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A Comparative Study of Different Synthetic Methods of Copper Metal-Organic Frameworks (Cu-MOF)

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The metal-organic framework of copper (Cu-MOF) was prepared using the reflux method and microwave method. The results of the two techniques were compared with each other to determine the best method to prepare Cu-MOF. Preparation of Cu-MOF using different techniques has shown that it influences the morphology of the MOF. The results showed that there was a correlation between the two methods. The obtained products were characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD), Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) and ultraviolet-visible (UV-Vis) spectroscopy. The SEM images showed that the microwave method synthesized particles were cubic while the reflux method produced amorphous material. The XRD spectra showed intense diffraction peaks at 2θ values of 17.61º, 20.47º, 25.34º, 29.59º, 43.01º and their miller indices were (511), (442), (731), (751) and (662), respectively. FTIR results revealed that the materials had functional groups such as (C=O, C-O, O-C=O and Cu-O), UV-visible results showed optical absorption band of Cu-MOF was at 274.18 nm for the microwav and 274.41 nm for the reflux methods. This band could be allocated to the charged transfer from the oxygen in carboxylate to Cu^{2+} ions.

Keywords: Copper, Metal-organic frameworks, Microwave method, Reflux method.

INTRODUCTION

Metal-organic frameworks (MOFs) are materials made up of metal bonded to functionalized organic molecules such as carboxylates, sulfonates, amines and pyridines [1]. The arrangement of both parts (metal and organic molecule) provides different crystalline compounds with one, two or three-dimensional porous structures ranging from microporous to mesoporous. Despite several publications on MOFs, these materials are still given a lot of attention due to their applications such as gas storage [2,3] drug delivery [4-6], sensors [7,8], catalysts [9] and adsorption [10-14]. Due to its high porosity [15], MOFs can be prepare using solvothermal, hydrothermal, mechanochemical, sonochemical and electrochemical methods [13]. Some of these methods take several hours to several days hence researchers are making efforts to come up with ways to prepare MOFs using cheaper and efficient ways in a short space of time.

MOFs are mostly prepared by the solvothermal method which has some disadvantages such as long reaction time which can be 20 h to 72 h, which can be tedious and laborious [16,17]. High-throughput screening of synthesis parameters in the formation of the metal-organic frameworks MOF-5 and HKUST-1 was obtained in 20 h [18]. In the study of one-pot synthesis of binary metal-organic frameworks (HKUST-1 and UiO-66) for the enhanced adsorptive removal of water contaminants, Azhar *et al.* [19] prepared HKUST-1 and UiO-66 by the solvothermal method which took 24 h.

Microwave heating is another method that has been used for the preparation of MOFs. CO_2 adsorption and catalytic application of Co-MOF-74 synthesized by microwave heating were done and it took 1 h for the reaction to complete [20]. Lee *et al.* [21] used the microwave method to synthesize porous metal-organic framework, nickel(II) dihydroxyterephthalate and studied its catalytic properties in the oxidation of cyclohexene. Microwave-assisted modulated synthesis of zirconium based metal-organic framework (Zr-MOF) for hydrogen storage applications was obtained after 5 min [22]. Synthesis of a metal-organic framework material, iron terephthalate by ultrasound,

microwave and conventional electric heating: a kinetic study [23] was synthesized in 20 min. It has been reported that the synthesis time is drastically reduced when microwave irradiation was used [23], which include uniform heating of the reaction mixture, increase in heating rate of the reaction, superheating of the reaction and enhancement of the precursor material. It is, therefore, important to come up with methods which are cheap, fast and commercially viable. The microwave synthetic route might be the key to easier and faster preparing MOFs with good chemical properties.

Solvothermal synthesis is sometimes referred to as reflux or the conventional heating method. This is because this method involves heating a mixture of organic bridging ligands (linkers) with a metal salt in high boiling solvent systems [24]. The energy used to drive this type of reaction is thermal energy varying from 79-179 ºC with the process lasting between 48 to 96 h [24]. It is further mentioned that this method produces fine particle powders which are not achieved by most conventional procedures. Thus in this study, the microwave (MW) was used to prepare Cu-MOF and was compared with the reflux method. The synthetic conditions were kept constant for both methods.

