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Performance Determination of Aluminium Metal Organic Framework in Carbon Dioxide Gas Adsorption

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ABSTRACT

The rapid escalation of atmospheric carbon dioxide (CO_2) concentrations has raised an alarming surge in global temperatures, consequently contributing to global warming. This phenomenon is irreversible and has detrimental consequences for our planet. Unfortunately, current technologies and methodologies have proven inadequate in mitigating atmospheric CO_2 levels to the good indoor air quality. Hence, the pressing need to conceive and develop innovative and cost-effective CO_2 removal techniques and technologies. Metal-organic frameworks (MOFs) have emerged as promising materials in the pursuit of effective CO_2 removal, owing to their distinctive properties. Characterized by their porous structures and expansive internal surface areas, MOFs exhibit a remarkable capacity for CO_2 adsorption. In this study, we embarked on the synthesis of MOFs employing aluminum chloride hexahydrate in conjunction with two distinct organic ligands, namely, benzene-1,3,5-tricarboxylic acid (BTC) and benzene-1,4-dicarboxylic acid (BDC). Our research endeavors aimed to study the influence of varying molar ratios of metal precursor to organic ligand on the adsorption capacity and structural characteristics of the resultant MOF structures. The results elucidated that Al-BDC possesses superior CO_2 adsorption performance relative to Al-BTC. Specifically, the 1:3 molar ratio of Al-BDC emerged as the highest CO_2 adsorption performance among all the assessed samples. This finding suggested the potential suitability of Al-BDC for CO_2 adsorption applications.

Keywords: *Adsorption, aluminium, carbon dioxide, metal organic framework, metal precursor*

1. INTRODUCTION

The two major carbon dioxide (CO_2) emissions sources are natural processes and human activities. The CO_2 emission from human activities is substantially lower than the amount of CO_2 released from natural processes [1]. Before the existence of many human activities that emit CO_2 into the atmosphere, the rate of removal by nature was almost equal to the emission rate of CO_2 from nature. The balance that existed for many thousand years has been broken since humans released CO_2 into the atmosphere without attempting to remove it [2]. The rapid increase in atmospheric CO_2 levels has resulted in rising global temperatures and global warming. Global warming can result in many irreversible negative consequences for our planet. The existing technologies and methods are insufficient to reduce atmospheric CO_2 to a reasonable level. Therefore, developing innovative CO_2 removal technologies and methods is imperative [3].

Metal-organic frameworks (MOF) are organic-inorganic hybrid crystalline porous materials [4]. The inorganic unit of MOF is the metal ion that acts as a joint, while the organic unit of MOF is an organic ligand that acts as a linker in the network structure [5]. The network structure of MOF can be 1, 2, or 3-dimensional [6]. The metal nodes connect the organic linker's arms to create a cage-like structure. The internal surface area of MOFs is extremely large because of their hollow structure. In addition, MOFs have the largest reported surface area of any known materials. MOFs also have a very high porosity due to the presence of long organic linkers. The long organic linkers provide large storage space and multiple adsorption sites inside MOFs [7, 8]. MOFs' distinct structural diversity makes them special compared to other porous materials. The unique properties possessed by MOFs include uniform pore structures, atomic-level structural uniformity, tunable porosity, wide varieties, flexibility in network topology, geometry, dimension, and chemical functionality [9].

Synthesis of a new type of material, metal-organic framework (MOF), through a solvent-free method, is developed attributed to the green chemical manufacturing direction. MOF can potentially become a widely used technology for the removal of CO_2 due to its unique properties and characteristics [10, 11]. The porous structure of MOF makes it an excellent physical adsorbent. In addition, the high adsorption capacity of MOFs enables them to adsorb large amounts of atmospheric CO_2. As a result, the invention and development of MOF can potentially reduce global warming [12]. Besides, the negative environmental impact of solvents can be avoided

when a solvent-free method is used to fabricate MOF [13]. The solvent-free synthesis method ensures that no environmental pollution occurs during MOF's mass production. This work studies benzene-1,3,5-tricarboxylic acid (BTC) and benzene-1,4-dicarboxylic acid (BDC) organic ligand on the aluminium metal-organic framework performance in carbon dioxide adsorption.

Current technologies and methods fall short in effectively reducing indoor CO_2 concentrations to the regulated levels stipulated by relevant authorities such as the Department of Occupational Safety and Health. The resultant elevated CO_2 levels have the potential to deteriorate indoor air quality, thereby precipitating health issues, including sick building syndrome and respiratory tract infections. In this research, the synthesis of MOFs utilizing aluminum chloride hexahydrate in conjunction with two distinct organic ligands, BTC and BDC. The primary objective was to assess the efficacy of these MOFs in adsorbing CO_2 under varying molar ratios with the target to be applied in the indoor air quality improvement.

