Sonochemical synthesis of MOF-5†

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High quality MOF-5 crystals of 5–25 μm in size were prepared for the first time using a sonochemical method in substantially reduced synthesis time (*ca.* 30 min) compared with conventional solvothermal synthesis (24 h).

Metal organic frameworks (MOFs) are a class of crystalline porous materials that are usually obtained by solvothermal reactions between metal ion salts and organic linkers. MOFs have attracted considerable scientific interest on account of their extremely high surface area and pore volume, which have potential applications in gas storage, separation, and heterogeneous catalysis.[1–4] In particular, several metal–organic crystalline solids have been highlighted recently for their high adsorption capacities[5–7] and selectivity[8,9] for CO_2, a greenhouse gas. Crystals composed of purely organic compounds are also being emerged for gas sorption.[10,11]

While there are a number of articles reporting new types of MOFs,[12,13] there are few reports on their synthesis. If one envisages industrial applications of functional MOFs, it is important to focus more attention on the synthesis of the materials. In this regard, alternative synthesis methods of MOFs, such as solvent-free synthesis,[14] microwave heating,[15–17] and electrochemical methods[18] deserve particular attention.

Sonochemical methods can lead to homogeneous nucleation and a substantial reduction in crystallization time compared with conventional oven heating when nanomaterials are prepared.[19,20] The main event in sonochemical synthesis or sonochemistry is the creation, growth, and collapse of a bubble that is formed in liquid, known as an acoustic cavitation, which generates extremely high local temperatures (5000–25 000 K) and pressures as well as an extraordinary heating and cooling rate.[21–24] The use of high-intensity ultrasound to enhance the reactivity of metals as a stoichiometric reagent has become a synthetic technique for many heterogeneous organic and organometallic reactions.[25–28] Suslick *et al.* reported a variety of sonochemical reactions in liquid–solid mixture synthesis, *i.e.* intercalation into layered inorganic solids, synthesis of amorphous metal powders,[19] and metal semicarbides.[24]

In the present work, a sonochemical technique was applied to the synthesis of MOFs, for the first time. MOF-5, having a simple cubic framework of zinc oxo clusters and terephthalate linkers and is a prototype material for a series of isoreticular MOFs, is chosen for this purpose. Here, the effects of various sonochemical synthesis parameters on the MOF-5 crystal properties were examined, and the properties of the sample were compared with those of a MOF-5 sample prepared using a conventional solvothermal method. In addition, 1-methyl-2-pyrrolidone (NMP) was used as the solvent because it is substantially more economical than the diethylformamide (DEF) used in previous work.[1,18]

The sonicator used in this study was a SONOPLUS HD 2200 (Bandelin, Germany) with an adjustable power output (maximum 200 W at 20 kHz). A horn type tube Pyrex reactor was custom-made and fitted to the sonicator bar, and synthesis was carried out in N_2. As a standard synthesis condition, MOF-5 was prepared using 1.34 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, Sigma-Aldrich) and 0.25 g of terephthalic acid (H_2BDC, 98%, Sigma-Aldrich). These reactants were dissolved in 40 ml of NMP (99%, SamJun, EP grade) at a molar ratio of $Zn(NO_3)_2 \cdot 6H_2O$: 0.33 H_2BDC: 25–90 NMP. The reaction mixture was stirred vigorously under nitrogen until a clear solution was obtained. The resulting solution was transferred to a 50 ml transparent horn type tube reactor and subjected to an ultrasonic treatment for 10 to 75 min at various power levels to obtain the MOF-5 crystals (hereafter, S-MOF-5). The substrate solution became increasingly dark with sonication, and white crystals began to precipitate in 8 to 30 min. As the power level was increased from 10 to 50% of the maximum power, the actual synthesis temperature attained increased from 129 to 164 °C with faster crystallization (see Table S1 in ESI†). For comparison, a MOF-5 sample was also prepared by convective heating (C-MOF-5) in an oven maintained at 105 °C in a 50 ml vial. The C-MOF-5 crystals began to form after 12 h and high quality crystals formed after 24 h.[5,17] For both S-MOF-5 and C-MOF-5, the remaining reactants were washed off with neat NMP, and the NMP was completely exchanged with chloroform by repeated decanting and immersion. The crystals were stored in chloroform for 2 days and finally vacuum-dried (5×10^{-3} Torr) at 120 °C for 24 h.