EXPERIMENTAL

All chemicals were purchased from the reliable commercial source and used without purification. Copper(II) nitrate trihydrate (99%, Acros Organics), *N,N*-dimethylformamide (DMF) (> 99%, Acros Organics), terephthalic acid (> 99% Acros Organics) and methanol (99%, Promark chemicals).

Preparation of Cu-MOF using the reflux method: The Cu-MOF was prepared according to Shooto *et al.* method [25]. DMF (80 mL) was transferred into a round bottom flask, then 1.04 g $Cu(NO_3)_2{\cdot}3H_2O$ and 1.02 g terephthalic acid were dissolved in the solvent by mild stirring. The solution was refluxed for 24 h at 120 ºC while stirring. The crystals were centrifuged and washed with methanol three times. The obtained crystals were then dried in an air oven at 40 ºC for 0.5 h and used for further characterizations.

Preparation of Cu-MOF using microwave heating: For comparison, Cu-MOF was also synthesized using microwave irradiation using Sineo MDS-6G (SMART) microwave digester with a frequency of 2450 MHz and installed power of 1800 W. The instrument was equipped with a platinum resistor temperature sensor with temperatures ranging from 0-300 ºC. In the typical experiment, 1.03 g $Cu(NO_3)_2{\cdot}3H_2O$ and 1.01 g terephthalic acid were dissolved in DMF by mild stirring in a beaker. The mixture was transferred into a microwave sample holder then placed into a microwave digester. The reactions were heated to 100 ºC for 1 h. The obtained product was treated the same as the product from the reflux method.

Characterization: Scanning electron microscopy images were obtained from a Nova Nano SEM 200 from FEI operated at 10.0 kV. The powders were identified using Shimadzu-XRD 700, X-Ray Diffractometer using Cu$K\alpha$ radiation (λ = 1.154056 Å). The scan range was 2θ with continuous scan mode and a scan speed of 1 degree per minute using a Cu source at scan range of 15-80º, current 30 MA and voltage of 40 kV. FTIR spectra were measured using Nicolet iS50 FTIR spectrometer manufactured by Thermo-Fischer Scientific, universal ATR with a diamond detector at a wavelength from 650 to 4000 cm^{-1}. Thermal studies were determined using Perkin Elmer, simultaneous thermal analyzer STA 6000 with scan temperature from 30 to 900 °C. The temperature ramp rate was 10º min^{-1} with a nitrogen gas flow of 20 mL min^{-1}. Ultraviolet-visible (UV-Vis) spectroscopy was determined by Perkin-Elmer Lambda 25 UV/Vis spectrometer, which collects spectra from 200 to 900 nm using the same solvent in the studied solution as a blank.

RESULTS AND DISCUSSION

SEM analysis: SEM images of Cu-MOF samples prepared under microwave irradiation at 100 ºC for 1 h are shown in Fig. 1 (a-b) while those prepared using the reflux method at 100 °C for 24 h in Fig. 1(c-d). It was observed that the product was composed of layers of cubic shape materials and similar results were observed by Tari *et al.* [26]. Comparing the images from the microwave irradiation with the reflux method, it can be seen that the structures from microwave are more cubic in shape than those from the reflux synthesis (Fig. 1c-d). This is because microwaves influenced the molecules during the reaction, due to a rapid increase in temperature [26]. This resulted in rapid superheating and caused a fast nucleation of Cu-MOF material. Under the reflux method, it was not possible to get well-shaped cubes. It has been reported that microwave irradi-ation accelerated not only nucleation but also crystal growth [17] hence more well-shaped particles were formed in the microwave synthesis. This shows that cubic Cu-MOF can be prepared by microwave irradiation in less time.