2. MATERIAL AND METHODS

2.1. Material

The source of metal precursor used was aluminium chloride hexahydrate, $AlCl_3 \cdot 6H_2O$ (99% purity) purchased from Alfa Aesar, United Kingdom and two types of organic ligands were used to synthesize aluminium metal-organic frameworks, namely benzene-1,3,5-tricarboxylic acid (BTC), and benzene-1,4-dicarboxylic acid (BDC) were both obtained from Sigma Aldrich, United States of America with purity more than 98.5%.

2.2. MOF Fabrication

The predetermined molar ratio of aluminium chloride hexahydrate to benzene-1,3,5-tricarboxylic acid (BTC) at 1:1 or and benzene-1,4-dicarboxylic acid (BDC) at 1:1 or 1:3, respectively were mixed and ground using a mortar and pestle (Table I). The aluminium chloride hexahydrate and BTC or BDC mixtures grinding were carried out at room temperature without adding any solvent or liquid additive. Attributed to the hydrated nature of the metal precursor, water was produced during the grinding process. Hence, after the grinding process, the mixtures were heated at 240°C for two hours by introducing the mixtures in an autoclave in order to crystalline the mixture and remove the moisture content. Subsequently, the products were cooled to room temperature.

Table 1 Fabrication composition of aluminium MOFs

MOFs	Aluminium molar ratio	BDC molar ratio	BTC molar ratio
Al-BDC-1:1	1	1	-
Al-BDC-1:3	1	3	-
Al-BTC-1:1	1	-	1
Al-BTC-1:3	1	-	3

2.3. Characterisation Physiochemistry Properties of MOFs

Scanning electron microscopy (SEM) (Hitachi S-3400N, Japan) was utilise to study the surface morphology of the synthesized MOFs, whereas energy dispersive X-ray (EDX) was applied to examine the elemental composition of synthesized MOF. Firstly, the MOFs samples were placed on a sample holder and coated with gold using a sputter coater machine (Quorum SC7620, United Kingdom) to enhance their conductivity before the analysis. The samples coated with gold and platinum were transferred to the SEM-EDX instrument to study their morphology and elemental composition. The morphology of the samples was observed using a magnification of 2,000. Three spots of the sample were used to examine the elemental composition to yield the average in EDX analysis for elemental composition.

X-Ray Diffractometer (XRD) (Shimadzu 6000, Japan) is applied to study and examine the crystallinity and structure of the synthesized MOF. The sample was placed on the holder and compressed to create a flat surface. Consequently, the sample was transferred to the XRD instrument for analysis. It is important to ensure that the door of the instrument was closed properly due to the radioactive nature of the radiation used in the analysis. A scan range of 5° to 30° and a scan rate of 2θ per minute were utilized. Each sample took approximately 15 minutes to complete the analysis.

2.4. Gas Adsorption Study

First, the samples and empty glass bottles were weighed and recorded. The sample was then placed into the glass bottle, and the mass of the bottle containing the sample was weighed and recorded. After that, the opening of the bottle was covered using a breathable porous bag to facilitate the flow of carbon dioxide into the bottle. Then, the glass bottle was placed inside the stainless-steel vessel for the CO_2 gas adsorption test. The upper inlet of the vessel was equipped with a tube to enable the flow of pure CO_2 gas into the pipe for a predetermined duration. Prior to the CO_2 gas adsorption test being completed, CO_2 gas adsorption capacity of the samples was calculated through the difference between the final and initial mass of the samples. The gas adsorption capacity of the prepared sample is calculated using the following equation.

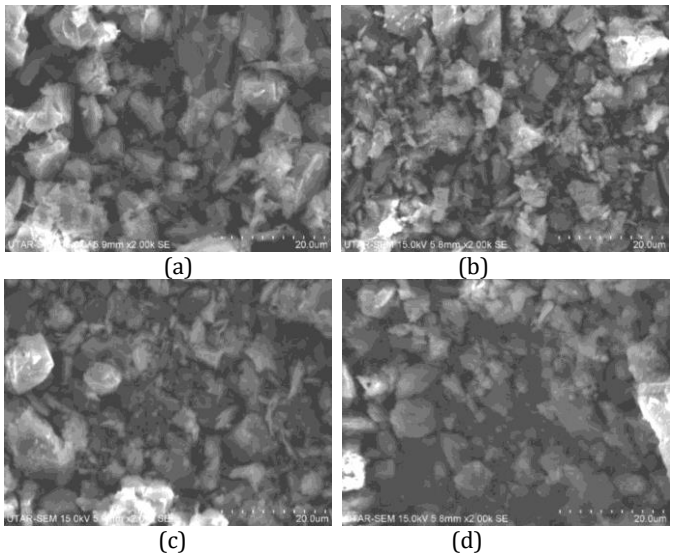
$$n_{ads} = (W_f - W_i)/W_i \div M_{CO2}$$

where n_{ads} is the mole of CO_2 adsorbed (mmol), W_i and W_f are the weight of the MOF before and after the adsorption (mg) and M_{CO2} is the molar mass of CO2 (44.009 mg/mmol).

