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Microwave enhanced synthesis of MOF-5 and its CO_2 capture ability at moderate temperatures across multiple capture and release cycles

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ABSTRACT

The metal-organic framework, MOF-5 ($Zn_4O(BDC)_3$), was prepared using solvothermal synthesis under microwave irradiation, followed by solvent exchange to improve molecular stability at high temperatures, and assessed for its ability to capture CO_2 at ambient pressure and temperatures up to 300 °C. The reaction product was characterised by X-ray diffraction, scanning electron microscope, N_2 physisorption, thermogravimetric analysis and CO_2 physisorption. Cyclic CO_2 physisorption showed the capacity of the MOF-5 crystals to be 3.61 wt% when cycled between 30 °C and 300 °C through 10 separate capture and release cycles. Above 400 °C MOF-5 underwent thermal decomposition and was no longer capable of capturing CO_2.

1. Introduction

Metal-organic frameworks (MOFs) are a relatively new class of porous solid with large pores, high apparent surface areas and high structural and chemical diversity [1–6] formed by metal atoms linked together with multi-functional organic ligands. To date, several hundred MOF structures have been reported, with the most well studied being MOF-5 comprising Zn_4O units connected by linear 1,4-benzenedicarboxylate (BDC) struts to form a cubic network. MOF-5 was first described by Li et al. in 1999 [2] followed by analysis of its reticular design using different carboxylate linkers in 2002 [3]. More recently, the structures, properties and possible applications as storage media have been investigated [4,6] including comparison with oxides, molecular sieves, porous carbon and heteropolyanion salts [1].

Typically, MOFs are synthesised by mass transfer techniques (e.g. diffusion of amine into a solution containing a metal salt and organic acid), hydrothermal and solvothermal methods [7,8], in which very long reaction times are needed (several days for hydrothermal and solvothermal methods, several weeks for diffusion synthesis). Hence, for large-scale production [9], improvements in the synthesis protocol are required, in particular a reduction in the synthesis time and increase in energy efficiency. In this respect, Choi et al. [10] reported a novel solvothermal synthesis technique for MOF-5 using microwave irradiation and Li et al. [11] achieved similar improvements using an ultrasonic synthesis methodology. We have previously demonstrated substantial improvements in reaction efficiency under microwave irradiation [12] and hence this work attempts to expand on the microwave synthesis technique of Choi et al. [10], to demonstrate the high efficiency synthesis of MOF-5. We then investigate the ability of MOF-5 to capture CO_2 across multiple capture and release cycles at atmospheric pressure, for the first time.

Carbon dioxide (CO_2) is a known greenhouse gas implicated in anthropogenic climate change. Consequently, efforts to reduce CO_2 emissions to atmosphere have intensified, including a focus on materials to efficiently capture gaseous CO_2 from complex mixtures. MOFs are promising new candidates for these applications [13]; for example, recent studies have concentrated on the ability of various MOF materials to adsorb methane [5,14] and hydrogen [5,15].

At present, the most developed technology for flue gas separation of CO_2 is solvent absorption, typically using aqueous alkanolamine solvents. The major drawbacks of solvent based CO_2 absorption processes are high energy requirements and environmental performance issues due to loss of alkanolamines as a consequence of their high volatility. Separation processes based on solid CO_2 sorbents [16] potentially lead to enhanced environmental and energetic benefits, however, in the development of solid state CO_2 capture one major challenge is to develop sorbents with high adsorption capacity for CO_2 at low partial pressures. In this regard, MOFs are considered strong candidates for CO_2 removal by adsorption. Millward and Yaghi [17] recently reported that MOF-177 was the most effective structure for CO_2 capture amongst a series of isoreticular MOFs with a capacity of 34 mmol CO_2/g at 43 bar. Equally promising was MIL-101, a novel mesoporous MOF

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reported by Ferey et al. with a storage capacity of 33 mmol CO_2/g at 50 bar condition [18]. More recently, chabazite zeolites and amino-functionalised MOF materials have been proposed for CO_2 adsorption due to their high surface area [19,20], with amino-functionalised MIL-53 MOF adsorbing ∼2.3 mmol/g CO_2 at 5 bar [19]. In this experiment, increasing pressure resulted in an increase in CO_2 adsorption, however, a CO_2 pressure of 13 bar was required to re-open pores on the MOF surface.

