a MOF structure [133]. HKUST-1 is the first industrial-scale manufactured MOF. However, whilst it has a high CO₂ uptake capacity, it is not stable under hydrothermal conditions. Water stability is significant during the removal of CO₂ in flue gas (mixture of SO_x, NO_x and H₂O). Therefore, increasing the hydrophobicity of HKUST-1 is an effective strategy to make it more durable for industrial applications. Zu et al. [136] reported a method of introducing graphite oxide to this MOF. MOF precursors were mixed to get the MOF product and then solid state graphite oxide were added in, and the mixture was heated at 85 °C for 21 h with stirring. Apart from incorporating another composite to modulate the hydrophobicity, reducing or blocking the material's contact with water molecules is another operational strategy. Zhang et al. explored a facile method for coating MOFs with PDMS (polydimethylsiloxane) using a thermal vapor deposition technique [123]. In their experiments, HKUST-1 undergoes a

PDMS coating process. It is heated in a sealed glass container with the existence of PDMS stamp under 235 ° C. Silicone molecules are generated from the degradation of PDMS and deposited on the surface of the MOFs as a thin layer [123]. In this section, we investigate a simple process to improve the hydrophobicity of HKUST-1 using a continuous flow reactor.

5.2 Experimental A: Synthesis of HKUST-1 and ZIF-8

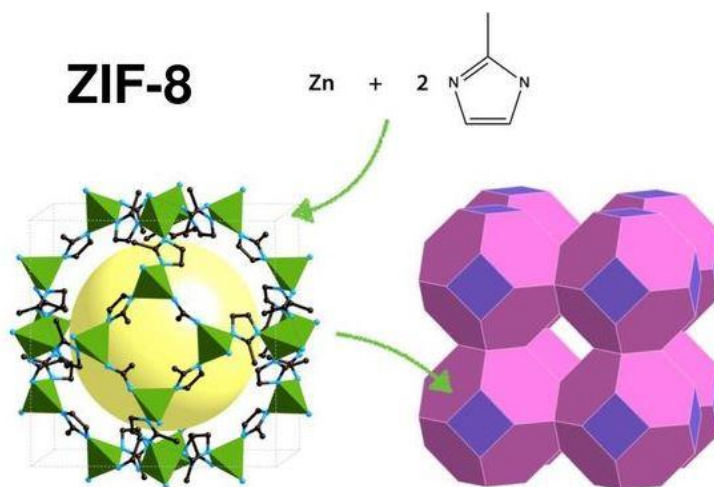
5.2.1 Materials and Sample Preparation

All of the chemicals used were purchased from Sigma Aldrich and used without further treatment. Commercial ZIF-8 and HKUST-1 were also bought from Sigma-Aldrich, which are named as Basolite® Z1200 and Basolite® C300, respectively.

5.2.1.1 Synthesis of ZIF-8

For the synthesis of ZIF-8, 4.93 gram of 2-methylimidazole and 26.55 mL of 35%wt. ammonia were dissolved in 1 L H₂O and preheated to 100 °C and introduced from downflow with a controlled flow rate of 20 mL min⁻¹, 6.59 gram of zinc acetate was introduced from upflow in 10 mL min⁻¹ (The molar ratio of

$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$: 2-methylimidazole: NH_4OH = 1:2:16, according to the stoichiometry). ZIF-8 formation mechanism is as follows [257]:



These two streams meet together at the mixing point and the resulting product flows through a cold water exchanger, and then a back pressure regulator. The whole process is depicted in Figure 5.1. The collected product was not highly pure due to the solvent present inside the pores. This continuous synthesis process therefore needs an activation process after synthesis. Most solid material is firstly isolated by centrifugation and then mixed with ethanol. This mixture was refluxed at around 80°C for 3 hours to remove the guest molecules. The mixture was centrifuged again to extract the activated product and then dried overnight at 70°C to obtain ZIF-8 powder. After measuring the

weight of the dried powder, the ZIF-8 conversion can be calculated as around 31 %.

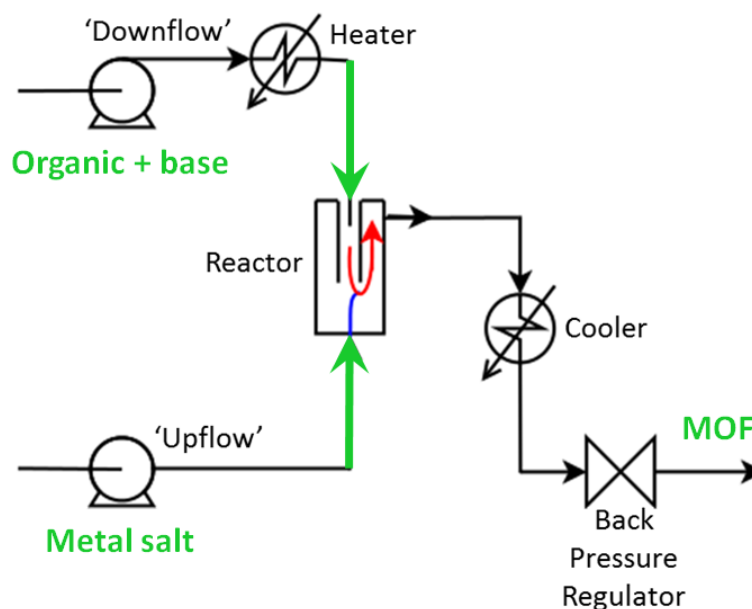
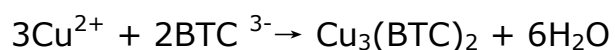
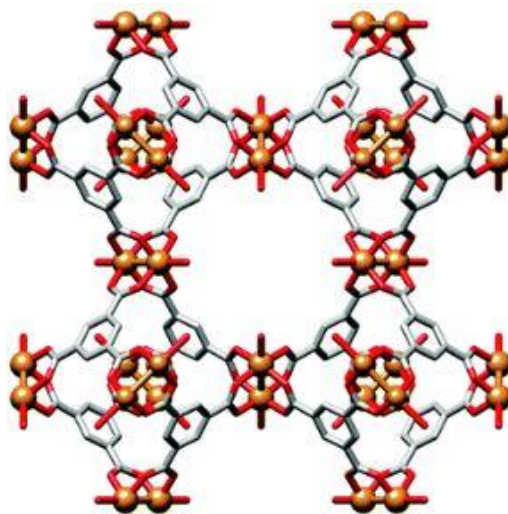


Figure 5. 1 MOF production using a continuous solvothermal flow reactor

5.2.1.2 Synthesis of HKUST-1

The reaction and activation process were the same for HKUST-1 and synthesized with a ratio of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$: trimesic acid: $\text{N}(\text{Et})_3 = 3:2:6$. In a typical synthesis, 6.98 gram of copper salt was dissolved in 250 mL H_2O , and 4.2 gram of trimesic acid with 8.32 mL triethylamine was dissolved in 500 mL ethanol. The reaction equation and the schematic of HKUST-1 are as follows:





5.2.2 Characterization

X-ray diffraction patterns of the materials were recorded with a Bruker D8 Advance diffractometer. The morphologies of materials were observed using scanning electron microscopy with an XL30 FEG-ESEM operating at 20 kV. Thermogravimetric analysis was performed on a thermobalance (TGA Q500-0829). The sample was heated from room temperature to 800 °C with a heating rate of 10 °C per minute under a gas flow of nitrogen or air (100 mL min⁻¹). A Q500-1360 instrument was used to measure CO₂ uptake capacity for the samples at room temperature. The N₂ adsorption-desorption isotherms were measured using a TriStar II 3020 at 77 K. ZIF-8 was degassed at 90 °C for 15 h and then at 120 °C for 3 h prior to analysis. HKUST-1 was degassed at

120 °C for 15 h. The BET surface area was obtained from the adsorption data.

5.2.3 Thermal and water stability test

A thermogravimetric analysis instrument (TGA Q500-0829) was used to examine the thermal stability of MOFs. ZIF-8 samples were thermally treated under N₂ atmosphere at temperatures of 450, 500, 550 and 600 °C for 5 hours, HKUST-1 samples were treated at 50, 100, 150, 200, 250 and 300 °C for 5 hours. Afterwards, the heated products were collected and characterized by SEM and XRD instruments.

A water exposure environment was prepared to test the water stability of MOFs: 25 mL deionized water was filled in a 250 mL sealed DURAN glass bottle. The sample was loaded onto gauze which was supported by a stainless steel stand to avoid direct contact with water. Then the glass bottle was transferred into a 90 °C oven for 1, 5 and 18 hours, respectively. The hydrothermally treated materials were then examined using SEM and XRD instruments.

5.2.4 Results and Discussions for ZIF-8

5.2.4.1 Crystal structure characterizations

Figure 5.2 shows the powder X-ray diffraction patterns of as-synthesized ZIF-8 (termed as Nott.ZIF-8 in this article) and the commercialized ZIF-8. It can be seen that these two patterns are consistent, and both match well with the simulated pattern. The sharp peaks on 7.3° (011) [258], 10.2° (002) and 12.7° (112) indicate that the product possesses a high purity and high degree of crystallinity [258]. The pattern for commercial ZIF-8 presents a smaller intensity ratio of (002) to (011) plane than Nott.ZIF-8. This difference also reflected in the crystal shapes from SEM imaging (Figure 5.3).

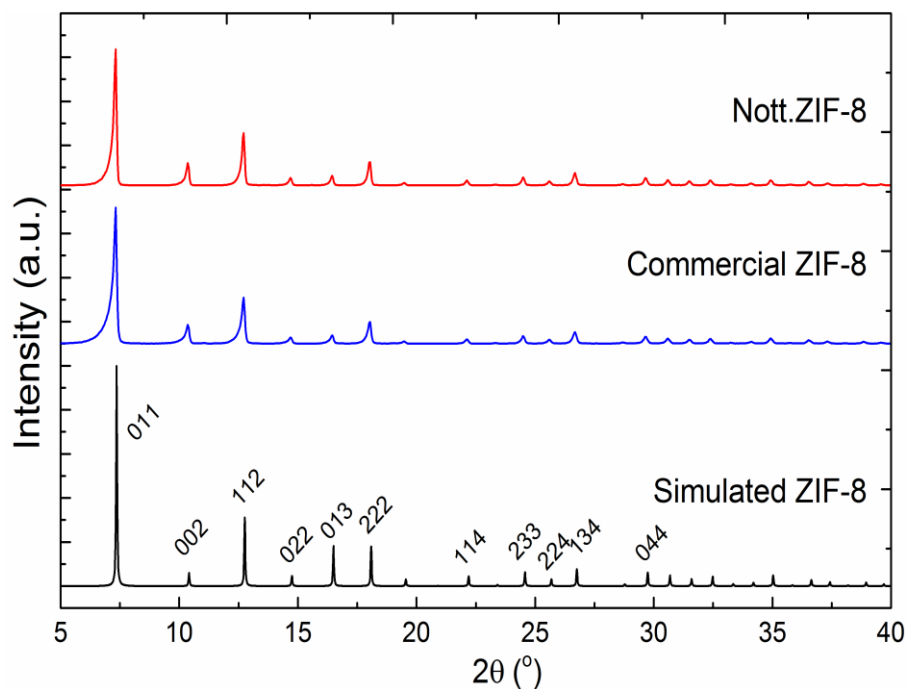


Figure 5. 2 XRD patterns for Nott.ZIF-8, commercial ZIF-8 and simulated ZIF-8

Obvious crystal morphology variation can be observed from SEM images (Figure 5.3). Bigger sized (0.5-2.5 μm) cubes with truncated edges were obtained from ZIF-8. Commercial ZIF-8 exhibits a much smaller size (200-300 nm) with a shape of rhombic dodecahedron. This difference implies that the crystal growth of Nott.ZIF-8 develops preferentially on the (100) face (Figure 5.4), which could be probably resulted from the chemicals influence (involved in the precursors and base).

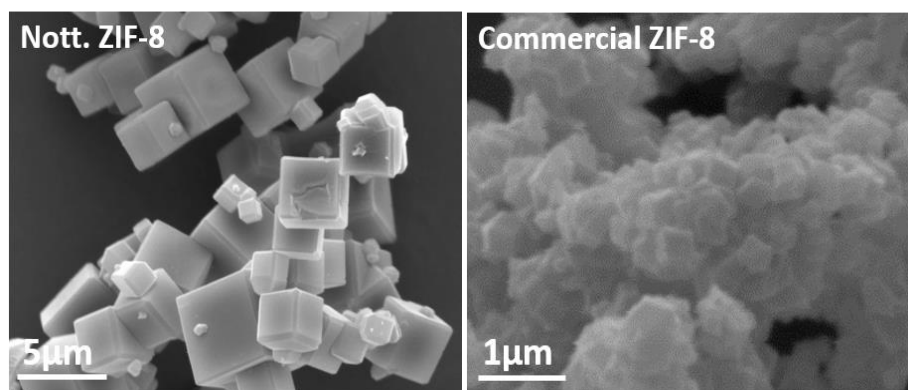


Figure 5. 3 SEM images of ZIF-8 products

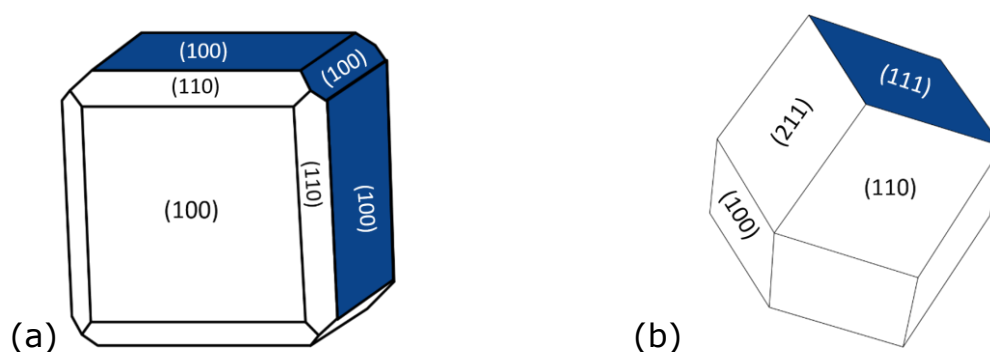


Figure 5. 4 The crystal faces for ZIF-8: (a) Nott. ZIF-8, (b) Commercial ZIF-8.

5.2.4.2 Thermal and Water Stability

In order to apply MOFs for industrial scale carbon capture, hydrothermal stability tests were needed to conduct to assess the quality of the MOFs [259]. ZIF-8 has been reported to possess a remarkable thermal and water stability [84]. Figure 5.5 illustrates Nott.ZIF-8 and commercial ZIF-8 decomposition curves in N_2 .

These two curves match well. Nott. ZIF-8 starts to lose weight at ~ 500 °C, while the commercial ZIF-8 tend to lose weight earlier. It can be inferred that Nott.ZIF-8 possesses a greater thermal stability than the commercialized product. The plain line before 500 °C suggests that our ZIF-8 almost contain no unreacted solvents or impurities [258].

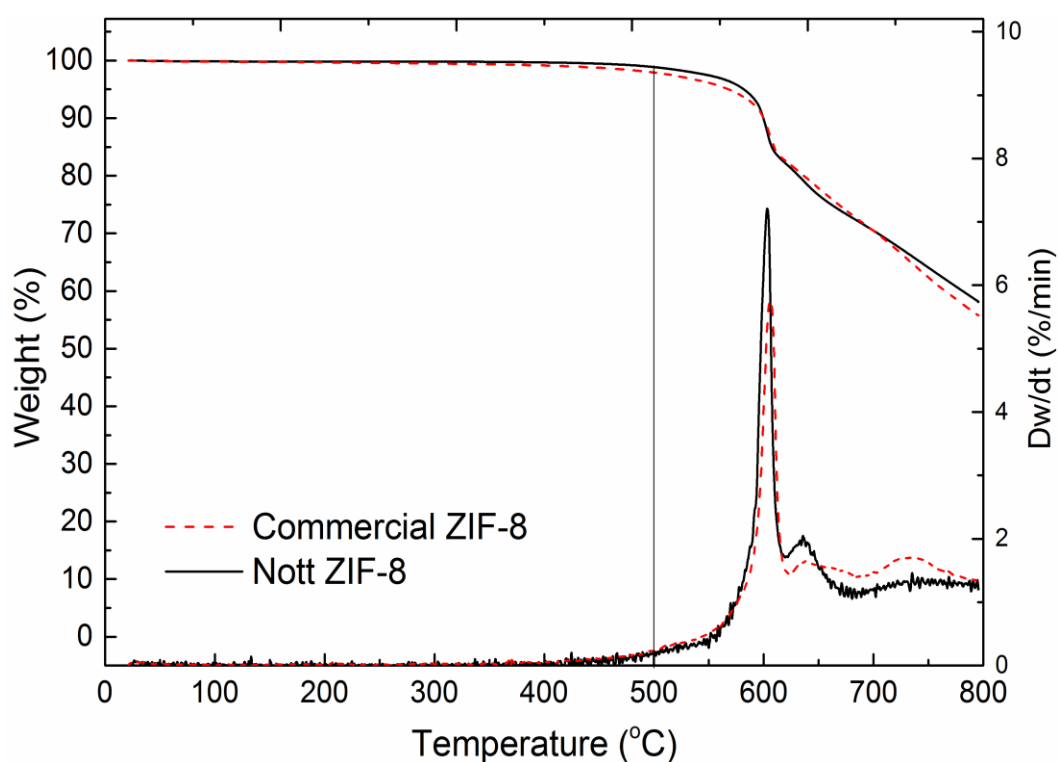


Figure 5. 5 Thermal decomposition in Nitrogen of ZIF-8

In order to assess the thermal stability of ZIF-8, further isothermal TGA decompositions tests were carried out. Figure 5.6 and Figure 5.7 present the crystallinities and morphologies

changes for the samples after heated in 450, 500, 550 °C for 5 hours. The XRD results indicate that both materials retained high integrity when heated at 450 °C for 5 hours. However, Nott.ZIF-8 was able to sustain a higher temperature treatment up to 500 °C, at which the commercial ZIF-8 has decomposed to ZnO. The crystallinity of Nott.ZIF-8 was noticeably eliminated at 500 °C and at 550 °C ZnO XRD peaks emerge.