3. RESULTS AND DISCUSSION

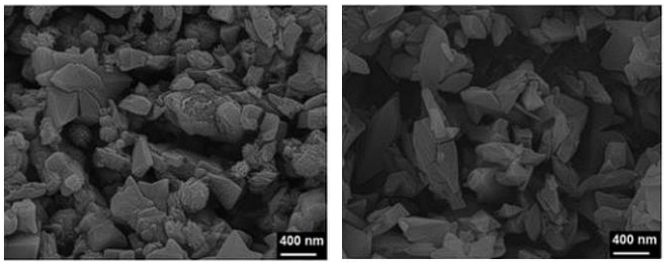
3.1. Physiochemical Properties of MOFs

In this study, Al-BDC synthesis was conducted using solvothermal methods in a hydrothermal autoclave reactor, which was similar to the literature mentioned previously. Upon comparing Figure 1(a) to (d), it is observed that the structure of the synthesized Al-MOFs is similar to the structure of MIL-53(Al) synthesized in the literature by Cihan and coworkers (Figure 2) [14]. It is interesting to note that there are notable differences between the structures of Al-BDC and Al-BTC. Al-BDC exhibited a more tightly packed and smaller trapezoidal crystal structure, whereas Al-BTC exhibited a more dispersed and larger trapezoidal crystal structure with the presence of a lumpy crystal. The presence of lumpy crystals indicated the unsuccessful crystal formation, as they did not break down into smaller trapezoidal crystals during the crystal formation process. The lumpy crystal formation might be attributed to the type of organic ligands used in the fabrication of MOF [15]. Furthermore, the formation of lumpy crystals was undesirable because it could negatively affect the performance of the samples in the CO_2 adsorption test and decrease their efficiency. Additionally, based on the SEM image of Al-BDC-1:1 and Al-BDC-1:3, it is observed that Al-BDC-1:3 exhibited a larger crystal structure as compared to Al-BDC-1:1. This observation suggested that the increase in the Al/BDC molar ratio results in a corresponding increase in the size of the crystal structure. For Al-BTC, when the ratio of Al/BTC increase, the formation of lumpy crystal decreases, and lead to the formation of trapezoidal crystal.



(a) (b) (c) (d)

Figure 1. SEM morphology of (a) Al-BDC-1:1, (b) Al-BDC-1:3, (c) Al-BTC-1:1, and (d) Al-BTC-1:3, respectively at 2,000x.



(a) (b)

Figure 2. SEM morphology of MIL-53(Aluminium) (a) 1,000x and (b) 2,000x [14]

The EDX analysis results indicated that Al-BDC and Al-BTC consist of carbon, oxygen, and aluminium (Table 2). The organic ligands used in the MOF fabrication, which were BTC and BDC, were the sources of carbon and oxygen. At the same time, the metal precursors, which were aluminium chloride hexahydrate were the sources of aluminium. The fabrication of MOF is considered to be successful because the samples comprised solely the metal precursor and organic ligand used in the fabrication of MOFs. In the case of Al-BDC, and Al-BTC, an increase in the metal precursor to organic ligand molar ratios led to a corresponding increase in the weight percentage of the metal elements present in the samples.

Table 2 EDX analysis of aluminium MOFs

MOFs	C (Wt%)	O (Wt%)	Al (Wt%)
Al-BDC-1:1	38.26	40.67	21.07
Al-BDC-1:3	40.96	43.54	15.49
Al-BTC-1:1	37.42	41.94	20.64
Al-BTC-1:3	40.41	45.44	14.16

The XRD analysis of Al-BDC and Al-BTC (Figure 3) illustrated that both Al-BDC and Al-BTC with different molar ratios exhibited two distinct peaks at 2θ of 24° and 2θ of 27°. In particular, the peak with the highest intensity for Al-BDC-1:1 occurred at 2θ of 24°, while for Al-BDC-1:3, it occurred at 2θ of 27°. Similarly, the highest intensity peak for Al-BTC-1:1 occurred at 2θ of 27° and 2θ of 24° for Al-BTC-1:3. The XRD patterns of the Al-MOF samples synthesized are coherent with the findings reported in the literature, and the peaks of all the Al-MOF samples are in good agreement with that reported in the previous work done by Moreno et al. [15]. It is observed that in the literature, peaks occurred at 2θ of 24° and 2θ of 27° which was identical to the Al-MOF samples synthesized, indicating that the Al-MOFs are well synthesized.