2. Experimental

MOF-5 was synthesised according to Choi et al. [10] as follows: In a typical experiment, 2.93 g of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, SIGMA), 0.55 g of terephthalic acid (H_2BDC, SIGMA) and 50 mL of 1-methyl-2-pyrrolidinone (NMP, SIGMA) were mixed together and transferred to sealed Teflon pressure vessels followed by heating for 30 min under irradiation in a commercial microwave system (Milestone Microwave Labstation, ETHOS SEL). The power output of the microwave (up to 1 kW) was adjusted to maintain the required reaction temperature. To study the effect of the temperature gradient during synthesis, MOF-5 was synthesised at an isothermal temperature of 105 °C (designated 'IT') as well as using a linear temperature ramp between 105 °C and 130 °C (designated 'LT'). For comparison, MOF-5 was also synthesised using a standard reflux apparatus with conventional heating at 105 °C for 4 h (designated 'Reflux') [9].

All products were filtered and washed with NMP three times, and then dried at 100 °C under vacuum for 12 h (designated IT-N, LT-N, and Reflux). To investigate the influence of post-synthesis solvent exchange, the products washed with NMP were variously stored in ethanol (designated IT-E), acetone (designated IT-A and LT-A) or chloroform (designated LT-C) for 24 h and then dried at 100 °C under vacuum for an additional 12 h.

The MOF-5 products were first characterised by X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD patterns were recorded with a Siemens D-5000 diffractometer using nickel-filtered Cu Kα radiation over the range of $5^\circ < 2\theta < 50^\circ$ in 0.03° increments with a 1-s time step. Images of the MOF-5 crystals were taken with SEM (Philip XL-30) using a 20 kV electron beam. The thermal stability of the samples was tested using thermogravimetric analysis (TGA, TA Instruments Q500) where 5 mg of sample was heated at 10 °C/min to 700 °C under air (60 mL/min). Nitrogen adsorption isotherms were measured with an Autosorb 1 (Quantachrome Instruments). Samples of a known weight (between 30 and 60 mg) were loaded into a sample tube and evacuated at 120 °C under vacuum (10^{-5} Torr) for 12 h. After evacuation, the sample and tube were weighed again to obtain the evacuated sample weight. The specific surface areas of the samples were calculated according to the Langmuir model.

CO_2 adsorption measurements were made using two complementary techniques; (i) volumetric measurement was performed by the Autosorb 1 at 30 °C from vacuum to a CO_2 pressure of 1 atm, and (ii) gravimetrically at a CO_2 flow rate of 60 mL/min using the TGA instrument across 10 capture and release cycles, also at atmospheric pressure. Prior to commencing measurement of the CO_2 adsorption capacity, the sample was evacuated (10^{-5} Torr) at 120 °C for 12 h. For the gravimetric method, after every adsorption step, the sample was heated to 300 °C under N_2 and then cooled prior to repeating the CO_2 capture step. This procedure ensured that every adsorption value was measured independently from the previous one.

3. Results and discussion

The crystal properties of MOF-5 prepared under microwave irradiation were compared with those of MOF-5 synthesised using

