IOP Conference Series: Materials Science and Engineering

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To cite this article: K C Chong *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **670** 012002

ICADME 2019 IOP Publishing
IOP Conf. Series: Materials Science and Engineering **670** (2019) 012002 doi:10.1088/1757-899X/670/1/012002

Preparation and characterization of chromium metal organic framework with trimesic or terephthalic acid in carbon dioxide adsorption

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Abstract. Greenhouse gases (GHGs) have greatly changed the global climate in the recent year. Metal organic frameworks (MOFs) is one of the solutions which can be utilized as gas adsorbents to capture carbon dioxide (CO2), the main contributor of greenhouse effect. MOF possesses good CO2 adsorption ability attributed to its high surface area to volume ratio and pore size. Nevertheless, the success of the MOF is greatly depend on the fabrication parameter such as fabrication methods, type of metal oxide, type of organic linkers used and the molar ratio of the reactant. In this study, chromium (VI) oxide, trimesic acid and terephthalic acid were used to fabricate MOFs by solvothermal method to investigate the performance of CO2 adsorption. The characterization tests by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) shows that Cr-TMA-1:5 amongst the rest of the fabricated MOF possess the shape of small irregular diagonal with highest surface area to volume ratio which was ideal in CO2 adsorption. Furthers, the result CO2 adsorption test carried by thermogravimetric analyser (TGA) suggested the MOF Cr-TMA-1:5 possesses the highest the CO2 adsorption capacity recorded at 0.099 mmol/g. This had revealed that MOFs composed of chromium (VI) oxide and trimesic acid possess the potential to be applied in CO2 adsorption.

1. Introduction

MOF is a crystalline porous solid that made by organic acids and inorganic metals and it consists of multiple metal-ligand bonds [1]. These bonds enable the formation of three-dimensional organic-inorganic hybrid networks. There are numerous types of metal-ligand combinations that can be casted by varying the use of metals and acids as well as method of formation [2,3]. These provide endless combinations of MOFs to be formed [4]. MOFs are well-known for their characteristics of adjustable pore size, tuneable internal surface properties, enormous specific surface areas which can extend beyond 6000m2/g and ultrahigh porosity that can achieve up to 90% free volume [5]. Therefore, optimizing the combination of metal complexes and organic linkers can change the affinity of pores towards the desired gases to be adsorbed. Also, MOFs have been investigated as existing potential CO2 adsorbents mainly due to its physical structural characteristics. Generally, MOFs have high porosities, small pore sizes (ranging from scale of ultra-micro to meso), high specific surface area (>6000 m2/g), low densities (0.2-1 g/cm3), excellent thermal and mechanical stabilities. Besides, MOFs are better than many other mesopores gas adsorbents as MOFs will not show hysteresis effect when the gas is removed from the micropores MOFs for regeneration [6]. Numerous MOFs with different metal ions and organic linkers have been synthesized and investigated in lab scale for CO2 adsorption by other researchers. According to a study, different starting materials which are cobalt ions, nickel ions, zinc ions and magnesium ions could yield various capacities for CO2 adsorption [7]. The metal ions in MOFs will be having interactions with molecules of CO2. Hence, it is suggested that metal with coordinative unsaturated sites in the framework shall be selected to fabricate an effective CO2 adsorbent. Besides, the property of the metal can also affect the stability of MOFs under humid conditions. The polarity of metal sites and CO2 must be considered as it will affect the interactions of adsorbate and adsorbent [8]. On the other hand, the selection of organic linkers is very vital in designing MOFs that can have good performance in adsorbing CO2. Generally, molecular size of linkers plays an important role in determining pore sizes between coordinated metal centers which can greatly influence the pore volume and surface area of the materials. In other words, longer molecules give higher porosity for better diffusion of CO2. Also, MOFs with functionalized organic ligands can adsorb CO2 better than MOFs with unfunctionalized pores. However, the selectivity of CO2 would be reduced if the pore sizes are too large [8]. Stoichiometry of reactants can also greatly affect the topographies and structural patterns of MOFs which may lead to different performances when they are applied for certain tasks. Hence, the molar ratio of organic and inorganic reactants used are very crucial in synthesizing MOFs [9].

2. Methodology

2.1. Materials

Metal oxides and organic acids were used in this study to fabricate MOF. In this study, the chosen metal oxide will be chromium (VI) oxide (CrO3) whereas organic acids that will be utilized were trimesic acid (TMA) and terephthalic acid (TPA). All the chemicals were obtained from Sigma Aldrich and used without further purification.

2.2. Synthesize and characteristic method

In this study, solvothermal method was applied to produce MOFs as it can form MOFs with nanoscale morphologies in short period of time [10,11]. First and foremost, predefined mass of metal oxide was dissolved in 12ml of deionized water. Later, the solution was mixed with predefined volume of organic acid and 12ml of ethanol solvent [12]. The mixture was stirred at room temperature until homogenous. Subsequently, the mixture was poured into a Teflon lined autoclave and heated in an oven at temperature range of 80˚C for 72 hours. The mixture was later cooled to room temperature and crystalline powders was formed. Lastly, the MOF was collected and shall be kept at room temperature and dry condition for further application. The composition of MOFs fabricated were tabulated in Table 1 where it were labelled according to the molar ratio of metal oxide to organic acid.

