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Yulia, Fayza
Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia

Marsya, Shavira
Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia

Bobby, Yohanes
Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia

Nasruddin
Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia

他

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Design and Preparation of Succinic Acid-Based Metal-Organic Frameworks for CO_2 Adsorption Technology

Fayza Yulia[1], Shavira Marsya[1], Yohanes Bobby[1], Nasruddin[1,*], and A Zulys[2]
[1]Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia,
Depok, 16424, Indonesia
[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia,
Depok, 16424, Indonesia

*Corresponding Author's email: nasruddin@eng.ui.ac.id

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Abstract: Increasing amount of CO_2 in the atmosphere caused by human activities has quickly become one of the most urgent environmental issues. CO_2 Capture and Storage (CCS) is a promising option as it can reduce the amount of CO_2 emissions in the atmosphere. It is critical to develop an efficient separation technique for capturing CO_2 from the gas streams. One of the technologies in CCS is utilizing a crystalline porous material called Metal-Organic Frameworks (MOFs). To take the advantages of MOF due to the ease of modification, we designed bio related ligand from natural products in the form of porous framework. Bio-MOFs discussed in this research is made from Chromium (III) Nitrate and Succinic Acid ($C_4H_6O_4$) as ligand. The synthesis is carried out through hydrothermal reaction method using water as solvent. This research measured Chromium-Succinate MOF's porous properties, thermal stability, morphology, and chemical functionalities by performing various test such as adsorption/desorption of N_2, thermogravimetric analysis (TGA), scanning electron microscope (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The results of this study show that this Bio-MOF based succinic acid (Cr-SA) has surface area of 233 m^2/g with pore volume of 0.66 cm^3/g. The porosity of Bio-MOF Cr-SA is comparable to other reported Bio-MOFs. Bio-MOF Cr-SA also has good thermal stability which can maintain its structure up to temperatures above 350ºC. From the Bio-MOF properties that have been investigated, it is expected that it would be a preliminary study for the use of succinic acid bio-ligands in MOF for CO_2 capture application.

Keywords: Bio-MOFs; CO_2 uptakes; Adsorbent Characteristics; Adsorption; Succinic Acid

1. Introduction

The emissions of Carbon Dioxide from burning fossil fuel have reached such an alarming rate, resulting in worldwide impact, the need for an effective method for reducing the amount of CO_2 emission has never been this high[1, 2]. In 2011, globally averaged atmospheric CO_2 at Earth's surface reached 390.4 ppm surpassing 390 ppm limit for the first time. This means the global atmospheric CO_2 level has risen more than 110 ppm compared when the industrial age begun at 1750[3]. Most of the CO_2 emission is caused by anthropogenic activities such as electricity generation that takes up 26% of total CO_2 emissions and road transport field which accounts for around 25% of CO_2 emissions[4]. Therefore, global CO_2 emissions can be drastically reduced by preventing the amount of CO_2 released by chemical reaction in power plants and mobile transportation into the atmosphere[5]. Many researches have been focusing on finding suitable method for specifically lowering the CO_2 released by burning fossil fuel; and one of which is Carbon Capture and Storage (CCS)[6]. CCS has been estimated to reduce 80%-90% CO_2 emission in power plant equipped with suitable CCS technologies[5]. Generally, based on the fundamental chemical process involved in the combustion of fossil fuels, there are three basic CO_2 separation and capture method: (1) pre-combustion capture; (2) oxy-fuel combustion; and (3) post-combustion capture [7]. This research is focusing on post-combustion capture by removing CO_2 from flue gas. This method is the most feasible on short-time scale and research in this area has future benefit on developing application in natural gas[8, 9]. One of the challenges of this method is finding the suitable material that has exact property, so that the CO_2 capturing process has high performance while still being cost-efficient and suitable for long-term use.

Adsorption process in CCS can be done using either chemical sorbent which involve the interaction between chemicals which lead to the formation of molecular structures that are CO_2-based, or physical sorbent that rely on porous material to form the bond between sorbent and sorbate[10]. Chemical sorbent consumes relatively higher energy compared to when using physical sorbent making it less-reliable at the moment; thus, most researches tend to focus on carbon capture by physical adsorption by considering materials and experimental investigations[9]. Moreover, in the few past decades, the development a material called Metal Organic Frameworks (MOF) has become hot topic in the field of material science[9]. MOFs are known for its high-porosity, adjustable pore, excellent sensitivity and adsorbing ability, making it suitable adsorbent in CCS application[11, 12]. Implementation of MOF-based CCS in post-combustion system is to limit the amount of CO_2 released to atmosphere. The goal is to create MOF that has high performance of separation, environmentally friendly, and cost-effective technologies. The green chemistry priority including renewability and recyclability cannot be achieved with the use of commercial MOF where most of the material comes from petrochemical feedstock. Biological MOF, known as Bio-MOF, can be a solution as it has green composition, cost-effectiveness, and recyclability[13].

