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# Synthesis and Characterization of Metal Organic Frameworks for Gas Storage

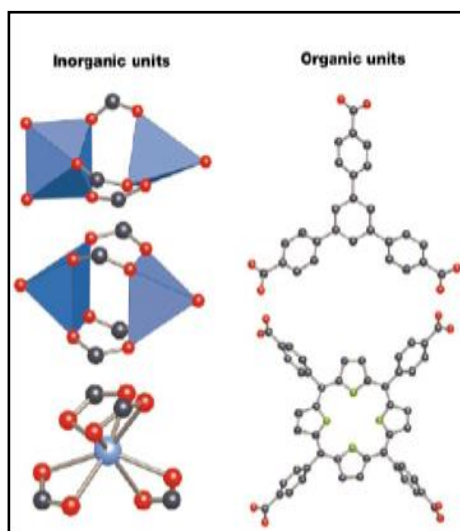
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**Abstract.** This research demonstrates the preparation of a metal-organic framework (MOF-199) using the solvothermal method. The solvothermal conditions for synthesis and activation were investigated by changing the synthesis time (24 - 48 h), the solvothermal temperatures (85 and 100 °C), and the effect of the ethanol: water solvent ratio (within the solvents range from 1:1 to 1:2 ratios). All synthesized samples were characterized using of x-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area (BET). The prepared MOF-199 at the optimal conditions (100 °C for 48 h, 1:1 of the ethanol: water) has up to 5518 m<sup>2</sup>/g m<sup>2</sup>/g surface area (BET), 0.693 cm<sup>3</sup> g<sup>-1</sup> specific volume, a 11.8 Å porous size, and 103 crystallinity. All MOF-199 samples were activated for 21 h at 60 °C.

## 1. Introduction

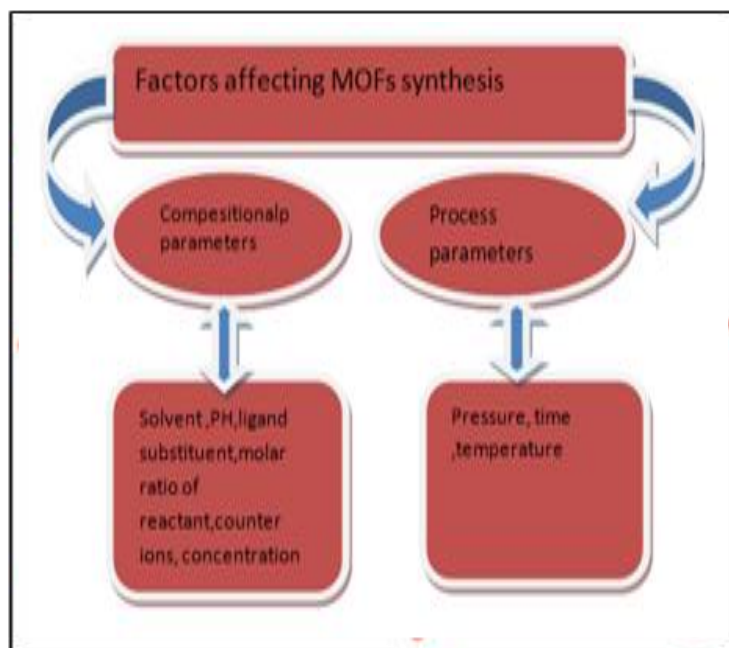
Metal-organic frameworks (MOF) are structured by porous with 1, 2 or 3-dimensional, metal ions (or clusters) in the MOFs structure act as joints to connect by organic linkers [1]. MOFs are synthesis as porous solids by reacting of metal ion salts with organic bridges. These novel porous solids were first invented by Tomic (1965 as the thermally stable metal organic framework).



**Figure 1.** Carboxylate MOFs. O:red; C: gray; N: green; blue: metal ion.

MOFs are porous solid with promising properties such as; up to 5900 m<sup>2</sup>/g surface areas, pores < 2 nm, up to 2 cm<sup>3</sup>/g pore volume, and 0.4 g/cm<sup>3</sup> density. These promising physical properties provided MOFs with an excellent potential for enormous applications as purification, separation, and gas storage [2]. The MOF-199 or HKUST-1 is considered one of important MOFs since it has a high pore volume, good stability upon water adsorption/desorption, large surface area, and high chemical stability [3]. Therefore, this study is focusing on the preparing of MOF-199 and gas storage ability.

