



SYNTHESIS OF METAL-ORGANIC FRAMEWORK-199: COMPARISON OF MICROWAVE PROCESS AND SOLVOTHERMAL PROCESS

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Abstract: In the present paper, a comparative study on the synthesis of the metal-organic framework–199 (MOF–199) using the microwave and solvothermal method was demonstrated. The obtained materials were characterized using X-ray diffraction, scanning electron microscope, nitrogen adsorption/desorption isotherms and thermal gravity. The microwave synthesis of MOF–199 was compared with the conventional hydrothermal synthesis. The results showed that MOF–199 could be obtained in a much shorter time with improved yield and textural properties under the microwave irradiation. It is supposed that the microwave energy emitted fast and uniformly, creating nuclei through the solution which quickly grew to crystals, and both the nucleation and crystallization were accelerated. This made the microwave synthesis advantageous over the solvothermal synthesis.

Keywords: MOF–199, comparative, microwave, solvothermal

1 Introduction

Metal-organic frameworks (MOFs) are crystalline porous solids composed of a three-dimensional (3D) network of metal ions held in place by multidentate organic molecules [1]. The spatial organization of these structural units leads to a system of channels and cavities in the nanometer-length scale, analogous to that found in zeolites. The correct selection of the structural subunits and the way in which they are connected allow a systematic modification of the pore structure of MOFs. Over the last decade, the elevated surface area and pore volume, and the flexibility of pore design characteristics of MOFs have sparked research aiming mainly at preparing new MOF structures and studying their applications in gas storage and separation [2,3].

The metal-organic framework–199 (MOF–199) ($[\text{Cu}_3(\text{BTC})_2]$ (BTC = 1,3,5-benzenetricarboxylate)), also known as HKUST–1, is one of the most important metal-organic frameworks due to its large surface area, high pore volume, and high chemical stability. Because of these properties, MOF–199 is a very potential candidate for gas storage [4], catalysis [5] and sensing applications [6, 7]. Especially, MOF–199 has been employed as an electrode modifier to detect glucose [8], to simultaneously determine hydroquinone and catechol [9], and to detect bisphenol A rapidly [10].

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Ever since the synthesis of MOF-199 was reported by Chui et al. [11], many papers have reported about the synthesis of MOF-199 by solvothermal methods [12] or microwave-assisted hydrothermal process [13], electrochemical methods [14]. However, the textural properties of MOF-199, including the surface area, pore volumes were different from each other because of the differences in the synthetic procedures. The study on MOF-199 synthesis by various methods with a large surface area, low cost, and high yield has been progressed.

The microwave-assisted hydrothermal synthesis is known to be advantageous for rapid heating, faster kinetics, phase purity, higher yield and reproducibility [15]. This process has been widely used to synthesize materials in science [16, 17] and is very established in the synthesis of MOFs as well [18, 19]. Despite these facts, only a few reports on the use of microwave synthesis of MOF-199 have been published [13].

In the present paper, we carried out the synthesis of MOF-199 using a domestic microwave device at ambient temperature and pressure. The solvothermal synthesis of MOF-199 was conducted for the sake of comparison.

2 Experimental

Materials

All the chemicals were used as received: benzenetricarboxylic acid (BTC, 95 %) and copper nitrate trihydrate (99 %) were acquired from Merck. Solvents (dimethylformamide (DMF), ethanol (EtOH) and methanol (MeOH) with 99 % of purity) were supplied from HiMedia, India.

Apparatus

Powder X-ray diffraction patterns of all samples were obtained by using a D8 Advance Bruker with Cu K α -radiation ($\lambda = 1.5406 \text{ \AA}$) monochromator. The morphology was examined using a scanning electron microscope (Hitachi S-4800). Thermogravimetric analyses (TGs) were conducted with TA instrument model DTG-60H Shimadzu. The nitrogen adsorption/desorption isotherms were performed after dehydration under vacuum at 393 K for 24 h using Micromeritics-ASAP 2020.