Table 1. The absorption of the MOF.

Metal Organic Frameworks	Chromium oxide, (mmol)	Trimesic acid, (mmol)	Terephthalic acid, (mmol)
Cr-TMA-1:1	1	1	Nil
Cr-TMA-1:2	1	2	Nil
Cr-TMA-1:3	1	3	Nil
Cr-TMA-1:4	1	4	Nil
Cr-TMA-1:5	1	5	Nil
Cr-TPA-1:1	1	Nil	1
Cr-TPA-1:2	1	Nil	2

Cr-TPA-1:3	1	Nil	3
Cr-TPA-1:4	1	Nil	4
Cr-TPA-1:5	1	Nil	5

2.2.1. Scanning Electron Microscope (SEM)

SEM (Hitachi S3400N) was used and it will be carried out under accelerated voltage of 12kV. SEM was used to observe the morphology of MOFs. Before the analysis was carried, the specimen was placed on sample holder and fixed on the holder with carbon tape. Later, a layer of gold will be sputtered on the surface of sample by sputter coated machine. The gold metal layer can increase the conductivity of sample as well as enhance the focused beam of electrons to penetrate through the sample and hence clearer image can be obtained.

2.2.2. Energy Dispersive X-ray (EDX)

The distinct atomic structures of MOFs will be formed by using different materials and mole fraction of metal and organic linkers. EDX was used to determine the elemental composition of MOFs. In this analysis, five different points will be chosen randomly for characterization and the average results was obtained based on the unique set of peaks obtained.

2.3. CO2 Gas Adsorption Study

The CO2 gas adsorption study was carried by thermogravimetric analyser (Simultaneous thermal analyser (STA) 8000) to study the CO2 adsorption performance of the MOFs (Figure 1). Initially, the initial mass of MOF sample was weighted and placed in the sample pan of TGA. Subsequently, the moisture content of the sample needs to be removed by increasing the temperature of TGA to 150˚C and nitrogen gas was flowed at the rate of 0.02 L/min. Before purging the gas of CO2 to measure the CO2 adsorption capacity of MOF, the sample of MOF was being cooled down from 150˚ C to room temperature. Lastly, the final mass of MOF sample was weighted and the difference of initial and final mass of MOF sample was the CO2 adsorption capacity of the MOF.

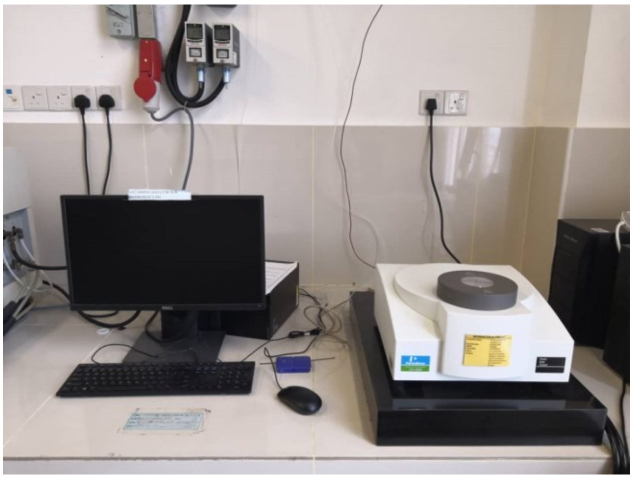

Figure 1. CO2 gas adsorption study by thermogravimetric analyser (TGA).

3. Results and Discussions

3.1. Morphologies of Metal Organic Framework

The morphologies of fabricated Cr-MOFs from TMA or TPA were captured from SEM analysis with magnification scale of 2,000 times as shown in Figure 2 and Figure 3. Both Cr-TMA and Cr-TPA MOF possess similar morphology which consists of randomly dispersed irregular diagonal shape of particles. Additionally, it was also noted the degree of crystallinity significantly enhanced and the sizes of crystal structure obtained was relatively smaller as the molar ratio of metal oxide to organic acid decreased. The comparison of the morphologies obtained between Cr-MOFs from TMA or TPA, the crystal structure of Cr-TMA series was relatively more oriented than Cr-TPA series. These may lead them to have higher surface area to volume ratio and hence have better gas adsorption.

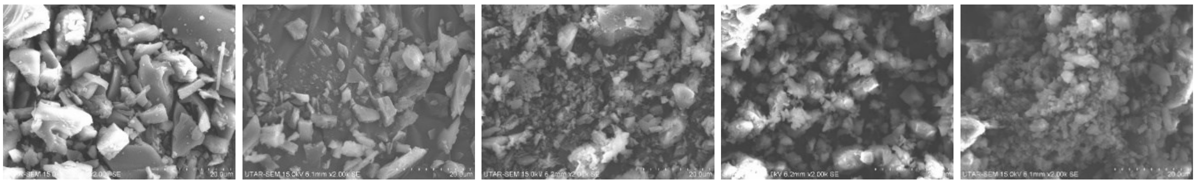
(a) (b) (c) (d) (e)

Figure 2. SEM Morphologies of Cr-TMA MOF, (a) Cr-TMA-1:1, (b) Cr-TMA-1:2, (c) Cr-TMA-1:3, (d) Cr-TMA-1:4, and (e) Cr-TMA-1:5.