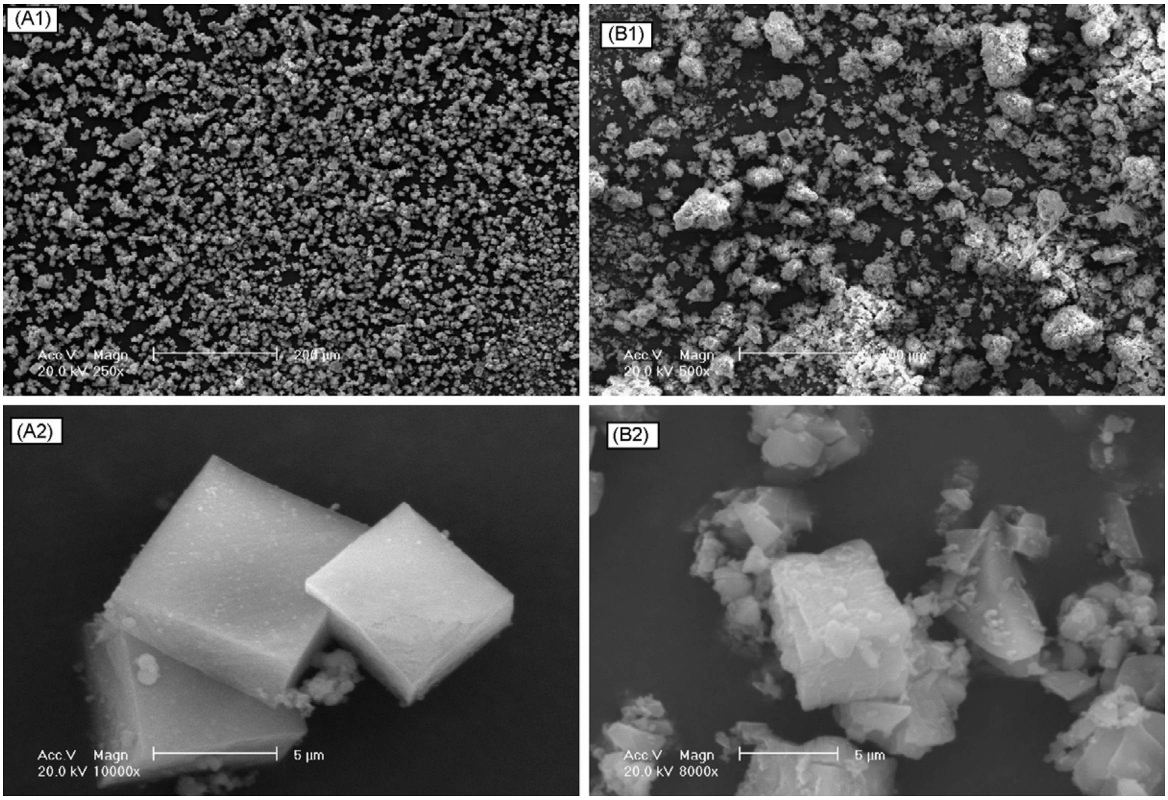

Fig. 1. Morphology of the MOF-5 samples: (A) synthesised under microwave irradiation at 105 °C for 30 min, and (B) synthesised with a conventional reflux apparatus at 105 °C for 4 h.

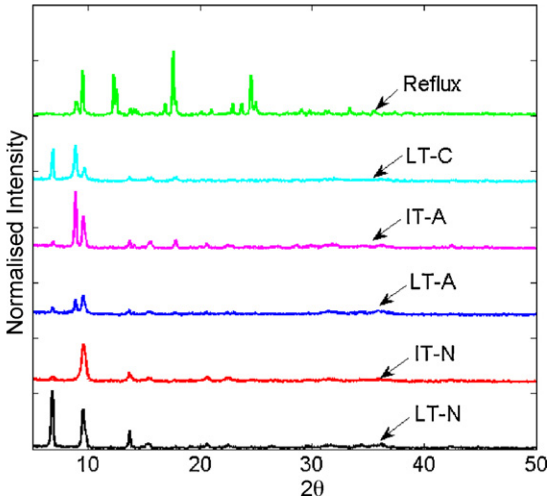

Fig. 2. XRD patterns of the various MOF-5 samples as indicated: LT—synthesised under microwave irradiation at a linear temperature ramp from 105 °C to 130 °C; N—sample washed with NMP during filtration without further solvent exchange; C—sample washed with NMP, followed by solvent exchange with chloroform. A—sample washed with NMP, followed by solvent exchange with acetone. IT—synthesised under microwave irradiation at an isothermal temperature of 105 °C; Reflux—synthesised using a conventional reflux apparatus at 105 °C for 4 h.

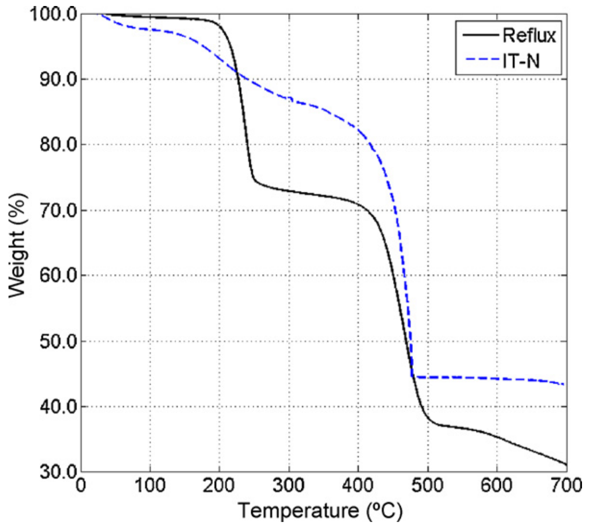

Fig. 3. Weight loss profiles measured using thermogravimetric analysis (TGA) for IT-N (synthesised under microwave irradiation at an isothermal temperature of 105 °C for 30 min) and Reflux (synthesised using a conventional reflux apparatus at 105 °C for 4 h). The samples were heated in air between 25 °C and 700 °C at a ramp rate of 10 °C/min. The air flow rate was 60 mL/min.

