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# Facile Syntheses of Metal-organic Framework $Cu_3(BTC)_2(H_2O)_3$ under Ultrasound

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Cu-BTC[$Cu_3(BTC)_2(H_2O)_3$, BTC = 1,3,5-benzenetricarboxylate], one of the most well-known metal-organic framework materials (MOF), has been synthesized under atmospheric pressure and room temperature by using ultrasound. The Cu-BTC can be obtained in 1 min in the presence of DMF (*N*,*N*-dimethylformamide), suggesting the possibility of continuous production of Cu-BTC. Moreover, the surface area and pore volume show that the concentration of DMF is important for the synthesis of Cu-BTC having high porosity. The morphology and phase also depend on the concentration of DMF : Cu-BTC cannot be obtained at room temperature in the absence of DMF and aggregated Cu-BTC (with low surface area) is produced in the presence of high concentration of DMF. It seems that the deprotonation of benzenetricarboxylic acid by base (such as DMF) is inevitable for the room temperature syntheses.

**Key Words**: Metal-organic frameworks (MOF), Rapid synthesis, Ultrasound, Cu-BTC, Morphology

## Introduction

The number of materials exhibiting permanent nanoporosity has rapidly expanded in recent years, due in large part to the discovery of metal-organic frameworks (MOFs) and coordination polymers, *etc*.[1-8] The major applications currently being considered for these compounds involve gas storage,[9-12] catalysis,[13-18] separations,[19-24] as carriers for nano-materials[25, 26] and drug delivery,[27, 28] *etc*. For these applications, their high surface areas and unique pore structures are likely to offer many potential advantages over existing compounds.

Cu-BTC [$Cu_3(BTC)_2(H_2O)_3$, BTC = 1,3,5-benzenetricarboxylate] also known as HKUST-1 has paid a good deal of attention since it was first reported by Chui *et al*. in 1999.[29] The paddle wheel complex built from the axial $Cu^{2+}$ ion and 1,3,5-benzenetricarboxylic acid ($H_3BTC$), is very interesting for their structural diversity, geometrical control and flexibility. There have been continuous efforts to improve the synthesis and activation of Cu-BTC.[30-33]

Various MOFs have generally been synthesized widely by slow diffusion techniques, conventional hydrothermal and solvothermal methods.[1-4] However, the reactions used to synthesize many MOFs, particularly those with good thermal stability, require hydro/solvothermal synthesis conditions. Since hydro/solvothermal reactions typically need up to several days, it is important to develop facile, rapid, inexpensive, commercially viable routes to the production of these compounds in order for them to be considered for applications.

Recently, microwave heating has been used for fast crystallization of porous materials.[34, 35] Microwave method has also shown positive effects of narrow particle size distribution[36, 37] and facile morphology control.[38, 39] The microwave irradiation has been applied for the synthesis of metal-organic frameworks also.[40-44] Due to rapid homogeneous heating and fast kinetics, microwave assisted hydrothermal method is applied successfully for decreasing reaction time of Cu-BTC synthesis up to a few minutes with high phase purity and high yield.[30]

Moreover, the ultrasonic synthesis method has attracted growing attention for the synthesis of nanomaterials, zeolites assembling and fabricating ZnO nanorods,[45-47] *etc*. This method has also shown to provide an efficient way to synthesize MOFs with short crystallization time and especially with low reaction temperature.[48] Very recently sonochemical technique has been also reported[31] to synthesize Cu-BTC under some specific conditions.

In this work we report a highly efficient route to synthesize Cu-BTC by using ultrasonic irradiation. The technique shows a facile synthesis within the shortest reaction time (ever reported) of one minute, at room temperature and ambient pressure. The particle size can remarkably be decreased up to 0.2 μm by this method compared with other heating techniques. The shape and size of porous materials are very important for applications such as membrane, catalysis and separation.[49-52] Several advantages, reported in the field of catalysis using small crystals[49-52] are: (a) catalysis is more effective; (b) coke deposition is less severe; (c) diffusion limitation is less severe; (d) template extraction and cation exchange are easier; (e) regeneration of used catalyst is less difficult for small crystals. Moreover, small particles are also effective to prepare membranes or films.

