

Sonochemical Synthesis of $\text{Cu}_3(\text{BTC})_2$ in a Deep Eutectic Mixture of Choline Chloride/dimethylurea

Sun-Hee Kim, Seung-Tae Yang, Jun Kim, and Wha-Seung Ahn*

Department of Chemical Engineering, Inha University, Incheon 402-751, Korea. *E-mail: whasahn@inha.ac.kr
Received April 25, 2011, Accepted June 14, 2011

Key Words : $\text{Cu}_3(\text{BTC})_2$, Ionothermal synthesis, Deep eutectic mixture, Sonochemistry

Metal organic frameworks (MOFs) are a class of porous polymeric material composed of metal ions or clusters linked together by organic bridging ligands. Their large surface areas accompanied by uniform pores,¹ open metal sites,² and diverse available post-synthesis functionalization routes³ make MOFs promising candidate materials for gas storage, separation, and heterogeneous catalysis.⁴

MOFs are typically synthesized by solvothermal reactions in organic solvents or in water,⁵ but have also been prepared in ionic liquids (ILs) recently; examples of the latter include Cu-BTC (BTC: 1,3,5-benzenetricarboxylate),⁶ Ln-BTC,⁷ Cd-BTC,⁸ Zn-BTC,⁹ and others.¹⁰ ILs have been attracting increasing attention as a solvent of choice for chemical synthesis, because of their unique integration of various properties such as essentially zero vapor pressure, excellent solvating properties, easy recyclability, and high thermal stability.⁹ The majority of the reports dealing with MOF synthesis have focused on ILs derived from 1-alkyl-3-methylimidazolium.¹¹ However, deep eutectic solvents (DESs), mixtures of two or more compounds that have melting points lower than that of either of their constituents, are known to exhibit solvent properties very similar to those of ILs¹⁰ and have been employed for MOF synthesis.^{8,9} They have advantages over other types of ILs such as ease of preparation as pure phases from easily available components, low prices, and relative unreactivity towards atmospheric moisture.¹² DES can act as both a solvent and a ligand during the MOF synthesis.¹³

MOFs can be synthesized by sonochemical method which has exhibited rapid synthesis kinetics, uniform particle morphology, and excellent phase purity in inorganic materials synthesis.¹⁴ The sonochemical method promotes homogeneous nucleation and reduces crystallization time considerably¹⁵ via the creation, growth, and collapse of an acoustic cavity, generating extremely high temperature (5000-25000 K)/pressure as well as fast heating and cooling rates.¹⁶ In the sonochemical synthesis route, in connection with this reaction mechanism, DESs are thought to create cavitation easily at relatively high temperatures due to their low vapor pressures, and thus have good potential as a reaction medium in the sonochemical synthesis of nanomaterials.¹⁷

In this work, we have chosen the widely investigated $\text{Cu}_3(\text{BTC})_2$ as a representative MOF material for sonochemical synthesis using choline chloride/dimethylurea

DES as a solvent (designated as S-CuBTC). To the best of our knowledge, this is the first report of sonochemical synthesis of a MOF structure in a DES. Effects of various synthesis parameters on the crystallization process of $\text{Cu}_3(\text{BTC})_2$ were examined, and the properties of the sample were compared to those of $\text{Cu}_3(\text{BTC})_2$ prepared via a conventional ionothermal synthesis route in an oven (designated as C-CuBTC).

In order to use MOFs for adsorption, rigorous guest removal from the pores has to be performed so as to achieve the highest possible surface area (and pore volume). This is typically accomplished by solvent washing and vacuum treatment. Since the mixture of choline chloride and 1,3-dimethylurea in a molar ratio of 1:2 used in this work has a eutectic temperature of around 70 °C, removal of the solvent guest before it solidifies inside the pores is challenging. Thus, an effective activation procedure for $\text{Cu}_3(\text{BTC})_2$ samples obtained under ionothermal synthesis conditions was briefly examined by conducting repeated sample washing with de-ionized water and ethanol in the manner described in entries I to V in Table 1. No apparent PXRD patterns or morphology changes were observed after washing step II (see Figure S1 and S2). The corresponding SEM images after different washing steps did not reveal any noticeable differences either, except that the DES coated at the external surface in the $\text{Cu}_3(\text{BTC})_2$ sample was removed. However, repeated washing (200 mL \times 2) by de-ionized water and ethanol was necessary to obtain the BET surface area of a high quality $\text{Cu}_3(\text{BTC})_2$, as shown in Table 1. Elemental analysis of the C-CuBTC sample after washing treatment IV confirmed the virtual elimination of DES; The

Table 1. Textural properties of C-CuBTC samples after different sequential washing steps

Step	Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)
I	de-ionized water washing once	31	0.02
II	de-ionized water washing twice	1449	0.60
III	Step II + ethanol washing once	1809	0.76
IV	Step II + ethanol washing twice	1822	0.76
V	Step II + ethanol washing twice ^a	928	0.41

^awashing after the eutectic mixture product solution cooled down to room temperature.

