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Synthesis of porous Cu-BTC with ultrasonic treatment: Effects of ultrasonic power and solvent condition

Farrukh Israr [a], Duk Kyung Kim [b], Yeongmin Kim [a], Seung Jin Oh [c], Kim Choon Ng [c], Wongee Chun [a,*]

[a] Department of Nuclear and Energy Engineering, Jeju National University, Jeju 690-756, South Korea
[b] Department of Chemistry, Auburn University at Montgomery, Montgomery, AL 36117, USA
[c] Mechanical Engineering Department, National University of Singapore, 9 Engineering Drive 1, 117576 Singapore, Singapore

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ABSTRACT

Cu-BTC (BTC = 1,3,5-benzenetricarboxylate) metal organic framework (MOF) was synthesized using different solvent conditions with ultrasonic treatment. Solvent mixtures of water/N,N-dimethylformamide (DMF), water/ethanol were used for the reactions with or without a variety of bases under 20 kHz ultrasonically treated conditions. Prepared crystals were purified through 30 min of sonication to remove unreacted chemicals. Treatment time and ultrasonic power effects were compared to get optimum synthetic condition. The characterization of MOF powders was performed by scanning electron microscopy, X-ray powder diffraction, infrared-spectroscopy, thermo-gravimetric analysis and specific surface determination using the BET method. Isolated crystal yields varied with different solvent and applied ultrasonic power conditions. A high isolated crystal yield of 86% was obtained from water/ethanol/DMF solvent system after 120 min of ultrasonic treatment at 40% power of 750 W. Different solvent conditions led to the formation of Cu-BTC with different surface area, and an extremely high surface area of 1430 m^2/g was obtained from the crystals taken with the solvent condition of water:DMF = 70:30.

1. Introduction

Metal organic frameworks (MOFs) are a new class of porous 3-D structures, which have attained a remarkable attention over the recent few years for certain applications such as gas storage, gas separation, catalyst materials [1–10], gas carrier for nano-sized materials [11,12], preparation of nano-inorganic materials [13] and drug delivery [14,15]. Their high surface areas and unique pore structures are key properties for such applications.

Cu-BTC (BTC = 1,3,5-benzenetricarboxylate), is a well-established MOF for hydrogen gas storage, gas storage and heterogeneous catalysis [16–21]. Cu-BTC resembles a paddle wheel complex built from Cu^{2+} ions and 1,3,5-benzenetricarboxylic acid (H_3BTC). It has three dimensional face centered cubic crystal structure with two different pore sizes of a square cross section with 0.9 nm diameter and a tetrahedral slot with 0.5 nm diameter [21]. Initially reported Cu-BTC was synthesized by solvo-thermal process at 180 °C [22]. The drawbacks associated with solvo-thermal process are long reaction time (12 h or more) and consumption of large amount of solvents for the reaction. Technological developments has been leading to the use of ultrasonic irradiation, microwave heating and mechanochemical techniques which were successfully employed for the synthesis of Cu-BTC [22–27]. Compared to the traditional techniques, sonochemical reaction is faster and easy to be controlled. In general, a wide variety of MOFs have been synthesized with ultrasonic technique. Safarifard et al. [28] has provided in-depth overview of ultrasonic synthesis of metal organic frameworks with emphasis upon inherent chemistry that involved in application of high energy ultrasonic waves to an initial reaction mixture. Similarly Masoomi et al. [29] has reported an ultrasonic synthesis of Zn (II) metal organic framework with nano-plate morphology.

Because bases added to the solution may help deprotonate from BTC for the formation of Cu-BTC, the effect of a variety of bases of NaOH, HN_4OH, and pyridine (Pyr) was also tested in this research work. Irradiation time and ultrasonic power effects were compared to get optimum synthetic condition. Purification of MOFs is important for further application of the porous materials. Additional ultrasonic irradiation was applied to remove unreacted chemicals for the purification purpose. Characterizations of isolated Ni-BTC crystals were performed by X-ray diffraction (XRD) measurement, scanning electron microscope (SEM), FTIR, X-ray photoelectron spectroscopy (XPS) techniques together with the BET surface area measurement.

* Corresponding author.
E-mail address: wgchun@jejunu.ac.kr (W. Chun).

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Table 1
Reaction conditions and results from synthesized Cu-BTCs by ultrasonic treatment and comparison with reported microwave assisted and mechano-chemically synthesized MOF.