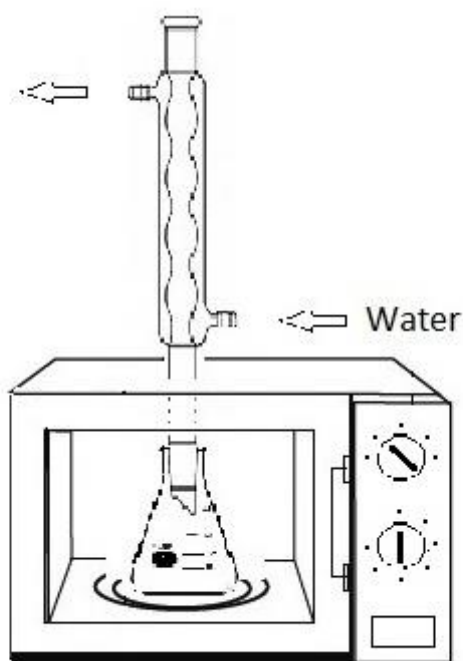
Preparation of MOF-199

In the solvothermal process (ST process), MOF-199 was synthesized according to a modified procedure [7]. Typically, an exact amount of BTC (0.0021 mol) and Cu(NO₃)₂·2H₂O (0.0032 mol) was dissolved in 21 mL of the mixture of ethanol:distilled water:DMF (1:1:1, w/w) and stirred magnetically for 5 minutes. The resulting mixture was loaded into a Teflon autoclave and placed in a dryer oven at 100 °C for derived time. The solid is collected by using centrifugation and washed

with DMF three times and dried at 180 °C for 8 hours. The MOF-199 synthesized by this process was named as ST-MOF-199.

In the microwave process, the same amount of reactants as mentioned in the ST process was loaded into a 250 mL Erlenmeyer flask and placed in a hand-made microwave device (made from a domestic microwave oven – Sharp R-203VN-M with a power of 250 W) (Scheme 1). The Erlenmeyer flask was attached to a reflux condenser, therefore the reactions were conducted under mild conditions (ambient atmosphere). The temperature in the Erlenmeyer flask was around 80–100 °C (measured through the condenser) depending on the irradiation time.

The solid was collected by using centrifugation and washed with DMF three times and dried at 180 °C for 8 hours. The samples synthesized by this process were named as MW-MOF-199.



Scheme 1. Hand-made microwave device used in the synthesis of MOF-199

3 Results and discussion

The phase structure obtained from the diffraction peaks of the samples was consistent with the theoretical patterns from the single crystal data, and with those previously reported [20, 21] of MOF-199.

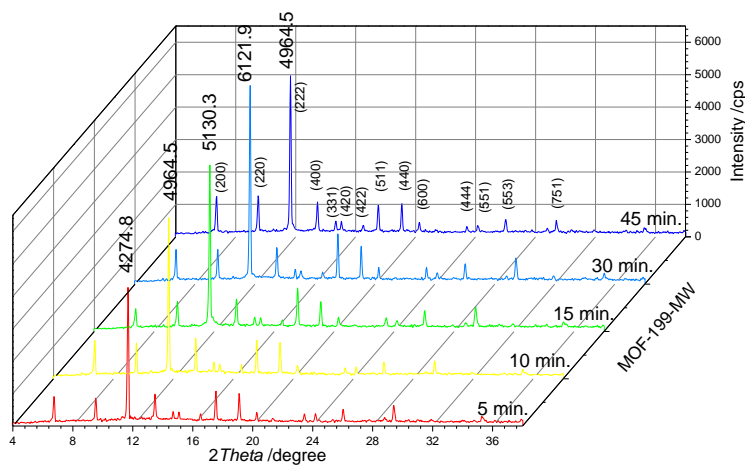


Fig. 1. XRD patterns of MOF-199 synthesized by MW-process

The sharp peaks with high intensity indicated that all the obtained MOF-199 had high crystallinity. For MW-MOF-199 (Fig. 1), the intensity of characteristic diffractions increased sharply at 30 minutes and then decreased slightly, while that of ST-MOF-199 also increased as the crystallization time increased for up 360 minutes, then decreased as the time went on (Fig. 2).