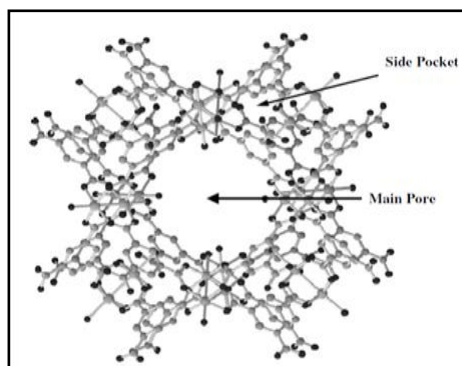
There are several factors that are affecting on the direct or indirect coordination behavior of the metal supply number, which reflect on the structure of the metal-organic frameworks (figure 2). The wise choice of these factors (solvents, reaction temperature, and reaction time) is a main aspect in the preparation of metal-organic frameworks. Many researches provide examples of the solvent system role in regulating and forming of different coordination environment for MOFs. There are could be two roles for the solvents used in the assembling process; the first role is to be mixed with metal ions, whereas, the second role is acting as a guest molecule in the final MOFs lattice structure [4,5]. Solvent work as an intermediate guide or structural agent during the crystal grows of the MOFs in synthesis process, however, solvents mainly may not be incorporated into MOFs synthesized. Experiments revealed the effect of water adding on solvation and re-arranging at different environments for self-assembly of the MOFs. Thus, the MOFs structure appeared to be tuned by changing ethanol: water ratio [3]. Solvothermal synthesis of MOFs is more beneficial than other non-conventional or conventional preparation methods due to pressures higher than 1 atm and the reaction temperature is over than 100° C in a closed system. In the solvothermal synthesis, the feasibility of crystallization process is advanced due to the improving of the solubility for the raw materials, thus a high-quality crystals formed at solvothermal synthesis [6]. The MOFs obtained by the solvothermal synthesis have open channels in the inorganic networks [7].



**Figure 2.** Factors effecting MOFs synthesis

MOF-199 is one of the firm MOFs which synthesis by solvothermal method of Cu<sup>2+</sup> as a metal and 1,3,5-benzenetricarboxylate (BTC) as organic linker [8]. The MOFs with structure containing zinc often their framework might be collapsed during the adsorption/ desorption of water process due to the high affinity of these types of MOFs for moisture. However, MOFs containing copper are often more stable [9]. MOF-199 is formed of metal-organic frameworks where copper (metal) acts as joints and connecting the 1,3,5-benzenetricarboxylate molecules as an anchor. The adsorption properties of the

MOF-199 are improved by the partial positive charges on metal sites. The cell unit of MOF-199 consists of symmetry cube with small octagonal cages and large cavities in their structure (figure 3).



**Figure 3.** Structure of MOF-199 [10].

## 2. Experimental

### 2.1. MOF-199 Synthesis

The general procedure of synthesizing MOF-199 using solvothermal preparation was depended on Schlichte's work [10], where 0.42 g BTC dissolved in 24 ml of 1:1 ethanol:water solvent. The materials were mixed until a clear solution was obtained (10 min). Then a 0.875 g copper (II) nitrate tri-hydrate was added and mixed thoroughly with the mixture further for 10 min. A blue solution was obtained after complete dissolving of mixture reached. Then, the blue mixture was transferred to a 50 ml stainless steel autoclave lined with Teflon. The reactor was heated at 100°C for specific time to achieve crystallization (table 1). At the end of the reaction time, the reactor left to cool at ambient temperature, and a blue powder collected. After that, the blue powder was filtered and washed with a 60 ml of 1:1 water and ethanol mixture. Finally, the blue powder was activated under vacuum using rotary evaporator for 21 h at 60°C and stored at 60°C in vials.

**Table 1.** Prepared MOF-199 samples

Synthesized samples	Synthesis time (h)	Synthesis temperature (°C)	Ethanol:Water ratios
Sample 1	24	25	1:1
Sample 2	24	85	1:1
Sample 3	24	100	1:1
Sample 4	30	100	1:1
Sample 5	48	100	1:1
Sample 6	48	100	2:1