Additionally, syntheses by conventional electric and microwave heating were also carried out for comparison. We also tried to point out the factors, such as pH (or DMF concentration) and reaction time, which affect the physicochemical properties (morphology, surface area and pore volume) of the Cu-BTC crystals.

## Experimental

An exact amount of 1,3,5-benzenetricarboxylic acid ($H_3$BTC, 0.5 mmol) was dissolved in a solvent mixture of ethanol (2 mL) and DMF (0.0, 0.2, 0.5, 1.0, 3.0 or 6.0 mL), and then mixed with an aqueous solution (4 mL) of cupric acetate dihydrate (0.5 mmol) in a sample vial and stirred magnetically for 10 min. The vial was set to the probe of an ultrasonic generator (VCX 750, Sonics & materials, Inc). The energy of the ultrasound was kept 20% of the maximum power (750 W) for all

reactions. The temperature of vials under ultrasound was room temperature (around 25 °C) during 5 min, and less than 40 °C even after sonication for 30 or 60 min due to natural cooling.

In case of conventional electric heating and microwave irradiation the reaction mixture was composed of $Cu(NO_3)_2 \cdot 3H_2O$ (3.65 mmol), $H_3BTC$ (2.00 mmol), 24 mL of 1:1 (w/w) water: ethanol mixture, which were loaded in specific Teflon-lined autoclaves, sealed and placed in a preheated electric oven or a microwave oven (Mars-5, CEM, maximum power of 1200 W) for a fixed time. The detailed microwave-synthesis procedure has been reported elsewhere.[41,53] After finishing the reactions, the vials or the autoclaves were allowed to cool down to room temperature and the solid products were recovered with centrifugation. The solid products were washed with water-ethanol mixture (1:1 v/v) to remove the unreacted $H_3BTC$ and dried overnight at 100 °C.

The phase and crystallinity of the samples were determined with an X-ray diffractometer (MO3X-HF, Model No. 1031, CuKα radiation). The crystal morphology was examined using field emission scanning electron microscope (Hitachi, S-4300). The nitrogen adsorption isotherms were measured at −196 °C with an adsorption unit (Micromeritics, Tristar II 3020) after evacuation of the obtained samples at 150 °C for 12 h. The surface areas and micropore volumes were obtained using the BET equation and t-plot, respectively. The yield of the solid product was calculated based on Cu. The reaction conditions and properties of the examined samples are summarized in Table 1 and Table 2.

## Result and Discussion

The reaction conditions for synthesizing Cu-BTC using conventional electric and microwave heating are optimized recently;[30] however, in the present work we report the synthesis route for remarkably smaller particle size of Cu-BTC in very short reaction time of 1 min. The synthesis method is established by ultrasonic irradiation at room temperature and ambient pressure. Water-ethanol-DMF was used as the solvent for this synthesis in reduced time because the Cu-BTC cannot be obtained under ultrasonic irradiation without DMF even after long reaction time of 2 h (see below).

Fig. 1 presents the XRD patterns of Cu-BTC, synthesized by sonochemical method for different reaction times. The solvent is composed of water (4 mL) - ethanol (2 mL) - DMF (1 mL). In this study, in accord with previous works, all the diffraction peaks matched exactly with the pure Cu-BTC,[29-32] and no additional peak of impurities was detected. The result of the XRD patterns suggests that pure Cu-BTC can be synthesized by sonochemical method within 1 min at room temperature and atmospheric pressure. The rapid syntheses of materials under