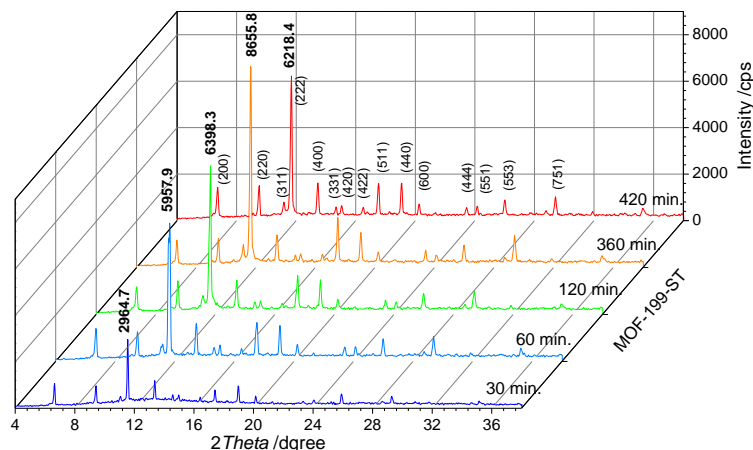


Fig. 2. XRD patterns of MOF-199 synthesized by ST-process

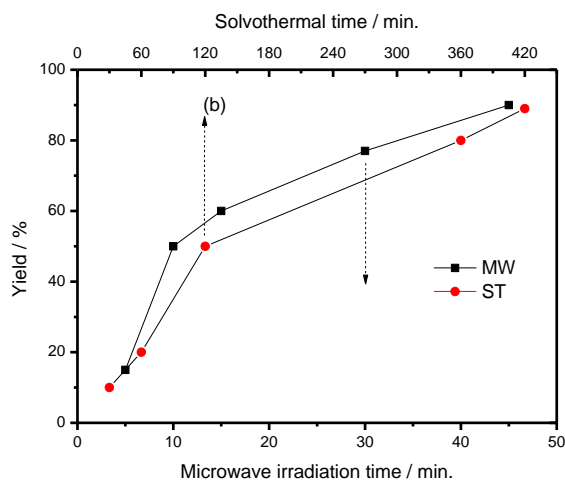


Fig. 3. Yield of MOF-199 at different time a) MW method and b) ST method

The yield of MOF-199 synthesized was calculated through the molar ratio of MOF-199 received and that calculated according to the $\text{Cu}_3\text{BTC}_2 \cdot 3\text{H}_2\text{O}$ formula proposed by Chui et al. [11]. The yield of MOF-199 is presented in Fig. 3. The yield of the MW process increased with the increase in the irradiation time from 0 to 30 minutes, with a larger increase (> 75 %). From 30 to 45 minutes, the increase is there but to a rather smaller extent (15 %). The yield of the ST process also increased with the increase in the reaction time but significantly more slowly than that of the MW process. In fact, the MOF-199 yield of the MW process reached 77.2 % after 30 minutes while that of the ST process was around 10 % at the same time and only reached 80.1 % after 360 minutes.

The increase in the crystallization time led to the increase in the MOF-199 crystal size due to Ostwald ripening where smaller crystals were consumed to form larger crystals. In the ST process, the nucleation and crystal growth were slow and therefore it spend much longer time. The combining the individual nanostructures into the larger particles at where group of surfaces is combined in a certain pattern, consequently, the large particles with the combine of several octahedron units were obtained in Fig. 4 b1–b4. Whereas, the microwave energy emitted fast and uniformly, creating nuclei through the solution, and these nuclei quickly grew to crystals. Both the nucleation and crystallization were accelerated. As a result, the particles with a more homogeneous shape formed (Fig. 4 a4–b4). As the crystallization time increased, the complete crystallization took place. A crystallized-dissolved equilibrium was possibly established as proposed by Seo et al. [13]. The dissolution combined with the crystallization resulted in the formation of smaller particles, and more tiny particles intermingled with larger particles (Fig. 4 a5 or b5). This explains the reduction in the intensity of X-ray diffraction of MOF-199 synthesized with long irradiation time or long solvothermal time.