According to the PXRD patterns of the samples obtained at different power levels shown in Fig. 1(a), most peaks of S-MOF-5 match well with those for MOF-5.[1] However, at power levels of 10 and 20%, XRD peaks not originating from MOF-5 were observed at $2\theta = 18$ and 26°. After examining the SEM images of those samples, it was established that those diffraction peaks were produced by impurity crystals with a plate morphology, which is quite different from the typical cubic MOF-5 crystals (Fig. S1, ESI†). The occurrence of these

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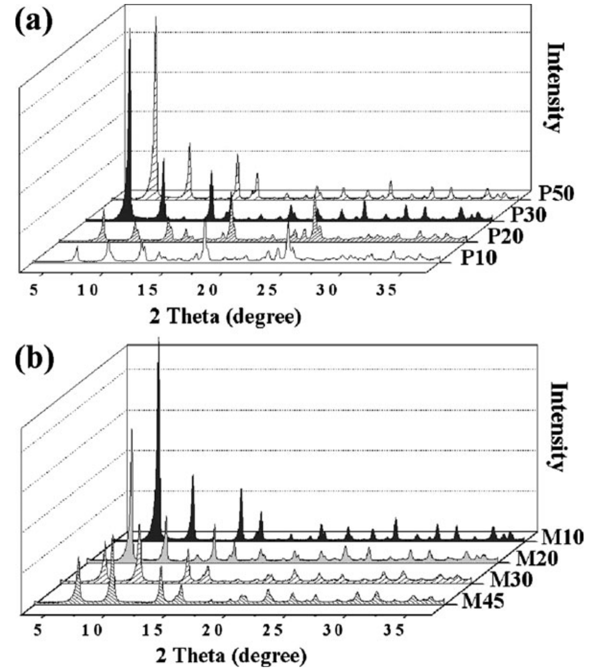

Fig. 1 PXRD patterns of the S-MOF-5 samples measured on a Rigaku diffractometer using Cu-Kα (λ = 1.5418 Å) radiation (a) at different power levels and (b) at different irradiation time at 30% maximum power level (P30), where P = power, M = sustained sonication time after the initial formation of white crystals is observed.

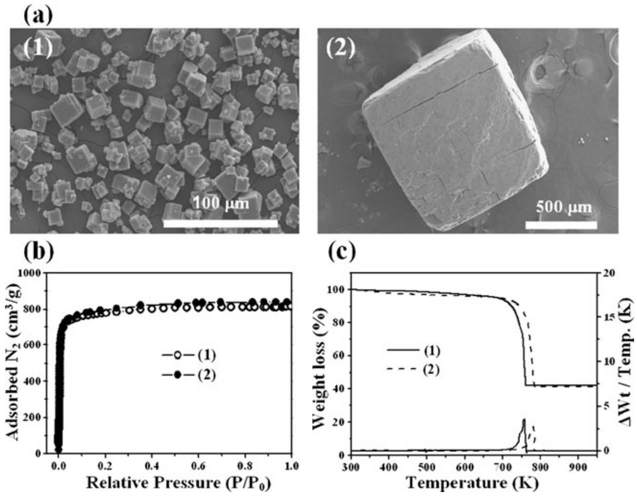

Fig. 2 Comparison of the physicochemical properties between S-MOF-5(1) and C-MOF-5(2): (a) SEM images, (b) N_2 adsorption isotherms, and (c) thermogravimetric analysis. S-MOF-5 was prepared at a 30% power level for 10 min sonication after observing the initial formation of white crystals. SEM analysis of the morphological features was carried out using a Hitachi S-4200 instrument.

impurity crystals were suppressed by increasing the power, and virtually homogeneous cubic crystals were obtained at both 30 and 50% power levels (P30 and P50, respectively, in Fig. 1(a)).