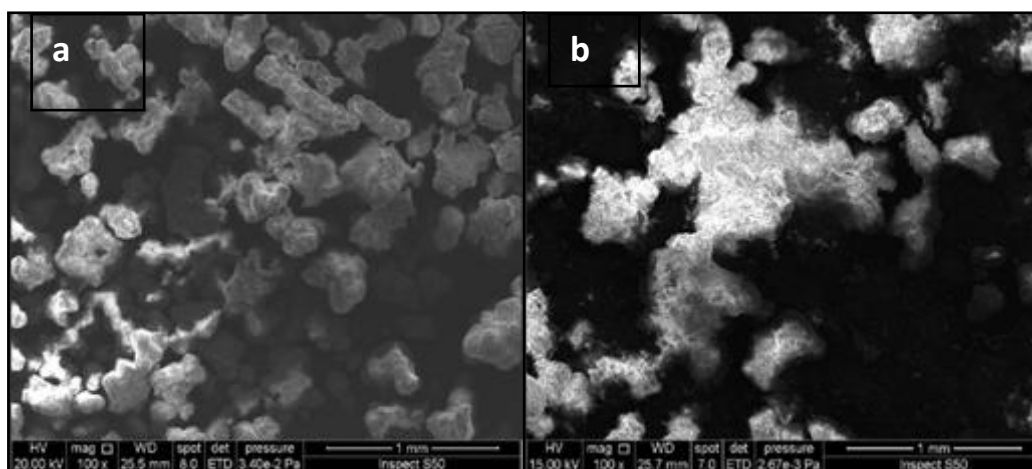
### 2.2. Determination of physicochemical properties

The physicochemical properties were characterized by using Langmuir surface areas (BET), a scanning electron microscope (SEM), and N<sub>2</sub> adsorption isotherms at 77 K ( using Quantachrome Novawin) to obtain the total pore volumes, and x-ray diffraction microscope (XRD, Bruker). The degree of crystallinity MOFs was calculated by the ratio of the peak intensities summation for the prepared MOF-199 to the peak intensities summation of the standard MOF-199 [13].

## 3. Results and discussion

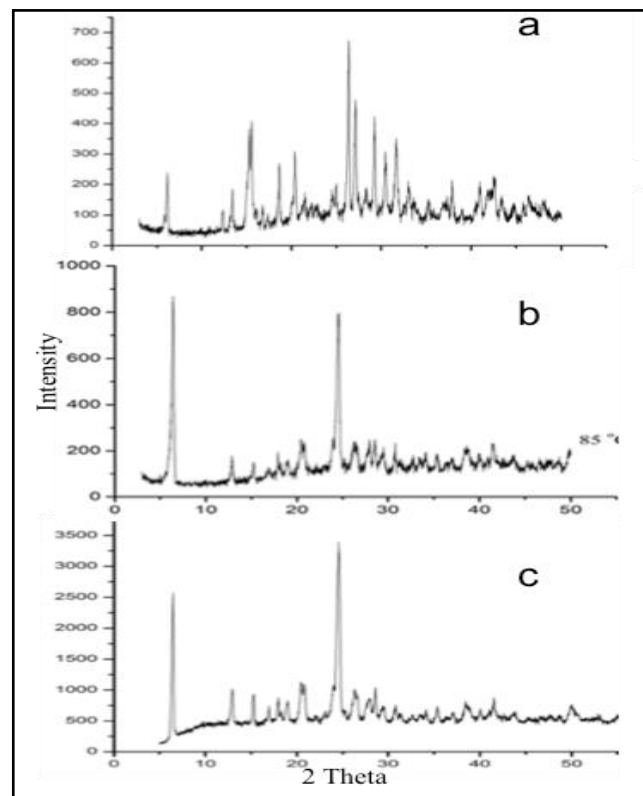
The morphology of the MOF-199 for all samples was studied using an SEM instrument. The SEM images study showed that by increasing the reaction time to 48 h was leading to the deforming of crystals

with sizes shrinking and diminishing of the octahedral crystal at 140 °C. The SEM images of crystals phase for selected synthesized samples MOF-199 showed in Figure 4. The morphology change in MOF-199 as reaction time is prolonging, which is directly related to drop in the yield production, denoted the re-dissolving of MOF-199 due to the prolonged reaction time. Studying the SEM images for the MOF-199 crystals showed that the octahedral shape of crystals phase becomes less obvious with prolong the reaction time. Representative images are shown in Figure 4, for synthesized MOF-199 samples with synthesis time 24 h and 48 h at 85°C and 100°C, respectively. The MOF-199 with these methods is solid dark blue with octahedral crystals shape (0.5-5 µm). For MOF-199 synthesis at 85°C, 24 h the octahedral crystals shape is clear, whereas, for MOF-199 synthesis at 100°C, 48h this shape was less clear and that tie well with Torrente-Murciano et al. results [13]. The SEM images study showed that by increasing the reaction time to 48 h and temperature to 140°C was leading to the deforming of crystals with sizes of crystal shrinking and diminished of the octahedral crystals.