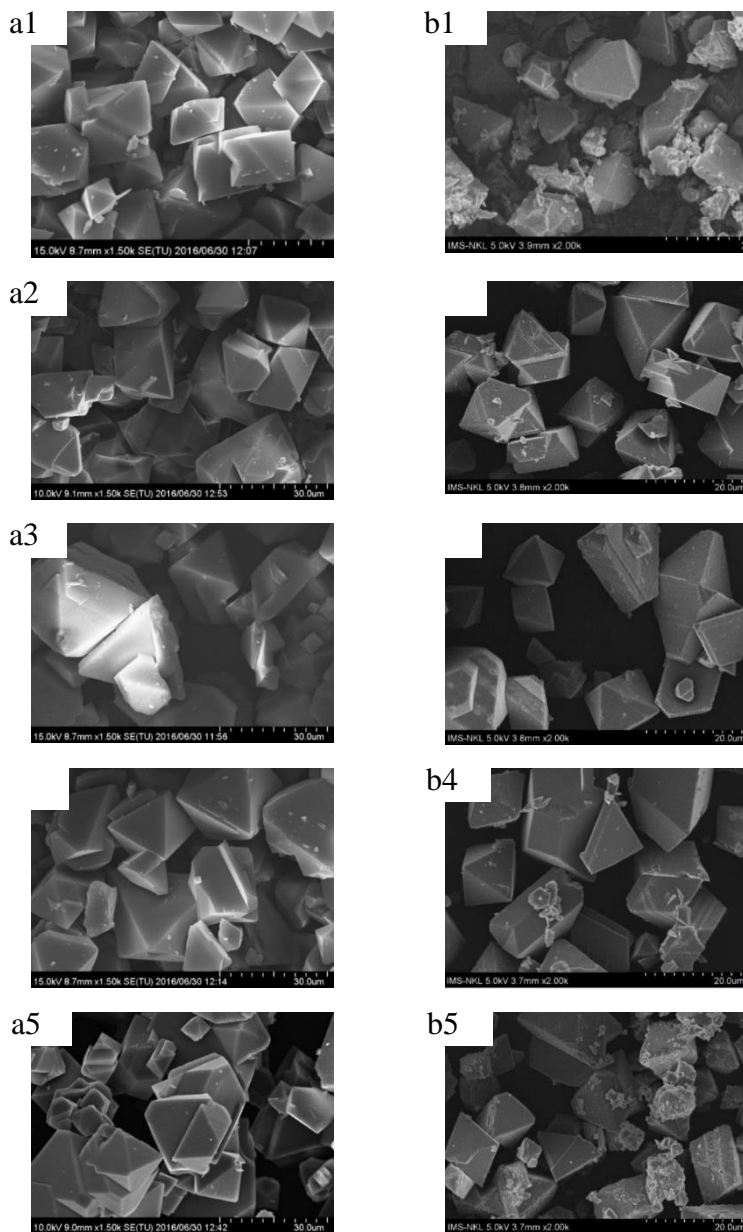


Fig. 4. SEM images of MOF-199 synthesized by MW process (a1: 5 min; a2: 10 min; a3: 15 min; a4: 30 and a5: 45 min) and ST process (b1: 30 min; b2: 60 min; b3: 120 min; b4: 360 min; b5: 420 min)

MOF-199 shows a considerable structural diversity in hydrate forms [20]. The thermal analysis is a useful tool for studying both thermal stability and their hydrate forms. Fig. 5 illustrates the TG diagrams of MW-MOF-199 and ST-MOF-199 in the nitrogen atmosphere. Three main steps of weight loss were observed. For MW-MOF-199, the first step was related to the loss of physically adsorbed water, and its exact height depended on the initial degree of hydration of the material. The chemical formula of as-synthesized MW-MOF-199 can be written as $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O}$ [20]. The as-synthesized MW-MOF-199 showed a weight loss (10.2 %) up to temperatures of 110–200 °C corresponding to the theoretical loss of 10.1 % for three water molecules. A second weight loss (7.6 %) up to 300 °C was assigned to the loss of three H_2O molecules from the structure (theoretical loss of 7.6 %), and the final loss of 54.4 % starting at 300 °C was attributed to the decomposition of the metal-organic structure (theoretical loss of 48.3 %). Meanwhile, the TG curve of ST-MOF-199 showed a continuous loss of 26 % up to 150 °C, a second loss of 7.5 % up around 300 °C and the final loss of 41.2 %. This may be due to the loss of twelve water molecules in $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3] \cdot 12\text{H}_2\text{O}$ (theoretical loss of 24.6 %), and then the loss of three structural water molecules (theoretical loss of 24.6 %), followed by decomposing the metal-organic structure starting at around 300 °C to leave copper oxides (the theoretical loss of 40.8 %). In this study, MOF-199 synthesized by the MW process was less hydrated than MOF-199 synthesized by the conventional solvothermal process.

