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Optimized synthesis of nano-scale high quality HKUST-1 under mild conditions and its application in CO$_2$ capture

Xueliang Mu$^{1,2}$, Yipei Chen$^{1,3}$, Edward Lester$^3$, Tao Wu$^{1,2,*}$

$^1$New Materials Institute, The University of Nottingham Ningbo China, Ningbo 315100, P. R. China
$^2$Municipal Key Laboratory of Clean Energy Conversion Technologies, The University of Nottingham Ningbo China, Ningbo 315100, P. R. China
$^3$Department of Chemical and Environmental Engineering, The University of Nottingham, Nottingham NG7 2RD, P. R. China

* Corresponding author: Tao.Wu@nottingham.edu.cn

Highlights

- A fast and efficient method was developed for the synthesis of HKUST-1
- Synthesis was conducted under low temperature and atmospheric pressure
- The MOFs was synthesized in nano-scale with high BET surface area and high yield
- Activation agent has shown significant influence on BET surface area of the MOFs
- The HKUST-1 prepared shows excellent CO$_2$ uptake capacity
Abstract
This study was focused on the development of an optimized method for the rapid synthesis of nano-scale HKUST-1 with high yield, high surface area and high CO\textsubscript{2} uptake capacity but under mild conditions. A series of HKUST-1 were synthesized under different conditions, such as preparation time, temperature, activation method, etc. It was found that the nano-scale HKUST-1 MOFs (T85-3-Pm4-120) was successfully synthesized at a high yield (87%) under low temperature (85\degree C) using a mixture of Triethylamine(TEA), Cu\textsuperscript{2+} and trimesic acid (TMA) with a molar ratio of 6:3:2. The highest porosity was achieved via this pristine HKUST-1 being activated (powder activation, drying at 120 \degree C) four times using methanol to remove impurities trapped in the pores. The best HKUST-1 MOFs (T85-3-Pm4-120) hereby prepared was then tested in CO\textsubscript{2} adsorption and exhibited an adsorption capacity of 2.5 mmol/g. It is therefore demonstrated that the new approach proposed in this study is a rapid and effective way to synthesize highly porous HKUST-1 MOFs under mild conditions, which is of comparable surface area and CO\textsubscript{2} uptake capacity with those MOFs prepared under harsh conditions.

Keywords: HKUST-1, nano scale, fast synthesis, mild synthesis condition, CO\textsubscript{2} adsorption

1. Introduction
Metal–organic frameworks (MOFs) are hybrid crystalline compounds consisting of organic ligands bridging inorganic moieties. MOFs exhibit unique structure and outstanding properties in porosity, pore size and surface area and have been used in various fields such as gas storage, adsorption, separation, and catalysis\textsuperscript{1}. Recently, more and more effort has been made to explore the application of nano-scale MOFs in areas, such as liquid phase catalysis\textsuperscript{2,3}, adsorption\textsuperscript{4} and drug delivery\textsuperscript{5}, etc.
HKUST-1, a copper-based MOF, is one of the first reported MOFs whose structure is based on Cu$^{2+}$ ions linked with 1,3,5-benzenetricarboxylate struts. The conventional solvothermal method for the preparation of HKUST-1 involves heating the solution up to 180 °C to form crystalline Cu$_3$(BTC)$_2$. The Cu$_3$(BTC)$_2$, synthesized at 75–120 °C, has to be kept in an autoclave for a long period, varying from 1 day up to a few weeks, to remove impurities that are trapped in the pores.

Although slow diffusion techniques require significantly long time for the synthesis of MOFs, it is still the preferred method for the synthesis of MOFs due to its tunable reaction conditions, such as, the control of the rate of nucleation and crystal growth by the control of concentration gradient (temperature gradient). Normally, the synthesis of MOFs with good thermal stability has to be conducted under hydro/solvothermal conditions. To date, commonly adopted methods for the rapid preparation of HKUST-1 include microwave heating, ultrasound irradiation, mechanochemistry, and solvothermal synthesis, which are summarized in Table 1. Normally, conventional solvothermal and electrochemical methods require long time to synthesize HKUST-1 with high surface area. Although mechanochemical, microwave heating and ultrasound irradiation methods can be used to produce HKUST in much shorter time, the surface area of the MOFs prepared via these methods is in micron scale and cannot meet some special requirements in catalysis when nano particles are preferred to enable higher mass transfer rate or to achieve higher thermal resistance. Because of this, there has been numerous work being carried out on the synthesis of nanoscale MOFs. However, there is still a need to develop cost-effective techniques for the preparation of nanoscale HKUST-1 MOFs under mild conditions, which are able to produce MOFs with high surface area (>1500 m$^2$/g).
Table 1 MOFs prepared under Different Methods

