에너지공학, 제24권 제2호(2015)
Journal of Energy Engineering, Vol. 24, No. 2, pp.51~54(2015)
http://dx.doi.org/10.5855/ENERGY.2015.24.2.051

Cost effective and low energy consuming hydrothermal synthesis of Ni based MOF

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(Received 24 April 2015, Revised 9 June 2015, Accepted 12 June 2015)

Abstract

The mesoporous metal organic framework structure of Ni-BTC was successfully synthesized in a low temperature and short operation time via hydrothermal synthesis process. Such operational route virtuously consumed less electrical and thermal energy. It proved time saving along with acceptable product yield (38%). The product was characterized through FESEM, FT-IR, XRD and N_2 gas adsorption measurement. Hightemperature stability of synthesized MOF was gauged by diffraction indexing of XRD patterns of as synthesized and heat treated samples of MOFs. The mathematically calculated particle size of Ni-BTC was found to be 42nm.

Key words : Mesoporous, Metal organic frameworks, hydrothermal process, diffraction indexing, particle size

1. Introduction

Porous metal-organic frameworks (MOFs) are an important class of advanced functional materials. These materials have unique coordination structures and variant configurations due to which MOFs have wide range of applications [1-3]. The features of MOFs such as exceptionally high porosities, with regular pores and extremely high surface areas, well-defined crystalline structures, and more accessible bulk volume are hallmark which have attracted the attention of both academia and industry[4].

Ni-BTC is one such an example of MOF which is known to belong to M(BTC)(M = Cr, Fe, Ni, Cu, Mo). It has iso-structural relationship along with permanent porous structure. Hydrothermal and solvo-thermal synthesis has been reported by O. M. Yaghi et al.[5] and Casey R. Wade et al.[6]. There has been significant research going on for micro and mesoporous materials as adsorbents for heat transfer applications in closed systems such as thermally driven adsorption chillers and heat pumps[7, 8]. For a cooling application, the choice of the adsorbent/adsorptive working pair is key factor. The best pair choice is determined by the amount of heat that can be extracted from the evaporator per adsorption cycle. In general, the present generation of adsorption chillers use silica gels as adsorbent. The key problem with silica gel adsorbents for these applications is that most of the water adsorption occurs at

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too high relative pressures. However in recent times nickel based MOF (ISE-1) [9] has been reported which have good adsorption properties such as consistent water loading capacity over large number of adsorption cycles. This metal organic framework is less hydrophilic than silica gel and readily releases water molecules at low desorption temperature.

The hydrothermal processes employed earlier had the drawback of high operating temperatures (180˚C) and longer reaction times (12 hours or sometimes more than that) along with consumption of large amount of solvents. Therefore an interest was there to investigate a hydrothermal process which is less time consuming and more economical.

Here we have adopted a low temperature synthetic approach for Ni-BTC powder. We conducted synthesis process at 130˚C for 8 hours and were able to obtain noticeable MOF yield. We applied diffraction indexing over diffraction patterns of as synthesized and heat treated Ni-BTC. This way we were able to gauge the crystalline nature of product in as synthesized condition and higher temperature stability at heat treatment temperature.

2. Materials and method

The chemicals including nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) and trimesic acid ($C_6H_3(COOH)_3$) were purchased from sigma Aldrich and used without further purification. A mixture of $Ni(NO_3)_2.6H_2O$ (0.84g) with $C_6H_3(COOH)_3$ (0.42g) was dissolved in 30ml de-ionized water, stirred for 30 minutes, then loaded in Teflon liner and heated at 130˚C in autoclave for 8 hours. After hydrothermal treatment solution was cooled down to room temperature. The solution was then filtered and green precipitates of Ni-BTC were recovered.The precipitates were then washed with de-ionized water and dried thoroughly.