**Table 1.** Reaction conditions and results for the synthesis of Cu-BTC by ultrasonic irradiation at room temperature from reactant mixtures containing solvent of water (4 mL) - ethanol (2 mL) - DMF (*x* mL)

| Sample No. | Reaction conditions | | | Reaction results | | | |
|---|---|---|---|---|---|---|---|
| | Amount of DMF (mL) | pH (reactant mixture) | Time (min) | Phase | Yield (%) | $S_{BET}$ ($m^2/g$) | Micropore volume ($cm^3/g$) |
| A | 1.0 | 3.32 | 1 | Cu-BTC | 81 | 1156 | 0.40 |
| B | 1.0 | 3.32 | 5 | Cu-BTC | 83 | 1150 | 0.40 |
| C | 1.0 | 3.32 | 30[a] | Cu-BTC | 82 | 838 | 0.28 |
| D | 1.0 | 3.32 | 60[a] | Cu-BTC | 85 | 850 | 0.29 |
| E | 0.0 | 2.81 | 1 | Unknown | ND[b] | ND | ND |
| F | 0.2 | 2.92 | 1 | Cu-BTC | 73 | 650 | 0.22 |
| G | 0.5 | 3.15 | 1 | Cu-BTC | 75 | 816 | 0.28 |
| H | 3.0 | 3.95 | 1 | Cu-BTC | 79 | 1017 | 0.35 |
| I | 6.0 | 3.62 | 1 | Cu-BTC | 80 | 877 | 0.31 |

[a]The reaction temperature is increased up to 40 °C after prolonged irradiation for 30 - 60 min. [b]ND: not determined

**Table 2.** Reaction conditions and results for the synthesis of Cu-BTC by conventional electric heating and microwave heating at 120 or 140 °C[a]

| Sample No. | Reaction conditions | | | | Reaction results | | |
|---|---|---|---|---|---|---|---|
| | Heating method[b] | Solvent | Time (min) | Temp. (°C) | Yield (%) | $S_{BET}$ ($m^2/g$) | Micropore volume ($cm^3/g$) |
| J | CEH | Water-ethanol | 1440 | 120 | 79 | ND[c] | ND[c] |
| K | CEH | Water-ethanol | 1440 | 140 | 73 | 890 | 0.32 |
| L | MW | Water-ethanol | 60 | 140 | 68 | 1080 | 0.39 |
| M | MW | Water-ethanol | 120 | 140 | 49 | ND[c] | ND[c] |

[a]Reactant composition: $Cu(NO_3)_2 \cdot 3H_2O$ (3.65 mmol), $H_3BTC$ (2.00 mmol), 24 mL of 1:1 (w/w) water : ethanol. [b]MW: microwave heating; CEH: conventional electric heating. [c]ND: not determined.

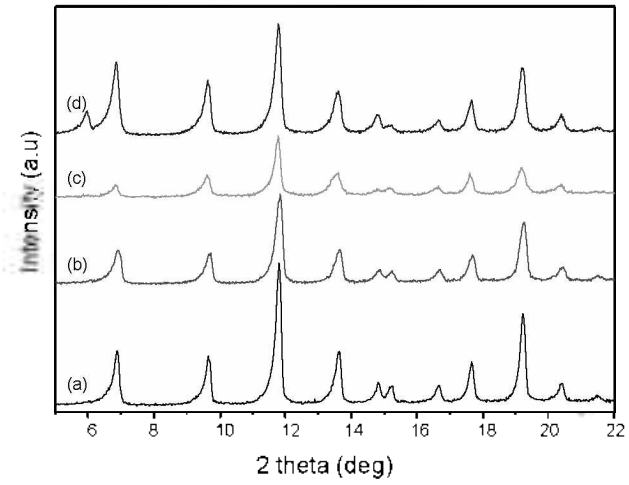


**Figure 1.** XRD patterns of Cu-BTCs prepared in various synthesis times by ultrasonic irradiation of reaction mixtures containing solvent of water (4 mL) - ethanol (2 mL) - DMF (1 mL): (a) 1 min (Sample A); (b) 5 min (Sample B); (c) 30 min (Sample C) and (d) 60 min (Sample D).