XRD analysis: The XRD analysis was done to determine the phase and the structure of Cu-MOF. The XRD patterns of Cu-MOF from microwave and the reflux method are shown in Fig. 2. The intense diffraction peaks were observed at 2θ values of 17.61º, 20.47º, 25.34º, 29.59º, 43.01º and their miller indices were (511), (442), (731), (751), (662), respectively [27,28]. The peak at 17.61º and 43.01º from the microwave method split into multiple peaks and resulted in broad peaks. Cu-MOF from this method also has peaks at 33.88º and 77.51º, which the reflux method does not show. The intensity of the peaks from the two methods varied. This could due to the hydration of the Cu-MOF samples since they are sensitive to moisture [27].

FTIR analysis: The FT-IR spectra of Cu-MOFs are shown in Fig. 3. The microwave shows a peak at 1696 cm^{-1} which is due to C=O stretching mode of the free carboxylic acid [18]. This peak disappeared in the spectrum of MOF made by the reflux method, which means that a COO group of the linker is coordinated to the Cu ions of MOF and that there is no free carboxylic aid [19]. The peaks at 1570 and 1497 cm^{-1} are due to the asymmetric and symmetric stretching modes of coordinated carboxylic acid, respectively [19]. The MOF prepared using the reflux method shows a peak at 1666 cm^{-1} which might be due to ν(C=O) [20]. Whilst the peaks at 1509 and 1387 cm^{-1} are due to asymmetric and symmetric modes of coordinated carboxylic acid respectively [19]. The peaks at 747 and 1015 cm^{-1} are assigned to the symmetric and asymmetric stretching mode of O-C=O and the stretching vibration of C-O of the