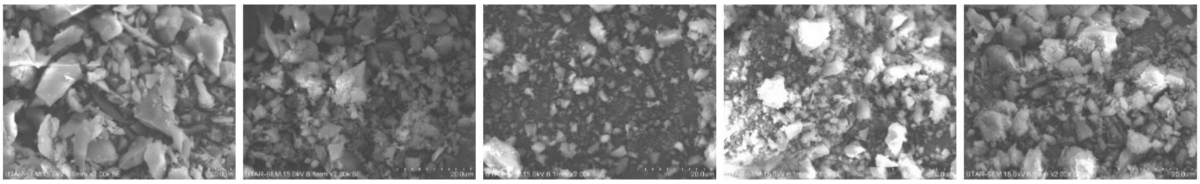
(a) (b) (c) (d) (e)

Figure 3. SEM Morphologies of Cr-TPA MOF, (a) Cr-TPA-1:1, (b) Cr-TPA-1:2, (c) Cr-TPA-1:3, (d) Cr-TPA-1:4, and (e) Cr-TPA-1:5.

3.2. EDX Analysis

The elemental content of each MOF sample was measured in term of weight percentage by employing EDX and the results was depicted in Table 2. There were only three elements being detected which were chromium, carbon and oxygen. These detected elements were coherent to the materials used to fabricate MOFs that were chromium (IV) oxide, terephthalic acid or trimesic acid. Due to the inhomogeneity of the samples, three readings were obtained from different spots for each sample to yield an average reading. The weight percentage of the chromium was observed decreases as the molar ratio of metal oxide to organic acid decreases (Table 2).

Table 2. EDX analysis.

MOFs	Carbon	Oxygen	Chromium	Carbon
Cr-TMA-1:1	16.29	40.84	42.87	16.29
Cr-TMA-1:2	46.13	42.26	11.61	46.13
Cr-TMA-1:3	46.60	43.11	10.30	46.60
Cr-TMA-1:4	50.60	39.21	10.19	50.60
Cr-TMA-1:5	48.18	45.00	6.82	48.18
Cr-TPA-1:1	48.92	39.59	11.49	48.92
Cr-TPA-1:2	41.08	48.45	10.47	41.08

Cr-TPA-1:3	38.83	50.89	10.27	38.83
Cr-TPA-1:4	44.95	45.05	9.99	44.95
Cr-TPA-1:5	44.94	48.93	6.12	44.94

3.3 Gas Adsorption Study

The gas adsorption study result reveal that the overall adsorption performance of Cr-TMA MOFs is better than Cr-TPA MOFs. It is interesting to note that both Cr-TMA and Cr-TPA MOFs illustreated the similar trend where the performance CO2 adsorption also increases as the molar ratio of metal oxide to organic acid decreases. Amongst all the MOFs fabricated in this study, Cr-TMA-1:5 has the highest adsorption capacity recorded at 0.095 mmol/g. This may be attributed by the morphologies of the MOFs. As the surface area to volume ratio of MOF, the CO2 adsorption increases. Hence, this has revealed that there was a great relationship between the molar ratio of metal to organic ligands, the types of organic ligands used during fabrication and the performance of CO2 adsorption.

Table 3. Gas adsorption study.

MOFs	Adsorption (mmol/g)	MOFs	Adsorption (mmol/g)
Cr-TMA-1:1	0.025 ± 0.0012	Cr-TPA-1:1	0.007 ± 0.0004
Cr-TMA-1:2	0.037 ± 0.0035	Cr-TPA-1:2	0.010 ± 0.0007
Cr-TMA-1:3	0.051 ± 0.0027	Cr-TPA-1:3	0.013 ± 0.0005
Cr-TMA-1:4	0.089 ± 0.0039	Cr-TPA-1:4	0.018 ± 0.0003
Cr-TMA-1:5	0.095 ± 0.0032	Cr-TPA-1:5	0.021 ± 0.0006

4. Conclusions

Various molar ratio of metal to organic ligands were used to fabricate ten different MOFs that were chromium oxide to organic acid of terephthalic acid or trimesic acid at ratio of 1:1, 1:2, 1:3, 1:4 and 1:5 respectively. The morphologies of Cr-TMA-1:5 from SEM has exhibited the most oriented and highest surface area to volume ratio will have the highest CO2 adsorption at 0.099 mmol/g among all the MOFs as observed in the gas adsorption study. This can also be proven by the EDX composition analysis as the materials used to synthesize MOFs were seemed to be fully incorporated to the MOFs and coherent with the elemental analysis of EDX. These results show that MOFs of Cr-TMA and Cr-TPA can be further developed to fight against global warming by adsorbing CO2.

Acknowledgments

The authors would like to thank Universiti Tunku Abdul Rahman for providing financial support in this work under the UTARRF (Project No.: IPSR/RMC/UTARRF/2017-C1/C04)

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