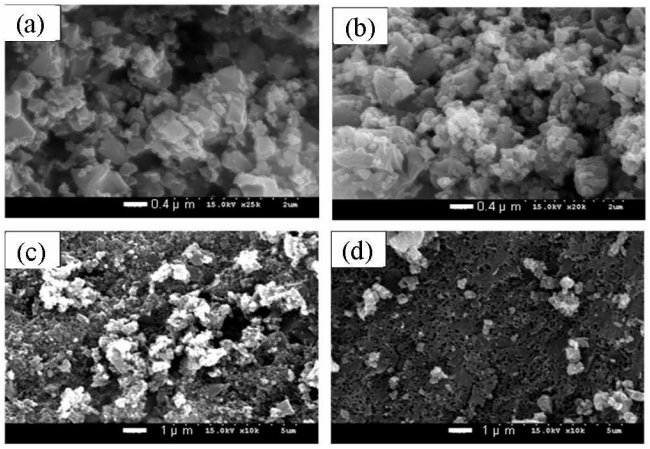


**Figure 2.** SEM images of Cu-BTCs prepared in various synthesis times by ultrasonic irradiation of reaction mixtures containing solvent of water (4 mL) - ethanol (2 mL) - DMF (1 mL): (a) 1 min (Sample A); (b) 5 min (Sample B); (c) 30 min (Sample C) and (d) 60 min (Sample D). The scale bars for (a), (b), (c) and (d) correspond to 0.4, 0.4, 1 and 1 μm, respectively.

ultrasound have been explained by cavitation.[54] So far, porous materials have been usually synthesized with batch processes due to long reaction time, preventing a continuous production.[53] The synthesis in 1 min may lead to continuous production of Cu-BTC.

Fig. 2, the SEM images of typical samples of Cu-BTC synthesized by ultrasound, shows that small and homogeneous particles are obtained only for short reaction times of 1 to 5 min. The images also suggest that, with increasing the reaction time from 5 to 60 min, the particles are gradually getting aggregated among themselves even though the Cu-BTC does not transform into another phase (Fig. 1).

In this study we found that ultrasonic synthesis of Cu-BTC is very much dependent on the solvent system. The synthesis

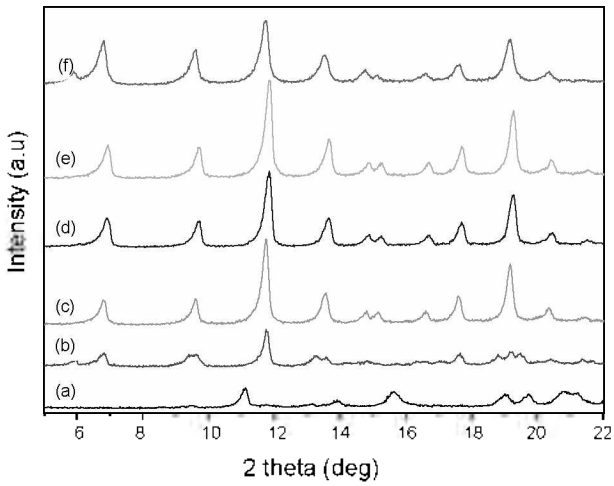


**Figure 3.** XRD patterns of Cu-BTC samples synthesized by ultrasonic irradiation for 1 min with different DMF concentrations in the solvent of water (4 mL) - ethanol (2 mL) - DMF(*x* mL): (a) 0.0 mL (Sample E); (b) 0.2 mL (Sample F); (c) 0.5 mL (Sample G); (d) 1.0 mL (Sample A); (e) 3.0 mL (Sample H) and (f) 6.0 mL (Sample I).