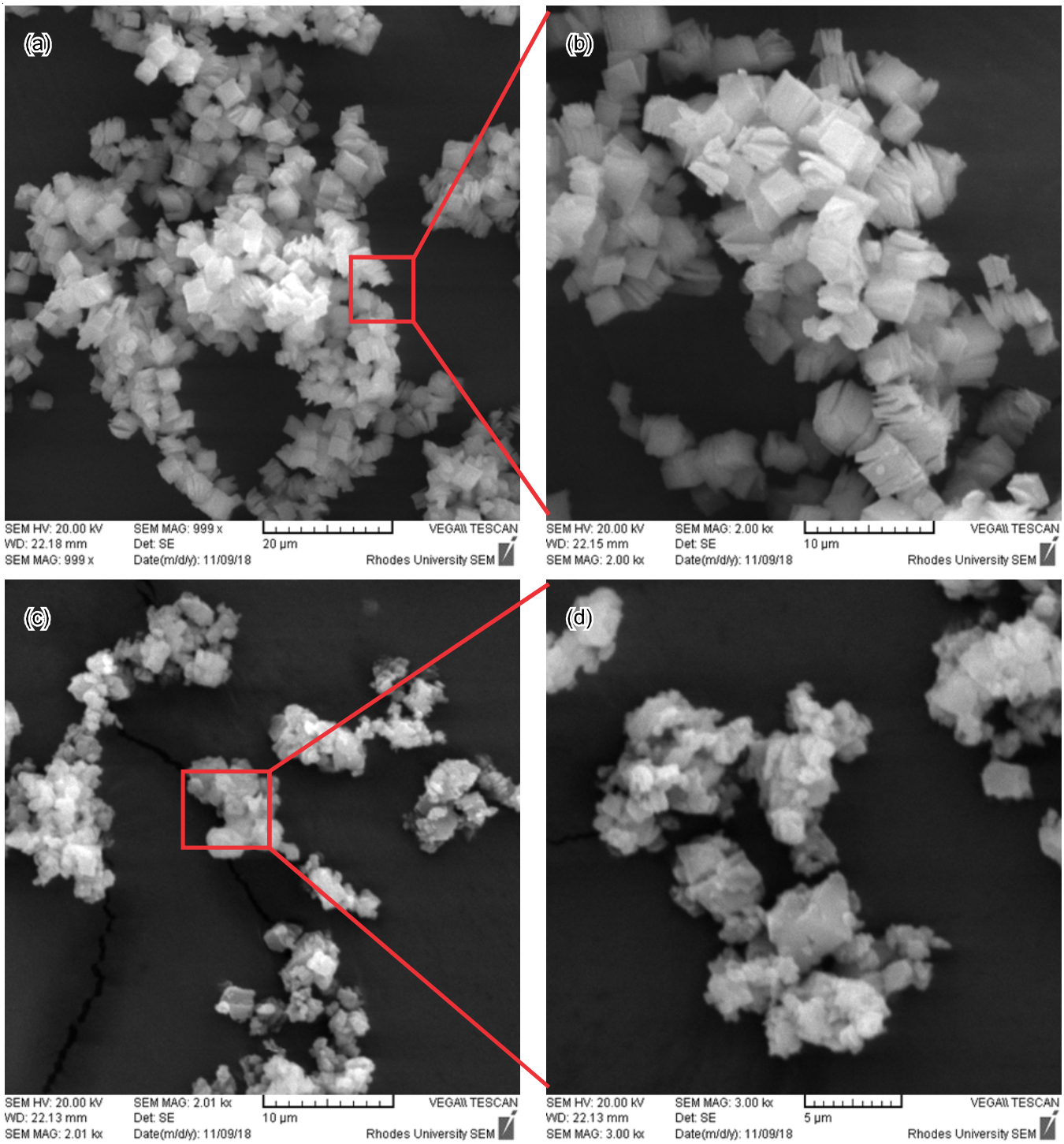

Fig. 1. SEM images of Cu-MOF (a-b) microwave (MW) and (c-d) reflux method (RH)

unreacted and reacted acid [28]. Other peaks at 747 cm^{-1} from both methods are due to C-H bends of the aromatic ring [27,28]. The bands at 572 cm^{-1} might be due to the bending modes of Cu-O [28].

TGA analysis: Thermal stability and percentage weight loss of Cu-MOF are shown in Fig. 4. The reflux method shows three weight losses at 185, 265 and 431 ºC, while the microwave shows three steps of weight loss at 179, 226 and 418 ºC. The first steps are assigned to solvent molecules from the washing steps whilst the second steps might be due to the disintegration of the MOF by losing the hydrogen and the oxygen bonds and the sides bond [18]. The last steps are due to the decomposition of the MOF and collapsing of the structures [19]. In comparing the two methods, the reflux method has an approximate total weight loss of 70% whilst microwave shows a total of 55%. The reflux method shows the highest combustible content [23].

UV-Vis analysis: The optical properties spectra of Cu-MOF prepared from microwave and reflux method are shown in Fig. 5. The samples were prepared with the ultrasonication and significantly absorbs light for wavelengths below 275 nm.