| Method            | Microwave heating\(^\text{19}\) | Ultrasound irradiation\(^\text{19}\) | Mechano-chemical\(^\text{20}\) | Conventional solvothermal\(^\text{21}\) | Electro-chemical\(^\text{22}\) |
|-------------------|----------------------------------|--------------------------------------|-------------------------------|--------------------------------------|-------------------------------|
| Surface area (m\(^2\)/g) | 1080                             | 1156 \(^\text{19}\)                 | 1421                          | 1000-1800                            | 1500-2100*                     |
| Particle Size (μm)  | 10                               | 0.2-0.4                             | >50 \(^\text{a}\)              | 1.5–3.5                              | 15.9*                         |
| Temperature (°C)   | 140                              | 25-40                               | -                             | 100-180                              | -                             |
| Synthesis Time (min) | 60                               | 1                                   | 20                            | 720-4320                             | 150                           |

* Basolite C300, Sigma-Aldrich. \(^\text{a}\) from SEM image\(^\text{20}\)

In this study, the effort was made to develop and optimize a new method for the preparation of HKUST-1 MOFs in a fast and efficient manner. Attempts were also made to control the MOFs in nanoscale with high surface area and high yield. The preparation conditions were optimized to enable the preparation of nanoscale HKUST-1, which was further studied to show its potential in CO\(_2\) capture.

2. Experiment

2.1. Preparation of HKUST-1

In this study, a novel hydro/solvo-thermal method was developed for the rapid preparation of porous HKUST-1 MOFs. Firstly, 0.03 mole of copper nitrate trihydrate (Sigma Aldrich, 98%) was dissolved in a 250 ml of deionized water to form Solution A, while 0.02 mole of trimesic acid (TMA) (Sigma Aldrich, 95%) and 0.06 mol Triethylamine (TEA) (Sigma Aldrich, 99.8%, anhydrous) were added in a 250 ml of ethanol (Sigma Aldrich, 99%) to form Solution B. These two solutions were then mixed and heated under constant stirring to the pre-set temperature level, i.e., 25, 50, 75, 80, 85°C, and kept isothermal for a period of time (3, 6 or 9 h). The solution was then cooled down to room temperature in an ice bath and centrifuged to produce pristine HKUST-1, which was activated using slurry state activation, powder state activation or slurry-powder state
activation to remove internal impurities. The slurry state activation refers to the activation of the centrifuged HKUST-1 after synthesis; the powder state activation refers to activation of the dried centrifuged HKUST-1; while the slurry-powder state activation refers to the slurry state activation followed by drying and further activation of the HKUST-1 powder. In this research, the activation agents used are ethanol and methanol. The activation process was 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. The activation process was conducted for 3 h. After that, the activated solution was centrifuged to obtain precipitation and dried at 120 °C to obtain final HKUST-1 powder. The sample being activated by slurry/powder state activation method using ethanol/methanol as the agent is denoted as Se/Pe or Sm/Pm (‘S and P’ stands for slurry state and powder state, while ‘e and m’ stands for ethanol and methanol). A suite of samples was screened under different conditions, such as reaction period (3, 6, and 9 h), reaction temperature (25, 50, 75, 80, 85°C), activation methods, and drying temperature (120 or 180°C) and are named as based on preparation conditions. For example, T85-3-Sm1Pm1-120 stands for a HKUST-1 being prepared under 85 °C for 3 hour, followed by firstly slurry state activation with methanol as the agent and drying at 120 °C using an air dryer, and then undergoing powder activation using methanol as the agent followed by drying at 120 °C.