Compound	Synthetic method	Solvent (volume ratio)	Base	Time (min)	Yield (%)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Reference
Cu-BTC_{DMF}	Ultrasound	H_2O:DMF (70:30)	None	120	73	1430	0.668	Present work
Cu-$BTC_{DMF+EtOH}$	Ultrasound	H_2O:EtOH:DMF (40:20:40)	None	120	86	1400	0.487	Present work
Cu-BTC_{NaOH}	Ultrasound	H_2O:EtOH (80:20)	0.2 M NaOH	120	33	926	0.345	Present work
Cu-BTC_{NH4OH}	Ultrasound	H_2O:EtOH (80:20)	0.2 M NH_4OH	120	81	792	0.305	Present work
Cu-BTC_{Pyr}	Ultrasound	H_2O:EtOH (60:40)	0.2 M pyridine	30	24	1190	0.422	Present work
Cu-BTC	Ultrasound	Ethanol:DMF:H_2O	None	5	62	1075	0.662	[31]
Cu-BTC	Ultrasound	Ethanol:DMF:H_2O	None	60	85	1100	0.565	[31]
Cu-BTC	Microwave assisted	EtOH:H_2O at 140 °C	None	30	88	1392	0.56	[23]
Cu-BTC	Microwave assisted	EtOH:H_2O at 180 °C	None	30	96	1206	0.75	[23]
Cu-BTC	Mechano-chemical	None	None	20	97	1119	0.59	[25]
Cu-BTC	Mechano-chemical	DMF	None	30	95	1421	0.74	[25]

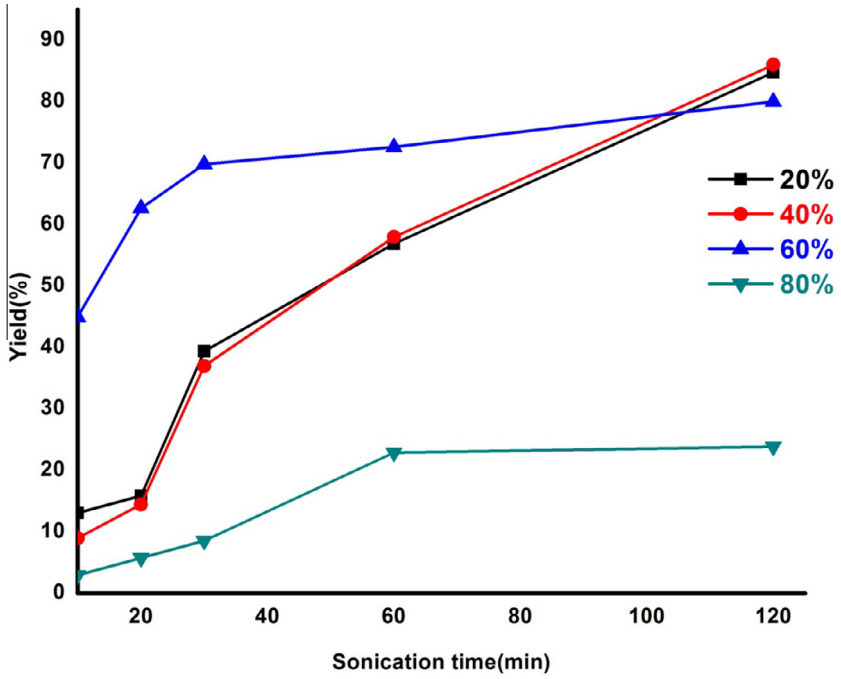

Fig. 1. Variation in yield with sonication time at different operating power levels.

2. Experimental

2.1. Materials

All materials including $CuCl_2{\cdot}2H_2O$ (99.5%, Alfa Aesar), 1,3,5-benzenetricarboxylic acid (99%, Alfa Aesar), DMF (99.8%, Alfa Aesar), ethyl alcohol (94–96%, Alfa Aesar), NaOH (pellets 98%, Alfa Aesar), NH_3 water (28% NH_3, Daejung Chem.) and pyridine (99.5%, Daejung Chem.) were used as received. De-ionized water was prepared by using lab scale distilled water equipment (Chang Shin, Model No. C-DIS1).

2.2. Sample preparation and ultrasonic irradiation

Ultrasonic power effect was tested based on isolated Cu-BTC yields. One to one molar ratio (5 mmol of H_3BTC and 5 mmol of $CuCl_2{\cdot}2H_2O$) of reactants were dissolved in mixed solvent of deionized water:ethanol:DMF = 40 mL:20 mL:40 mL. The solutions were treated with 20 kHz ultrasound (VCX 750, 750 W, tip diameter of 13 mm, Sonics & materials, Inc. USA) at different power levels of 20%, 40%, 60%, and 80% for given treatment times of 20–120 min at room temperature.

Traditionally synthetic processes of Cu-BTC either delivered hydrothermal [30], ultrasonic [22], microwave assisted [31,32] or mechanochemical [33], have employed typical solvent mixtures for effective dissolution of metal precursor and carboxylate ligands prior to the treatment. Effect of different solvent conditions was tested with fixed ultrasonic power of 40%. One to one molar ratio (5 mmol of H_3BTC and 5 mmol of $CuCl_2{\cdot}2H_2O$) of reactants was dissolved in mixed solvent systems of water/DMF, water/ethanol/DMF, water/ethanol with 0.2 M NaOH, water/ethanol with 0.2 M NH_4OH, and water/ethanol with 0.2 M pyridine. The effect of a