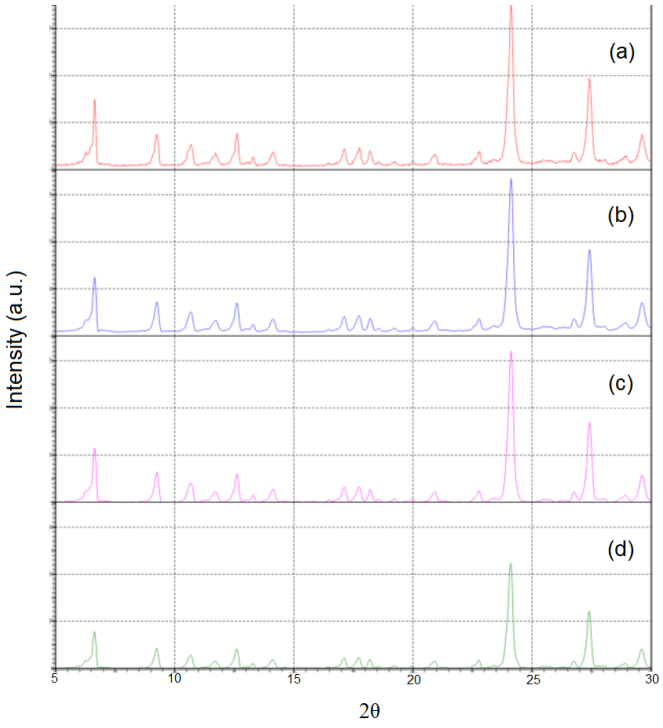


Figure 3. XRD analysis of (a) Al-BDC-1:1, (b) Al-BDC-1:3, (c) Al-BTC-1:1, and (d) Al-BTC-1:3

3.2. Effect of BDC and BTC Organic Ligand on the Performance of Aluminium MOFs in CO_2 Adsorption

The weight of the MOF was measured before and after the test. The difference between the two weights represents the quantity of CO_2 adsorbed by the MOFs during the adsorption test. The MOF with the greatest CO_2 gas adsorption is considered the most effective sample, as it adsorbed the largest amount of CO_2. Table III illustrates the CO_2 gas adsorption results for Al-BTC and Al-BDC, respectively. It is observed that Al-BDC-1:3 exhibited a better CO_2 adsorption performance compared to Al MOFs at 0.045 mmol/g. This result aligns closely with the observations reported in prior literature studies and the SEM morphology in the previous section [16]. The consistent findings suggest that MOFs with a more refined crystal structure exhibit an increased surface area-to-volume ratio. This phenomenon contributes to an increased level of porosity within the material. This resemblance with the results obtained by other researchers not only exhibit the robustness of the results but also reinforces the broader understanding of how the structural properties of MOFs impact CO2 adsorption [17]. Relative to other Al MOFs fabricated in this study, Al-BDC-1:3 possess the finest crystal structure as observed in the SEM morphology, therefore, it had a better overall CO_2 adsorption performance than another Al MOFs.

Table 3 CO_2 gas adsorption study by aluminum MOFs

MOFs	CO_2 gas adsorption (mmol/g)
Al-BDC-1:1	0.021 ± 0.004
Al-BDC-1:3	0.045 ± 0.009
Al-BTC-1:1	0.029 ± 0.012
Al-BTC-1:3	0.035 ± 0.006

4. CONCLUSION

In this study, Al-BDC and Al-BTC MOFs were successfully synthesized using solvent-free fabrication method. The physical and chemical properties of the MOF samples were examined using various types of characterization instruments. The EDX analysis results indicated that all of the MOFs comprise solely the metal precursors and organic ligands used in the fabrication process. Other elements were not observed in the MOF samples. Then, both Al-BDC and Al-BTC exhibited trapezoidal crystal structures. The XRD results revealed that the synthesized MOF samples were in good agreement with the XRD patterns reported in the literature, which had similar peaks occurring at the same degrees. The results of the CO_2 adsorption test revealed that Al-BDC-1:3 exhibited the best adsorption performance. The results from this study suggested that the types of metal precursors, organic ligands, and metal precursor to organic ligand molar ratios used in the fabrication of the MOFs will have a significant impact on the formation and the size of the crystal structure, which will directly affect the adsorption ability of the MOFs.

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