2.2. Characterization

Morphology and particle size of the synthesized HKUST-1 MOFs were analyzed by using a Scanning Electron Microscope (SEM, ZEISS Sigma VP/Oxford Instruments). The high quality SEM images, which show around 100 particles, were processed using ImageJ to find out particle size distribution (particle size is determined based on the Feret’s dimension). Structure of the solid
phase and crystallinity were analyzed by using a Powder X-ray diffraction (XRD) with a scanning rate of 0.02°/s (2θ) using monochromatic 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 following the method described elsewhere. Thermal decomposition behavior was studied using a thermogravimetric analyzer (TGA, NETZSCH STA49 F3), which involved the heating of the sample from 35 to 900 °C at a heating rate of 10 °C/min under N$_2$ atmosphere. The pH value of the solution was measured by using a METTLER TOLEDO pH analyzer (FiveEasy Plus- FE28). The crystallinity of each sample was studied to distinguish any possible variation of the crystal pattern. The crystallinity percentage (%C) was defined as the ratio of the sum of the relative intensity of the five most intense peaks and can be calculated using Eq.(1).

\[
%\text{Crystallinity} = \frac{\sum_{i=1}^{5} l_i^{\text{sample}}}{\sum_{i=1}^{5} l_i^{\text{sample of reference}}} \times 100 \quad \text{(Eq. 1)}
\]

In this calculation, the C300 (C300 is commercial product acquired from Sigma) was used as the reference (100% crystallinity).

- CO$_2$ adsorption testing

CO$_2$ adsorption was conducted in a TGA system (NETZSCH STA49 F3) following the procedures adopted by others. Initial treatment of the activated sample was carried out in N$_2$ at 150 °C for 12 h. The adsorption was carried out using ultra purity CO$_2$ and N$_2$ (99.999%). A gas mixture of 133 mL/min of CO$_2$, 100 mL/min of N$_2$ and 100 mL/min of protective gas (N$_2$) was introduced into the sample chamber. Temperature and pressure of the adsorption chamber was maintained at 27 °C and 1 bar, respectively.
CO\textsubscript{2} isotherm of the HKUST-1 MOFs at 27 °C was obtained using the Micromeritics ASAP 2020. The degas 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\textsuperscript{27}.

The CO\textsubscript{2} and N\textsubscript{2} adsorption–desorption cycle at 27°C was obtained using the TGA. Approximately 10 mg HKUST-1 MOFs was pre-treated at 150°C for 2 h in a nitrogen environment. The adsorption-desorption cycle was carried out at a flowrate of 60 mL/min of CO\textsubscript{2} (99.999%) gas and 40 mL/min of N\textsubscript{2} (99.999%), respectively.

3. Results & Discussion

3.1. Screening synthesis of HKUST-1

In this study, the effect of synthesis temperature, time, pretreatment temperature and activation methods on the synthesis of HKUST-1 MOFs was investigated. The first attempt was made to find out an optimal reaction duration and temperature for the synthesis of MOFs. From Fig. 1, it can be seen that the variation in reaction time from 3 h to 9 h showed no significant impact on the specific surface area for samples in Region I. That means 3 hours provide sufficient time to allow the synthesis reaction to complete, which is shorter than the time required for conventional HKUST-1 synthesis (≥24h)\textsuperscript{21}. This is due to the addition of the alkaline TEA, which is consistent with the finding that the alkaline TEA could accelerate the deprotonation of H\textsubscript{3}BTC and promote the nucleation of particles into nanoscale\textsuperscript{28}. Furthermore, in Region II, the pristine HKUST-1 had gone through the pretreatment in an air dryer under two different temperatures, 120 and 180 °C. The results indicated that 120°C does not have a negative effect on the pores in the HKUST-1.
It can be seen from Fig. 1 that in Region III, the two samples prepared at 50 and 85°C showed significantly different BET surface areas. It is obvious that 85°C favors the formation of HKUST-1 with large BET surface area. This low temperature (85°C) is much lower than the temperature (180 °C) adopted for the synthesis of HKUST-1 MOFs by Chui et al. The low temperature level can inhibit the formation of the by-product (Cu$_2$O) and therefore contribute to a high selectivity and yield.

After synthesis, the pristine HKUST-1 has to be activated to remove the impurities (unconverted reactant or byproduct) that are trapped in the pores. The activation can also activate the metal sites, which are always surrounded by water and other gas molecules. As shown in Region IV, pristine HKUST-1 was activated via either slurry state or powder state activation by ethanol or methanol. The BET surface area of T85-3-Se1-120 and T85-3-Pe1-120 was lower than that of T85-3-Sm1-120 and T85-3-Pm1-120. It is reported that methanol is a better activation agent and can remove more impurities than ethanol. It is clear that the BET surface area of T85-3-Pe1-120 and T85-3-Pm1-120 was higher than that of T85-3-Sm1-120 and T85-3-Pe1-120, which suggests that powder state activation is more efficient in the removal of impurities from pores.