the conventional refluxing apparatus. Under consistent synthesis conditions, i.e. at a temperature of 105 °C using 10 mmol $Zn(NO_3)_2{\cdot}6H_2O$, 3.3 mmol H_2BDC and 50 mL NMP, it required >4 h to synthesise MOF crystals using a standard refluxing apparatus compared to 30 min under microwave irradiation.

Fig. 1(A and B) shows the SEM images of the MOF-5 samples synthesised under microwave irradiation at 105 °C for 30 min and synthesised in a conventional refluxing apparatus at 105 °C for 4 h, respectively. It can be observed that the crystals were typically cubic-shaped with dimensions of approximately 5–10 μm. A comparison of these SEM images shows that the MOF-5 crystals synthesised under microwave irradiation (Fig. 1A) are more structured and cubic-shaped than those synthesised by conventional refluxing method (Fig. 1B). This indicates that MOF-5 crystals of a higher quality can be synthesised in less time using microwave heating [10].

XRD patterns for the MOF-5 samples synthesised under microwave irradiation and in a conventional refluxing apparatus are shown in Fig. 2. The main peak at $2\theta = 9.87^\circ$ corresponding to the MOF-5 crystal plane [21–23] is observed in all samples, confirming that MOF-5 crystals were successfully synthesised under microwave irradiation and using the conventional refluxing method. This is consistent with the SEM results (Fig. 1). Another two characteristic peaks for MOF-5 at $2\theta = 7.25^\circ$ and 13.96° appear in the microwave heated samples, consistent with the results of Huang et al. [21], Hafizovic et al. [22] and Saha et al. [23].

A further characteristic peak for the MOF-5 crystal plane at $2\theta = 24.76^\circ$ [21–23] at relatively low intensity is shown in the sample synthesised by conventional refluxing method, indicating the existence of MOF-5 crystals in this sample. This confirms the SEM results (Fig. 1B). However, several unidentified peaks at $2\theta = 12.71^\circ$ and 17.63° which do not correspond to MOF-5 crystal planes indicate that a mixture of MOF-5 and an unidentified framework were obtained in this sample.

In addition, the morphology and XRD patterns were qualitatively different (Figs. 1 and 2). Under the refluxing conditions employed, it was impossible to obtain pure MOF-5 crystals; a mixture of MOF-5 and an unidentified framework resulted, whereas the morphology and XRD patterns for MOF-5 synthesised under microwave irradiation (Fig. 2) were consistent with those previously reported [2,24].

When the reaction products were subjected to thermogravimetric analysis (TGA), the Reflux-sample showed negligible weight loss until 200 °C, followed by a sharp weight loss in the range of 200–254 °C, followed by a further sharp weight loss in the range 410–508 °C (Fig. 3). In contrast, the microwave-irradiated sample (IT-N) exhibited steady continuous weight loss to around 425 °C followed by a sharp drop in weight in the range 420–478 °C. The weight loss profiles are quantitatively indicative of MOF-5 framework stability.

The weight loss below 200 °C corresponds to the volatilisation of NMP [25]. The little weight loss of Reflux-sample in this range shows that little NMP solvent remains in the pores of Reflux-sample. However, approximately 7.2 wt% is lost below 200 °C in the product synthesised at isothermal temperatures under microwave irradiation, i.e. it shows that more NMP solvent is absorbed in the pores of MOF-5 structures of the product synthesised under microwave irradiation than that of conventional refluxing method. This indicates that the pores of the former are more structured than the latter.

Weight loss from 200 °C to 508 °C likely correspond to the decomposition of the MOF-5 framework [26]. SEM images (Fig. 1) show that the products synthesised by conventional refluxing method have a poor pore structure, while the XRD patterns (Fig. 2) confirm that this is a mixture of MOF-5 crystals and another (unidentified) framework. A comparison of the weight loss profiles show that the decomposition of this MOF mixture occurred earlier than that of pure MOF-5 crystals synthesised under microwave irradiation, indicating a less stable structure for the mixed framework material. The different framework structures for the Reflux and IT-N samples observed in the TGA data are in agreement with the XRD patterns. At temperatures above ∼508 °C, for both samples, the dramatic weight loss was due to decomposition of the organic ligands in the framework.