After fixing the sonic power level at 30%, the duration of the sonic treatment (M) was varied from 10 to 45 min. As shown in Fig. 1(b), high quality MOF-5 crystals were obtained after maintaining the sonication treatment for 10 min (M = 10) after observing initial crystal formation. However, further increases in irradiation time quickly deteriorated the crystal quality (see Fig. S2, ESI†), which might be due to the high temperatures generated by the prolonged irradiation. The textural properties of the S-MOF-5 samples deteriorated in accordance with the crystal quality observed by the XRD patterns at different sonication times (Table S2, ESI†).

Fig. 2(a–1) and (a–2) show the SEM images of the S-MOF-5 and C-MOF-5 samples. Both samples were single phase cubic crystals but S-MOF-5 was 5–25 μm in size, which is approximately 60 times smaller than C-MOF-5 (*ca.* 900 μm) on average. Such a size difference is commonly observed in sonochemistry.[20] In a typical solvothermal synthesis of MOF-5, the reaction temperature was kept near 100 °C, which is significantly below the 155 °C attained in the sonochemical synthesis condition (P30 and M10) for high quality S-MOF-5 crystals. When the reaction for C-MOF-5 was carried out at 155 °C, the quality of the crystals produced was inferior to the S-MOF-5: C-MOF-5 crystals showed a larger size with a distorted cubic morphology (see Fig. S3, ESI†).

The nitrogen adsorption isotherms of the S-MOF-5 and C-MOF-5 sample were obtained using a Micromeritics ASAP-2020 sorptometer at liquid nitrogen temperature. The samples were degassed at 120 °C for 24 h (5×10^{-3} Torr) before the adsorption measurements. The specific surface area of the samples was calculated using the Langmuir method. As shown in Fig. 2(b), both S-MOF-5 and C-MOF-5 samples exhibited type I isotherms with no hysteresis. S-MOF-5 had virtually the same textural properties to those of C-MOF-5. The Langmuir surface area of S-MOF-5 was 3208 $m^2 g^{-1}$ with a total pore volume of 1.26 $cm^3 g^{-1}$, while the corresponding values for C-MOF-5 were 3200 $m^2 g^{-1}$ and 1.21 $cm^3 g^{-1}$, respectively. Fig. 2(c) shows the thermogravimetric analysis results of S-MOF-5 and C-MOF-5. The thermal stability of the samples was tested using a thermogravimetric analyzer (TGA, SCINCO thermal gravimeter S-1000): 10 mg of the sample was heated at 10 °C min^{-1} to 700 °C under an airflow (30 ml min^{-1}). S-MOF-5 showed a steady continuous weight loss to *ca.* 430 °C followed by a sharp drop in weight at 430–470 °C. On the other hand, C-MOF-5 showed negligible weight loss until a sharp weight loss occurred within the temperature range of 450–520 °C. This minor difference in the TGA profiles was attributed to S-MOF-5 having a substantially smaller particle size than C-MOF-5.[17]

Usually, an organic liquid is not an effective medium for sonochemistry because the high vapor pressure of common organic solvents greatly reduces the intensity of cavitational collapse and hence the resulting temperatures and pressures.[29] However, NMP was proven effective as a synthesis medium for MOF-5, since the boiling point of NMP is 202 °C and its vapor pressure was sufficiently low under the MOF-5 synthesis conditions used in this study (155 °C). In addition, it was not necessary to place a cooling water bath over the sonochemical synthesis vessel. In fact, the synthesis temperature decreased when external water cooling was applied, and MOF-5 crystals could not be obtained even at a 70% power level.