In Region V, it shows that repeated slurry activation resulted in lower BET surface area, which might be due to the destruction of micropores to form larger pores and subsequently result in lower BET surface area. However, repeated powder state activation shows different impacts on BET surface area, as shown in Region VI. Four times of powder state activation result in the highest surface area around 1542.4 m$^2$/g.
The combination of slurry-powder state activation was applied to activate pristine HKUST-1 and the BET surface area of individual samples is shown in Region VII in Figure 1. It is found that the BET surface area of T85-3-Sm1Pm1-120, T85-3-Se1Pm1-120 and T85-3-Sm1Pe1 was higher than that of their respective samples being activated once via slurry state activation. For example, T85-3-Sm1Pm1-120 has a BET surface area of 1264.6 m$^2$/g, which is higher than that of T85-3-Sm1-120 (954.4 m$^2$/g). In addition, it was found that the BET surface area of T85-3-Sm1Pm1-120 was higher than that of T85-3-Sm1Pe1-120 (1022.7 m$^2$/g), which again proves the powder state activation using methanol as the activation agent is a reliable and efficient method. However, the BET surface area of one more times of powder activation by methanol (T85-3-Sm1Pm2-120) was reduced. Therefore, it can be concluded that slurry state activation removes the impurities in the pores but does not significantly contribute to the formation of higher BET surface area.

Among the 17 samples prepared, the highest BET was found for T85-3-Pm4-120, which is 1542.4 m$^2$/g. There are also other five samples, i.e., T85-3-Pm1-120, T85-3-Pm2-120, T85-3-Pm3-120, T85-3-Pm5-120, and T85-3-Sm1Pm1-120, that have BET surface area greater than 1100 m$^2$/g. The highest BET surface area is attributed to the cleaning of pores, which is associated with a final HKUST-1 yield of 67%.
Fig. 1 Screening of HKUST-1 with large specific surface area. I, reaction period; II, Drying temperature; III, synthesis temperature; IV, slurry/powder state activation using methanol/ethanol as the activation agent; V, repeated slurry state activation using methanol as the activation agent; VI, repeated power state activation using methanol as the activation agent; VII combination of slurry and powder activation. (T25, T50, T75, T80, T85-A stand for reaction temperature at 25, 50, 75, 80, 85°C. T50-3, T50-6, T50-9 stand for reaction duration of 3, 6, and 9 h at 50°C, respectively. T50-3-Se1-180 indicate the pristine HKUST-1 yielded at 50°C with a duration of 3 h was activated once using slurry state activation method and dried at 180°C. Sm1 means slurry state HKUST-1 was washed by using methanol. Pe1 means powder state
HKUST-1 was washed by using ethanol once. Sm1Pm1 means slurry state washing firstly, and then followed by powder state washing.)

3.2. The nano HKUST-1 formation and its morphological features

To understand how the morphology of HKUST-1 is affected by synthesis conditions and powder activation process, SEM analysis was conducted with morphological features of different samples shown in Fig. 2 (I) – (IV). It is evident that all samples are of nano-particle size (<100 nm) but form agglomerates. In the Region I of Fig. 2 and Fig. 3, the samples synthesized under 50°C for 3/6/9h were similar in morphology, but particle size of the samples decreased with the increase in synthesis period. That means longer synthesis period favors the formation of smaller nanoscale particle.

Regarding the influence of synthesis temperature on the morphology of HKUST-1, as shown in Region II of Fig. 2 and Fig. 3, the samples synthesized from 25 to 85°C after 3 h demonstrated differences in particle size distribution and average particle size. The SEM image (Fig. 2(II)) shows similar morphology, which are featured with small spherical particles. Under low temperature (25°C), it shows crystal structure with blocky shape and obvious sharp edges and has the highest average particle size of 93.6 nm, whereas samples prepared under higher temperatures (50, 75, 85°C) are more spherical and are of smaller particle size. It was obvious that the MOFs prepared at 50°C and 85°C formed are of similar average particle size (~72 nm) as shown in the Region II of Figure 3(b). However, the peak (53.8-67.5 nm) of T85-3-Se1-120 is higher than the peak (67.5-87.2 nm) of T50-3-Se1-120 in the Region II of Figure 3(a).
In this study, further investigation was conducted to understand the influence of powder activation and slurry activation process on the samples prepared under the optimal synthesis temperature of 85°C. It was found that when the pristine sample had undergone powder activation using methanol as the activation agent twice, the average particle size was the smallest (76.0 nm) with the peak of particle distribution in the range of 67.5-81.25 nm. However, the particle size increased when the sample had undergone more times of powder state activation, which could be attributed to the crystal growth of the primary particle during the activation process, i.e., the precursors being washed out of the pores to form new MOFs on the surface of the primary MOF particle.