of Cu-BTC has already been reported[30, 31] using water-ethanol or water-ethanol-DMF as solvent; however, to the best of our knowledge the quantitative role of DMF under ultrasonic treatment has not been reported so far. To understand the quantitative effect of DMF on the syntheses, the amount of DMF was varied from 0.0 mL to 6.0 mL (Sample A and Samples E - I). Fig. 3 presents the XRD patterns of Cu-BTC synthesized from different DMF contents in the solvent system (0.0 mL to 6.0 mL, Sample A and Samples E - I), illustrating very small amount of DMF (0.2 mL) is sufficient to synthesize Cu-BTC (even though the porosity is relatively poor) within 1 min, whereas only water-ethanol solvent yields an unknown phase similar to the one reported in the previous work.[30] In our previous work it has been observed that DMF is very promising solvent for the deprotonation of benzenedicarboxylic acid to remove occluded benzenedicarboxylic acid in a MOF.[55] In this present study, it is also found that DMF is indispensable for the synthesis at ambient pressure, and the presence of DMF may lead to facile deprotonation of $H_3BTC$ under ambient condition. The pH of the reactant mixtures was also measured to estimate the allowable acidity range to synthesize small and homogeneous particles under ultrasound. XRD patterns and SEM images (Figs. 3 and 4) suggest that, even though 0.2 mL DMF is sufficient to synthesize pure Cu-BTC with considerable yield, at least 1.0 mL (up to 3.0 mL) DMF (pH: 3.32 - 3.95) is required for homogeneous and small particles (Samples A and H). It is found that further addition of DMF to the reactant mixture leads to the aggregation of the crystals. Actually there is an optimum DMF concentration for the synthesis of highly porous Cu-BTC in 1 min under ultrasound. As shown in Fig. 5 and Table 1, the surface area and micropore volume increase with DMF concentration and decrease with further increase of the concentration, illustrating the existence of an optimum concentration of DMF. When the DMF concentration is too low the deprotonation rate will be surely low; however, too high DMF concentration causes the aggregation of Cu-BTC crystals probably due to conden-