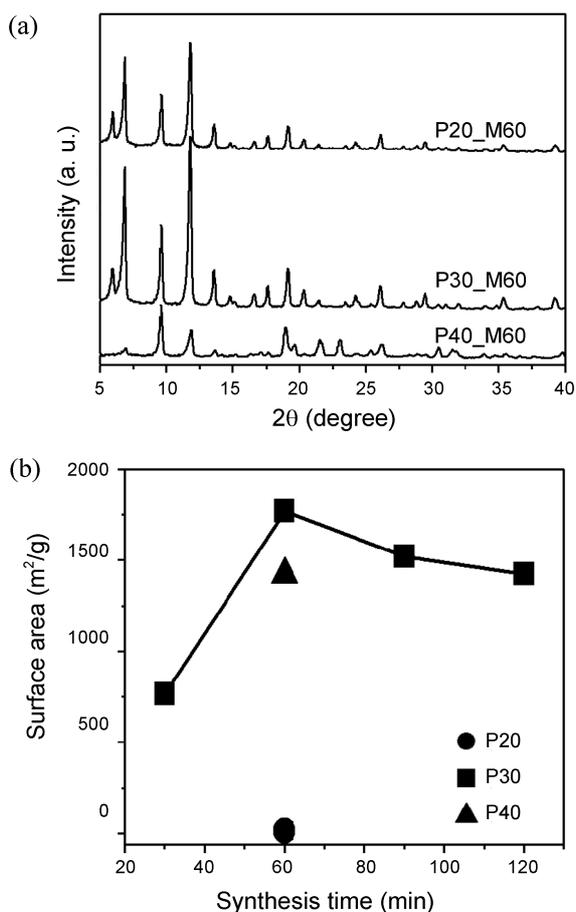


Figure 1. (a) PXRD patterns and (b) relationship between surface area and sonication time of S-CuBTC, where P = sonication power, M = sonication time.

elemental analysis results of C-CuBTC are as follows: C, 37.7; H, 5.3; N, 10.6%, S-CuBTC: C, 36.1; H, 5.2; N, 10.4% (after washing step I) and C-CuBTC: C, 30.4; H, 2.7; N, 0.2%, S-CuBTC: C, 30.0; H, 2.7; N, 0.0% (after washing step IV).

It was also noted that washing should be performed before the product/DES solution mixture is cooled below the eutectic temperature of the DES; once solidified, the same washing treatment resulted in only partial recovery of the BET surface area due to occlusion of DES molecules (Step V in Table 1).

The PXRD patterns and the BET surface areas of the S-CuBTC samples obtained at different synthesis times in sonochemical process is shown in Figure 1, where all the diffraction peaks could be indexed to crystalline Cu₃(BTC)₂.¹⁸ First, the synthesis time for S-CuBTC was found to be significantly reduced, from 36 to 1 h, compared with C-CuBTC. As the ultrasonic power level was varied at 20, 30, and 40%, the synthesis temperature increased steadily from 100 and 145 to 167 °C, respectively. However, the best quality MOF crystals in terms of PXRD intensity and the BET surface area were obtained at 30% ultrasonic power level, due to optimum cavitation.¹⁹ Usually, organic liquids are known to be an ineffective medium for sonochemistry,