3. Characterization

The crystallinity and phase purity of synthesized MOF was analyzed using X-ray diffractometer (Rikagu D/MAX 2200H, Bede model200). The X-ray diffraction (XRD) measurement was performed using a Cu-K_α radiation source of wavelength λ=1.5406Å and the diffraction intensity was recorded in 2Θ range of 5-80˚ with a step of 0.02˚. The particle size of synthesized powders was calculated by using the Debye-Scherrer (DS) equation (1), as shown below:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where "D" is crystallite size, "λ" is the radiation wavelength (1.5406 Å), "β" is the full width half maximum (FWHM) for diffraction peak, "Θ" is the diffraction angle. "k"is the shape factor and an average value for "k" was assumed as 0.9. The FT-IR spectrum was collected on a BRUKER IFS66/S Fourier transform IR spectrophotometer in KBr disk at room temperature. The scanning electron microscopy (SEM) observation was done on JEOL, JEM1200EX II set up equipped with field emission gun. The measurement of N_2 adsorption was performed on a Quanta chrome AUTOSORB-1-MP apparatus at −196°C, and the specific surface area of the investigated sample was calculated using the multiple-point Brunauer-Emmett-Teller (BET) method. The sample was out gassed under vacuum at 150°C for 12 h, prior to the adsorption measurements.

4. Results and Discussion

4.1. Ni-BTC

Ni-BTC has been synthesized previously at room temperature[10] and by high temperature process[11] using different solvents. In this work we have synthesized Ni-BTC by employing intermediate temperature of 130°C for 8 hours operation without using any conventional organic solvents. The process yield was 38% based on stoichiometric calculations and is 25% less than those reported[10]. There appeared to be a slight mismatch between the obtained XRD pattern of as prepared Ni-BTC (Fig. 1) as compared

to the one reported in literature[9].

Here the diffraction peaks were shifted to lower angles. The most commonly cited reasons[12] for such kind of discrepancy are changes in cell parameters typical for solid solutions, induced compressive stresses and to some extent equipment error. The diffraction peaks were observed at 2Θ values of 4°, 10°, 13°, 15°, 18°, 20°, 22°, 24°, 25.5°, 28° and 30°, are tabulated along with their (h k l) and inter planner spacing values "d" (Table. 1). The calculated value of lattice parameter "a" for Ni-BTC was 44.1 Å. For heat treated sample, major comparable diffraction lines appeared on almost similar angles as were those for as prepared sample (Fig. 1(a) &(b)), But in addition to those, there were few additional peaks at 2Θ values of 12°, 14°, 23° and 24.5°. Those additional peaks might be a result of localized oxide formation within the MOF structure due to which diffraction pattern of heat treated sample gave somewhat distorted image. The observed FT-IR spectrum of synthesized compound is shown in (Fig. 2) depicted C=O stretch at

1780cm^{-1}, O-H band between 1400 and 1600cm^{-1} and C-O stretch at 1200 and 1350cm^{-1}. The adsorption isotherm for Ni-BTC (Fig. 3) resembled typical type II category[13-16] which is a principle characteristics of solids with micro pores. The measured