For comparison purpose, the slurry state activation using methanol as activation agent was also conducted. The samples, T85-3-SmX-120 (X=1, 2, 3), were prepared and are shown in Fig. 2(III). These samples showed different morphologies and demonstrated that particle size can be reduced followed by the additional times of slurry state activation, which is shown in the Fig. 3a (III). It can be seen from Fig. 3b (III) and (IV) that slurry state activation leads to the formation of samples with smaller particle size compared with powder state activation. However, although slurry activation process can lead to the formation of smaller size nano particles, it cannot form nano-scale HKUST-1 particle with BET surface area greater than 1100 m²/g (as shown in Region V of Fig. 1). Despite the increase in particle size after 3 times of powder state activation, the specific surface area of T85-3-PmX-120 (X=1, 2, 3, 4) increased from 1115.3 to 1542.4 m²/g as a result of multiple powder state activations. Therefore, it can be concluded that to form nanoscale sample with large surface area, the sample shall be prepared under 85°C and activated via powder state activation for at least two times.
Fig. 2 Morphology of HKUST-1 MOFs prepared under different preparation conditions. I, reaction time. II, synthesis temperature. III, slurry state activation. IV, powder state activation.
Fig. 3 Particle size (based on Feret’s diameter) of each synthesized sample vs different preparation method (results obtained from ImageJ). a, particle size distribution. b, average particle size (average Feret’s diameter). I, reaction time. II, synthesis temperature. III, slurry state activation process. IV, powder state activation.

Table 2 Structural properties of samples prepared under 85°C

| PREPARATION METHOD | $S_{BET}^1$ (m²/g) | $S_{LANGMUIR}^2$ (m²/g) | $V_{TOTAL\_PORE}^3$ (cm³/g) | $V_{MICRO\_PORE}^4$ (cm³/g) | %$V_{MICRO\_PORE}^5$ | pH* |
|-------------------|--------------------|--------------------------|-----------------------------|-----------------------------|----------------|-----|
| T85-3-N-120       | 503.5              | 580.1                    | 0.31                        | 0.20                        | 0.65           | 3.63|
| T85-3-Se1-120     | 769.6              | 904.7                    | 0.58                        | 0.29                        | 0.50           | 3.60|
| T85-3-Sm1-120     | 954.4              | 1197.7                   | 0.49                        | 0.40                        | 0.82           | 3.86|
| T85-3-Pm1-120     | 1032.3             | 1235.4                   | 0.55                        | 0.45                        | 0.82           | 7.01|
| T85-3-Pe1-120     | 1003.0             | 1161.1                   | 0.47                        | 0.38                        | 0.81           | 6.07|
| T85-3-Sm2-120     | 687.5              | 719.7                    | 0.49                        | 0.23                        | 0.47           | 4.78|
| T85-3-Sm3-120     | 493.5              | 516.4                    | 0.36                        | 0.16                        | 0.44           | 5.63|
| Sample          | BET Surface Area (m²/g) | Langmuir Surface Area (m²/g) | Total Pore Volume (cm³/g) | Micro Pore Volume (cm³/g) | Micro Pore Volume Percentage (%) | pH Value |
|-----------------|-------------------------|-------------------------------|---------------------------|--------------------------|----------------------------------|----------|
| T85-3-Pm2-120   | 1292.3                  | 1452.4                        | 0.56                      | 0.47                     | 0.84                             | 7.70     |
| T85-3-Pm3-120   | 1354.6                  | 1579.3                        | 0.63                      | 0.54                     | 0.86                             | 7.87     |
| T85-3-Pm4-120   | 1542.4                  | 1647.9                        | 0.65                      | 0.57                     | 0.88                             | 8.17     |
| T85-3-Pm5-120   | 1241.0                  | 1358.2                        | 0.53                      | 0.46                     | 0.87                             | 8.20     |
| T85-3-Sm1Pm1-120| 1264.6                  | 1437.8                        | 0.57                      | 0.49                     | 0.86                             | 6.22     |
| T85-3-Sm1Pm2-120| 541.6                   | 731.2                         | 0.45                      | 0.24                     | 0.53                             | 6.88     |
| T85-3-Sm1Pe1-120| 1022.7                  | 1184.5                        | 0.48                      | 0.40                     | 0.83                             | 6.18     |

Note: 1. Specific surface area by BET. 2. Specific surface area by Langmuir. 3. Total pore volume by original Horvath-Kawazoe. 4. Micro pore volume by t-plot. 5. Micro pore volume percentage in total volume. *

*pH values of solution were measured after activation.