Typically, high quality MOF-5 crystals were obtained using DEF as the solvent, which is costly even for industrial grade. In order to confirm the effect of the solvent on MOF-5

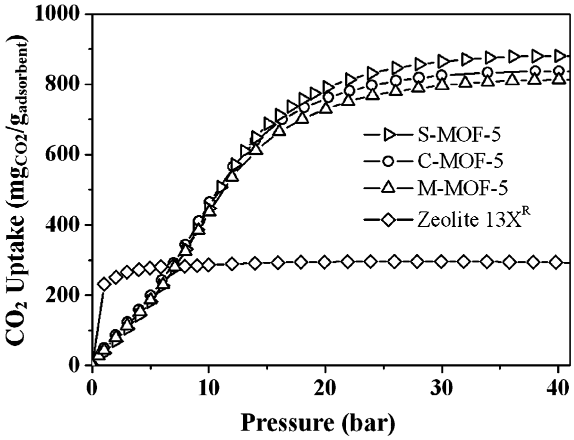

Fig. 3 CO_2 high-pressure isotherms of the MOF-5 samples at 25 °C: S-MOF-5, C-MOF-5 and M-MOF-5 samples were synthesized by sonochemical, solvothermal and microwave heating, respectively.

synthesis, S-MOF-5 was also prepared using DEF as the solvent. With DEF, it took *ca.* 30 min to observe the initial crystal formation (8 min with NMP), and the resulting crystal quality was not as good as that prepared in NMP (see Fig. S4, ESI†) because of the relatively low boiling point of DEF (177 °C). Indeed, superior performance of NMP to DEF in MOF-5 preparation is a unique feature in sonochemical synthesis. In addition, S-MOF-5 was prepared with different amounts of NMP ranging from 25–75 in molar ratio (see Fig. S5†), which confirmed that more dilute synthesis conditions are desirable for producing better quality MOF-5 crystals.[17]

Finally, the high-pressure CO_2 adsorption isotherm of a S-MOF-5 was measured using a magnetic suspension balance (Rubotherm, Germany) with *in situ* density measurements in a closed system. The samples were initially conditioned at 120 °C in a vacuum (5×10^{-3} Torr) for 24 h. High-pressure adsorption was carried out using ultra high purity CO_2 in the pressure range 0–40 bar at 25 °C. Fig. 3 shows the CO_2 adsorption isotherms of S-MOF-5 and C-MOF-5, which yielded 880 and 837 mg CO_2 g^{-1}, respectively, at 40 bar. After reaching *ca.* 80% of the maximum adsorption capacity at 17 bar, the amount of adsorbed CO_2 began to increase only moderately.

Also plotted in Fig. 3 is a high-pressure CO_2 adsorption isotherm for a MOF-5 sample prepared by us earlier[17] using microwave heating (M-MOF-5). Whilst the differences in adsorption capacity should be interpreted with caution, Fig. 3 indicates that the sonochemical method is a effective synthesis technique for MOFs. The CO_2 capacity of commercial zeolite 13X is *ca.* 289 mg g^{-1} at 10 bar and saturates to 78% of the maximum capacity at 1 bar.

In summary, MOF-5 crystals were prepared for the first time using a sonochemical method (S-MOF-5). The synthesis time for MOF-5 was reduced substantially and significantly smaller crystals were obtained. Their physicochemical properties were similar to those of crystals prepared under conventional convective heating (C-MOF-5). Sonochemical synthesis of MOF-5 has many benefits. Equipment is cheaper than a microwave unit and power consumption is very low, since no induction period is needed before sonicator stabilization and the synthesis time is very short. Successful implementation of economical 1-methyl-2-pyrrolidone (NMP) as a synthesis solvent for MOF-5 instead of DEF is an added advantage of this solvothermal synthesis, which can be beneficial in the large scale production.

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