CHEMISTRY OF MATERIALS

Communication

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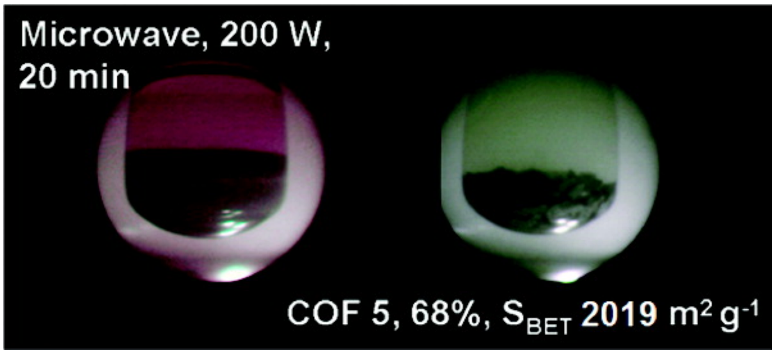
Chem. Mater., **Article ASAP** • DOI: 10.1021/cm802981m



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Rapid Microwave Synthesis and Purification of Porous Covalent Organic Frameworks

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Received November 2, 2008
Revised Manuscript Received December 11, 2008

There has been a great deal of interest recently in microporous materials such as crystalline metal organic frameworks (MOFs)[1] and amorphous microporous organic polymers.[2] The first "covalent organic frameworks"[3] (COFs) were reported in 2005. COFs are crystalline porous aromatic framework materials linked by boroxine or boronate-ester groups. Since this initial report,[3] a number of other studies have described crystalline boroxine or boronate-ester COFs,[4,5] with apparent Brunauer−Emmett−Teller (BET) surfaces areas (S_{BET}) of up to 4210 m^2 g^{-1} in some cases (COF-103).[5] This is interesting, for example, in terms of the potential of these materials for gas physisorption.[6] The first COF (COF-1)[3] was synthesized by solvothermal self-condensation in sealed pyrex tubes of 1,4-benzenediboronic acid (BDBA). The product was reported to be a staggered $P6_3/mmc$ hexagonal layered material linked by planar boroxine rings ($S_{\mathrm{BET}} = 711$ m^2 g^{-1}). COF-5 was mesoporous ($S_{\mathrm{BET}} = 1590$ m^2 g^{-1}) and had an eclipsed boron nitride arrangement.[3] Choice of solvent was important, as was control over reaction rates to ensure that the thermodynamic, ordered crystalline products are obtained. The use of a sealed reaction vessel ensured that H_2O was available to maintain reversible conditions. These considerations (solubility, reaction rates, nucleation and growth, ability of structures to 'self-heal') are likely to be generally important for the synthesis of any ordered, crystalline porous polymers. Subsequent COFs were also synthesized solvothermally in sealed tubes (reaction times typically 72 h) under a variety of conditions.[4,5]

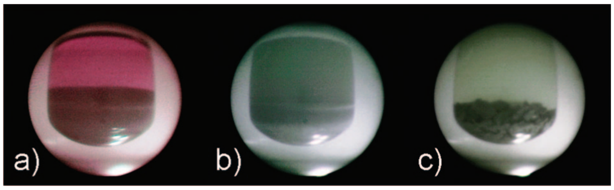

Figure 1. Digital camera images recorded from the observation port of the microwave reactor showing COF-5 reaction and purification: (a) gray-purple COF-5 powder formed after initial synthesis; (b) removal of trapped HHTP-oxidation impurities by microwave extraction process (acetone); (c) second microwave extraction results in purified gray COF-5 powder ($S_{\mathrm{BET}} = 2019$ m^2 g^{-1}).

Microwave reactors are well-known for their impact on small molecule organic chemistry due to accelerated reaction times, cleaner products, and higher yields in many cases.[7] Less-emphasized advantages of using microwave reactors are the potential for continual online monitoring, simultaneous control of reaction temperature and pressure, and (recently) visual monitoring of the phase behavior in reactions. There are an increasing number of reports concerning the synthesis of organic polymers by microwave heating[8] but much less attention has been given to microporous materials. Notably, Ni and Masel synthesized IRMOF materials using microwaves,[9] and recently, Bae et al. have used microwave heating to produce MOFs with very high CO_2/CH_4 gas separation selectivities.[10] We synthesized COF-5[3] under microwave heating conditions by preparing in a 3:2 molar ratio solution of 1,4-benzenediboronic acid (BDBA; 185 mg, 1.116 mmol) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP; 241.5 mg, 0.745 mmol) in a 1:1 mixture of mesitylene: 1,4-dioxane (20 mL). This mixture was sealed under nitrogen in a 35 mL glass microwave tube and heated by microwave irradiation at 100 °C with stirring for 20 min at a power of 200 W using a CEM S-Class Explorer 96-position microwave reactor with digital camera attachment. A gray precipitate was observed to form in the reaction vessel (Figure 1a). The supernatant solution became purple in color which we ascribe to the formation of an oxidized form of HHTP.[3]