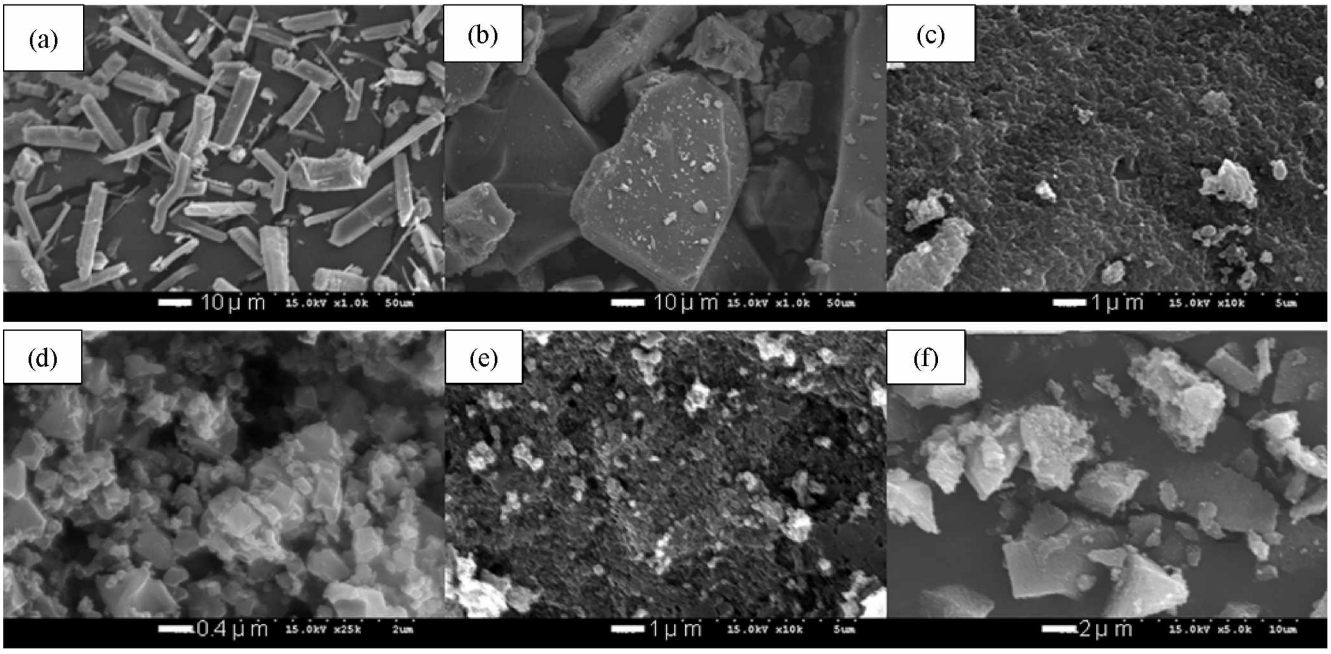


**Figure 4.** SEM images of Cu-BTC samples synthesized by ultrasonic irradiation for 1 min with different DMF concentrations in the solvent of water (4 mL) - ethanol (2 mL) - DMF(*x* mL): (a) 0.0 mL (Sample E); (b) 0.2 mL (Sample F); (c) 0.5 mL (Sample G); (d) 1.0 mL (Sample A); (e) 3.0 mL (Sample H) and (f) 6.0 mL (Sample I). The scale bars for (a), (b), (c), (d), (e) and (f) correspond to 10, 10, 1, 0.4, 1 and 2 μm, respectively.

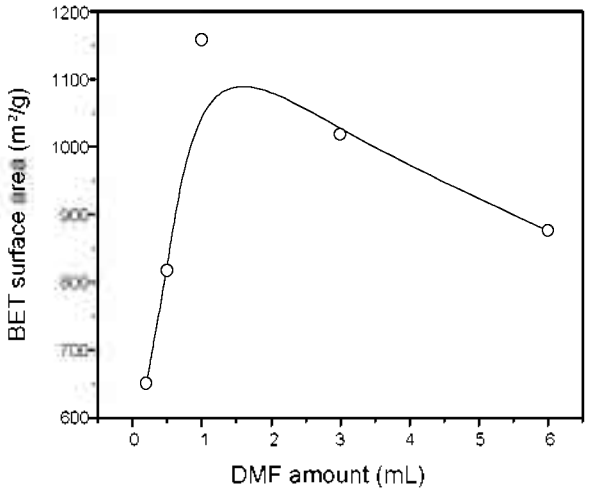


**Figure 5.** The change of BET surface area with DMF concentration in the syntheses of Cu-BTC under ultrasound for 1 min (Samples A and F - I in Table 1). The solvent consists of water (4 mL) - ethanol (2 mL) - DMF (*x* mL).

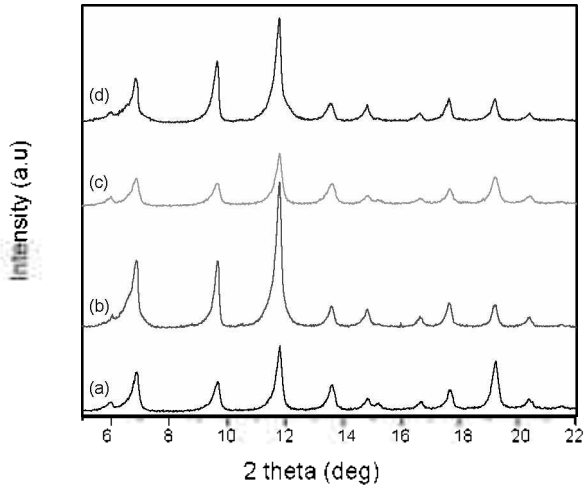


**Figure 6.** XRD patterns of Cu-BTC samples synthesized by conventional electric heating and microwave methods: (a) Sample J; (b) Sample K; (c) Sample L and (d) Sample M.

sation of terminal functional group (such as carboxylic acid or hydroxyl group) of Cu-BTC crystals.

For a comparative study we also carried out some syntheses under conventional electric heating and microwave irradiation using water-ethanol as solvent for a few reaction times and temperatures. The results shown in Fig. 6 and Table 2 are in accord with the previously reported results.[30] Fig. 7 shows the SEM images of conventional electric heating and microwave irradiation products having the particle size of about 20 and 10 μm respectively, whereas Cu-BTC by ultrasonic irradiation has particle size of about 0.2 - 0.4 μm (Fig. 2). Moreover the product yields (Table 1 and Table 2) confirm that, the syntheses of Cu-BTC by sonochemical method (when the DMF ≥ 1.0 mL) are more quantitative than conventional electric and microwave heating methods.