Fig. 4 Nitrogen adsorption and desorption isotherms of the synthesized HKUST-1. For each sample, top line is the adsorption isotherm, bottom line is the desorption isotherm.
### 3.3. Nitrogen isotherm analyses

It is found that N$_2$ adsorption rate increases at a low relative pressure ($0.0 < P/P_0 < 0.1$) (as shown in Fig. 4), the shape of each line indicates that they are Type I isotherm according to the IUPAC (International Centre for Theoretical and Applied Chemistry) classification $^{26,30}$. Samples with Type I isotherm are of microporous (<2nm) structure $^{31}$. The hysteresis loop at a higher relative pressure ($P/P_0 > 0.4$) indicates capillary condensation of mesopores for N$_2$, which contributes to the stacking combination of large particle of HKUST-1$^{32}$ or the creation of defects under such synthesis method $^{33}$. That is, the hysteresis loop for T85-3-n-120 and T85-3-Pm1-120 would be due to the defects, because this loop was the cavitation phenomenon$^{34}$ that occurs when the pore size is less than 6 nm. Besides, the hysteresis loop for T85-3-PmX-120 ($X=2,3,4,5$) at $P/P_0 > 0.8$ appeared due to larger pores over 10 nm $^{35}$. This loop is caused by the interparticle pores of nanoparticle agglomerate$^{36}$.

The influence of activation process on the surface properties of HKUST-1 was also investigated in this study. As shown in Table 2, BET surface area after activation is in the range of 503-1542 m$^2$/g, which is very close to the values reported by Diring $^{37}$ and Ameloot$^{38}$, but much higher than those obtained by Chui$^{7}$. Regarding total pore volume, the reported values are in the range of 0.21 - 0.79 cm$^3$/g $^{39}$, whereas the effective pore volume was reported as 0.82 cm$^3$/g $^{40}$. In this study, the as-synthesized samples exhibited a total pore volume of 0.31-0.65 cm$^3$/g, which is comparable with reported data. The relatively low N$_2$ adsorption capacity of the raw material (T85-3-N-120) is attributed to some micropores being blocked by TEA and/or its derivatives. The high N$_2$ adsorption capacity indicates that the modulator is absent from the pores after activation. The percentage of micropore volume shown in Table 2 suggests that these samples are comprised of
plenty of micropores. It can be seen from Table 2 that activation process (powder, slurry and combination activation) has significant influences on pore properties (BET, Langmuir, Total pore volume, Micropore volume, and Microporosity). As for slurry activation, both methanol and ethanol can be used as the agent to clean the interior of pore and therefore improve N\textsubscript{2} adsorption capacity. However, more times (>2) of slurry state activation using methanol as the activation agent would result in smaller BET surface area. This is associated with the decrease in the percentage of micropores, which means excessive times of slurry state activation might damage micropores and form more mesopores.

As shown in Table 2, the slurry state activation followed by power state activation once led to the formation of HKUST-1 with better pore properties. However, powder state activation is more effective in the removal of impurities trapped in pores and multiple powder state activation could result in high BET surface area (T85-3-PM4-120, 1542.4m\textsuperscript{2}/g).

Meanwhile, the pH value of the solution after activation was monitored by using a pH meter, the results of which are shown in Table 2. It is clear that pH value generally increased with BET specific surface area, which is associated with the removal of impurities and TEA derivatives. It is speculated that powder state activation retained the high BET surface area and did not damage the pore structure of HKUST-1. Therefore, the powder state activation by methanol is considered as an appropriate method for the treatment of the pristine HKUST-1.

3.4. XRD analysis

XRD analysis was conducted to show the crystalline phases of the porous HKUST-1. It can be seen that all the diffraction peaks in Fig 5 (a) and (b) match well with the pattern of C300 and
simulation, indicating that these samples are pure phase of HKUST-1. From Fig 5, it is evident that the XRD peak positions and relative intensities of the synthesized MOFs also agree well with those of the simulated HKUST-1 (red spikes labelled by star at the bottom of Fig. 5)\textsuperscript{41}. Due to the low temperature condition adopted for the synthesis of HKUST-1, the diffraction peaks of Cu\textsubscript{2}O (36.7 °, PDF#04-003-6433) do not show in the XRD spectrum, which means that (Cu\textsubscript{2}O) was not formed.