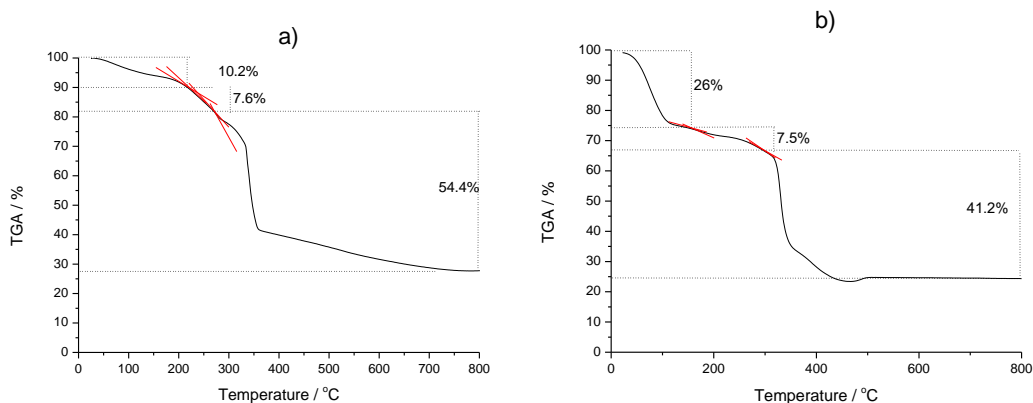


Fig. 5. TG diagrams of MOF-199 synthesized by a) MW process and b) ST process

The textural properties of MOF-199 were investigated by using nitrogen adsorption/desorption isotherms (Fig. 6). The isotherm curves belonged to type I according to the IUPAC classification which is characteristic of the microporous materials. The specific surface areas calculated from the BET model tended to increase as the synthesized time increased and then, slightly decreased at samples with long synthesized time. In fact, the specific surface areas for MW-MOF-199 synthesized at 15, 30 and 45 min were 1554, 1635 and 1635 $\text{m}^2 \cdot \text{g}^{-1}$, respectively, while those

for ST-MOF-199 at 120, 360 and 420 min were 1525, 1567 and 1554 $\text{m}^2\cdot\text{g}^{-1}$, respectively. Table 1 lists the specific surface areas of MOF-199 synthesized with different processes. It is worth noting that the specific surface area of MOF-199 obtained with the MW process is significantly higher than that prepared with other processes. The high surface area of MW-MOF-199 revealed that microwave energy enhanced the nucleation and crystal growth, reduced agglomeration and produced homogeneous particles with larger surface areas. Furthermore, the MW process required short time and provided a high yield compared with the conventional solvothermal process.

Table 1. Specific surface area of MOF-199 synthesized with microwave process and other processes

Methods	Specific surface area calculated with BET model ($\text{m}^2\cdot\text{g}^{-1}$)	Time (hours)	Temp. ($^{\circ}\text{C}$)	Ref.
Microwave-assisted Solvothermal synthesis	1656	1	140	[13]
	1200–1400	15	110	[22]
Ambient pressure synthesis	1239	12	150	[23]
Electrochemical synthesis	1300–1500	4	20–30	[14]
Solvothermal synthesis	1500	18	110	[12]
Microwave synthesis	1636	0.5	100	The present study

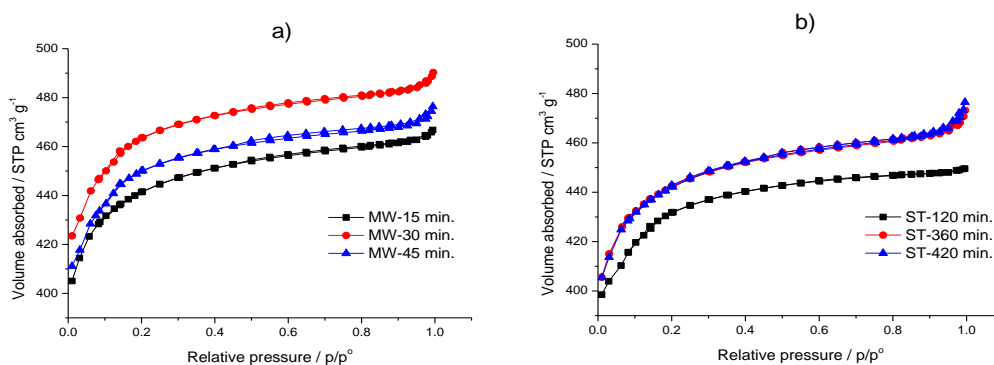


Fig. 6. Nitrogen adsorption/desorption isotherms of MOF-199 synthesized by a) MW process and b) ST process synthesized at different time

4 Conclusions

A comparative study on the synthesis of MOF-199 by solvothermal and microwave processes has been demonstrated. The microwave process is advantageous for high yield, less reaction time and mild condition (ambient temperature and atmosphere). The obtained MW-MOF-199 had higher crystallinity with defined octahedron-shaped crystals and large surface area compared with that obtained from the solvothermal process. The size of MW-MOF-199 was easily controlled by adjusting the irradiation time.

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