It can be clearly seen from SEM images (Figure 5.7) that the increase in temperature results in the shapes of both materials being distorted, to some extent. The size of materials gradually became smaller due the shrinkage caused by thermal treatment. The commercial ZIF-8 expresses an earlier morphology change (~500 °C). From XRD and SEM results it is possible to conclude that Nott.ZIF-8 possesses a higher thermal stability. This could be probably due to the stronger chemical bonding of Nott. ZIF-8.

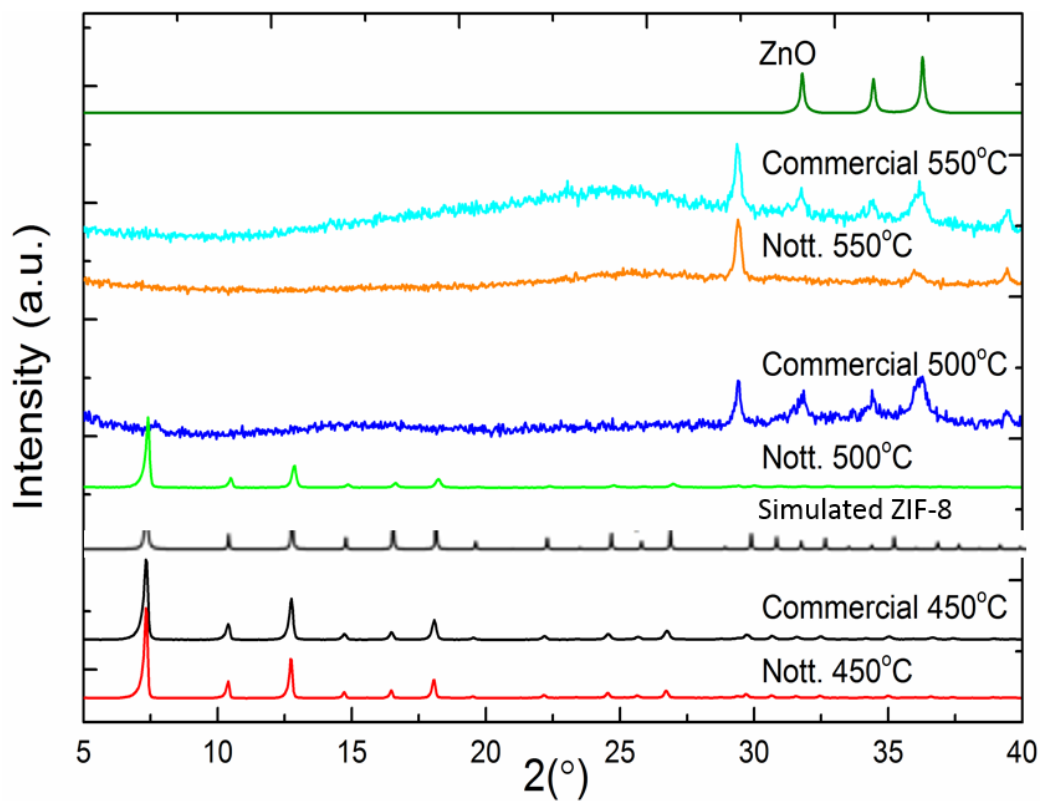


Figure 5. 6 XRD patterns of ZIF-8 after thermal treatments at different temperatures for 5 h.

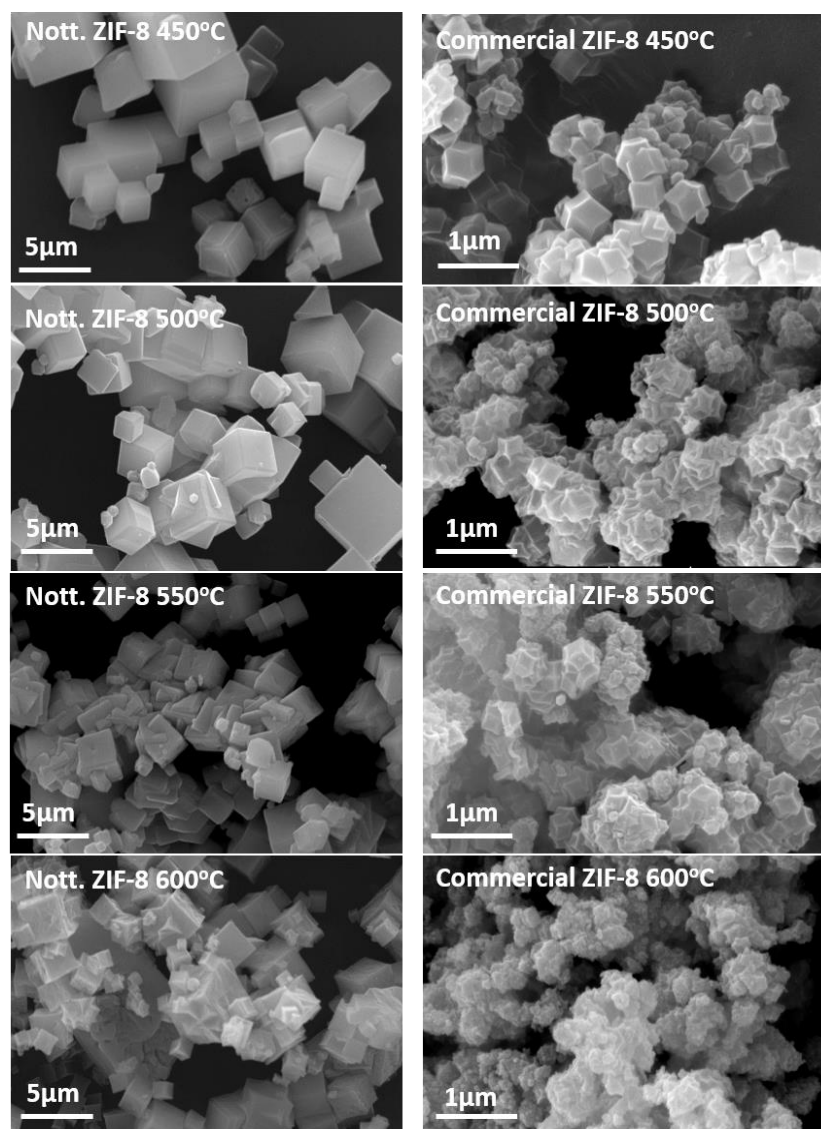


Figure 5. 7 SEM images of ZIF-8 after different temperatures thermal treatments for 5 hours.

In addition to thermal stability, it is also important to examine the water stability of MOFs since water vapour exists in industrial flue gas and a dehydration step would be impractical [260]. Figure 5.8 shows the XRD patterns before and after water vapour

exposure at 90 °C for different times of ZIF-8. The patterns for both samples retained high integrity even after exposed in water vapor for 18 hours, which indicates that ZIF-8 is more tolerant of moisture than HKUST-1.

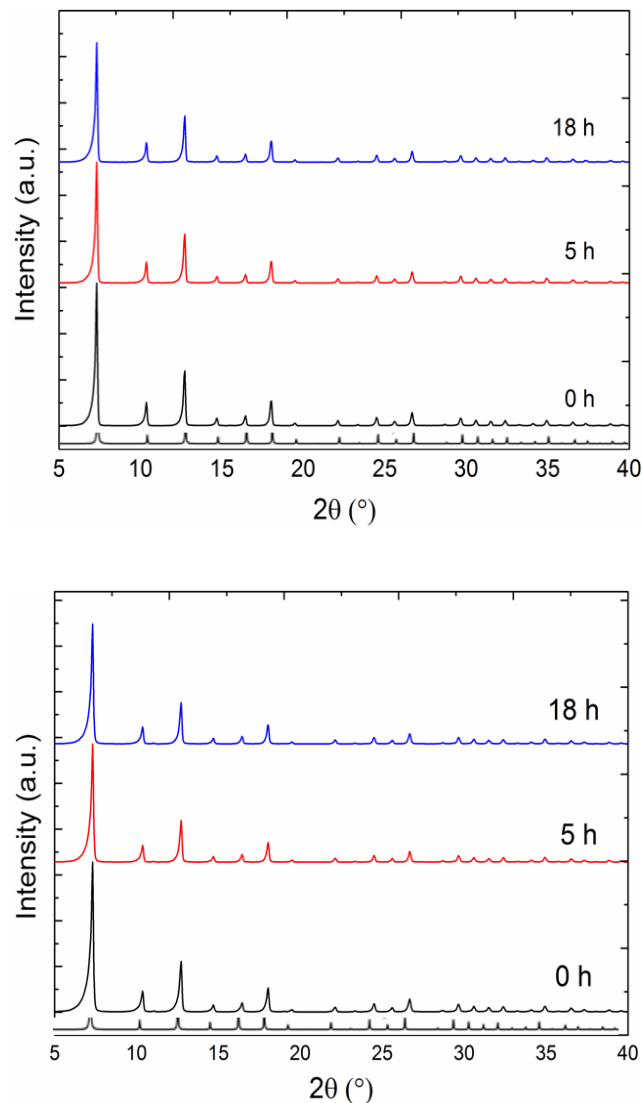


Figure 5. 8 XRD patterns of top: Nott. ZIF-8 and bottom: Commercial ZIF-8 after exposure to humidity for different times. (the bottom pattern in each figure represents the simulated ZIF-8)

5.2.4.3 Textural properties

The nitrogen adsorption isotherms at 77 K are shown in Figure 5.9. The two curves almost overlap with no hysteresis loop existing. According to the classification of IUPAC (International Union of Pure and Applied Chemistry), the shapes of the curves indicate that the isotherms for both are Type I [172, 238]. This implies microporous character, which means that most adsorption takes place below a partial pressure of p/p_0 0.1. The Nott. ZIF-8 exhibits a BET surface area as high as $1707 \text{ m}^2 \text{ g}^{-1}$ and the commercial one $1711 \text{ m}^2 \text{ g}^{-1}$.

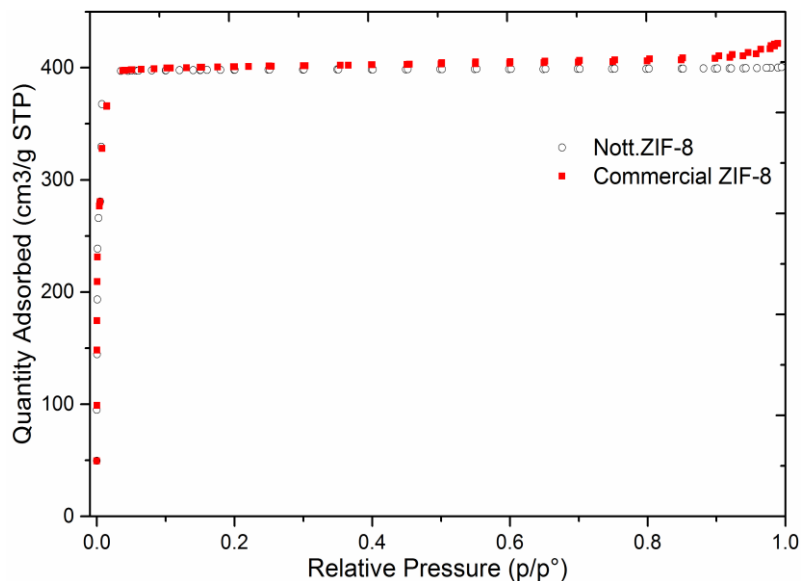


Figure 5. 9 Nitrogen isotherms for Nott. ZIF-8 and commercial ZIF-8

In addition, their pore volumes were determined to be 0.62 and 0.65, respectively (Table 5.1). These values compare well with those reported previously and the high surface area suggests that the guest molecules inside the pores are absent after activation process [234]. The similar surface area further proves that using the continuous reactor is a feasible method of production.

Table 5. 1 Texture properties of Nott.ZIF-8 and commercial ZIF-8.

	S_{BET} (m²/g)	V_p* (cm³/g)
Nott. ZIF-8	1707	0.62
Commercial ZIF-8	1711	0.65

* V_p: total pore volume at 0.99 p/p₀

5.2.4.4 CO₂ adsorption test

The CO₂ uptake capacity of pristine materials and thermally treated materials were evaluated using a TGA. The results are shown in Table 5.2. Nott.ZIF-8 lost CO₂ uptake ability after being held at 550 °C for 5 hours in N₂, while commercial ZIF-8 lost this ability after 500 °C thermal treatment. This CO₂ uptake test results were in good agreement with SEM and XRD records. CO₂ adsorption capacity of commercial ZIF-8 was slightly higher than

Nott.ZIF-8 except after going through 500 °C heat treatment for 5 hours. This can be attributed to the higher surface area and total pore volumes of the commercial product, but the difference is very small. Table 2 exhibits that with the increased temperature in heat treatment CO₂ adsorption capacity of ZIF-8 decreased gradually. Once the samples decomposed, the CO₂ uptake drops dramatically as well for both samples.

Table 5. 2 CO₂ uptake for Nott.ZIF-8 and commercial ZIF-8 at 25°C, 1bar

CO₂ uptake at 25°C	Nott.ZIF-8	Commercial ZIF-8
No treatment	2.69%	2.71%
5h@450°C	2.42%	2.50%
5h@500°C	2.39%	0.55%
5h@550°C	0.87%	0.18%

5.2.5 Results and Discussions for HKUST-1

5.2.5.1 Crystal structure characterizations

The continuous as-synthesized HKUST-1 (termed as Nott. HKUST-1 later) and commercial HKUST-1 were characterised by SEM and XRD. It can be estimated from SEM images (Figure 5.10)

that Nott. HKUST-1 possesses very small crystal sizes ranging approximately at 30-100 nm, while the commercialized HKUST-1 presents larger crystal sizes ranging from 2 to 10 μm .

XRD patterns in Figure 5.11 compare the as-synthesised and commercial HKUST-1. The position of each peak for as-synthesized and commercialized HKUST-1 is in good agreement. However, the different intensity ratios of (200) to (220) plane can be visibly observed. The ratio of commercial HKUST-1 shows smaller than that of Nott. HKUST-1. This can be attributed to the water adsorption of HKUST-1 [261] and is difficult to avoid since HKUST-1 will rapidly adsorb water in the air during the experimental procedures [262]. Also, this difference presented in XRD patterns implies the shape variation of samples.

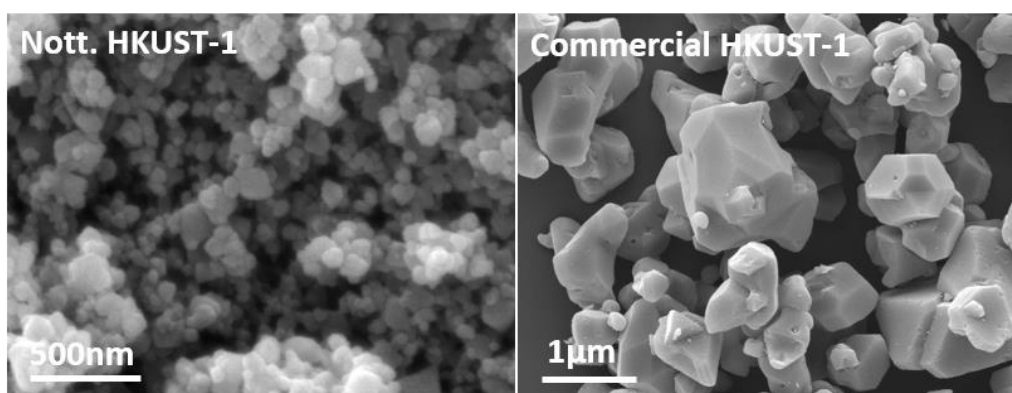


Figure 5. 10 SEM images for Nott.HKUST-1 and commercial HKUST-1.

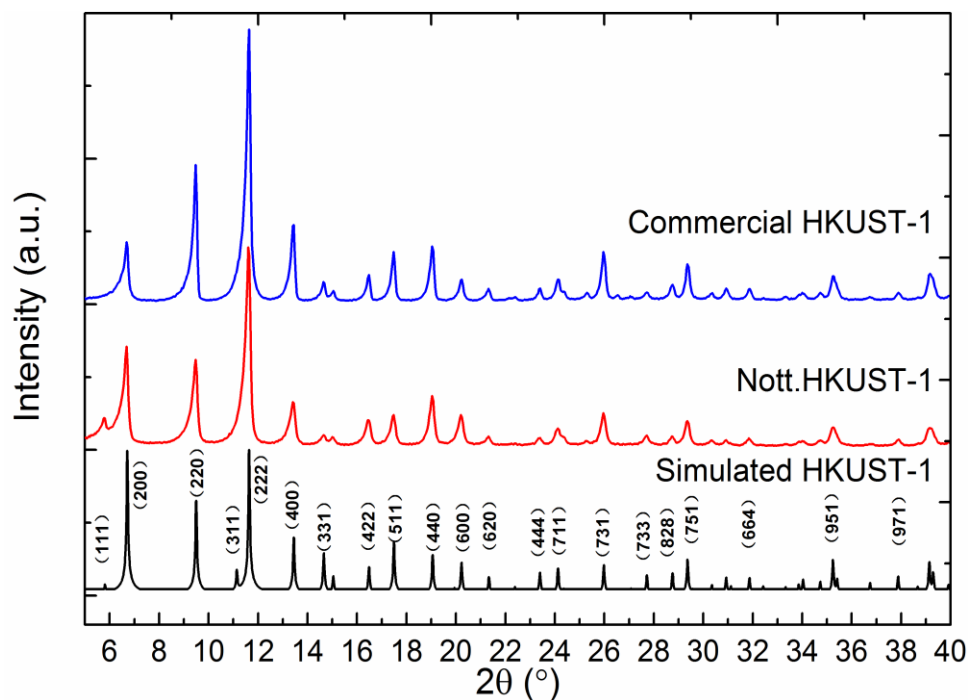


Figure 5. 11 XRD patterns for Nott.HKUST-1, commercial HKUST-1 and simulated HKUST-1.