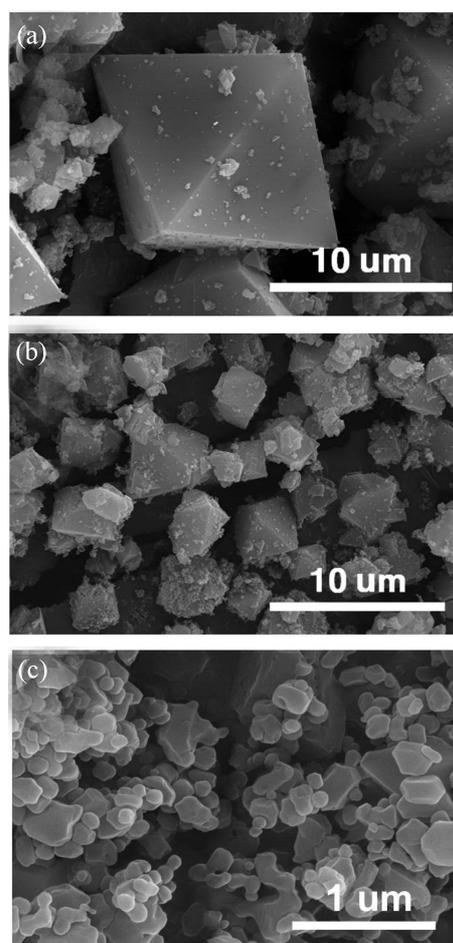


Figure 2. SEM images of (a) C-CuBTC, (b) S-CuBTC (P30_M60), and (c) S-CuBTC in a mixed solvent (de-ionized water:EtOH:DMF = 2:1:3, v/v).

because their high vapor pressures greatly reduces the intensity of cavitation collapse and hence the resulting temperatures and pressures.²⁰ DES, in this regard, was proven to be an effective synthesis medium for Cu₃(BTC)₂, since it has essentially zero vapor pressure.

Intensity of the PXRD peaks of S-CuBTC grew steadily with sonication time to a maximum value after 60 min at 30% ultrasonic power level, but started to decrease again afterwards up to 120 min (Figure S3). The BET surface area of the S-CuBTC also increased to the maximum level (1771 m²/g) in 60 min and then steadily decreased afterwards (see Table S1). This indicates that prolonged synthesis can lead to structural deterioration in MOFs.^{14a}

The morphologies of C-CuBTC and S-CuBTC, respectively, are shown in Figure 2. According to the SEM images, S-CuBTC crystals range in size from 3–5 μm, and are smaller than those synthesized using the conventional solvothermal method (10–30 μm). Such a size reduction is commonly observed in sonochemistry. Whilst a significant reduction in particle size (to 1/20–1/100 th) has been reported when sonochemical was applied to the synthesis of MOF-5 or -177 in organic solvents,^{14a,b} a lesser extent of size reduction (to 1/3–1/6 th) was observed for Cu₃(BTC)₂ in DES in

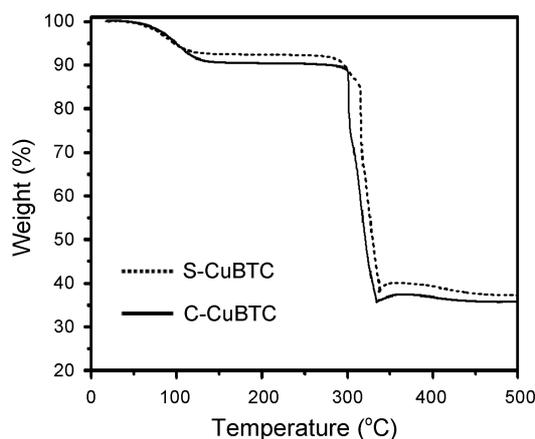


Figure 3. TGA measurement profiles of CuBTC samples prepared by different synthesis methods.

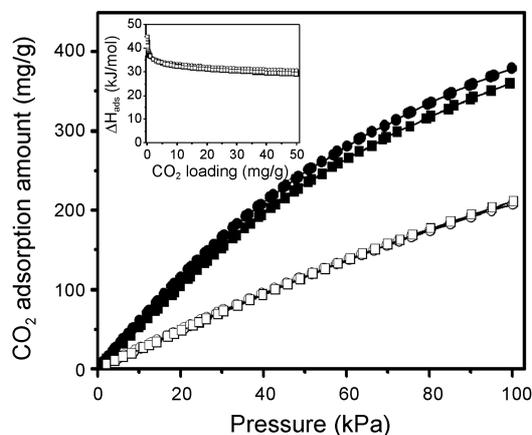


Figure 4. CO₂ adsorption isotherms of (■□) C-CuBTC, and (●○) S-CuBTC samples at different adsorption temperature (closed symbols: 0 °C; open symbols: 25 °C). Inset shows corresponded heats of adsorption.

this work. Furthermore, the CuBTC sample sonochemically prepared in a mixed organic solvent²¹ (Figure 2(c)) also produced smaller crystals than those of S-CuBTC prepared in DES (Figure 2(b)). These size changes can be attributed to the higher viscosity of DES, which would slow down the rate of nucleation.²²

Figure 3 shows the TGA analysis results for the CuBTC samples. C-CuBTC showed 10 wt % loss until a sharp loss occurred within a temperature range of 300–330 °C. S-CuBTC also showed 7 wt % loss to *ca.* 320 °C, followed by a sharp drop in weight in a temperature range of 320–330 °C. Thus, it was established that the thermal stability of S-CuBTC is close to that of C-CuBTC despite the crystal size of S-CuBTC being smaller than that of C-CuBTC.