Nitrogen adsorption isotherms (Fig. 8) of the Cu-BTCs (at −196 °C after evacuation at 150 °C for 12 h) obtained by conventional electric heating, microwave irradiation and sonochemical method show the permanent porosity of the obtained Cu-BTCs. As listed in Table 1 and Table 2, however, BET surface area of Cu-BTC (without aggregation) synthesized by ultrasonic method (1156 $m^2/g$) is higher than the surface areas of Cu-

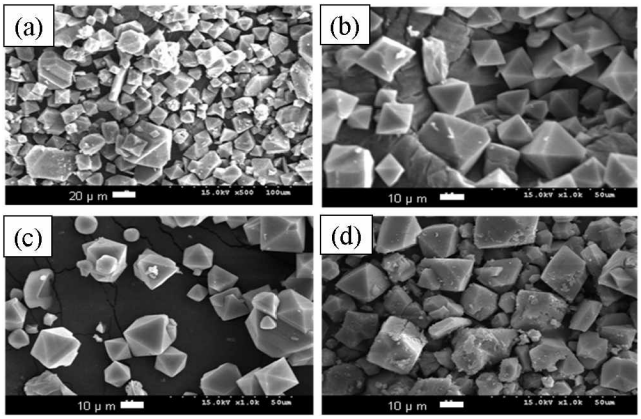


**Figure 7.** SEM images of Cu-BTC samples synthesized by conventional and microwave methods: (a) Sample J, (b) Sample K, (c) Sample L and (d) Sample M. The scale bars for (a) and (b) - (d) correspond to 20 and 10 μm, respectively.

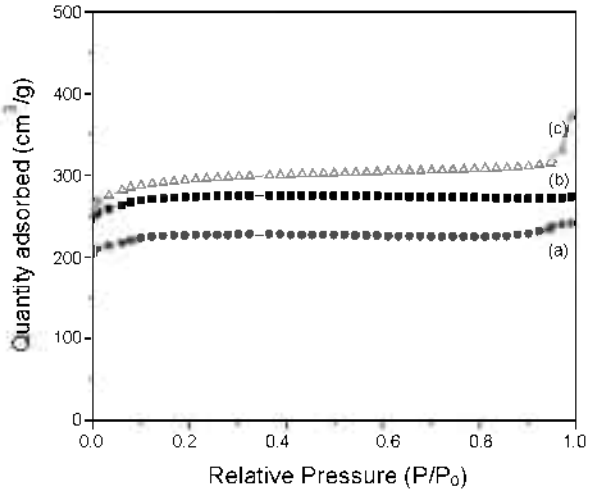


**Figure 8.** Nitrogen adsorption isotherms of synthesized Cu-BTCs: (a) Sample K, (b) Sample L and (c) Sample A.

BTCs synthesized by conventional electric heating (890 $m^2/g$) and microwave heating (1080 $m^2/g$). In harmony with the surface areas, the micropore volumes were found to be 0.32, 0.39 and 0.40 $cm^3/g$ for samples synthesized by conventional electric heating, microwave irradiation and sonochemical method, respectively. It is also clear that aggregated samples show surface area much lower than the area of fine particles (Table 1, Sample I).

## Conclusion

The Cu-BTC, one of the most well-known metal-organic framework materials (MOF), can be readily synthesized under ultrasonic irradiation within 1 min at room temperature and ambient pressure, suggesting a possibility of continuous production of Cu-BTC at ambient conditions. Base such as DMF is indispensable for the ultrasonic synthesis at room temperature, illustrating the role of DMF in the deprotonation of benzenetricarboxylic acid. Suitable concentration of DMF is needed for small (around 0.2 - 0.4 μm), highly porous and homogeneous Cu-BTC; however, high DMF concentration causes the aggregation of Cu-BTC crystals. The synthesized Cu-BTC under ultrasonic irradiation shows improved surface area and pore volume compared with conventional or microwave synthesis at high temperature without additional DMF.

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