5.2.5.2 Thermal and Water Stability

A TGA was used to explore the degradation of HKUST-1. Figure 5.12 presents the degradation process of the two samples. The first stage of weight loss centering at about 100 °C can be mainly attributed to the removal of free water. The complete collapse of Nott.HKUST-1 structure was observed at around 320 °C, while the commercial HKSUT-1 collapsed at a higher temperature of about 340 °C. This indicates that the commercialized HKSUT-1 possess a higher thermal stability. In addition, the Nott.HKUST-

1's weight was lost gradually in the temperature range of 100 °C to 290 °C, which might be a process of unreacted reactants or guest molecules removal [169]. This also reflects on its lower surface area. The TGA curve for commercial HKUST-1 exhibits a plateau at this temperature range, indicating the absent of guest molecules in the pore interior.

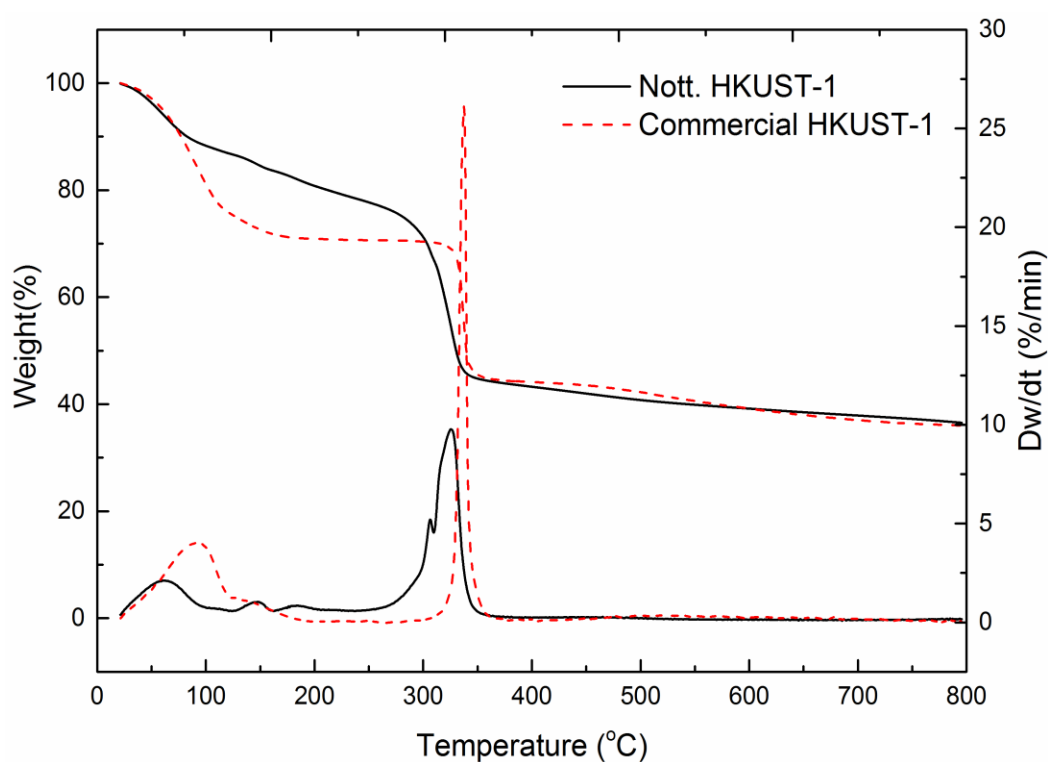


Figure 5. 12 Thermogravimetric analysis of two HKUST-1 in N₂ atmosphere.

Subsequently, both samples were heated in N₂ for 5 hours at different temperatures. The samples were collected and analyzed

by XRD and SEM. Figure 5.13 and Figure 5.14 have shown the results.

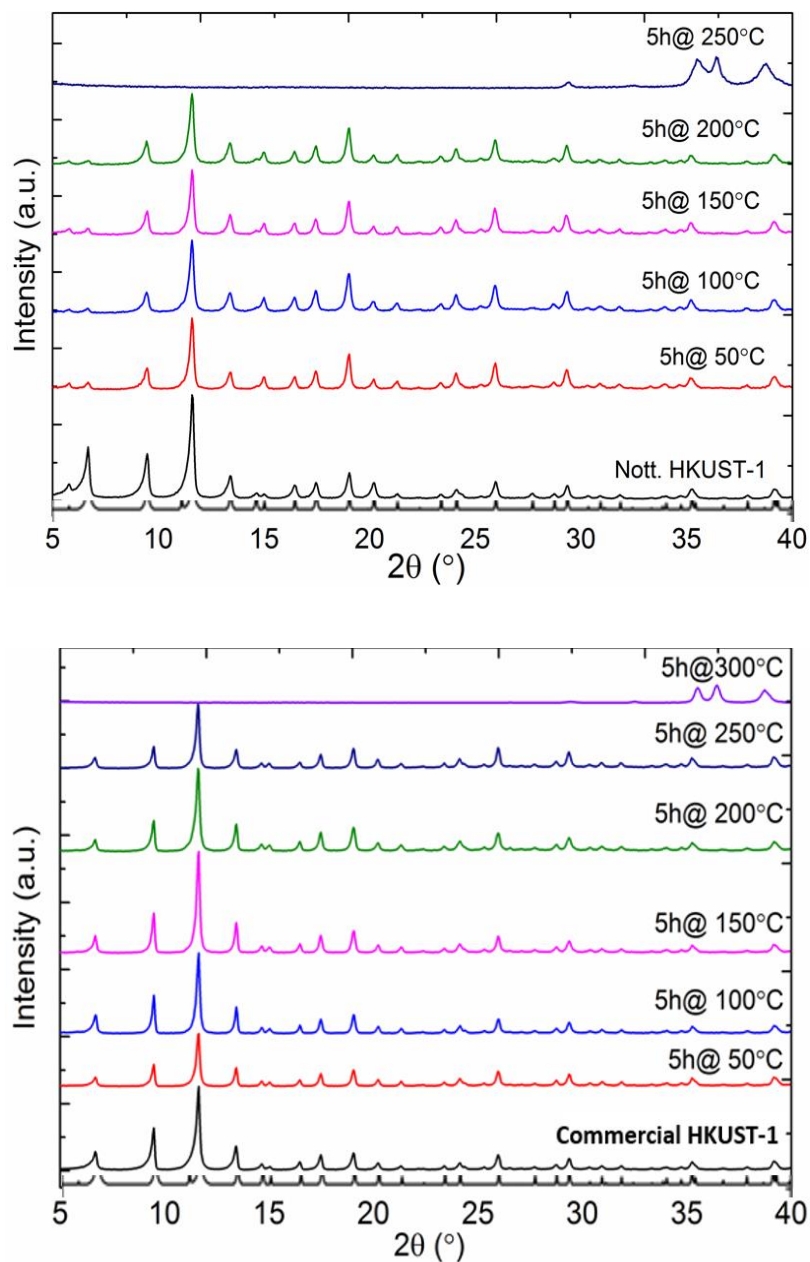


Figure 5. 13 XRD patterns of HKUST-1 after thermal treatments for 5h (the bottom pattern in each figure represents the simulated HKUST-1)

The XRD patterns show that the commercial HKUST-1 maintains its structure until heated at 300 °C, while the crystal structure of Nott.HKUST-1 decomposed when exposure at 250 °C for 5 hours. The dramatic decrease of the intensity on (200) plane for Nott. HKSUT-1 can be probably resulted from crystalline water loss. Through the comparisons it can be concluded that commercial HKUST-1 has a higher thermal stability than Nott.HKUST-1. This might be due to its stronger chemical bonding.

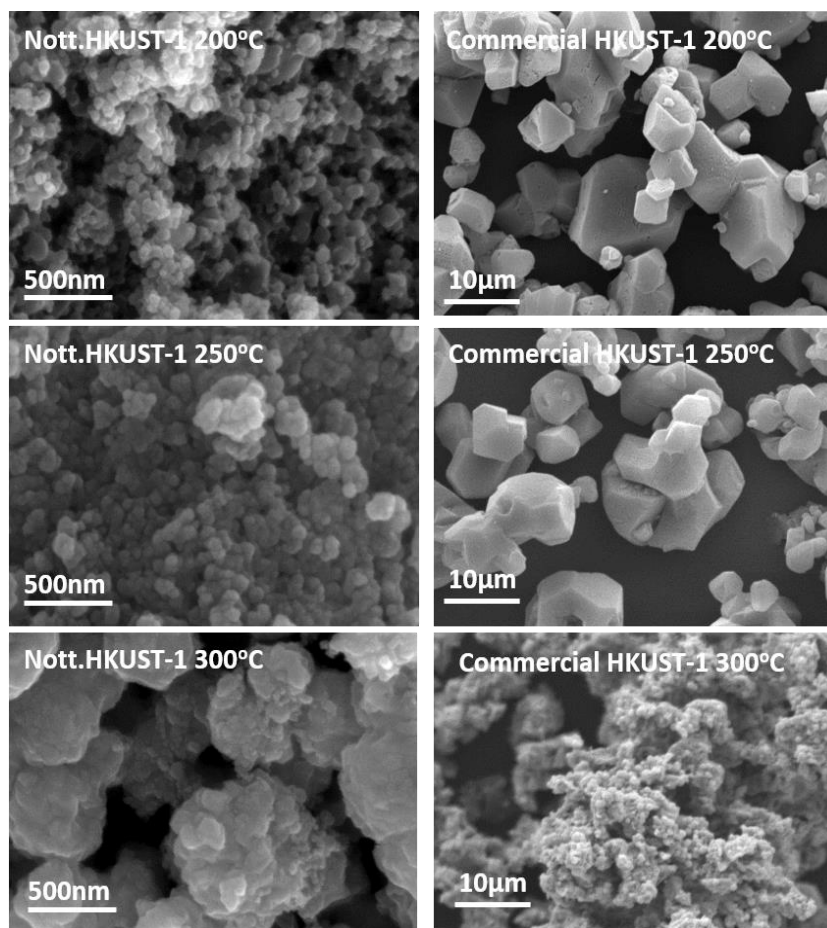


Figure 5. 14 SEM images of two HKUST-1 after thermal treatment with different temperatures for 5 h.

HKUST-1 is known as a material which is highly sensitive to water [123]. The same process of hydrothermal treatment as that of ZIF-8 was conducted to assess the materials stability in a humid atmosphere. Figure 5.15 shows that after 1 hour moisture treatment a significant loss of structural integrity happened, meaning a collapse of the framework structure. The degraded

sample's XRD patterns are consistent with that reported by Al-Janabi [263].

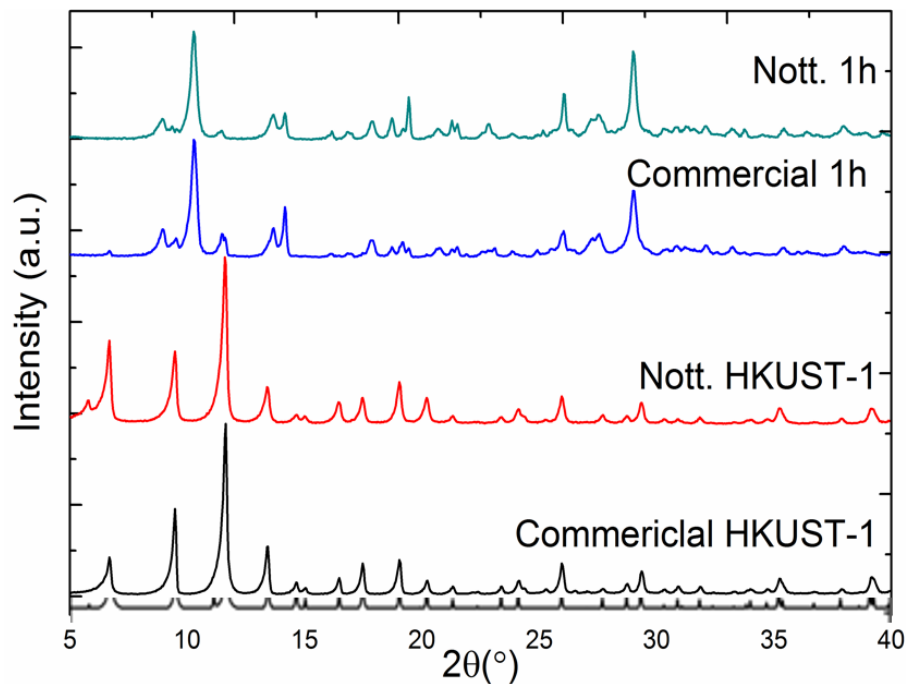


Figure 5. 15 XRD patterns of Nott.HKUST-1 and commercial HKUST-1 before and after exposure at 90 °C water vapor for 1 hour.

5.2.5.3 Textural properties

Figure 5.16 shows the nitrogen adsorption isotherm curves for Nott.HKUST-1 and commercial HKUST-1. According to IUPAC classification the shape of these two curves belongs to Type I isotherm, indicating microporous structure (<2nm) of these two samples. The surface area of commercial HKUST-1 shows higher than Nott.HKUST-1 (Table 5.3). This might be because of some

contaminant molecules remaining in the Nott.HKUST-1 pore structure. This is also in agreement with the TGA results that Nott. HKUST-1 presents a weight loss between 100°C and 300°C. However, our synthesized HKUST-1 takes advantage of low cost and low energy consumption compared to the expensive commercial HKUST-1, and this is the first reported HKUST-1 synthesized continuously with a high yield (64%) under mild conditions (50°C and ambient pressure) and comparable surface area of 1322 m²/g.

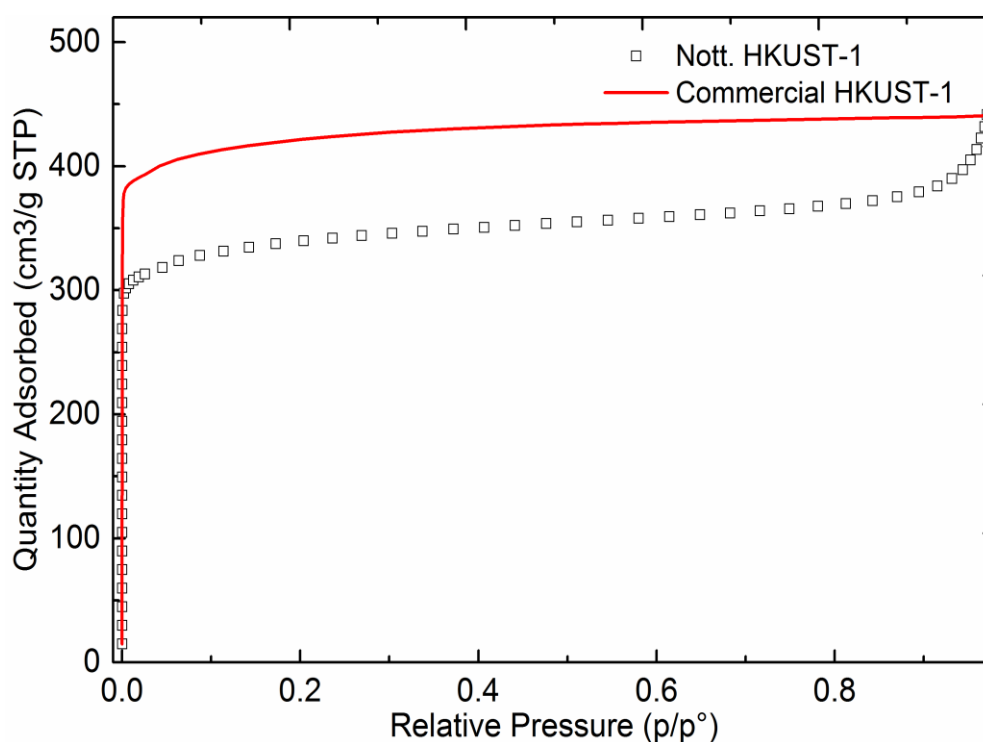


Figure 5. 16 Nitrogen adsorption isotherms for the two HKUST-1 samples.

Table 5. 3 Textural properties of Nott.ZIF-8 and commercial ZIF-8.

	S_{BET} (m^2/g)	V_p^* (cm^3/g)
Nott. HKUST-1	1322	0.63
Commercial HKUST-1	1678	0.69

5.2.5.4 CO₂ adsorption test

CO₂ uptake experiment was carried out by TGA at 25 °C under the atmospheric pressure. Three same TGA tests were conducted in order to ensure the repeatability and the average value was used. Nott. HKUST-1 adsorbed 10.2% CO₂ and commercial HKUST-1 adsorbs about twice of the Nott.HKUST-1 (19.8%). The test value for the commercialized one was similar to that tested by other researchers [60]. It is noticed that the CO₂ uptake amount is around 16% percent higher than that of HKUST-1 synthesized in Chapter 3. The reasons of these were 1) two different TGA instruments were used (one in UK, one in China), 2) the lower temperature leads to a higher CO₂ uptake.

5.2.6 Conclusions

According to the comparative study it can be concluded that the continuous production of ZIF-8 and HKUST-1 using the

counter-current mixing reactor is possible. Compared to commercial material, Nott.ZIF-8 has a higher thermal stability, which can be probably explained by its larger crystal size. Although the thermal stability of Nott.HKUST-1 is lower than commercial one the cost is rather low to synthesize HKUST-1 in this method. In addition, the surface area and the yield is relatively high compared to others reported recently.