The Langmuir surface area of the Refluxed sample was 108 m^2/g, compared with 811 m^2/g (Table 1) for the microwave-irradiated sample (IT-N). As has been widely reported, the starting materials, their concentration, solvent type, synthesis temperature and synthesis time all affect the final MOF crystal properties [27]. However, our experiments have demonstrated that the heating mode

Table 1
Langmuir surface areas and adsorbed amounts of CO_2 at atmospheric pressure of the various MOF-5 products.

MOF-5 product	Surface area (m^2/g)	Uptake of CO_2 (volumetric method) (wt%)	Uptake of CO_2 (gravimetric method) (wt%)
LT-N[a]	1263	3.81	3.61 ± 0.034[b]
IT-N	811	3.50	3.30 ± 0.073
LT-A	322	2.13	2.19 ± 0.154
IT-A	388	1.80	2.26 ± 0.094
Reflux	108	1.38	1.12 ± 0.093

[a] Sample-id: LT—synthesised under microwave irradiation at a linear temperature ramp of 105 °C to 130 °C for 30 min; N—sample washed with NMP during filtration without further solvent exchange; IT—synthesised under microwave irradiation at an isothermal temperature of 105 °C; A—sample washed with NMP, followed by solvent exchange with acetone; Reflux—synthesised using conventional refluxing apparatus at 105 °C for 4 h.

[b] Standard deviation from 10 individual measurements.

also plays an important role in the synthesis, confirming the observations of Choi et al. [10]. Harris et al. [28] previously reported that microwave heating can lead to order of magnitude increases in reaction rate compared with conventional heating [29], principally due to localised (i.e. molecular) superheating, resulting from (i) dipolar polarisation (the principal heat-generating pathway for the solvents resulting in rapid molecular rotation induced by the electric field oscillation), (ii) enhanced refluxing within the sealed vessel, (iii) the presence of electrically conducting materials and (iv) the generation of gas plasma from absorbed gases. In the case of MOF-5, the superheating effect explains why it is possible to synthesise metal-organic framework materials using short reaction times compared with published literature on conventionally heated hydrothermal or solvothermal synthesis [30].

The Langmuir surface area is closely related to the quality of crystal growth, which in turn depends on reaction temperature. MOF crystal growth occurs via: (i) nucleation of MOF growth sites and then (ii) targeted anisotropic growth of MOF crystals [31]. Reaction temperature is highly likely to dynamically control the rate of both steps. Thus, it is likely that microwave heating provides favourable conditions for the nucleation of MOF growth sites and the growth of MOF crystals, leading to a higher Langmuir surface area.

We also investigated whether a constant (105 °C), or slowly increasing (105 °C to 130 °C over 30 min), reaction temperature was most beneficial. When assessed using XRD, the crystals produced from the ramped temperature experiment (LT-N) showed a stronger intensity for the 1st peak at $2\theta = 6.75^\circ$ than the constant experiment (IT-N, Fig. 2) showing enhanced crystallinity of LT-N over IT-N. The Langmuir surface area was also higher (LT-N = 1263 m^2/g vs IT-N = 811 m^2/g). We were unable to reproduce the very high surface areas (3200 m^2/g) reported by Choi et al. [10] using any of the microwave-irradiated synthesis experiments or post-synthesis solvent exchange, although our data were consistent with those of Panella et al. [24] (1014 m^2/g).

In order to improve the specific surface area and pore volume, and stabilise the framework, guest molecules are often removed using post-synthesis solvent exchange. However, the boiling point and polarity of the solvent must be considered in order to avoid damage to the original framework. To assess this we performed solvent exchange experiments with ethanol, acetone, and chloroform. The XRD patterns in Fig. 2 show a comparison between MOF-5 that has undergone solvent exchange (LT-C, LT-A, and IT-A) and MOF-5 containing the original solvent (NMP; LT-N and IT-N). In the former, the peaks at $2\theta = 8.6^\circ$ increased significantly whereas the peaks at $2\theta = 9.5^\circ$ decreased. In addition, the SEM images in Fig. 5 indicate changes in the surface roughness following solvent exchange and the TGA results (Fig. 4) show the weight loss at temperatures less than 240 °C was 27.7% for the MOF-5 without solvent exchange, but only 10.0% with solvent exchange, suggesting it is easier to remove NMP using ethanol, acetone or chloroform in a post-synthesis step. This also results in an increase in the apparent surface area, possibly due to increased sensitivity to atmospheric conditions following exposure during the solvent exchange process. Panella et al. [24] reported on the sensitivity of MOF-5 following exposure to atmospheric conditions and reported that, following exposing of MOF-5 samples to air for 6 weeks a qualitatively different XRD pattern was obtained, indicative of sample instability. The Langmuir surface area of the decomposed sample also decreased from 1014 m^2/g