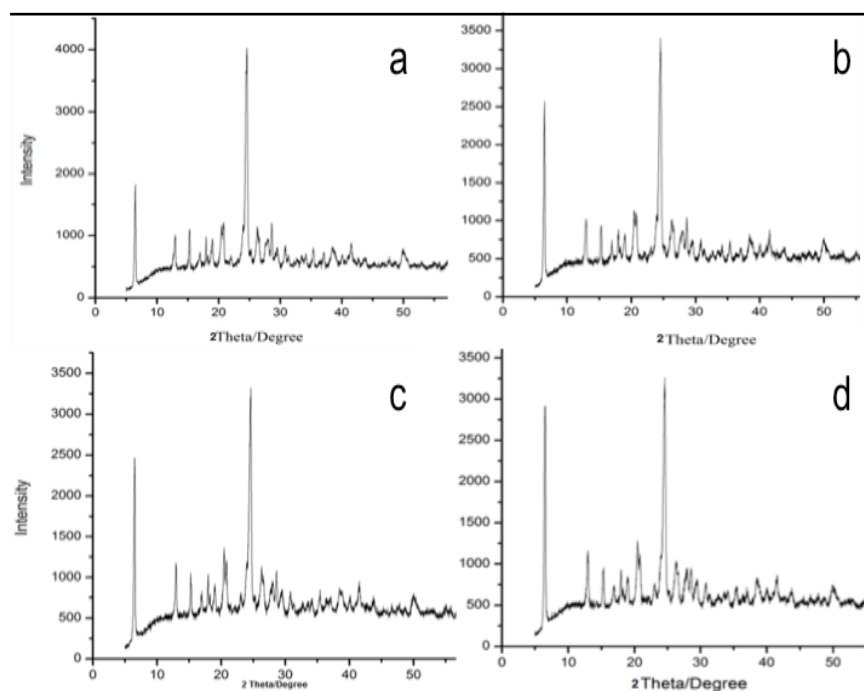


**Figure 4.** SEM for synthesized MOF-199 at a) 85°C for 24 h and b) 100°C for 48h.

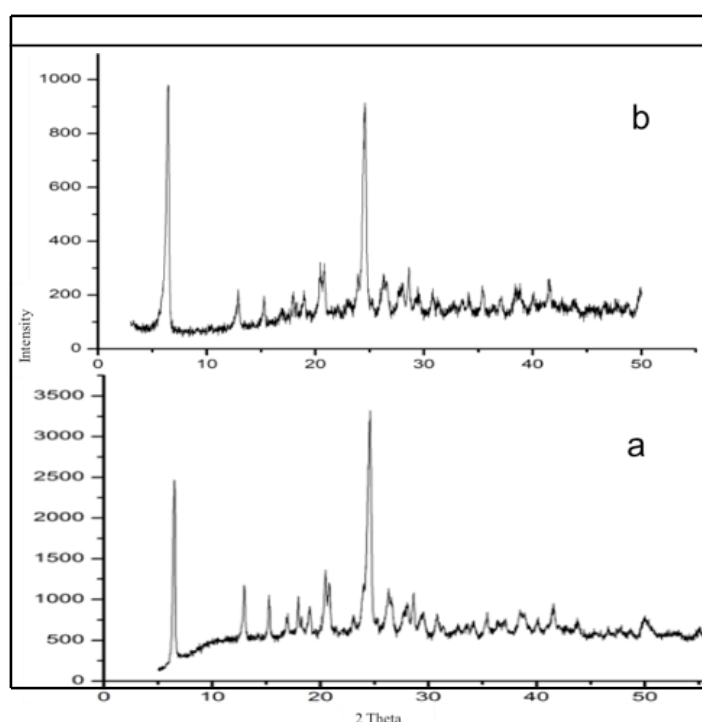
XRD pattern of MOF-199 usually exemplifies its crystalline phase with identification peaks at  $2\theta \approx 6.5^\circ$ ,  $9.5^\circ$ ,  $11.5^\circ$ , and  $13.4^\circ$  [10]. XRD Powder patterns for MOF-199 in figures 5 - 7 showed good agreements with a typical XRD pattern of MOF-199 with good crystallinity. Figure 5 demonstrated the effect of the varying the solvothermal temperatures (25 -100 °C) and fixing other conditions (1:1 ethanol:water ratio, and 24 h synthesis time) on the framework structure of MOF-199. At 25°C synthesis temperature, MOF-199 phase was not pure with slightly appearance of distinguished peaks (see Fig 5.a). The intensity of peaks for different MOF-199 samples was varying as a result of the raising the solvothermal temperature from the 25°C up to 100°C. When comparing these results to degree of crystallinity for the MOFs (see table 2, it must be pointed out that the degree of crystallinity for synthesized MOF-199 samples increased with the increasing of the solvothermal temperature up to 100°C. From Figure 5, it can be concluded the optimum temperature with high crystallinity of the sample is at 100°C, therefore, this temperature will be fixed and the next step will be finding the effect of reaction time at constant temperature. Figure 6 shows the effect of the changing the reaction time (24, 30, and 48 hours) at 100°C solvothermal synthesis temperature and 1:1 Water:Ethanol ratio on MOF-199 structure. MOF-199 formation is noted by the present of peaks at  $2\theta \approx 6.5^\circ$ ,  $9.5^\circ$ ,  $11.5^\circ$ , and  $13.4^\circ$  even at 18 h. It was clear that by prolonging solvothermal synthesis time up to 48 h the intensities of the peaks were increased and that means by prolonging crystallization time in that range the crystallinity increasing as shown in table 2.