5.3 Experimental B: Post-synthetic modification of HKUST-1 using DDSA

5.3.1 Initial Post-Modification Experiments

The second part of the experiments work was an attempt to improve the hydrophobicity of HKUST-1 by incorporating DDSA (Dodecenylsuccinic anhydride) into the samples as a coating. The rig configuration is described in Figure 5.17. HKUST-1 was firstly made by the reaction of Benzene 1,3,5-tricarboxylic acid (TMA) and $\text{Cu}(\text{NO}_3)_2$ using the same procedures as described in Section 5.2. Triethylamine (TEA) was added in the TMA to facilitate the deprotonation process to obtain more uniform products. DDSA was added in the third flow and met HKUST-1 in a T-mixer. The DDSA molecule structure is shown in Figure 5.18.

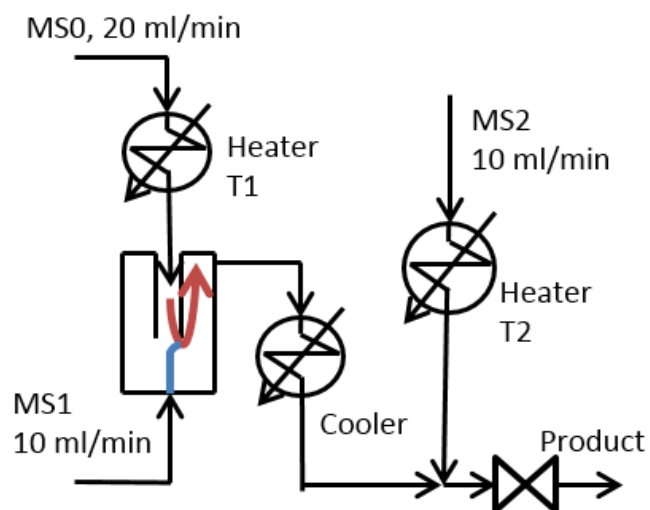


Figure 5. 17 Rig configuration of DDSA incorporation experiments

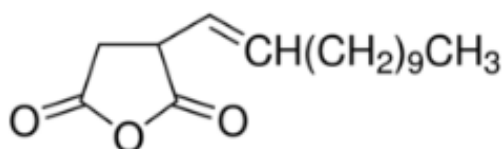


Figure 5. 18 DDSA molecule structure

Before doing the experiments, the health and safety issues caused by this new chemical addition should be assessed. According to the safety data sheet, DDSA can cause skin irritation and serious eye irritation. Therefore, PPE (Personal protective equipment) should be worn to minimize exposure to hazards.

In the first trial, ethanol was used as the solvent of DDSA, and the DDSA solution was preheated to different temperatures of 100, 150 and 200 ° C. The collected suspension was centrifuged at 400 rpm for 3 to 5 minutes. The preparation methods for different samples have been listed in Table 5.4. The sediment was then dried in the oven at 70 ° C overnight. The reason to increase the temperature was for the purpose of opening the ring structure of DDSA.

Table 5.4 1 (a) Synthesis conditions of products made by HKUST-1 and DDSA

Sample ID	Compositions					
	MS0		MS1		MS2	
	Reagents	Solvent	Reagents	Solvent	Reagents	Solvent
CYC-1A						
CYC-1B	TMA+TEA	Et(OH)	Cu(NO ₃) ₂	H ₂ O	DDSA	Et(OH)
CYC-1C						
CYC-1D						

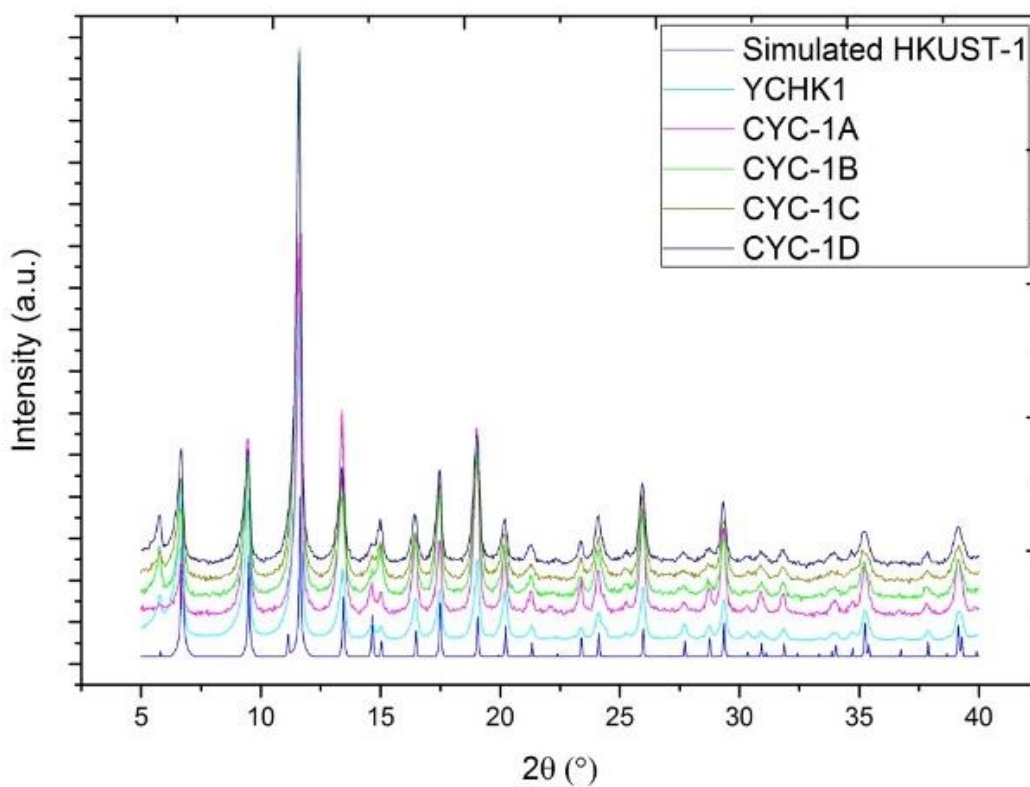
Table 5.4 2 (b) Synthesis conditions of products made by HKUST-1 and DDSA

Sample ID	Concentration of Cu ²⁺	Ratio	X	Flow Rate	T1	T2
	M			ml/min	°C	°C
		MS0:MS1:MS2		MS0:MS1:MS2	MS0	MS2
				2		
		(TMA:TEA):M+: (DDSA:X)				
CYC-1A	0.12	(2:6):3:(2:0)	None	20:10:10	50	RT
CYC-1B	0.12	(2:6):3:(2:0)	None	20:10:10	50	150
CYC-1C	0.12	(2:6):3:(2:0)	None	20:10:10	50	200
CYC-1D	0.12	(2:6):3:(2:0)	None	20:10:10	50	100

TMA=Benzene 1,3,5-tricarboxylic acid; TEA=Triethylamine;

Et(OH)=Ethanol; DDSA=Dodecenylsuccinic anhydride

Figure 5.19 illustrates that the products' XRD patterns retained integrity as the same as HKUST-1, indicating that DDSA did not damage the structure of HKUST-1.



(YCHK1 represents the NOTT.HKUST-1)

Figure 5. 19 Comparison of the XRD patterns for DDSA treated HKUST-1 and pristine HKUST-1

FTIR experiments were carried out to find out if DDSA was successfully deposited onto the surface of HKUST-1. The results are shown in Figure 5.20. However, there is no difference

detected between the samples with and without DDSA, which implies DDSA was probably not present in the products.

Further water stability test was performed in a 250 mL sealed DURAN glass bottle. The glass bottle was filled with 25 ml deionized water. The sample was loaded onto gauze which was supported by a stainless steel stand to avoid direct contact with water. Afterwards, the glass bottle was heated in an oven to 90 °C and kept for 1, 5, 18 hours. The treated material was then characterized by XRD to compare the differences in the patterns and thus the hydrothermal stability was evaluated. However, according to the XRD results, even after 1 h exposed in the humid glass bottle the framework structure collapsed for all four samples. The first attempt therefore failed.

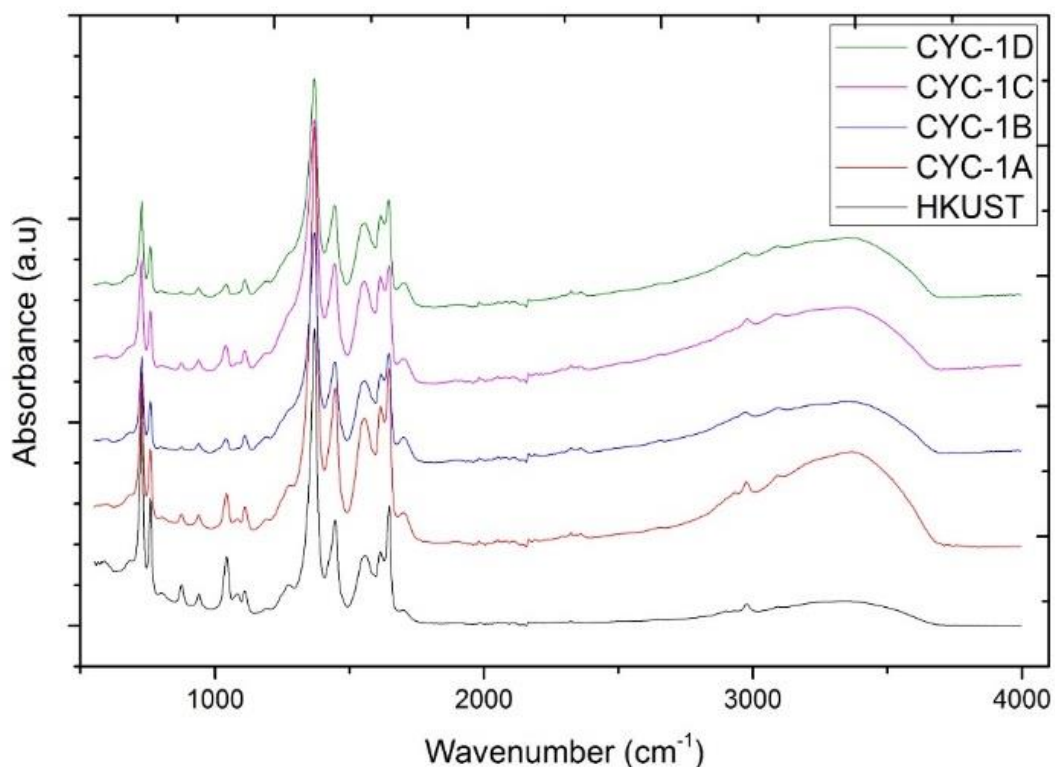


Figure 5. 20 FTIR results for the treated products synthesized at different T2 temperature.

5.3.2 Second Post-Modification Experiments

Afterwards, the second trial was conducted in order to open the anhydride ring of DDSA. It was demonstrated by Wang et al. [264] that a base solution can help open the ring of DDSA to facilitate its coating on HKUST-1. As trimethylamine (TEA) was used as the deprotonation agent in the ligand precursor when synthesizing HKUST-1, for the purpose to involve as less chemicals as possible TEA was used again as the solvent in DDSA

solution. The synthesis process was the same described previously in Section 5.2.1.

The sample labels for the new synthesized samples and their corresponding conditions are listed in Table 5.5. In sample CYC-3A and CYC-3B ammonium was used as the solvent because of its weak basicity, for the reason that HKUST-1 is sensitive to a strong base. Different T2 temperatures were used. The XRD patterns prove that the crystal structure was not damaged.

Table 5.5 (1) Synthesis conditions of products made by HKUST-1 and DDSA with base addition

Sample ID	Compositions					
	MS0		MS1		MS2	
	Reagents	Solvent	Reagents	Solvent	Reagents	Solvent
CYC-2A						
CYC-3A	TMA+TEA	Et(OH)	Cu(NO ₃) ₂	H ₂ O	DDSA+X	Et(OH)
CYC-3B						

Table 5.5 (2) Synthesis conditions of products made by HKUST-1 and DDSA with base addition

Sample ID	Concentration of Cu ²⁺	Ratio	X	Flow Rate	T1	T2
				ml/min	°C	°C
		MS0:MS1:MS2		MS0:MS1:MS2	MS0	MS2
CYC-2A	0.12	(2:6):3:(2:6)	TEA	20:10:10	50	RT
CYC-3A	0.12	(2:6):3:(2:2)	NH3	20:10:10	50	RT
CYC-3B	0.12	(2:6):3:(2:2)	NH3	20:10:10	50	100

Figure 5.21 displays the XRD patterns for the samples. Compare with the untreated HKUST-1 sample, the DDSA (with base solvent) modified sample shows no big difference, meaning the structures were not destroyed by the chemicals addition.

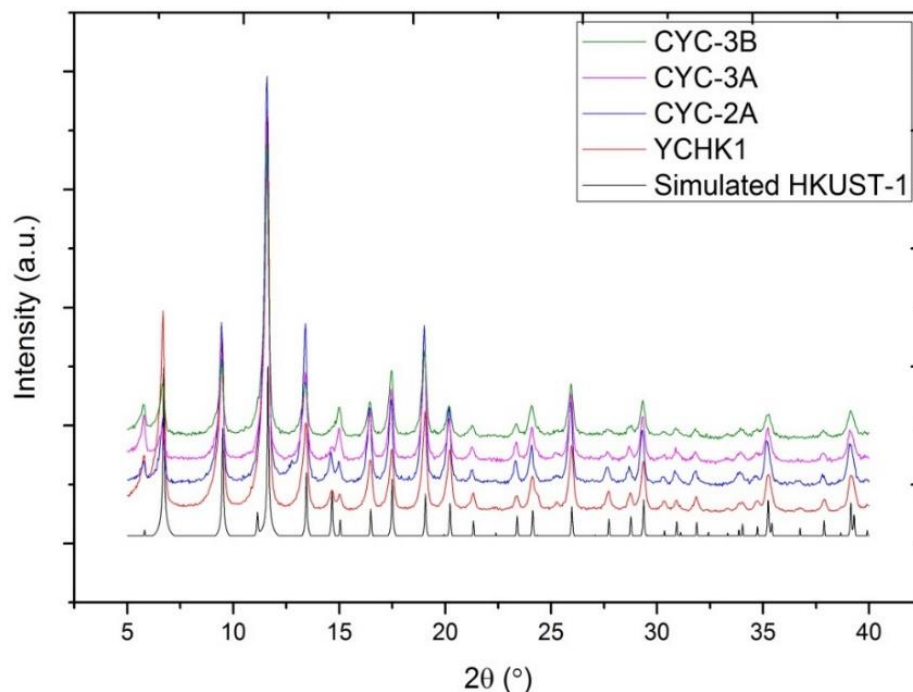


Figure 5. 21 XRD patterns for products synthesized by HKUST-1 and DDSA with base addition

To determine whether DDSA is present in the sample, FTIR instrument was used and the result for the comparison before and after treatment was exhibited in Figure 5.22. It can be notified that the sample produced by HKUST-1 and DDSA with TEA addition (CYC-2A) presents a difference in FTIR absorbance

in the wavenumber band near 1600 cm^{-1} . This band is referred as the absorbance of double carbon bonds which exist in DDSA. However, for the NH_3 added samples (CYC-3A and CYC-3B) there was no difference in this range. Therefore, it is speculated that DDSA was present in the sample CYC-2A, but not in sample CYC-3A and CYC-3B.

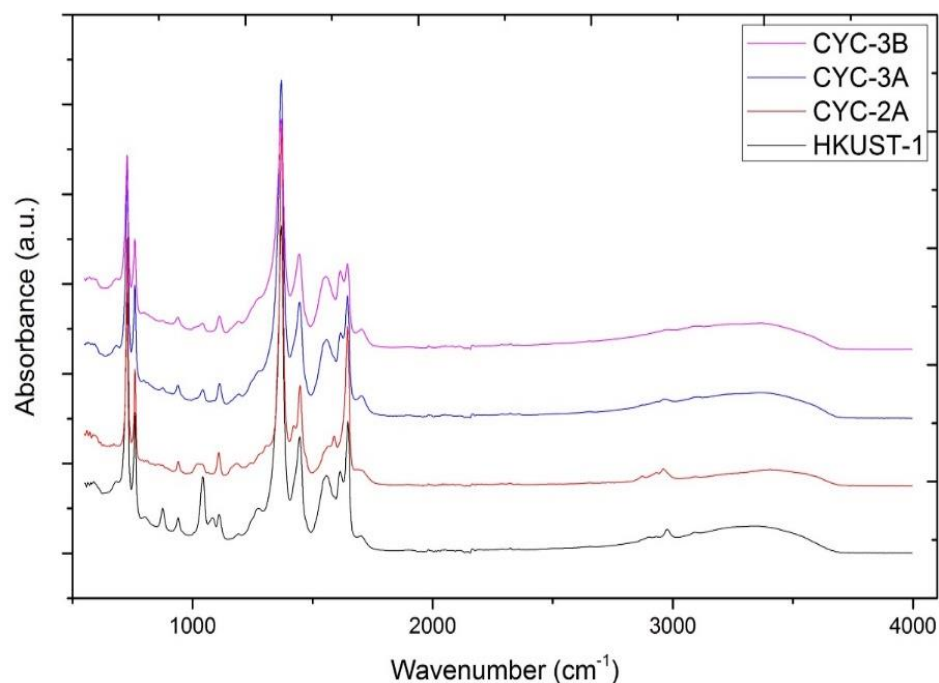


Figure 5. 22 FTIR absorbance results for products with and without DDSA (+TEA) addition.

To test the water stability of the modified samples, hydrothermal tests were conducted as it has been described in

Section 5.3.1. The samples after the hydrothermal tests were collected and sent to the XRD test. The result is illustrated in Figure 5.23 (for sample CYC-2A) and Figure 5.24 (for sample CYC-3A and CYC-3B).

Sample CYC-2A maintained structural integrity after 1 hour when exposed to the humid environment, although its structure was destroyed after 5 hours exposure. However, both of the samples CYC-3A and CYC-3B underwent a structure breakdown after 1 hour hydrothermal treatment. This phenomenon implies that the hydrophobicity is not changed in this trial.