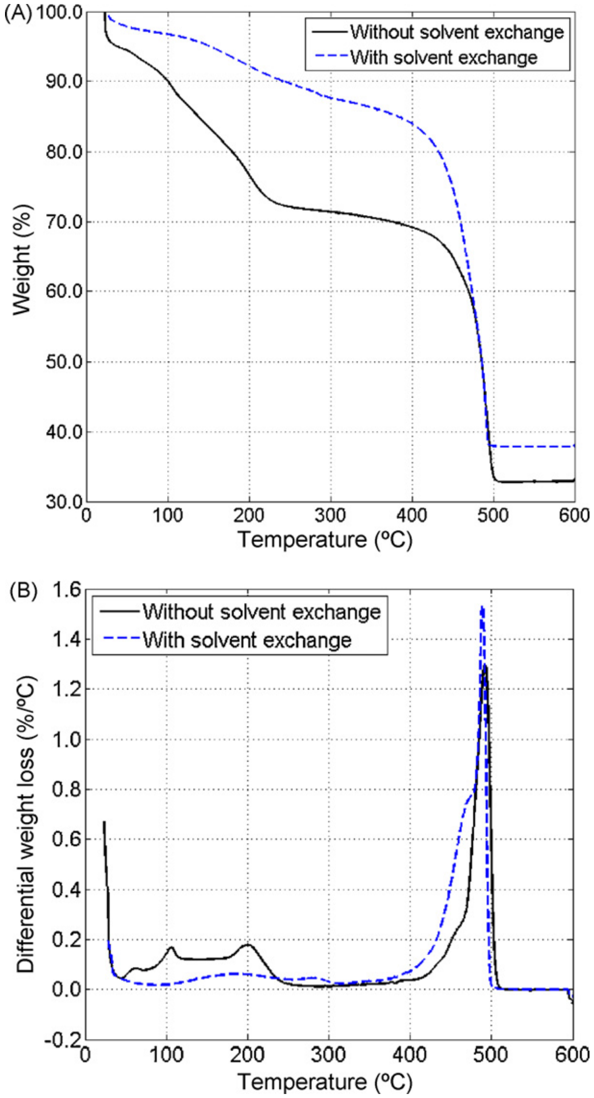

Fig. 4. Weight loss (A) and differential weight loss (B) profiles measured using thermogravimetric analysis of the MOF-5 products synthesised under microwave irradiation at an isothermal temperature of 105 °C for 30 min showing the influence of solvent exchange. The solid line represents the sample washed with NMP during filtration without any additional solvent exchange and the dashed line is for the sample washed with NMP followed by solvent exchange with ethanol.

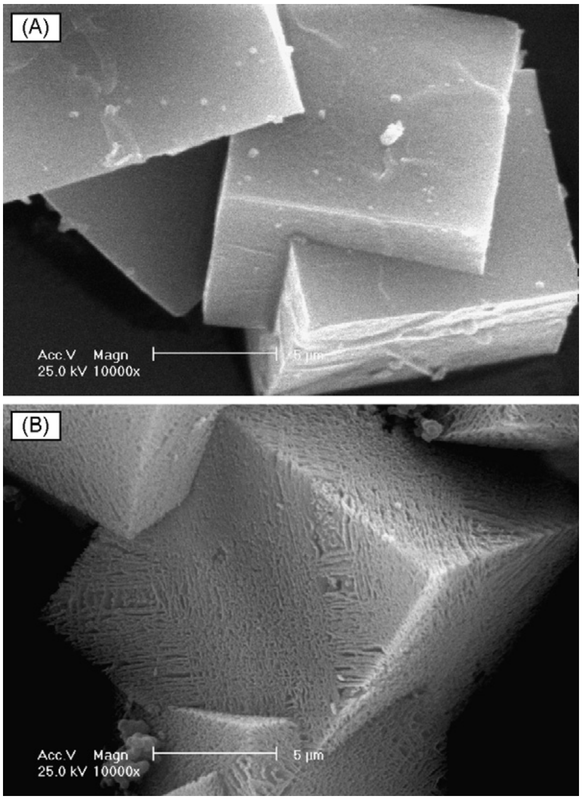

Fig. 5. SEM micrographs of the surface of individual MOF-5 crystals for samples synthesised under microwave irradiation at an isothermal temperature of 105 °C for 30 min. (A) A sample washed with NMP during filtration without further solvent exchange and (B) a sample washed with NMP followed by solvent exchange with ethanol.