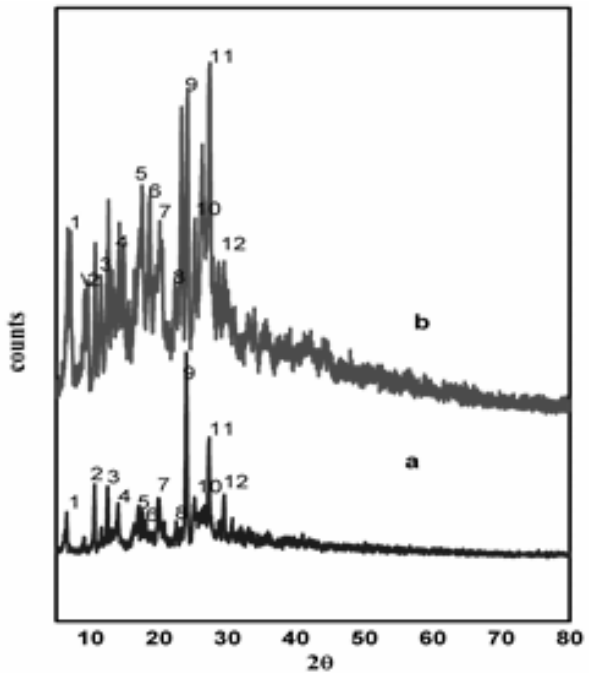

Fig. 1. XRD patterns of Ni-BTC

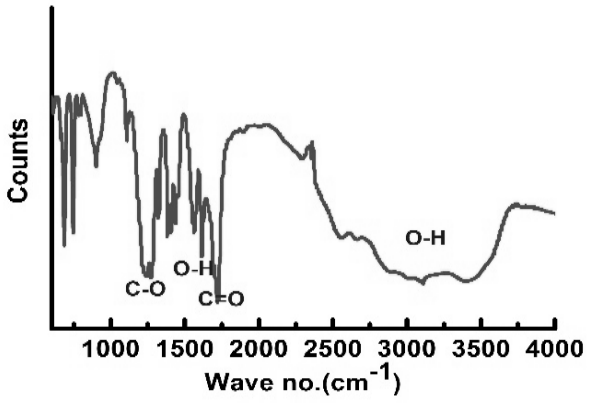

Fig. 2. FT-IR of Ni-BTC

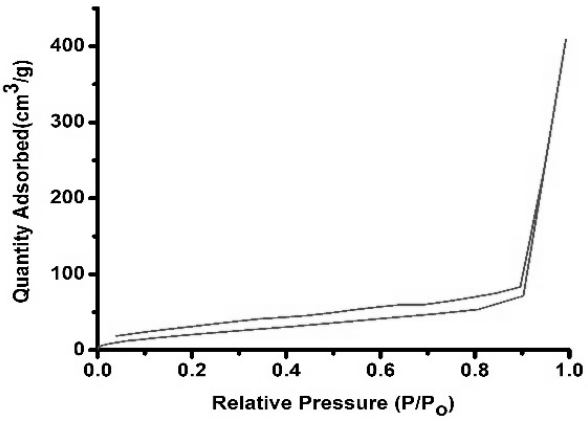

Fig. 3. Adsorption isotherm for Ni-BTC

Table 1. Indexing of Diffraction pattern for Ni-BTC

Peak No.	1	2	3	4	5	7	8	9	10	11	12
2θ	4	10	13	15	18	20	22	24	25.5	28	30
d	2.207	0.884	0.68	0.59	0.492	0.422	0.404	0.37	0.35	0.318	0.298
(h k l)	(100)	(211)	(311)	(321)	(420)	(511)	(521)	(600)	(620)	(631)	(711)

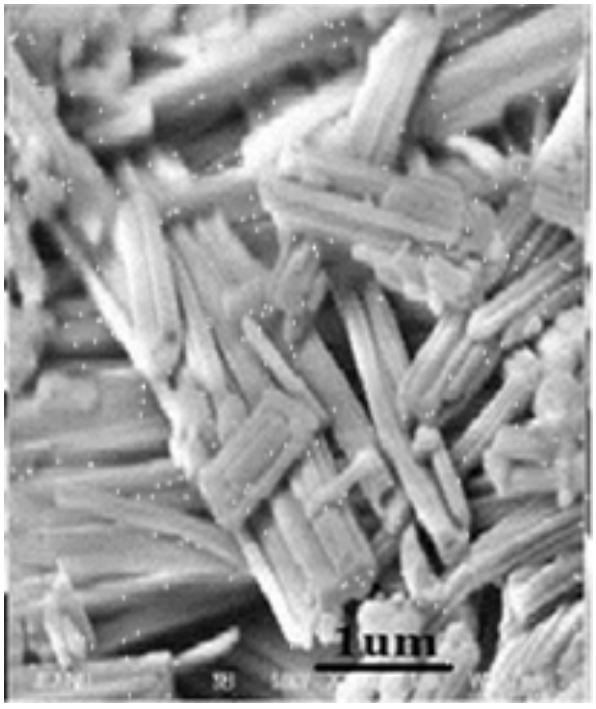

Fig. 4. Micro structure of Ni-BTC

BET surface area was 137m^2/g. The crystal shape as revealed in microstructure (Fig. 4) was nano rods with high aspect ratio. The value of calculated crystal size was found to be 44nm.

5. Conclusion

In contrast to conventional synthesis processes reported earlier, comparatively an intermediate or low temperature operational approach has been employed and Ni-BTC was synthesized with acceptable yield (38%). A low temperature and reduced time during synthesis makes this approach economically more feasible. The low temperature synthesis proved to be energy savior and provide a potential adsorbent.

The examination of diffraction pattern of heat treated Ni-BTC revealed a visible distortion in structure. This showed that Ni-BTC tend to destabilize at temperature around 200˚C or higher.

6. Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science, ICT & Future Planning (No. 2014R1A2A1A01006421).

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