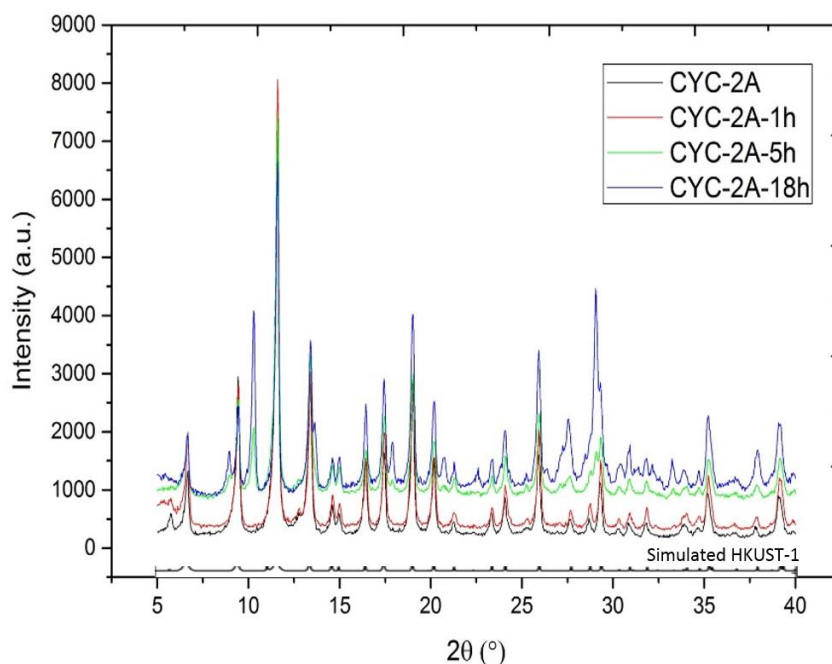


Figure 5. 23 XRD patterns for sample CYC-2A after exposure in humid environment for 1h, 5h, and 18h.

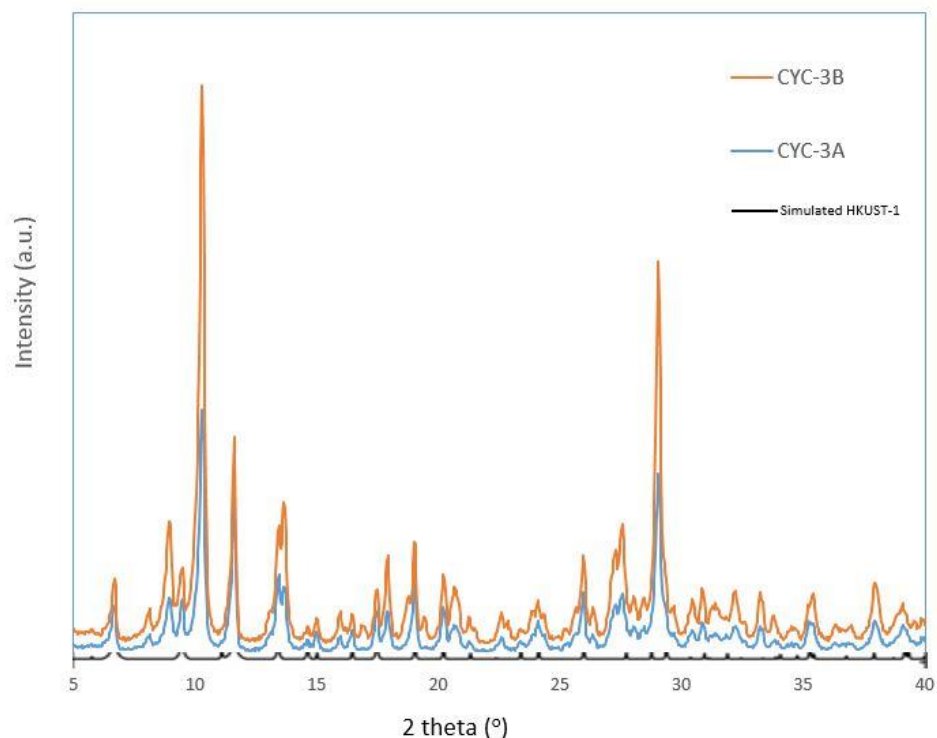


Figure 5. 24 XRD patterns for sample CYC-3A and CYC-3B after exposure in humid environment for 1 h.

5.3.3 Conclusions:

In this work, DDSA was successfully coated onto the surface of HKUST-1 in one of the experiments, and this coating successfully enhanced the hydrophobicity of HKUST-1. This coating did not enable the HKUST-1 to survive exposure of 5 hours in 2 % water vapor, but it is an improvement compared to the original HKUST-1 whose structure collapsed after 1 hour.

Chapter 6 Synthesis of Hybrid Materials in a Continuous Rig

6.1. Background and Theory

6.1.1 Nucleation and crystal growth

The mechanism of crystallization generally involves two steps: nucleation and crystal growth. Nucleation is the initiation process where the first small solid aggregates are generated [265].

Nucleation process involves phase change from liquid to solid, so the driving force decreases when the temperature rises. However, higher temperature leads to a faster diffusion of atoms into clusters, which contributes to an enhancement of the nucleation rate [266].

As a result, the nucleation rate exhibits a maximum during the process of increasing temperature to an infinite value (as depicted in Figure 6.1). Another factor that will influence the nucleation rate is flow rates, because the increased flow rates improve mixing and thus the nucleation rate [267].

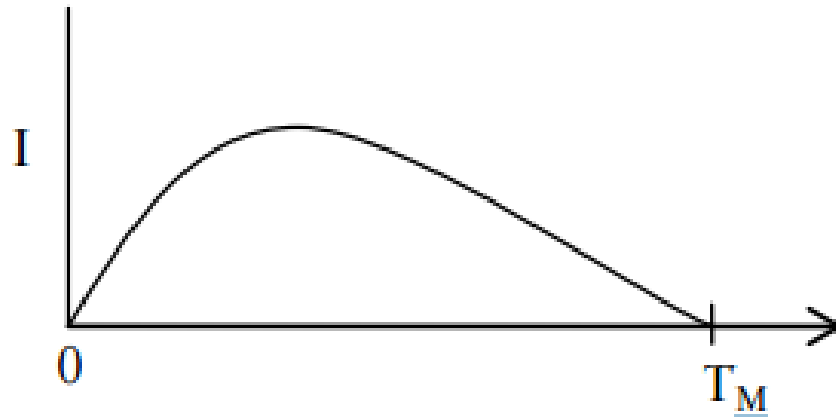


Figure 6. 1 nucleation rate trends with temperature, (y-axis means nucleation rate, x-axis means time) [268]

Nucleation can be homogeneous or heterogeneous [269]. Heterogeneous nucleation occurs between any two phases between solid, liquid or gas. The nucleus form at preferential sites such as solid wall and grain boundaries. Due to the lower effective surface energy at these sites the free energy barrier is diminished and the nucleation process is hence promoted [270]. On the contrary, homogeneous nucleation desires a nucleus forming at the interface of a new phase, which means it occurs more difficultly. Figure 6.2 illustrates the difference between homogeneous and heterogeneous.

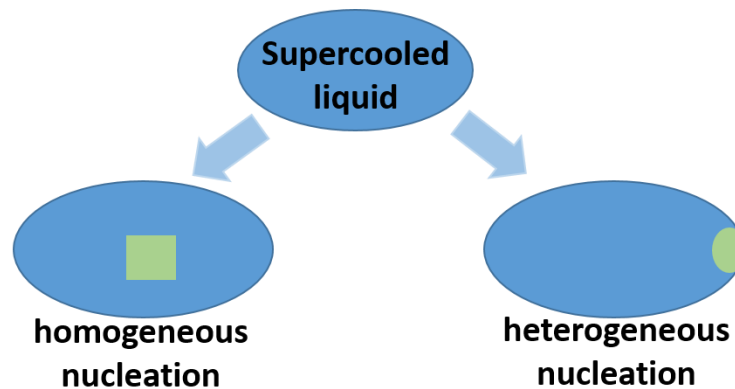


Figure 6. 2 Homogeneous nucleation and heterogeneous nucleation. Blue color represents liquid and green shape represents solid.

The second process of crystal formation is crystal growth. The nuclei start growing into visible size the moment they are stably formed. The final shape of the crystal is determined by the relative growth rates of each face. A crystal can be polyhedral ultimately even if it starts from a spherical seed, as several factors (e.g. impurities and solvents) are able to affect the growth rate on individual faces [271].

6.1.2 Supercritical fluids

A supercritical fluid (SCF) is defined as any substance at higher temperature and pressure than its critical point [272]. As for water, its critical pressure is 221 bar, and critical temperature is 374 °C [273]. Above this condition the discrete liquid and gas phase no longer exist, which means the two phases have the

same temperature, pressure and density. The phase diagram (Figure 6.3) clearly shows this phenomenon. Additionally, small changes in temperature or pressure near the critical point, creates large changes in density. Compared to ambient liquid water, supercritical and near-critical water have very different properties. Both of them are excellent solvents for non-polar molecules due to their low polarity and reduced density. What is more important is that supercritical water is advantageous over a lot chemical solvents because it is its non-toxic [274].

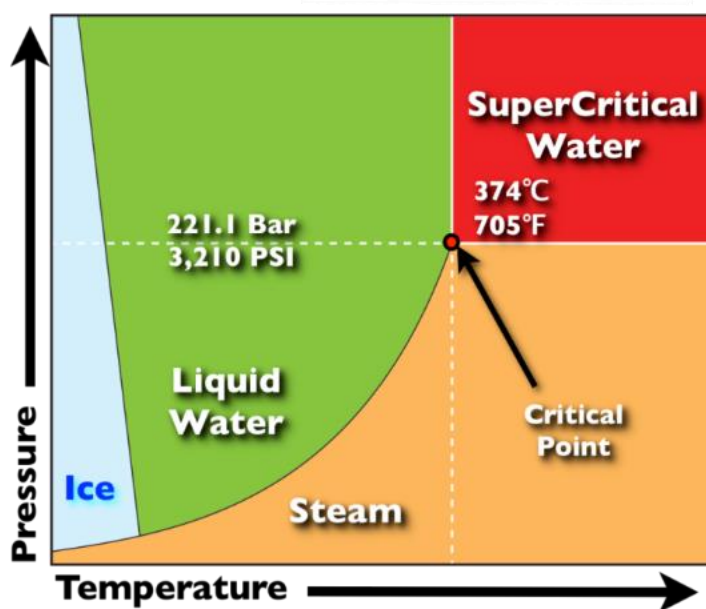
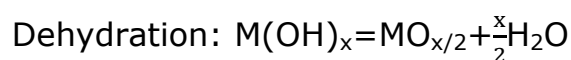
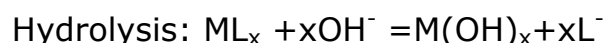


Figure 6. 3 Phase diagram for water [275]

It was first suggested by Adschiri et. al. [276] in 1992 that metal oxide nanoparticles can be generated by using supercritical

conditions in a continuous flow system. The concentrations of H^+ and OH^- increases due to the increased K_w of water. According to Adschiri et. al. [276] a dehydration process of metal salts occurs after the metal salts hydrolyze immediately. The two processes are as follows:



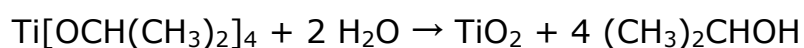
6.2. Aims and Objectives

Titanium dioxide (TiO_2), also known as titania, is widely used to decompose organic compounds [277], because it absorbs ultraviolet light (UV) at the wavelength less than 390 nm and creates active oxygen which comes from the oxidation of water and oxygen in air. Organic pollutants then can be decomposed by the active oxygen because of its strong oxidizing property [278]. Also, TiO_2 has other numerous applications in different areas including sunscreens, water purification and biomedical [279]. In addition, TiO_2 can be used for photocatalytic reduction of CO_2 to CO and CH_4 , while ZIF-8 is a widely used to adsorb CO_2 . Therefore, we considered to develop a new hybrid materials that combines ZIF-8 and TiO_2 , which can firstly adsorb CO_2 and then

in-situ convert CO₂ by TiO₂. In recent years hybrid composites have attracted much attention, as the product combining properties from two kinds of materials can be multifunctional and thus enhancing the applications.

6.3. Experimental Section

TiO₂ was made by the hydrolysis of Titanium isopropoxide (TTIP) in the flow reactor. The chemical reaction was as follows:



The continuous flow reactor is depicted in Figure 6.4. The titania precursor was prepared by dissolving 0.05 M TTIP in isopropanol (isopropyl alcohol, IPA) and then was introduced upstream with a controlled flow rate of 10 ml/min. Pure distilled water as the solvent was preheated to 400 °C and flowed 20 ml/min downwards to meet the TTIP solution. These two precursors mixed in counter currently reactor, followed by the cooling exchangers and a back pressure regulator. The whole system was operated under a high pressure (around 240 bar) condition. As it has been mentioned in the background section, the critical point of water is 374 °C and 221 bar. Therefore, the

titanium was synthesized in a supercritical condition, which has the advantages of narrow size distribution and small average particle size.

The product collected from the outlet of the reactor mixed with 10 vol.% nitric acid solution (HNO_3), to adjust the pH value to obtain the TiO_2 deposit. Afterwards, the suspension liquid was centrifuged at 400 rpm for 3 minutes in a centrifuge. Two layers can be clearly seen after centrifuging, a white precipitate layer of TiO_2 and a transparent upper layer. The wet sediment was dried in a vacuum oven overnight at 70°C . The TiO_2 purity in the product was examined by EDX technique, which showed TiO_2 accounted for 95 wt % of the sample.

6.3.1 TiO_2 effect on the hybrid samples

ZIF-8 was synthesized continuously and the product was proven comparable with the commercial zif-8 in terms of thermal stability, surface area, and CO_2 uptake stability. ZIF-8 synthesized without activation was noted as T0N in this report. Based on the same synthesis method of T0N, varieties of samples were made to explore any changes induced by TiO_2 . Figure 6.4 shows the construction change of the reactor and for different products.

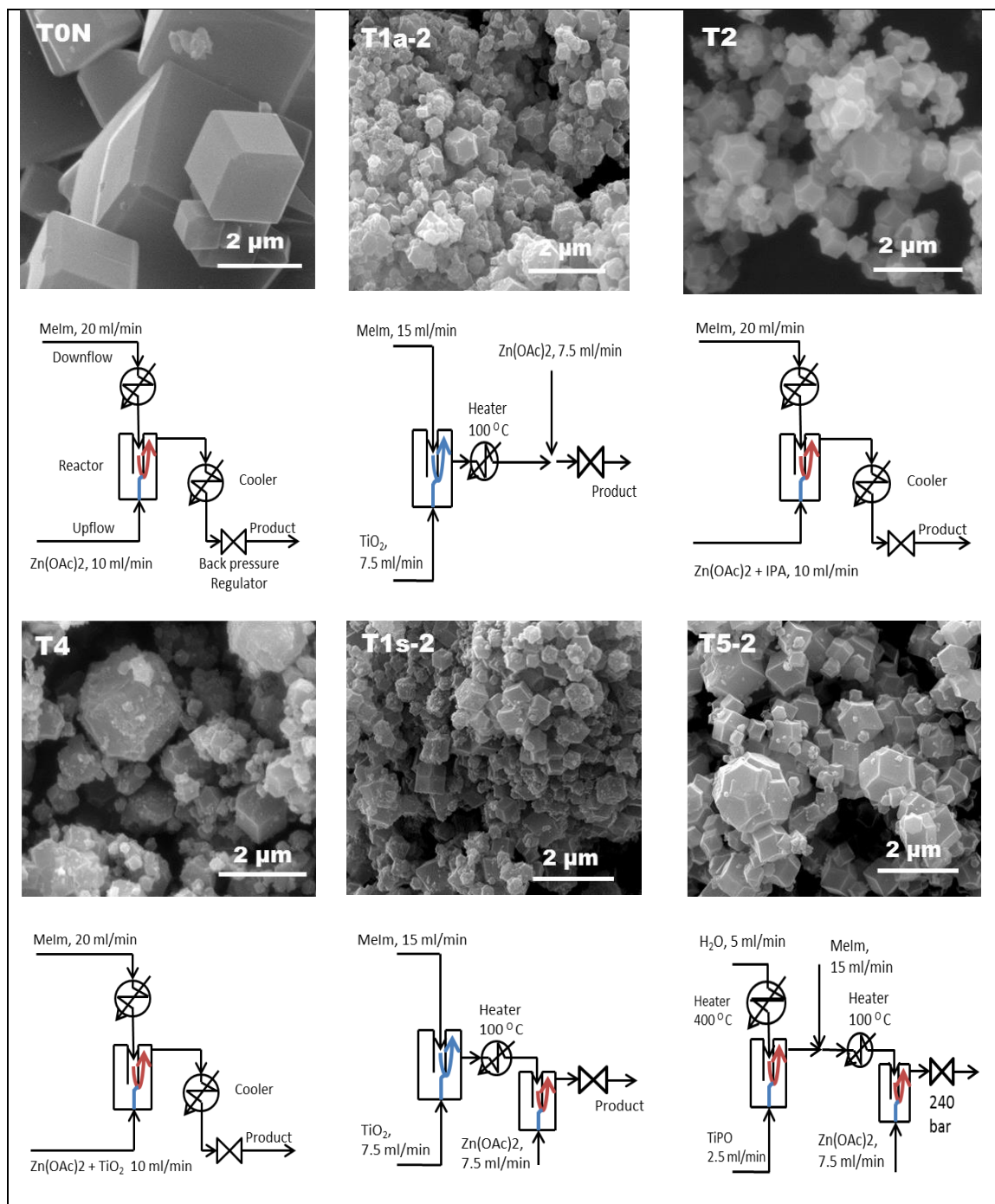


Figure 6. 4 Reactor constructions and morphologies for T0N, T1a-2, T2, T4, T1s and T5-2

The first hybrid sample made was marked as T1a-2. As the diagram shows, zinc acetate was introduced from a third flow into the system and met the previous flow in a T-mixer. The crystal shape of T1a-2 was truncated rhombic dodecahedron and the average particle size was much smaller than that of T0N. The change in morphology might be caused by TiO_2 addition or IPA addition (chemical impact) or the difference in residence time (RT).