**Figure 5.** XRD analysis of MOF-199 samples for 24h @ a) 25°C, b) 85°C, and c) 100°C



**Figure 6.** XRD pattern of MOF-199 synthesized at  $T=100\text{ }^{\circ}\text{C}$  for a) 18 h, b) 24 h, c) 30 h, and d) 48 h



**Figure 7.** XRD pattern of MOF-199 synthesized at 100°C, 48 h and solvent ratio a) 1:1 ethanol: water, b) 1:2 ethanol :water

Figure 7 demonstrated the influence of water content (1:1 - 1:2) in solvent for sample 5 and sample 6, all the synthesis conditions have been fixed. The Diffractogram data of crystals synthesized obtained with different solvent volume show the same typical pattern of MOF-199 [13]. Although, the varying the water content has not led to any difference in the XRD patterns for synthesized MOF-199, there was significantly different in the characteristic peaks intensity. At 1:1 ethanol:water, the characteristic peaks intensity have the highest intensity (figure 7a) with the high surface area (table 2). At 1:2 ethanol:water, the water content was doubled thus the crystallization process decreased because of the low concentration of raw materials. Therefore, high degree of crystallinity and high surface area were obtained at 1:1 ratio. Crystallinity results using equation two are listed in Table 2. MOF-199 synthesized sample with the highest crystallinity was obtained from the solvothermal condition of 85°C for 24 h. Nevertheless, from a comparison of the crystallinity for the MOF-199 and the BET surface area results (table 2), it is seen that the MOF-199 at 100°C for 48 h has the highest surface area (5518 m<sup>2</sup>/g) with high crystallinity off 103%. Surface area of synthesized MOFs determined using N<sub>2</sub> adsorption at 77K using the BET method. It was found that the surface area increasing reflects positively on activity of the catalyst [14]. The obtained value of MOF-199 surface area listed in Table 3, these values (5518 m<sup>2</sup>/g at 100°C for 48h) were higher than the value obtained by Jiang (1247 m<sup>2</sup>/g at 100°C for 13h) compared with time and temperature of the reaction [15]. It can be concluded that the synthesized MOF-199 in this research was approximately comparable with the standard with high relative crystallinity (Table 2). As shown, the optimum solvothermal for the synthesis of MOF-199 for the chosen operation conditions are 100 °C, 48h and 1:1 ethanol:water ratio. The solvothermal conditions are chosen based on the XRD patterns of the MOFs follow the pattern of typical XRD of MOF-199 with the high crystallinity and the highest surface.

**Table 2.** Surface area and crystallinity of samples

Synthesized Sample	Synthesis time (h)	Synthesis temperature (°C)	Surface area m <sup>2</sup> /g	Crystallinity%
Sample1	24	25	-	122
Sample2	24	85	2679	106
Sample3	24	100	2902	100
Sample4	30	100	3635	100
Sample5	48	100	5518	103
Sample6	48	100	-	94

#### 4. Conclusion

This research presented a study for the influence factors on the solvothermal synthesis of MOF-199. In this study, it was obtained an optimized procedure that maximizes the surface area and crystallinity of MOF-199 (up to 5518m<sup>2</sup>/g and 103, respectively) while varying the solvothermal synthesis time and temperatures.

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