It can be seen from Table 3 that the synthesis temperature has significant impacts on the crystallinity of the samples. In the samples of TX-3-Se1-120 (X=25, 50, 75, 80, 85), the crystallinity percentage of T85-3-Se1-120 is very close to that of the C300 (%Crystallinity=95.4%), which demonstrates that the low synthesis temperature (85°C) can lead to the formation of HKUST-1 with appropriate crystal structure. After the samples were further processed via powder state activation, the crystallinity percentage of each sample did not vary significantly compared with the variation in temperature. The crystallinity percentage is improved until 5 times of powder state activation. However, further powder state activation does not show much influence on crystallinity percentage. Therefore, to obtain the highest crystallinity percentage of HKUST-1, the sample shall be prepared under 85°C with the four times of powder activation process.

In addition, the hydration degree of the HKUST-1 could be determined by the I\textsubscript{200}/I\textsubscript{220} ratio\textsuperscript{42}. where higher I\textsubscript{200}/I\textsubscript{220} ratio indicates a smaller hydration degree. Normally, a smaller hydration degree indicates that more copper coordination sites are accessible for other molecules, such as CO\textsubscript{2}. The T85-3-Pm4-120 shows the highest value of I\textsubscript{200}/I\textsubscript{220}, which suggests that it can capture more CO\textsubscript{2} than any other samples. This result suggests that the proper condition (T85-3-Pm4-120) lead to the formation of HKUST-1 with desired properties in CO\textsubscript{2} adsorption.
Fig. 5 XRD spectrum of each sample. (a) HKUST-1 activated by repeated powder state activation. (b) HKUST-1 synthesized under different reaction temperatures. * indicates simulated PXRD data from single crystal data.

Table 3 XRD patterns of relative peak intensity based on the HKUST-1 peak intensity of (222)

| Sample       | $I_{(200)}$ | $I_{(220)}$ | $I_{(222)}$ | $I_{(400)}$ | $I_{(420)}$ | %Crystallinity | $I_{(200)}/I_{(220)}$ |
|--------------|-------------|-------------|-------------|-------------|-------------|----------------|-------------------|
| T85-3-Pm5-120| 30.2        | 30          | 100         | 24.0        | 7.4         | 98.3           | 1.01              |
| T85-3-Pm4-120| 38.5        | 28.7        | 100         | 18.8        | 6.7         | 98.9           | 1.34              |
| T85-3-Pm3-120| 27.5        | 28.1        | 100         | 23.2        | 6.1         | 94.9           | 0.98              |
| T85-3-Pm2-120| 22.8        | 27.3        | 100         | 19.2        | 6.1         | 90.0           | 0.84              |
| T85-3-Pm1-120| 20.2        | 24.2        | 100         | 20.4        | 6.5         | 87.9           | 0.83              |
| T85-3-Se1-120| 14.3        | 27.2        | 100         | 29.3        | 15.1        | 95.4           | 0.53              |
| T80-3-Se1-120| 17.3        | 25.4        | 100         | 21.7        | 13.9        | 91.5           | 0.68              |
| T75-3-Se1-120| 7.8         | 43.7        | 100         | 48.6        | 10.6        | 108.2          | 0.18              |
| T50-3-Se1-120| 5.2         | 47.7        | 100         | 63.0        | 13.3        | 117.7          | 0.11              |
| T25-3-Se1-120| 17.1        | 26.8        | 100         | 26.2        | 13.6        | 94.3           | 0.64              |
| C300         | 16.0        | 47.6        | 100         | 27.4        | 3.8         | 100.0          | 0.34              |