Residence time can be calculated as $\text{RT} = \text{Amount of a substance in a reservoir (usually in mass or volume)} / \text{Rate of input or output of the substance from the reservoir}$. The flow rates were kept as 30 ml/min for both T0N and T1a-2, while the volume of T-piece is smaller than that of the reactor, so T1a-2 owned a shorter residence time than T0N. It was demonstrated by Munn et al. [280] that an increased residence time can cause the morphology to move towards a cubic shape (Figure 6.5). Additionally, it is stated in literature that a reduced residence time causes the average particle size to decrease [281].

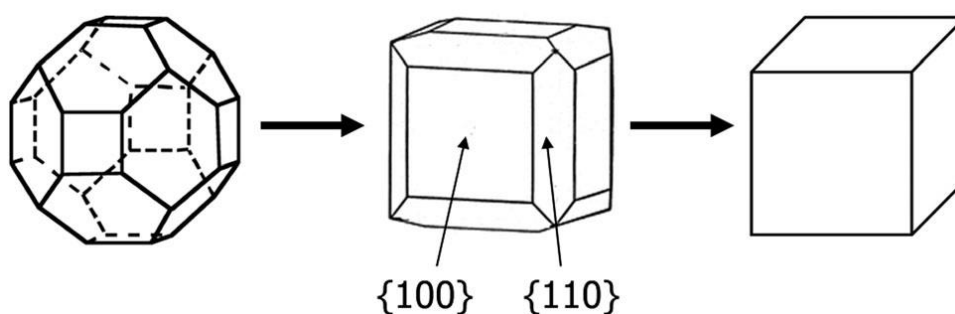


Figure 6. 5 Growth of truncated rhombic dodecahedron particles to form cubic particles [281].

However, the addition of IPA and TiO_2 could explain the morphology and size change. Zamaro et al. [282] demonstrate that the evolution of the reaction can be influenced by different solvents i.e. crystal growth rates can be altered by solvents which changes the crystal morphology. Further experiments were carried out to figure out the influence of chemical additions and the residence time change. T2 and T4 were synthesized via the same rig configuration as T0N to observe IPA and TiO_2 impact on morphology. The TiO_2 flow in T0N was pre-made by the hydrolysis of TTIP, the ratio of IPA to water in the suspension liquid was 1:2. Hence, the identical ratio was kept in the downflow stream of T2 and only IPA was added to that stream. While for T4, zinc acetate was dissolved in the pre-prepared TiO_2 . The design can be clearly seen from Figure 6.4. Another rig

configuration was designed for T1b to evaluate the impact of residence time, as presented in Figure 6.6.

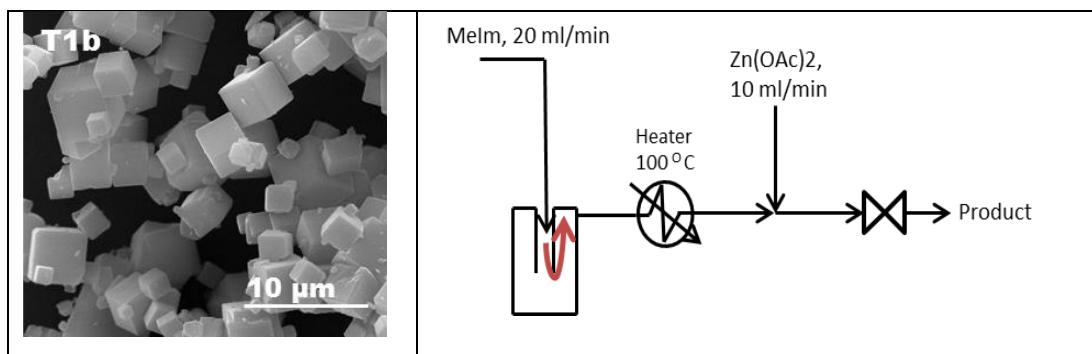


Figure 6. 6 T1b synthesized via a T-mixer

By comparing the SEM images of T0N and T2, it is possible to conclude that IPA facilitates the growth on the (110) face leading to a dodecahedron shape. The overall particle size of products from T2 was much smaller than T0N, probably because of the way that IPA solvent enhances nucleation rates. To make the comparison of size distribution between samples more clearly, ImageJ was used to facilitate observation (Figure 6.7). The processes to use ImageJ in particle analysis are as follows: 1) Draw the particles separately by hand using transparent paper; 2) click "image-Type-8 bit"; 3) set measurement scale and unit by clicking "analyze-set scale"; 4) click "process-binary-make binary" in the ImageJ software; 5) click "image-adjust-threshold"; 6) click "analyze-analyze particles"; 6) the software will show the

size (area) for all identified particles and from an size analysis table; 7) in order to ensure the data reliability, the number of particles will be remained above 80.

Figure 6.7 shows that T4 has a broader size distribution than T2. Although a majority of the particles appeared to be between 0.1 and 0.5 μm^2 , a small amount of particles exist with size above 0.6 μm^2 .

The size distribution of T0N and T1b does not show much difference (Figure 6.7), which means the T-piece mixer almost has no effect on the size and shape of the product. It is therefore possible to conclude: a) IPA modifies the crystallization rate and thus the crystal size and shape; b) The addition of TiO_2 enhances the size distribution of the product.

However, TiO_2 is also present in the T1a-2 sample, although the size distribution is not as broad as T4. The reason for the appearance of few particles with bigger size particles in T4 might be due to the TiO_2 (pre-mixed in zinc acetate) decreasing the nucleation rate, thus enhancing the size distribution and generating bigger size particles than T1a-2. More work is needed to prove this mechanism.

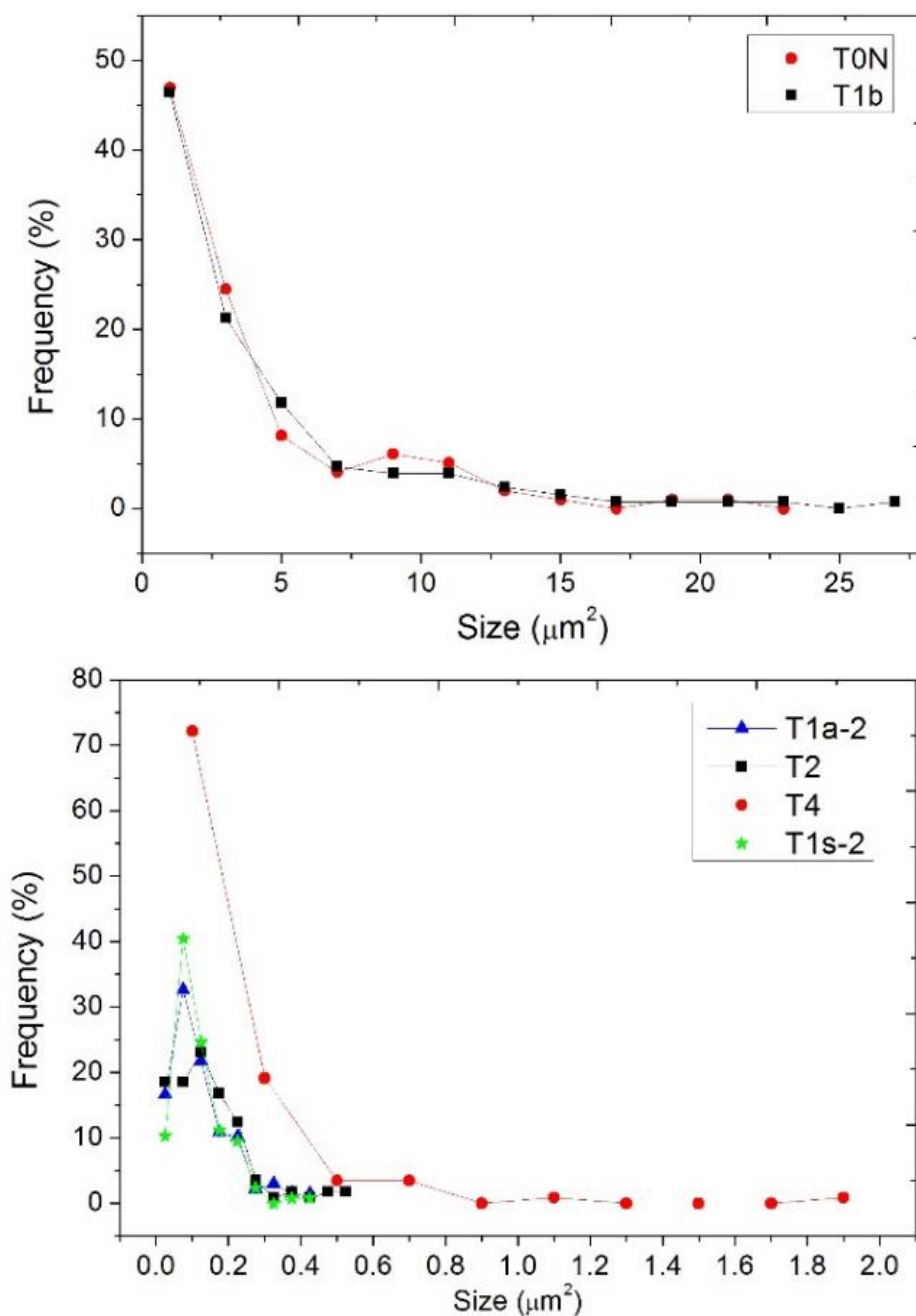


Figure 6. 7 ImageJ size distribution analysis for T0N, T1b, T1a-2, T2, T4 and T1s-2.

The XRD pattern shows all samples maintaining a uniform ZIF-8 structure. There is a small peak for T1a-2 and T4 (marked as

red circle in Figure 6.8), which is probably evidence of TiO_2 incorporation but in small quantities. However, the integrated XRD patterns illustrate that TiO_2 did not damage the MOF framework, which is important.

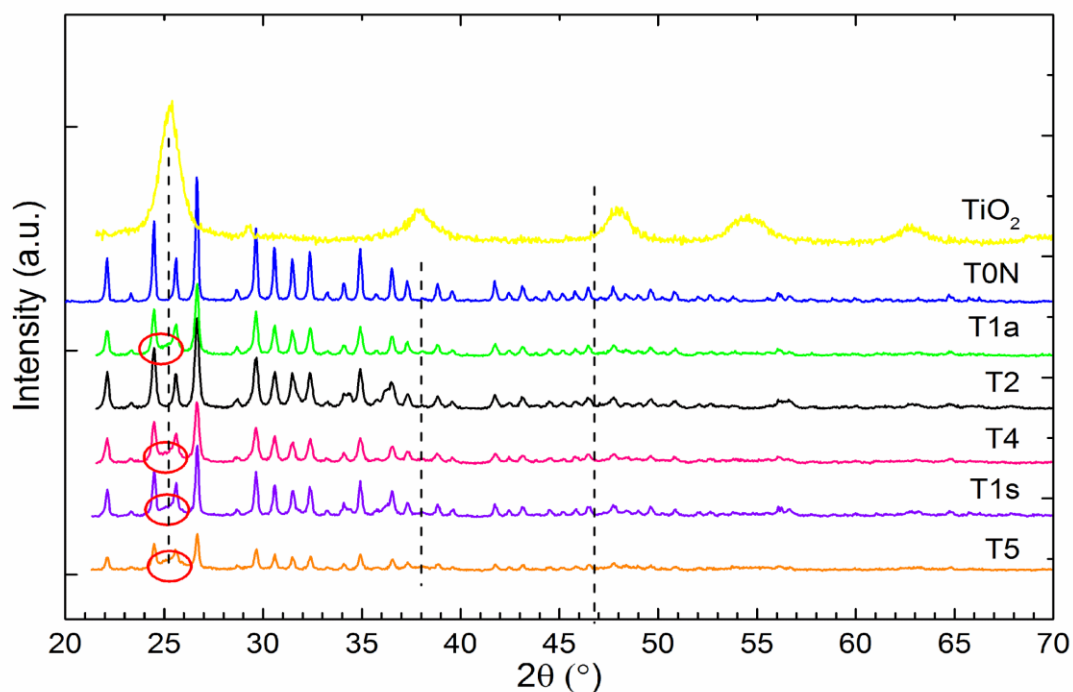


Figure 6. 8 XRD patterns for TiO_2 , T0N, T1a, T2, T4, T1s and T5.

In order to get more information about the sample composition TGA tests were carried out. It can be obviously seen from Figure 6.9 that only T0N underwent a weight loss in the range of $100\sim 180^\circ\text{C}$. This corresponds to the contaminant molecule removal, which will be analyzed in details later in this section.

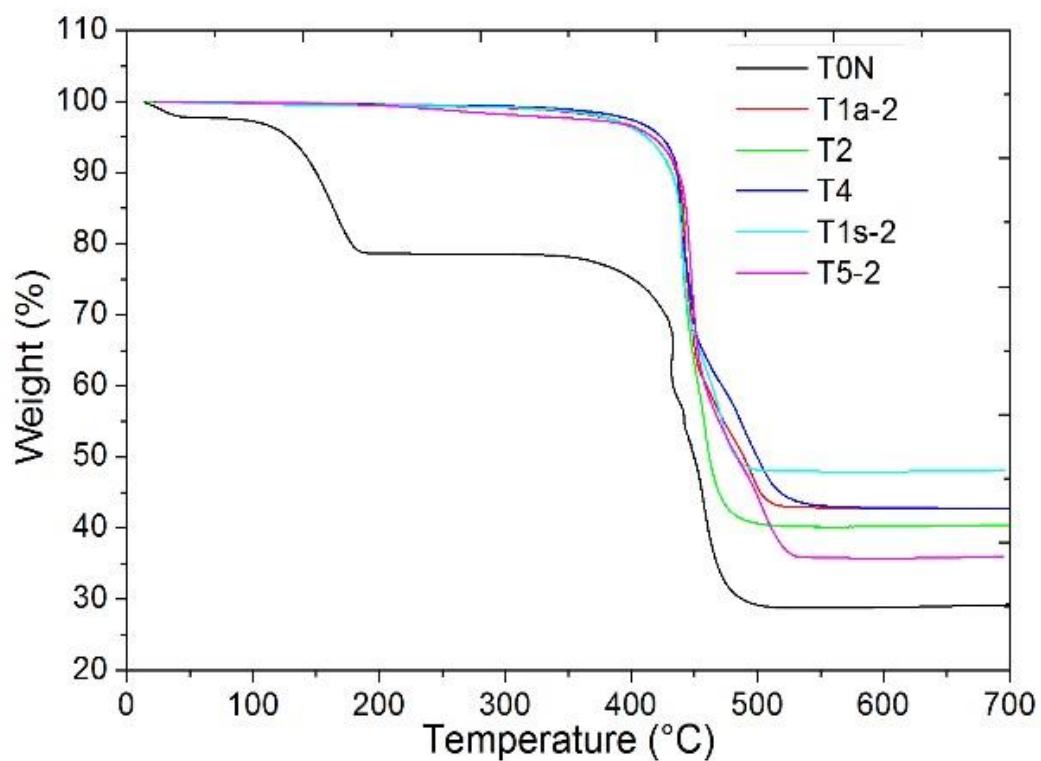


Figure 6. 9 TGA curves for T0N, T1a-2, T2, T4, T1s-2, T5-2.

Subsequent UV-visible tests are given in Figure 6.10. UV-visible spectrogram shows obvious absorbance in the wavelength band between 250 to 350 nm for T1a-2, T4 and the TiO_2 pre-made by TTIP. This wavelength range also fits with TiO_2 adsorption spectrogram from another literature [283].

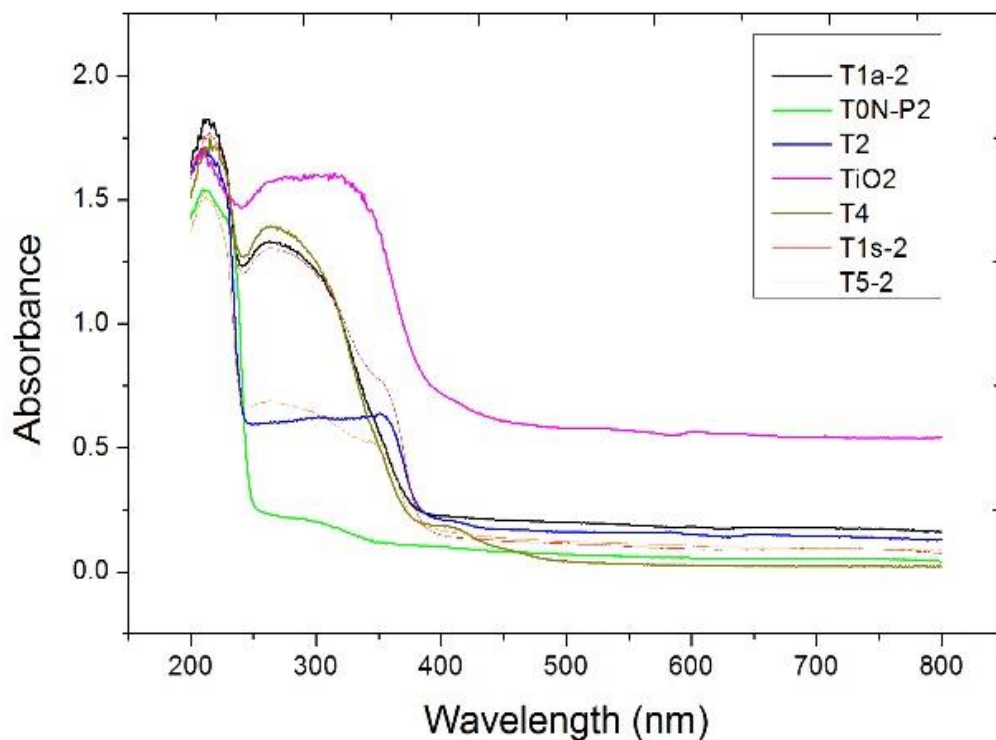


Figure 6. 10 UV-Vis curves for T1a-2, T0N-P2, T2, TiO₂, T4, T1s-2, T5-2.