Finally, a series of CO₂ adsorption isotherms for the CuBTC samples were measured and the results are compared in Figure 4. All samples exhibited high adsorption capacities for CO₂ (208, and 211 mg/g, respectively, for C-, and S-CuBTC at 25 °C). All the experimental adsorption data were fitted to the Langmuir-Freundlich equation. The heats of adsorption were then calculated by applying the

Clausius-Clapeyron equation (Eq. (1)) at low-loading regions (< 50 mg/g), as delineated below, and the results are plotted in the inset of Figure 4.

$$\left[\frac{\partial \ln P}{\partial (1/T)} \right]_q = \frac{-\Delta H}{R} \quad (1)$$

where P is pressure, T is temperature, q is the amount adsorbed, R is the gas constant, and ΔH denotes the heat of adsorption. The heats of adsorption extrapolated to zero coverage were in a range of 43.0–44.6 kJ/mol, and the asymptotic heat of adsorption values estimated were 30.2, and 28.9 kJ/mol for C-CuBTC, and S-CuBTC, respectively. Therefore, virtually identical adsorption properties were established for all three kinds of CuBTC samples prepared by different methods.

In summary, high quality Cu₃(BTC)₂ metal organic framework samples were prepared by ultrasonic over a choline chloride/dimethylurea eutectic mixture in significantly reduced synthesis time accompanied by crystal size reduction. The prepared Cu₃(BTC)₂ crystals showed virtually identical BET surface areas and CO₂ uptake capacities to values reported in the literature to date for highly crystalline materials. Ionothermal synthesis of Cu₃(BTC)₂ using a recyclable DES as a solvent can be environmentally benign and less costly than that prepared using *N,N*-dimethylformamide (DMF), but the more demanding washing/activation process described herein needs to be addressed.

Experimental Section

Synthesis of CuBTC. In a typical synthesis, 2.54 g copper(II) nitrate hydrate (Sigma-Aldrich, 98%) and 1.05 g benzenetricarboxylic acid (H₃BTC, Sigma-Aldrich, 95%) were dissolved in a mixture of choline chloride (Sigma-Aldrich, ≥ 98%) and 1,3-dimethylurea (DMU, Sigma-Aldrich, 98%) in a molar ratio of 1:2 (10.00 and 12.60 g, respectively) and heated above the eutectic temperature (*ca.* 69–71 °C).^{10a} The substrate mixture was held at 100 °C for 36 h in a convection oven. For sonochemical synthesis, a liquid phase substrate mixture was transferred to a 50 mL transparent horn type custom-made Pyrex reactor fitted to an ultrasonic generator. The ultrasonic generator used was a VCX500 (SONICS, USA; maximum 500 W at 20 kHz). The solution mixture was subjected to ultrasonic treatment for 30 to 120 min at various power levels. All the product samples were washed with de-ionized water and ethanol before being cooled to room temperature, and dried at 80 °C for 5 h and activated at 180 °C for 12 h under vacuum (5×10^{-3} torr).

Characterization. The crystallinity of the CuBTC samples was measured by powder X-ray diffraction (PXRD) using CuK α ($\lambda = 1.54 \text{ \AA}$) radiation (Rigaku). Nitrogen adsorption-desorption isotherms were measured using a BELSORP-mini instrument (BEL Japan, Inc.) at 77 K. The specific surface area of the CuBTC samples was calculated by the Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy (SEM) was performed using a Hitachi S-4300

electron microscope. Elemental analyses were carried out using an EA-1112 (Thermo Electron Corp., USA). The thermal stability of the samples was evaluated using a thermogravimetric analyzer (TGA, SCINCO thermal gravimeter S-1000); 10 mg of the sample was heated at 10 °C/min to 500 °C under airflow (30 cm³/min).

CO₂ Adsorption-desorption Measurements. Adsorption isotherm data for CO₂ on each CuBTC sample were measured using a BELSORP-mini (BEL, Japan). Prior to the measurements, each sample was heated at 180 °C for 12 h under a vacuum condition. The sample was then maintained at 0 and 25 °C, respectively, during adsorption measurements using a constant temperature water bath equipped with ethanol coolant. Adsorption isotherms were obtained for each material at pressures up to 101.3 kPa.