to 570 m^2/g. Hence to maintain the quality and sorption capacity of the MOF-5 crystals, both an appropriate solvent and storage conditions are required.

CO_2 adsorption isotherms for the microwave-irradiated sample IT-N were measured from vacuum to 1 atm at 0 °C, 30 °C, and 40 °C (Fig. 6). All isotherms showed type I behavior, characteristic of microporous materials. It has previously been reported that MOFs show potential for pressurised gas storage, e.g. Millward and Yaghi [17], reported that MOF-5 at 35 bar and ambient temperature has the ability to absorb CO_2 at 21.7 mmol/g. While these conditions are appropriate for high pressure applications, e.g. pressure swing adsorption, there is no data of the CO_2 capture capacity of MOF-5 at ambient pressure, nor any on its ability to capture and release CO_2 across multiple cycles. To assess these we modified an existing technique [32] using an atmospheric pressure thermogravimetric analyser (Fig. 7) as follows:

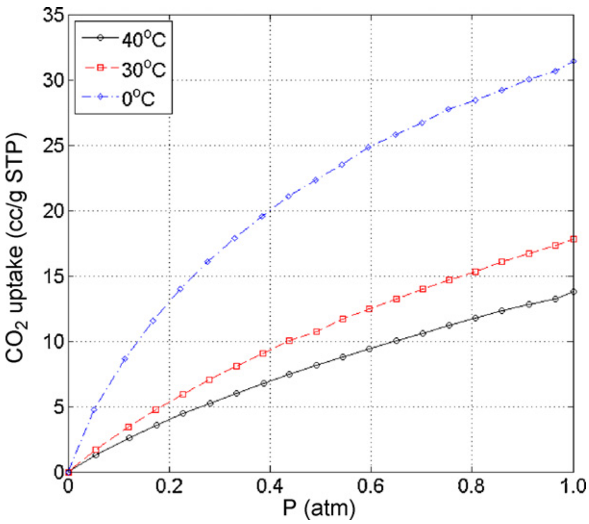

Fig. 6. CO_2 adsorption isotherms for sample IT-N at 0 °C, 30 °C and 40 °C. Sample IT-N was synthesised under microwave irradiation at an isothermal temperature of 105 °C for 30 min.

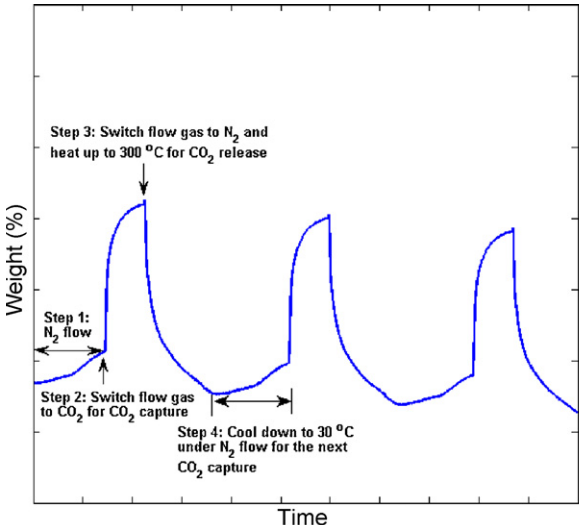

Fig. 7. Methodology for measuring the CO_2 adsorption across multiple cycles using the TGA instrument.

Step 1: Prior to commencing measurement of the CO_2 adsorption capacity, samples were degassed at 120 °C (10^{-5} Torr) for 12 h. The 5 mg samples were dispersed evenly on a platinum pan and purged under N_2.
Step 2: The gas flow was then switched from N_2 to CO_2 until the weight reached steady state, indicating the maximum capacity of the sorbent has been reached.
Step 3: The gas flow was then switched to N_2 and the sample heated at a rate of 5 °C/min to 300 °C to initiate CO_2 release from the framework. The N_2 flow at 300 °C was maintained for 10 min.