As the background states, data obtained from powder UV-visible measurement is unable to be quantitatively analyzed. With the purpose of acquiring quantitative data energy-dispersive x-ray spectroscopy (EDX) test was performed. The results are displayed in Table 6.1. The tiny amount of TiO₂ appeared in T0N should be the residues from the reactor which can be ignored. Both T1a-2 and T4 have around 30 wt% TiO₂ which means TiO₂ was heavily inserted into the ZIF-8. It is worth noting that BET surface area (Figure 6.11) decreases as the increase of titania

concentration but not dramatically. This demonstrates ZIF-8 was coated on TiO₂ but did not create a closed shell.

Table 6. 1 BET and EDX results for TiO₂, T0N, T1a-2, T2, T4, T1s-2 and T5-2.

Sample Name	TiO ₂	T0N	T1a-2	T2	T4	T1s-2	T5-2
BET surface area (m ² /g)	174	673	1548	1605	1552	1440	1569
TiO ₂ % from EDX test (wt%)	95	0.25	32.60	/	29.08	34.45	5.04

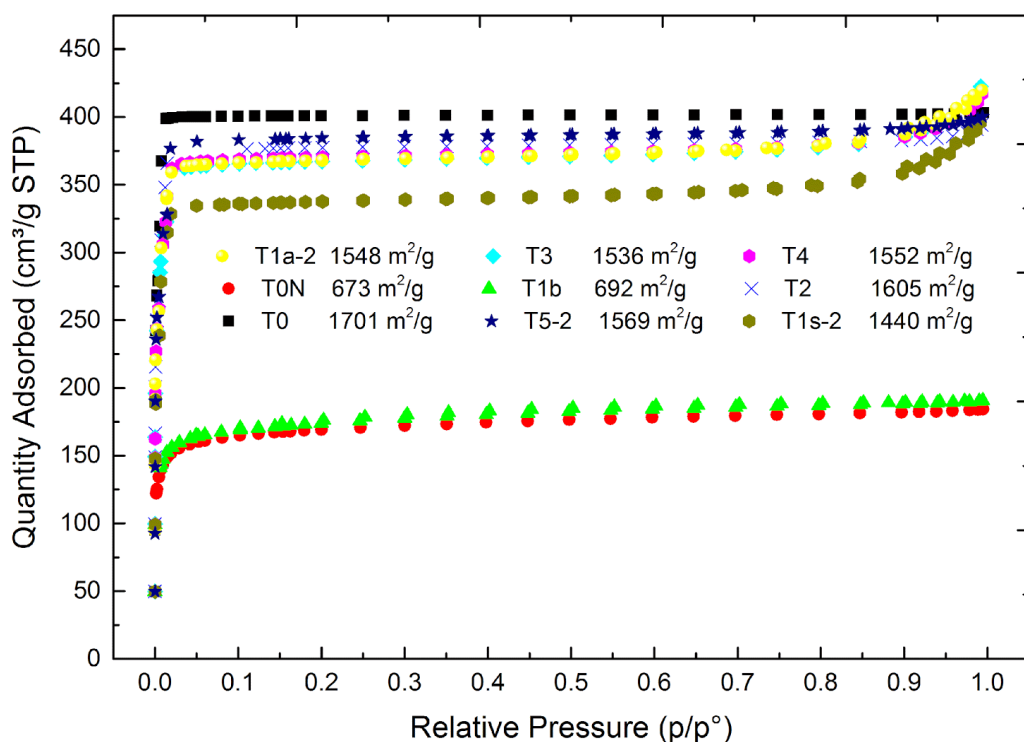


Figure 6. 11 BET surface area data for different samples.

T1s-2 and T5-2 were made in order to create further comparisons. For T1s-2, zinc acetate was introduced into a second reactor rather than a T-piece mixer. This is the only difference from the T1a-2 synthesis process. The comparison made between these two samples indicates no significant differences as caused by the different mixers. T5-2 was made by fresh TiO_2 rather than a pre-made suspension. In the synthesis of T5-2 the pressure for the whole system was 240 bar due to the synthesis condition requirement for TiO_2 . As a result, this variable was considered when making comparisons between different particles.

According to Table 6.1 the TiO_2 content dramatically decreased in T5-2 sample, which has an agreement with the UV-Vis result. In order to keep flowrate and chemical concentration constant, the flow rate of water and TTIP (also noted as TiPO in the figure) was to be fixed as low as possible. The low flow rate gave an increase in the residence time in the primary reactor resulting in titania forming with a bigger average particle size. Titania particles with bigger sizes leads to the low titania concentrations in terms of number of particles per cm^3 .

6.3.2 Reactor and T-piece comparison---T0, T0N, T1b

In the previous chapters two typical MOFs (ZIF-8 and HKUST-1) were made using the reactor designed by our group. In this section the effect of both T-piece and reactor on the synthesis of ZIF-8 was investigated. As seen in Figure 6.12, T0 and T0N were synthesized in a reactor and T1b was synthesized via a T-piece. The T0 product was post activated by ethanol to remove contaminant molecules trapped in the pores while T0N was not. T1b was synthesized via a T-piece.

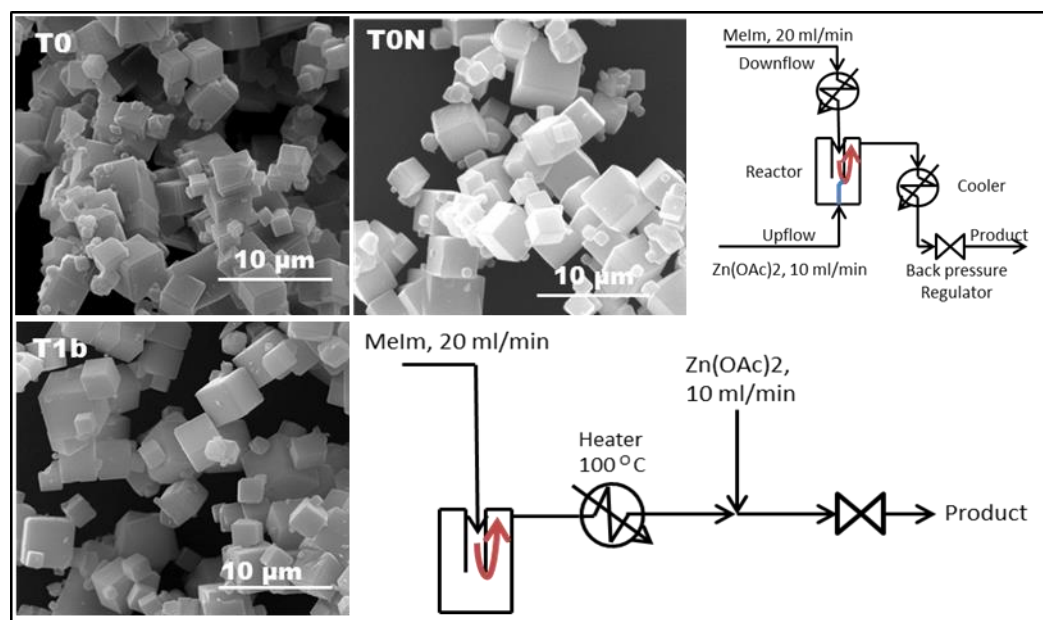


Figure 6. 12 Reactor constructions and morphologies for T0, T0N and T1b.

It is hard to quantify the size distribution directly from SEM images, so ImageJ software was used and the results are shown in Figure 6.13. There is little difference from SEM images and ImageJ size analysis, which indicates that the T-mixer has the same impact on the morphology of the products. XRD patterns show the structures retained their integrities in all samples (Figure 6.13).

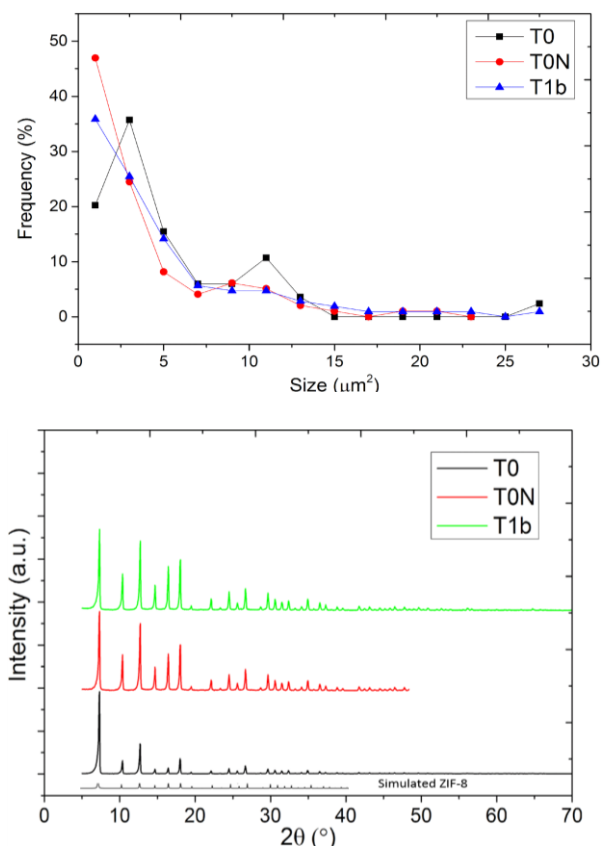


Figure 6. 13 ImageJ and XRD patterns for T0, T0N and T1b.

More information can be obtained from thermal analysis and BET surface area measurements. It can be observed from Figure

6.14 that there was no weight loss step for contaminant removal for T0 because it was already activated by ethanol. The total decomposition process underwent a weight loss of 65.1%, which was in a good agreement with the calculated data 64.2 % (Activated ZIF-8 ($\text{C}_8\text{H}_{10}\text{N}_4\text{Zn}$, MW=227.58 g/mol) decomposed to ZnO (MW=81.39 g/mol)).

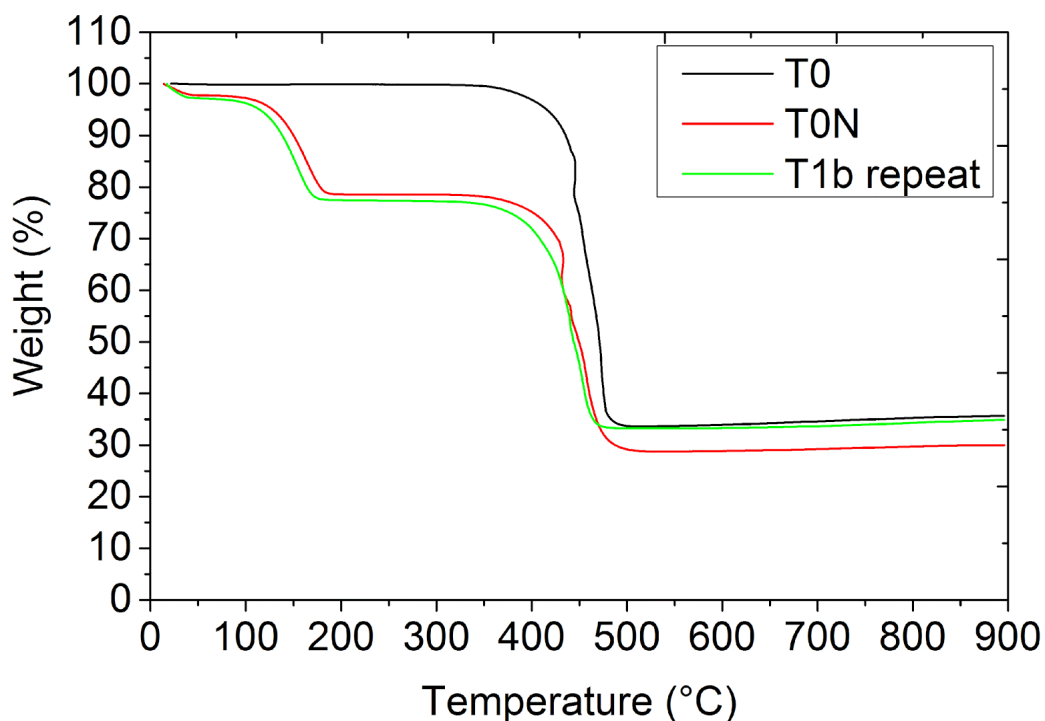


Figure 6. 14 TGA curves for T0, T0N and T1b

The contaminant molecules composition of ZIF-8 without activation (T0N) can be calculated from the weight change: $(2.56-2.04)/2.56=20.3\%$. This fits well with the first weight loss

step in TGA of both T0N and T1b (22.5%), which therefore indicates that the 1st weight loss corresponds to all guest molecules removal (H₂O and NH₃ solvent molecules trapped in the pores). The 2nd weight loss stage was related to the decomposition of the framework. The final weight losses of samples T0N and T1b differed by 6%, but as these two samples have the same guest molecules composition and similar BET surface area (Table 6.2), the 6% variation could probably be caused by the different impurities contents.

Table 6. 2 Yield and conversion comparison

ID	Production rate (g/h)	Zn ²⁺ flow rate (mol/h)	Calc. stoi. product (g/h)	Conversion (%)	S _{BET} (m ² /g)
T0	2.04	0.036	8.19	24.9%	1701
T0N	2.56	0.036	8.19	31.3%	673
T1b	2.64	0.036	8.19	32.2%	692

Table 6.2 summarizes the values of yields and BET surface areas for these three samples. According to this table, samples without post activation (T0N and T1-b) seem possessing higher yields than sample T0, this is due to the impurities removal in the

activation process, which is agreement with the results of BET surface area.

It can be concluded that the type of reactor has no impact in this case. Ethanol activation can boost the surface area by 60%.

6.3.3 Pressure Effect---T0N, T0N-P, T2, T2-P

As mentioned before, T5-2 was synthesized under pressure of 240 bar, to make the samples to be comparable the pressure impact on the products must be investigated. T0N and T2 were selected to be synthesized again under such high pressure and the new product were noted as T0N-P2 and T2-P, respectively. Figure 6.15 illustrates the rig configurations and SEM images for these four samples. The SEM images show no obvious difference. Further shape size analysis by ImageJ would be done afterwards. XRD patterns (Figure 6.16) show the MOF structure was not damaged, and the morphology observed from SEM images and ImageJ appeared to show no significant difference.

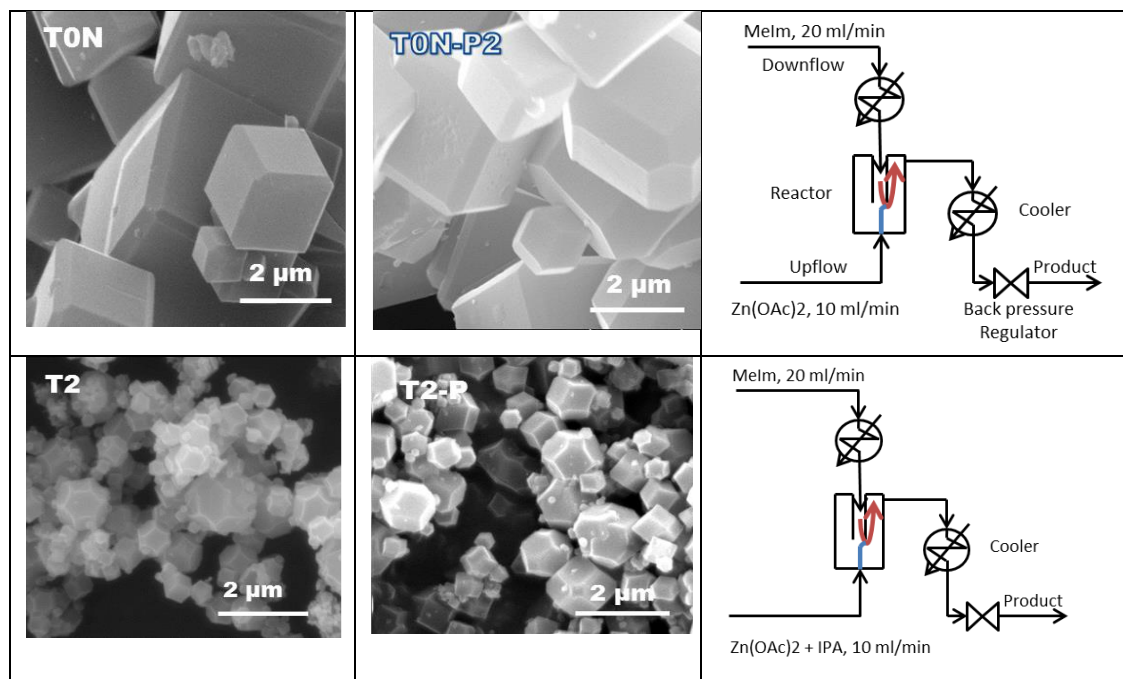


Figure 6. 15 Reactor constructions and morphologies for T0N, T0N-P2, T2 and T2-P.