The resulting gray-purple powder was filtered under nitrogen and washed with acetone which had first been dried over 5 Å molecular sieves. To further purify the product and

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(1) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705−714.

(2) (a) Jiang, J. X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z.; Cooper, A. I. *Angew. Chem., Int. Ed.* **2007**, *46*, 8574–8578. (b) Kuhn, P.; Antonietti, M.; Thomas, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3450–3453. (c) Jiang, J-X.; Su, F.; Trewin, A.; Wood, C. D.; Niu, H.; Jones, J. T. A.; Khimyak, Y. Z.; Cooper, A. I. *J. Am. Chem. Soc.* **2008**, *130*, 7710. (d) Makhseed, S.; Samuel, J. *Chem. Commun.* **2008**, 4342–4344, DOI: 10.1039/b805656k. (e) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, 230. (f) McKeown, N. B.; Gahnem, B.; Msayib, K. J.; Budd, P. M.; Tattershall, C. E.; Mahmood, K.; Tan, S.; Book, D.; Langmi, H. W.; Walton, A. *Angew. Chem.* **2006**, *118*, 1836;Angew. Chem. Int. Ed. **2006**, 45, 1804.

(3) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170.

(4) (a) Tilford, R. W.; Gemmill, W. R.; zur Loye, H. C.; Lavigne, J. J. *Chem. Mater.* **2006**, *18*, 5296–5301. (b) Côté, A. P.; El-Kaderi, H. M.; Furukawa, H.; Hunt, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2007**, *129*, 12914–12915. (c) Hunt, J. R.; Doonan, C. J.; Le Vangie, J. D.; Côté, A. P.; Yaghi, O. M.; Mastalerz, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 445–447.

(5) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortes, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316*, 268–272.

(6) (a) Li, Y. W.; Yang, R. T. *AIChE J.* **2008**, *54*, 269–279. (b) Han, S. S.; Furukawa, H.; Yaghi, O. M.; Goddard, W. A., III *J. Am. Chem. Soc.* **2008**, *130*, 11580–11581.

(7) Kappe, C. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250–6284.

(8) (a) Wiesbrock, F.; Hoogenboom, R.; Schubert, U. S. *Macromol. Rapid Commun.* **2004**, *25*, 1739–1764. (b) Germain, J.; Svec, F.; Fréchet, J. M. J. *Chem. Mater.* **2008**, *20*, 7069–7076. (c) Brown, S. L.; Rayner, C.; Graham, S.; Cooper, A. I.; Rannard, S.; Perrier, S *Chem. Commun.* **2007**, *21*, 2145–2147.

(9) Ni, Z.; Masel, R. I. *J. Am. Chem. Soc.* **2006**, *128*, 12394–12395.

(10) Bae, Y. S.; Mulfort, K. L.; Frost, H.; Ryan, P.; Punnathanam, S.; Broadbelt, L. J.; Hupp, J. T.; Snurr, R. Q. *Langmuir* **2008**, *24*, 8592–8598.

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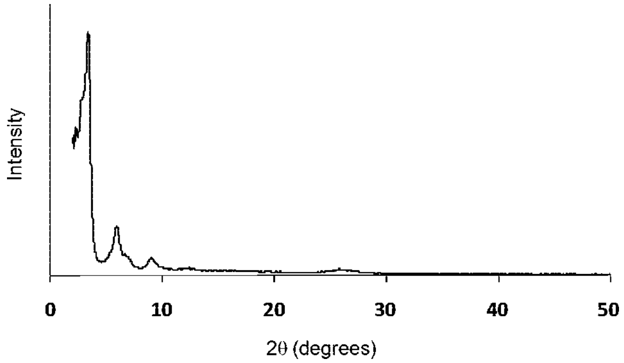

Figure 2. Powder diffraction pattern for COF-5 produced by microwave technique.

to remove any starting materials or impurities trapped in the porous structure, the microwave reactor was employed for extraction purposes by heating the isolated COF-5 powder with 30 mL of dried acetone (55 °C, 20 min, 200 W). This extraction was repeated twice (images b and c in Figure 1) and this was found to remove all of the purple coloration (Figure 1c). The final purified COF-5 was isolated as a gray solid in 68% yield (235 mg) based on the starting materials.