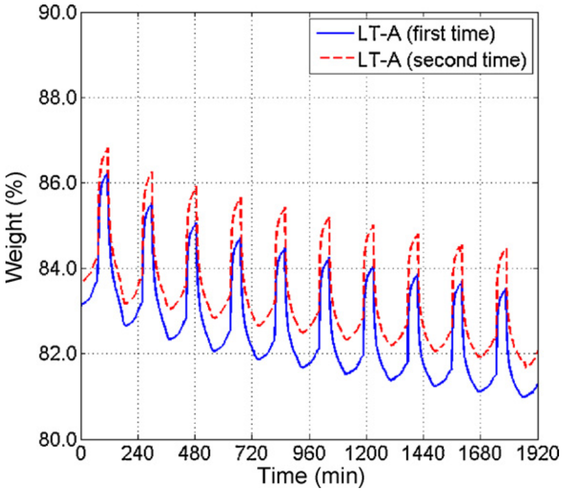

Fig. 8. Multiple CO_2 capture and release cycles using MOF-5 (LT-A) measured using the TGA apparatus. Sample LT-A was synthesised under microwave irradiation at a linear temperature ramp from 105 °C to 130 °C for 30 min followed solvent exchange with acetone. Data for two sets of sequential cycles are shown.

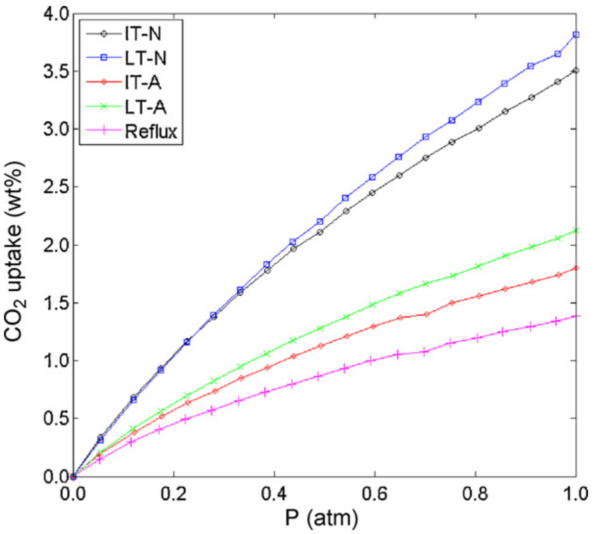

Fig. 9. CO_2 adsorption isotherms for the various MOF-5 samples measured using physisorption at 30 °C. LT—synthesised under microwave irradiation at a linear temperature ramp from 105 °C to 130 °C; N—sample washed with NMP without further solvent exchange; A—sample washed with NMP, followed by solvent exchange with acetone. IT—synthesised under microwave irradiation at an isothermal temperature of 105 °C; Reflux—synthesised using a conventional reflux apparatus at 105 °C for 4 h.

Step 4: Finally, the sample was cooled to 30 °C under N_2 in preparation for the next CO_2 capture cycle. Steps 2, 3 and 4 were repeated up to 10 times (Fig. 8).

In order to ensure methodological reliability, sample LT-A was then processed through two sets of 10 cycles as indicated above. The maximum measured uptake of CO_2 was 3.6%. We then compared this data with CO_2 physisorption measurements (Fig. 9 and Table 1) which showed consistency between the techniques. For comparison, the mesoporous silica MCM-41 and a multi-walled carbon nanotube (CNT) sample were also subjected to the same set of cyclic conditions. MOF-5 showed superior capacity for CO_2 across multiple cycles at atmospheric pressure compared with both the MCM-41 (1.45 wt%) and the CNT sample (0.55 wt%).

4. Conclusions

The metal-organic framework, MOF-5 ($Zn_4O(BDC)_3$) was synthesised by two different methods; a standard refluxing technique and under microwave irradiation in batch pressure vessels. The microwave-assisted method produced higher quality crystal structures, with better CO_2 adsorption properties in considerably less time than the reflux apparatus. Furthermore, the refluxed sample showed lower capacity for CO_2 than either of the microwave-irradiated samples. New data for CO_2 capture at ambient pressure showed good agreement volumetric and gravimetric assessment methods for CO_2 capture capacity, up to 3.8 wt% CO_2 at atmospheric pressure and up to 300 °C.

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