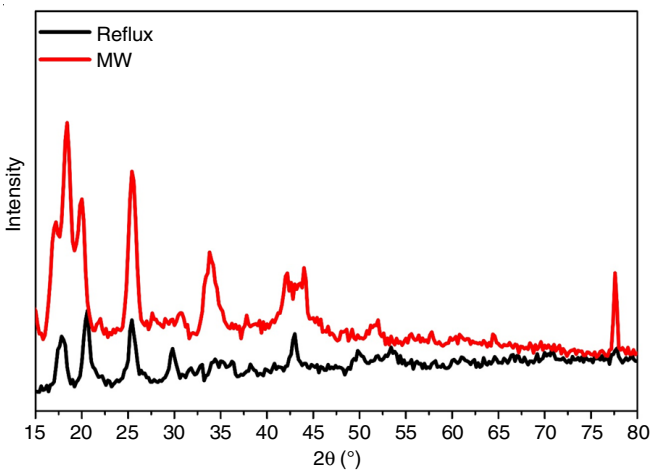

Fig. 2. XRD patterns of Cu-MOF from microwave (MW) and reflux (RH) method

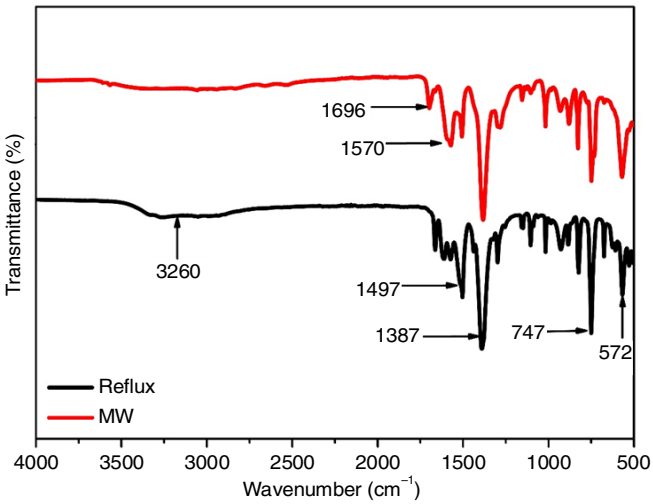

Fig. 3. FTIR spectra of Cu-MOF from microwave (MW) and reflux (RH) method

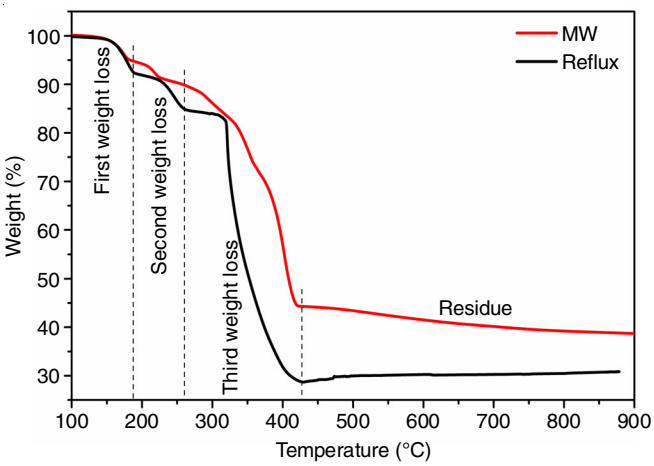

Fig. 4. TGA curve of Cu-MOF from microwave and reflux method

The main optical absorption bands of Cu-MOF were at 274.18 for the MW and 274.41 nm for the reflux methods. This band at 274 nm could be allocated to the charged transfer from the oxygen in carboxylate to Cu^{2+} ions, similar results were obtained by Gupta *et al.* [29]. The results of Cu-MOF prepared using microwave had a high-intensity absorption peak as compared to the peak of Cu-MOF prepared using the reflux method.

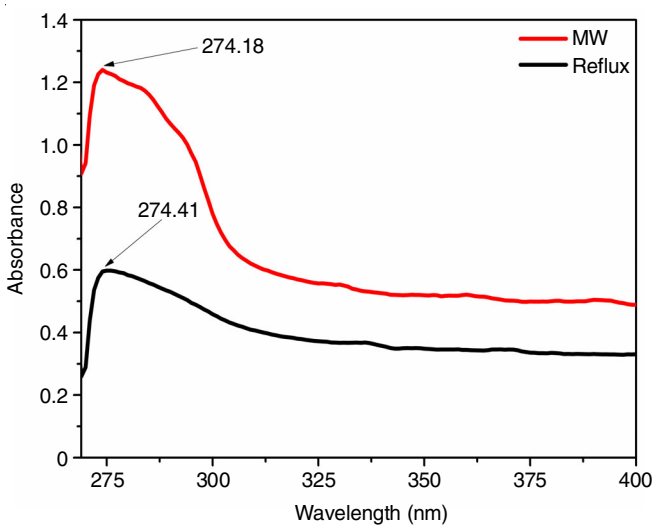

Fig. 5. UV-vis absorption spectra of Cu-MOF from microwave (MW) and reflux (RH) method

Conclusion

Copper metal-organic framework (Cu-MOF) was successfully synthesized using microwave and reflux methods. The materials were confirmed by SEM, TGA, FTIR, UV-Vis and XRD techniques. The microwave method appears to be efficient for preparing Cu-MOF as it reduced the time from 24 to 1 h and the material produced was more uniform compared to that obtained using the reflux method. SEM analysis revealed that the microwave method produced cubic-shaped particles and the reflux method produced irregular shapes. In FTIR, the main optical absorption band of Cu-MOF was at 274.18 cm^{-1} for the microwave and 274.41 nm for the reflux methods. This band could be allocated to the charged transfer from the oxygen in carboxylate to Cu^{2+} ions.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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