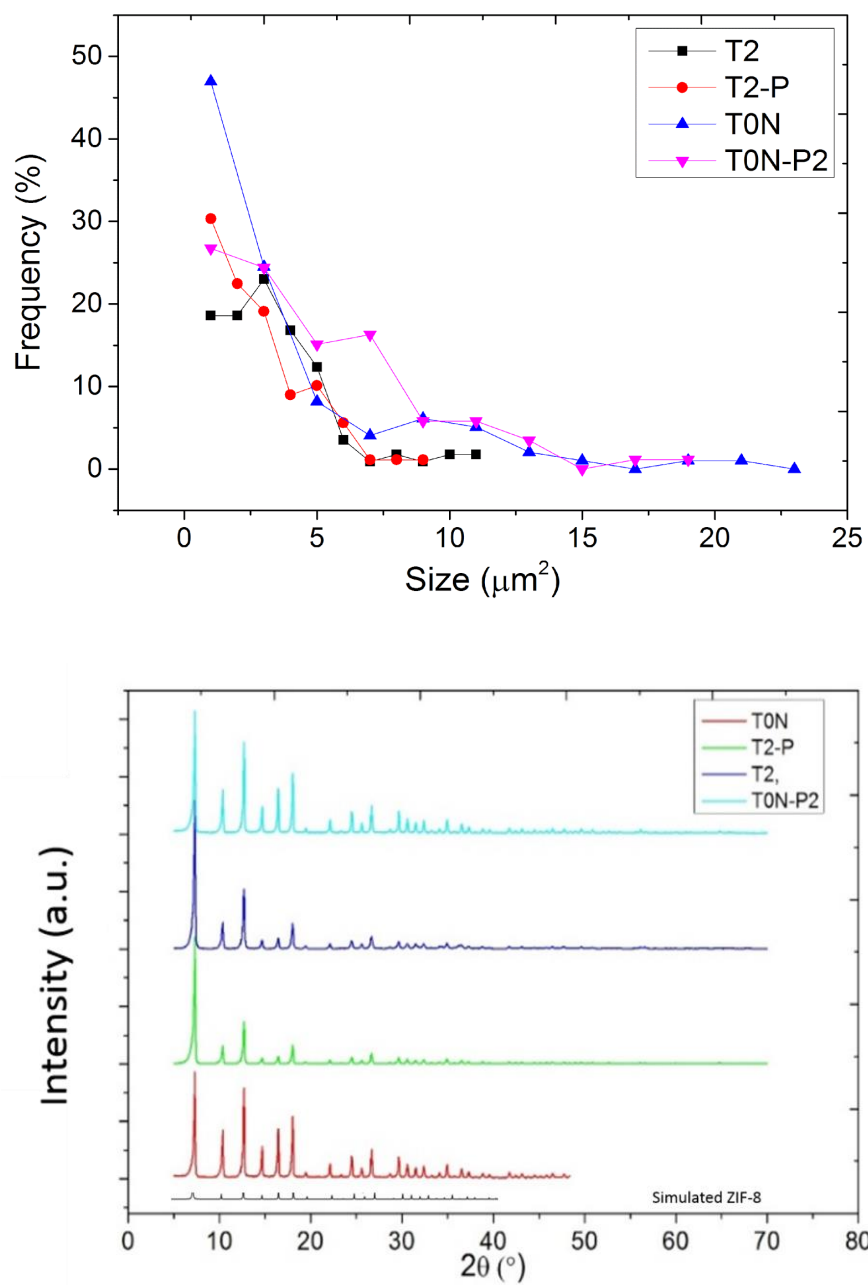


Figure 6. 16 Figure 6.16 ImageJ size distribution analysis and XRD patterns for T0N, T2-P, T2 and T0N-P2.

The surface area with products generated using high pressure were higher than those synthesized at ambient pressure. The

relative intensity values at $2\theta = 7.31^\circ$ and 10.24° observed from XRD pattern, and the increase of the surface area can be probably explained by the change of faces (011) and (002) growth [284]. In addition, the TGA curves of T0N-P in Figure 6.17 shows a significant variety from T0N. The disappearance of 1st weight loss stage indicates guest molecules were pressurized out by the high pressure. Thus, this should probably be another key reason causing the surface area of T0N-P2 increased more than two times than T0N.

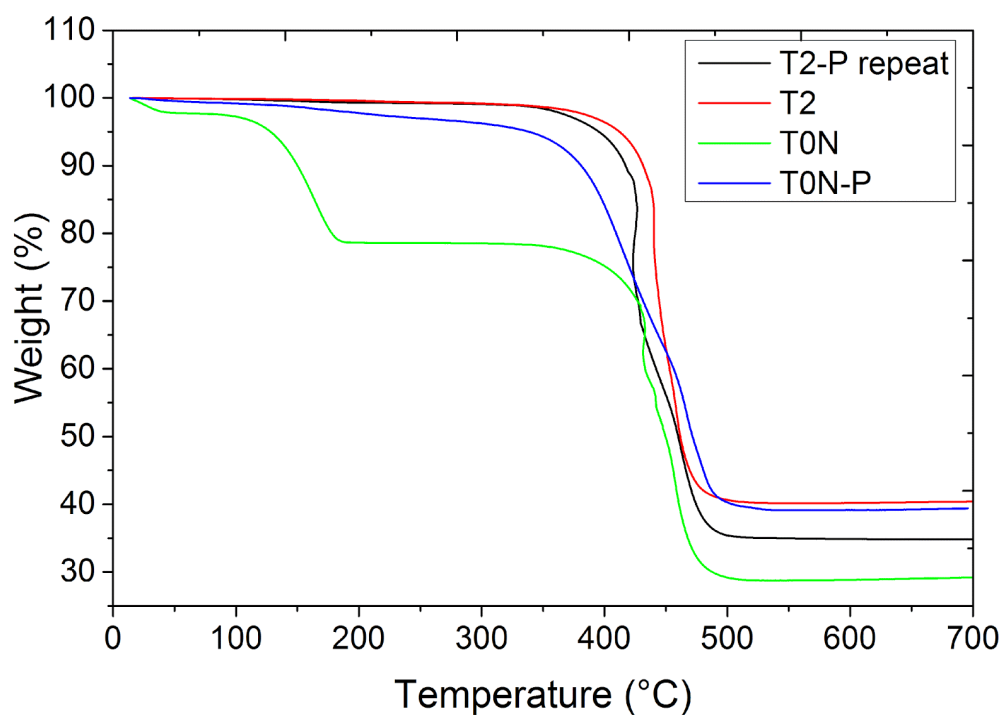


Figure 6. 17 TGA curves for samples synthesized under a high pressure.

Figure 6.18 is the nitrogen isotherm curves for the samples synthesized under high pressure and ambient pressure. There are T0N-P, T0N-P1 and T0N-P2 appeared in this figure. This is because sample T0N-P was made by three times, since the BET result of the first product (T0N-P) indicates the structure was damaged but which was of little possible. In the process of synthesis some black coloured powders were observed in T0N-P after drying process, which might be sulfide residue left in the reactor from another user. The unusual low surface area of T0N-P can be probably caused by the destruction of the MOF structure resulting from sulfides pollutants. Therefore, T0N-P was made again and noted as T0N-P1, the result was within the expectation. In order to confirm T0N-P1 was the correct product other than T0N-P, a third synthesis was made and the product was named as T0N-P2. T0N-P2 has a good agreement with T0N-P1, which means the result of T0N-P was not reliable and should be ignored.

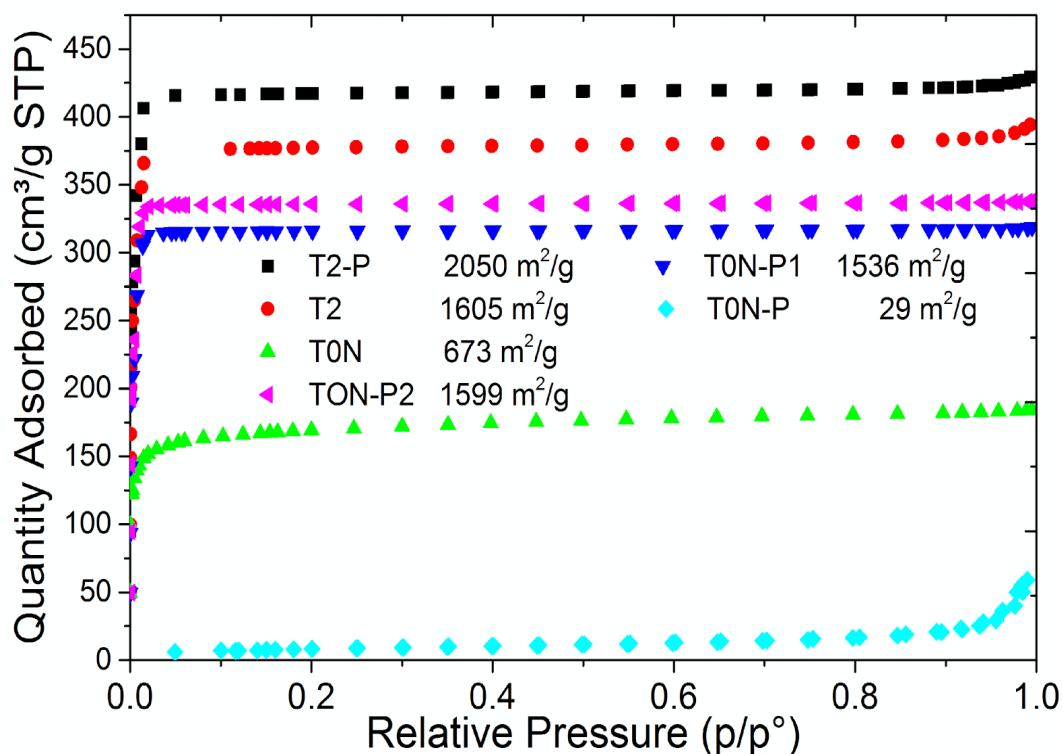


Figure 6. 18 nitrogen isotherm curves for the samples (T0N, T0N-P, T2, T2-P and T2) synthesized under high pressure and ambient pressure.

Table 6.3 gives yield and conversion calculation data. It can be seen that both sample T0N-P2 and sample T2-P show a notable increase compared to sample T0N and T2-P with regards to the conversion value. Therefore, it is clear that high pressure synthesis can lead to the enhancement of the conversion for the products.

Table 6. 3 Comparisons for the yield and conversion of T0N, T0N-P2, T2 and T2-P.

Sample No.	Production rate (g/h)	Zn ²⁺ flow rate (mol/h)	Calc. stoichiometry product (g/h)	Conversion (%)
TON	2.56	0.036	8.19	31.3%
TON-P2	3.69	0.036	8.19	45.1%
T2	1.25	0.036	8.19	15.3%
T2-P	1.75	0.036	8.19	21.4%

6.3.4 Conclusions

In summary, different hybrid nanoparticles TiO₂@ZIF-8 were synthesized and compared in this work. Owing to the addition of IPA (must exist in TiO₂ suspension), the crystallization rate was modified which impacts on particle size and shape. Around 30 wt.% of TiO₂ can be achieved in the hybrid product, and the surface area did not decrease significantly with the incorporation of TiO₂ which is key to ensuring successful use in future applications.

To make the synthesis process more feasible and effective, fresh TiO₂ incorporation experiments were carried out. However, due to the low flow rates in the system, blockage might occur, and this impacts on the final concentration of available TiO₂ in the hybrid product. Further experiments are needed to conduct

to improve the fresh TiO_2 incorporation because half of the synthesis time can be saved in this way rather than using premade TiO_2 .

Chapter 7 Conclusions and Future Work

7.1 Conclusions

The main work in this thesis focused on the synthesis of two MOFs: HKUST-1 and ZIF-8. Both batch and continuous synthesis were studied, and afterwards the characterizations of our produced samples were conducted by a series of techniques. The continuous rig applied here follows on from that was invented by the Lester group from University of Nottingham. MOFs, emerged as the new materials with their significantly high surface area, are widely studied in the region of gas adsorption in the past researches. In this thesis, CO₂ adsorptions of HKUST-1 and ZIF-8 products were investigated.

In Chapter 1, the current situation of how the greenhouse gases adversely influences the global climate was stated. According to The Intergovernmental Panel on Climate Change (IPCC), Carbon dioxide took up the most part in the global greenhouse gas emissions.

MOFs are also studied as the potential materials in the carbon capture application. In this chapter, several synthesis methods developed by researchers were reviewed. It is found that batch solvo/hydrothermal synthesis methods were generally employed as the conventional technology, but by this method it requires a long reaction time sometimes up to several days and is hard to control crystal growth; a range of crystal sizes are often formed by batch synthesis. The key strategy to overcome these drawbacks is to reduce the reaction time. A number of novel synthesis approaches have been reported, such as microwaves, ultrasound and mechanochemical.

However, the production of MOFs cannot be easily scaled-up by using batch processing due to the equipment limitations. Therefore, novel methods by employing continuous synthesis progress were developed in the recent publications.

In this thesis, both batch and continuous synthesis were studied. The rigs used in these two synthesis processes were shown in Figure 1.10 and Figure 1.14, respectively in Chapter 1. The main experimental instruments involved in the batch synthesis include heating jacket, reflux condenser, centrifuge and

oven. Also, the invention history for the continuous rig used in this thesis was stated in Chapter 1. The reactor was once in a T-piece designed for the supercritical water hydrothermal synthesis, but which will cause the poor product reproducibility when the supercritical solvent present in the stream due to particle accumulation and blockage in the reactor and the inlets. Consequently, frequent cleanings have to be conducted even between runs. Moreover, emergent shutdown had to be executed to avoid safety issues. To investigate further for the inner mechanism of the reactor, two modelling techniques (LAI and CFD) were conducted in the previous efforts. According to the modelling result, it is found that the driving force for the turbulent flow mixing came from the buoyancy forces, rather than the inertial forces from the process pumps. Therefore, a strong convection would occur during the mixing of two precursor streams, leading to a poor efficiency in supercritical water hydrothermal synthesis.

Subsequently, a new reactor patented as Nozzle Reactor was designed by Lester group, by using which reactor the blocking problem in the synthesis process can be avoided. In order to test the product producibility, CeO_2 was chosen to be synthesized by

five times with 9 hours per run. Only minimal particle accumulation was observed and no blockages occurred during all the runs. According to the data of temperature and pressure recorded by the software, as well as the surface area of these five CeO₂ samples, the conclusion can be drawn that this new design of Nozzle Reactor can manufacture product with a high reproducibility.

A pilot scale of this rig has been built in Nottingham, which belongs to Promethean Particles Ltd. The maximum fluid flowrate can achieve as high as 400 ml/min.

In chapter 2 the experimental instruments involved in this thesis to characterize samples or test the properties of products were introduced. These techniques include Powder X-ray diffraction (XRD), scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX/EDS), Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet-Visible Spectroscopy (UV-Visible).

The main experiments carried out in this thesis starts to be written in Chapter 3. A novel batch method to synthesize HKUST-

1 under a mild condition (50 °C, atmospheric pressure) was developed. The equipment used has been described in Chapter 1. Compared to those reported in the previous reports, this synthesis method possesses the advantages as follows: (i) the process was conducted safely under ambient pressure and mild temperature; (ii) both of the BET surface area (1610 m²/g) and CO₂ adsorption ability (8.08% at 1 atm and 27 °C) were higher than those reported in much of the other methods. The novel point in this synthesis approach is in the activation process. This is the first time to activate HKUST-1 in the powder state to our knowledge. This procedure can make the impurities removed more efficiently.

Subsequently, the post-immersion experiments were carried out for the purpose to further increase the surface area of our product. The batch synthesized HKUST-1 was immersed in a solvent which was mixed by sodium chloride, methanol and water for overnight, and then washed by methanol again. The surface area has an obvious increasement from 1615 to 1910 m²/g, and the CO₂ adsorption amount under 1atm and 27 °C also rose from 8.08% to 9.33%.

For the purpose to shape the product in a macro body, experiments were conducted in Chapter 3 to press HKUST-1 samples into pellets. Under the proper applied pressure, the structure will not be destroyed and the surface area decreases only in a reasonable range.

A second synthesis method of HKUST-1 was reported in Chapter 4. Nano scaled HKUST-1 can be obtained by adding one base triethylamine in the organic precursor. This chemical plays a role in deprotonating the organic ligand, and thus accelerates the reaction rate and then rapidly decreases the particle size. The average particle size is around 65nm, much smaller than the product obtained in Chapter 3. Meanwhile, the BET surface area and CO₂ adsorption capacity keeps comparative with those nano particles reported in the other literatures.

After screening the optimal batch synthesis method, continuous synthesis process was investigated in Chapter 5. Two MOFs HKUST-1 and ZIF-8 were successfully produced by the counter-current mixing reactor mentioned in Chapter 1, and comparisons with the commercial products manufactured by BASF. The thermal stability tests reveal that our ZIF-8 possess a higher

thermal resistance than the commercial one. Although the thermal stability of Nott.HKUST-1 is lower than commercial one the cost is rather low to synthesize HKSUT-1 in this method. It is found that the framework of HKUST-1 is easy to be destroyed in the humid environment. However, water stability is of significant importance in the removal of CO₂ in flue gas. In Chapter 5, a method for the post modification of HKUST-1 was developed. Dodecenylsuccinic anhydride (DDSA) was incorporated into the pristine HKSUT-1 and improve the hydrophobicity to some extent.

The method to continuously synthesize ZIF-8 was further modified to produce hybrid materials. In Chapter 6, TiO₂@ZIF-8 was synthesized, Around 30 wt% of nanoparticle TiO₂ can be obtained in the hybrid products, and the surface area did not decrease a lot with the incorporation of TiO₂, which will be potential for the future application.

7.2 Future Work

Although a lot of experiments have been carried out about the synthesis and post modifications of MOFs in this 4-years project, there are still further work needed to be done.

Following on from the work on pellets press in Chapter 3, further mechanical stability assessment can be made for the pellets. Also, different binders (e.g. kaoline, cellulose, polyvinyl alcohol) can be tried to add in the process of making pellets to enhance the mechanical strength of samples. After obtaining the pellets with optimal mechanical strength and surface area, the pellets can be packed in a tube to undergo the CO₂ breakthrough test, which can mimic the carbon capture process in the real application.

In Chapter 5, the modified HKUST-1 sample with DDSA additive has a higher hydrophobicity compared with our untreated HKUST-1 and the commercialized HKUST-1. However, the structure of DDSA modified HKUST-1 still collapsed after exposure in a 2% water vapor environment at 90 °C for 5 hours. This is obviously cannot meet the requirements for the industrial carbon capture application. Therefore, further efforts are needed to be made to significantly improve the water stability of HKUST-1, with the precondition that not highly adversely influence the carbon capture ability. The other hydrophobic chemicals can be tried to add in the post-synthesis process, such as

perfluorodecanoic acid, 2-methoxybenzoic acid and 2-(Trifluoromethoxy) benzoic acid.

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