Powder X-ray diffraction (PXRD) data was obtained for the material from the loose powder mounted on a zero background holder, measured in reflection geometry (PANalytical MPD diffractometer). The diffraction pattern (Figure 2) confirmed the crystallinity of the material and revealed no diffraction peaks which could be attributed to the starting materials. The diffraction pattern was comparable to that published previously.[3]

The sample was dried in a vacuum desiccator (24 h) and then transferred to a standard gas sorption sample holder for outgassing at 90 °C under dynamic vacuum (1×10^{-5} bar). High levels of porosity were confirmed by measuring the N_2 gas adsorption/desorption isotherm for the desolvated material at 77.3 K (Figure 3a). The isotherm shape was reversible type IV and essentially identical to that reported previously,[3] including the characteristic "double step" in the relative pressure range $P/P_o = 0-0.2$.

The BET model was applied to these data over the same relative pressure range reported previously[3] ($P/P_o = 0.05-0.1$), which resulted in an apparent BET surface area of 2019 $m^2\ g^{-1}$ (correlation coefficient = 0.998).[11] This is significantly higher than the reported S_{BET} for COF-5 of 1590 $m^2\ g^{-1}$.[3] In principle, this might be explained by different particle sizes. Indeed, SEM analysis (images b and c in Figure 3) suggested that the primary particulate size (<500 nm, Figure 3c) might be rather smaller than that observed for COF-5 produced using solvothermal methods.[3] We suggest, however, that the microwave solvent extraction method (see discussion above) leads to more efficient removal of residues or better preservation of porosity. This is supported by the increase in surface area of COF-5 after microwave purification from 901 m^2/g (as synthesized, no extraction) to 1467 m^2/g (after first extraction using microwave) to the final surface area of 2019 m^2/g after the second purification step. Experiments are currently underway to deconvolute these possible influences. The 20 min reaction time achieved by microwave heating is more than 200 times faster than the reported solvothermal reaction time of 72 h.[3,12] From a safety perspective, microwave synthesis under these conditions was found to generate only a very small over pressure (≤0.1 bar) within the sealed reaction vessel. This observation prompted us to study the reaction in an open vessel using microwave heating. To do this, a 100 mL round-bottom flask equipped with reflux condenser and magnetic stirring bar was fitted into the microwave reactor cavity. The reaction was carried out under similar reaction conditions to those employed in the sealed vessel (40 mL 1:1 mixed solvent; 500 mg monomers total; 100 °C; 200 W; continual stirring; 20 min.). The material was purified by washing with dried acetone.[3] Again, COF-5 was isolated as a pale gray powder, this time in 95% yield based on the BDBA monomer. The analytical data for this material (FTIR, PXRD) were comparable to those obtained for the material produced by microwave heating in a sealed reaction vessel. The BET model was applied to these data over the same relative pressure range reported previously[3] ($P/P_o = 0.05-0.1$) which resulted in an apparent BET surface area of 2027 $m^2\ g^{-1}$ (correlation coefficient = 0.998) (see the Supporting Information). The success of this open vessel approach demonstrates that an overpressure is not required in these syntheses.[13] This result

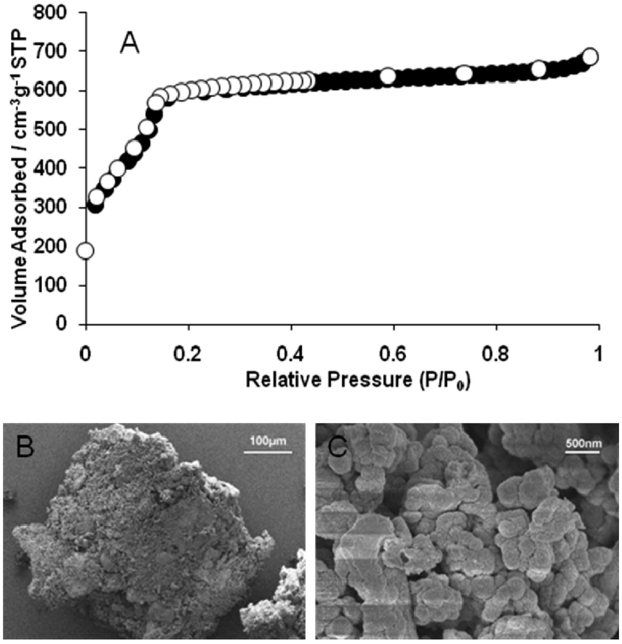

Figure 3. Physical characterization of microwave synthesized COF-5 material. (a) N_2 gas adsorption isotherms for COF-5 measured at 77.3 K; (b, c) FE-SEM images of microwave-synthesized COF-5 showing (b) bulk powder agglomerates and (c) nanoscale morphology.