Acknowledgments. This work was supported by the Carbon Dioxide Reduction & Sequestration R&D Center (CDRS) and Inha University in Korea.

References

1. Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.
2. Britt, D.; Furukawa, H.; Wang, D.; Glover, T. G.; Yaghi, O. M. *PNAS* **2009**, *106*, 20637.
3. Kitaura, R.; Fujimoto, K.; Noro, S.; Kondo, M.; Kitagawa, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 133.
4. (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Wang, Q. M.; Shen, D.; Bulow, M.; Lau, M. L.; Deng, S.; Fitch, F. R.; Lemcoff, N. O.; Semanscin, J. *Micropor. Mesopor. Mater.* **2002**, *55*, 217. (c) Alaerts, L.; Seguin, E.; Poelman, H.; Thibault-Starzyk, F.; Jacobs, P. A.; DeVos, D. E. *Chem.-Eur. J.* **2006**, *12*, 7353.
5. Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. *Science* **2005**, *309*, 2040.
6. Liu, L.; Wei, H.; Zhang, L.; Li, J.; Dong, J. *Stud. Surf. Sci. Catal.* **2008**, *174*, 459.
7. Himeur, F.; Stein, I.; Wragg, D. S.; Slawin, A. M. Z.; Lightfoot, P.; Morris, R. E. *Solid State Sci.* **2010**, *12*, 418.
8. Liao, J. H.; Wu, P. C.; Bai, Y. H. *Inorg. Chem. Commun.* **2005**, *8*, 390.
9. Zhang, J.; Wu, T.; Chen, S.; Feng, P.; Bu, X. *Angew. Chem. Int. Ed.* **2009**, *48*, 3486.
10. (a) Parnham, E. R.; Drylie, E. A.; Wheatley, P. S.; Slawin, A. M. Z.; Morris, R. E. *Angew. Chem.* **2006**, *118*, 5084. (b) Liao, J. H.; Wu, P. C.; Huang, W. C. *Cryst. Growth Des.* **2006**, *6*, 1062. (c) Xu, L.; Choi, E. Y.; Kwon, Y. U. *Inorg. Chem. Commun.* **2008**, *11*, 1190. (d) Chen, S.; Zhang, J.; Wu, T.; Feng, P.; Bu, X. *Dalton Trans.* **2010**, *39*, 697. (e) Lin, Z.; Slawin, A. M. Z.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4880.
11. Kuang, D.; Brezesinski, T.; Smarsly, B. *J. Am. Chem. Soc.* **2004**, *126*, 10534.
12. Parnham, E. R.; Drylie, E. A.; Wheatley, P. S.; Slawin, A. M. Z.; Morris, R. E. *Angew. Chem. Int. Ed.* **2006**, *45*, 4962.
13. Parnham, E. R.; Morris, R. E. *Acc. Chem. Res.* **2007**, *40*, 1005.
14. (a) Son, W. J.; Kim, J.; Kim, J.; Ahn, W. S. *Chem. Commun.* **2008**, 6336. (b) Jung, D. W.; Yang, D. A.; Kim, J.; Kim, J.; Ahn, W. S. *Dalton Trans.* **2010**, *39*, 2883. (c) Qiu, L. G.; Li, Z. Q.; Wu, Y.; Wang, W.; Xu, T.; Jiang, X. *Chem. Commun.* **2008**, 3642. (d) Haque, E.; Khan, N. A.; Park, J. H.; Jhung, S. H. *Chem.-Eur. J.* **2010**, *16*, 1046.
15. Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414.
16. Suslick, K. S. *Science* **1990**, *247*, 1439.
17. Flannigan, D. J.; Hopkins, S. D.; Suslick, K. S. *J. Organomet. Chem.* **2005**, *690*, 3513.
18. Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148.
19. Mason, T. J.; Lorimer, J. P. In *Applied Sonochemistry*; Wiley-VCH Verlag GmbH Press: Weinheim, Germany, 2002; p 77.
20. Lickiss, P. D. In *The New Chemistry*; University of Cambridge Press: UK, 2000; p 76.
21. Li, Z. Q.; Qiu, L. G.; Xu, T.; Wu, Y.; Wang, W.; Wu, Z. Y.; Jiang, X. *Mater. Lett.* **2009**, *63*, 78.
22. Cao, G. In *Nanostructures & Nanomaterials*; Imperial College Press: UK, 2004; p 56.