Note: %Crystallinity was based on Eq. 1.
3.5. **TGA analyses**

The HKUST-1 \((\text{Cu}_3\text{BTC}_2\text{(H}_2\text{O})_3\cdot x\text{H}_2\text{O}, x\approx 3)\) was tested in TGA to show its thermal stability. As shown in Fig. 6, these samples have similar TG curves from 35 to 900°C. At temperatures below 120°C, the weight loss is due to the desorption of physisorbed water or gases. This was followed by the release of water trapped in the pores when the temperature was raised up to 180°C. The HKUST-1 was then heated up to 350°C and exhibited modest loss of weight, as shown in DTG curve of the Fig. 6. However, the weight loss increased significantly when temperature was raised above 350°C. At higher temperatures, some metal were reduced and MOFs were decomposed to form carbon. The weight loss levelled off at higher temperatures when MOFs were completely transformed into \(\text{CO}_2\), \(\text{CO}\), \(\text{Cu}\), \(\text{Cu}_2\text{O}\), and \(\text{CuO}\). This finding is consistent with what has been reported by others, the MOFs retained its molecular formula but lost the microporous nature after being heated to 350 to 427°C.\(^{43}\)
Fig. 6 TGA analysis of T85-3A-Pm1, Pm2, Pm3, Pm4, Pm5 and Sm1Pm1-120 from 35°C to 900°C within N2 atmosphere.

### 3.6. CO2 adsorption analyses

It was found that the presence of divalent metals significantly increased CO2 binding strength and resulted in higher selectivity in CO2 adsorption. Due to its crystalline structure and the existence of Cu²⁺ metal ions, HKUST-1 is expected to have high affinity toward CO2. Normally, CO2 adsorption can be evaluated by two methods, i.e., static and dynamic adsorption. In this study, the static adsorption test was carried out at 27°C with pressure from 0-1 bar. In the dynamic test, a thermogravimetric study using pure CO2 was carried out at 27°C.

The CO2 uptake of T85-3-PmX-120 (X=1,2,3,4,5) and T85-3-Sm1Pm1-120 is shown in Fig. 7. The CO2 uptake capacity of T85-3-Pm4-120 sample exhibits a steep rise in a short time, and reach a maximum of 8.12% wt. (1.84 mmol/g), at 27°C and 1 bar. It is generally believed that CO2 adsorption capacity is dependent on pore volume of the adsorbent. The larger the microporosity, the higher the CO2 adsorption capacity. Besides, the I200/I220 ratio of each sample can be used as an indicator for CO2 adsorption capacity.
To reveal the CO$_2$ adsorption property of T85-3-Pm4-120, CO$_2$ adsorption isotherm was obtained and is shown in Fig. 8. The CO$_2$ recycle of T85-3-Pm4-120 was measured at 27°C under 1 bar. The results showed that the CO$_2$ desorption process finished rapidly during N$_2$ purging under the same conditions and the CO$_2$ adsorption capacity remains almost unchanged after ten adsorption/desorption cycles, which demonstrated the good adsorption stability of T85-3-Pm4-120. It is clear that T85-3-Pm4-120 has a CO$_2$ uptake of 11 wt% (2.5mmol/g) under static adsorption, which is higher than reported data under similar experimental conditions as shown in Table 4.
Fig. 8 CO$_2$ isotherm of T85-3-Pm4-120 at 27°C, inset graph is CO$_2$ recycle of T85-3-Pm4-120

Table 4 Comparison of CO$_2$ adsorption capacity for others’ HKUST-1

| Literature         | Adsorption manner    | Adsorption capacity mmol/g | Adsorption temperature °C |
|--------------------|----------------------|----------------------------|----------------------------|
| Sheng et al. 46    | Dynamic adsorption   | 1.82                       | 30                         |
| Chugh et al. 47    | Dynamic adsorption   | 1.45                       | 30                         |
| Shen et al. 48     | Static adsorption    | 0.15                       | 20 (0.75 bar)              |
| Yunxia et al. 49   | Dynamic adsorption   | 1.8                        | 32 (5 bar)                 |
| This research      | Dynamic adsorption   | 1.84                       | 27 (1 bar)                 |
| This research      | Static adsorption    | 1.95                       | 27 (0.75 bar)              |
| This research      | Static adsorption    | 2.5                        | 27 (1 bar)                 |

4. Conclusions

In conclusion, the optimized hydro/solvo-thermal approach developed in this research is a cheap and efficient method for the synthesis of nanoscale HKUST-1 MOFs under low temperature and atmospheric pressure using methanol as the activation agent. Both the slurry and powder state
activation methods were found to have significant influence on the specific surface area, micropore volume and mesopore size, while powder state activation is more effective in the removal of impurities trapped in HKUST-1. The **T85-3-Pm4-120** showed a high BET surface area of 1542.4m$^2$/g and an average size of 87 nm. It was also found that the HKUST-1 prepared in this study showed a high CO$_2$ adsorption capacity with an uptake around 11wt% (2.5mmol/g) at 27$^\circ$C and 1 bar.

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