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[11] S_{BET} can vary with the relative pressure range chosen for the calculation. We determined two other values as follows: (i) $P/P_o = 0.05-0.2$; $S_{BET} = 2234\ m^2\ g^{-1}$; correlation coefficient = 0.991; (ii) $P/P_o = 0.05-0.3$; $S_{BET} = 1945\ m^2\ g^{-1}$; correlation coefficient = 0.993. We report here S_{BET} calculated over the same relative pressure range used to characterize COF-5 (ref 3), which does also give rise to the highest correlation coefficient (0.998).

[12] It is not clear that all of the solvothermal syntheses reported for COF (and MOF) materials actually require the full reaction time that is specified. This highlights an additional advantage of this particular microwave reaction system; that is, the ability to continuously observe the contents of the reactor (Figure 1) and to ascertain whether or not a product has formed.

does not, however, disprove the need for H_2O to facilitate reversibility because the reflux condenser retains any condensate quite efficiently in the reaction flask.

In addition to the synthesis of COF-5, microwave heating was utilized to synthesize COF-102, showing that this method is applicable to the synthesis of both 2D and 3D COFs. COF-102 was prepared by the self-condensation of tetraphenyl boronic methane (200 mg) in a 1:1 mixture of mesitylene: 1,4-dioxane (20 mL). This mixture was sealed under nitrogen in a 35 mL glass microwave tube and heated by microwave irradiation at 100 °C with stirring for 20 min at a power of 200 W. The resulting white powder was filtered under nitrogen and washed with THF (anhydrous). The microwave reactor was again employed for extraction purposes by heating the isolated COF-102 powder with 30 mL of dried THF (65 °C, 20 min, 200 W). An apparent BET surface area, S_{BET}, of 2926 $m^2\ g^{-1}$ (correlation coefficient = 0.999) was obtained by N_2 adsorption. This is broadly comparable to the S_{BET} of 3472 m^2/g reported for COF-102 prepared by conventional solvothermal methods as analyzed by Ar adsorption.[3] The PXRD and FTIR of COF-102 are comparable to those reported previously in the literature (see the Supporting Information). Interestingly, measurements suggested quite low hydrogen uptakes for COF-102, at least at low pressures (<1.7 wt % at 1 bar, 77.3 K). This is surprising given the very high surface area and might be attributed to the apparently low isosteric heat of sorption for H_2 on this material (−6.5 kJ/mol, see the Supporting Information, Figures S20 and S21).

In conclusion, mild microwave synthesis offers a highly convenient method for the rapid production of COFs − in this case, 200 times faster than solvothermal methods[3] − both in sealed and in unsealed reaction vessels. The frameworks produced have physical properties that are comparable to materials prepared by solvothermal synthesis and, potentially, surface areas that are somewhat higher in the case of COF-5. The precise origin of this latter effect requires further elucidation but may be related to the microwave extraction process. These microwave preparations are also particularly amenable to integration with high throughput synthesis protocols for the discovery on new materials. We believe that these synthesis protocols may supplant traditional solvothermal processes and are currently evaluating the applicability of such methods to a broader range of COFs and other microporous organic polymers.

Acknowledgment. We thank EPSRC (EP/C511794/1), NWDA, and ERDF for financial support.

Supporting Information Available: FTIR of starting materials, COF-5 (open and sealed vessel), and COF-102. FE-SEM of COF-5 and COF-102. Powder XRD analysis of starting materials, COF-5 (open and sealed vessel) and COF 102. Gas adsorption analysis; full isotherm and surface area for COF-5; and full isotherm, surface area, H_2 sorption, and heat of adsorption (H_2) for COF-102 (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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(13) COFs were also produced by conventional reflux heating for 72 h: Tilford, R. W.; Mugavero, S. J.; Pellechia, P. J.; Lavigne, J. J. *Adv. Mater.* **2008**, *20*, 2741–2746. Tilford, R. W.; Gemmill, W. R.; zur Loye, H. C.; Lavigne, J. J. *Chem. Mater.* **2006**, *18*, 5296–5301.