Bio-MOF uses ligand that is taken from natural sources and mostly found in living organism such as amino acids, peptides, nucleobases and saccharides[14, 15]. These ligands come with various shape and size that offer the potential to utilize multiple coordination sites and functional group. They also can be useful in controlling hydrogen-bond and creating flexible and robust MOF structure. Bio-ligand offers opportunity for researcher to create various combination based on chirality, aromaticity, cyclic or aliphatic features that they desired[14]. This advantage makes Bio-MOF a promising solution for CO_2 capture, separation, photoluminescent, and catalyst[14].

Utilizing multidentate N- or O- donor ligand and multifunctional carboxylic acid in the formation of MOF structures had been widely used to increase the gas adsorption performance[16]. Succinic Acid (SA) is a natural acid that is commonly found in foods such as vegetables and fruits with an affordable price[17]. This carboxylic acid groups have interesting behavior due to the conformational flexibility, coordination diversity, and attracting the CO_2 molecules. The SA ligand design with the lanthanide group had also been investigated[18-21]. However, the MOF design of SA and transition metal are still less explored.

To demonstrate its feasibility as a ligand on MOF for transition metals, we performed a synthesis using the hydrothermal method of Bio-MOF based on metal ion Chromium (Cr) and Succinic Acid. Their high affinity and chemical structure that can be used to make an excellent MOF in term of porosity and coordination chemical bond will determine the adsorbing quality of the product for gas adsorption application. Herein, we report the new topology of Bio-MOF Cr-SA which is equipped with adsorbent physical characteristics such as structure, porosity, thermal stability, chemical functionalities and morphology. It is expected that in the future, this research can become the guidance in the use of natural succinic acid ligands with transition metals for CO_2 capture applications.

2. Methodology

2.1 Materials

Chrome(iii)Nitrate and Succinic acid used in this experiment were purchased from Aldrich Chemical Co. Inc. and used as received. Other materials needed for performing this experiment are sodium sulphate, NaOH, N,N-dimethylformamide (DMF) from Merck, demineralized water and Ethanol where those chemicals are widely available in market.

2.2 Synthesis Procedure

The Synthesis of Chromium-Succinate MOF is done using hydrothermal method as illustrated in Fig. 1 [20]. The procedure begins by dissolving 0.46 g of Chromium Nitrate in 30 mL water then reacting the solution with 0.13 g Succinic Acid and 0.008 g Sodium Sulphate. Sodium Hydroxide is then added until the pH of the solution is 5.0. Solution is then placed inside autoclave to be heated in the oven for 18 hours at 160°C. Furthermore, the autoclave is cooled to room temperature. After cooling, DMF is dropped on the sample to remove the unreacted substance, then the sample is heated at 80°C for 5 hours[22]. Afterwards the MOF is separated from the solution using centrifugation. In the sample that has been formed, MOF is then dropped by ethanol to then be heated at 80°C for 5 hours to eliminate the remaining DMF in the pores. Finally, drying process is carried out for 12 hours at 80°C. After drying process is complete, the sample is ready for characterization.

2.3 Adsorbent Characterization

Characterization is done using various tests by referring to literature[22]. The presence of functional group is tested using Spectrophotometer FTIR (Fourier Transform Infra-Red). The method is carried out on KBr using Thermo Scientific™ Nicolet™ iS™5. The thermal stability is analyzed by the TGA Q500 instrument. The sample is heated to a temperature of 550°C with a heating rate of 10°C/min below the flow of oxygen. Morphology, microstructure, and particle size are measured using SEM (Scanning Electron Microscopy) by JEOL FESEM at a voltage of 20 kV and MOF's. N_2 adsorption/desorption isotherm is measured in an ASAP-2020 adsorption apparatus (Micromeritics).

3. Result and Discussion

3.1 Synthesis

The synthesis process of succinic acid-based Bio-MOFs is carried out using the solvothermal method which refers to the synthesis of succinate-sulfate MOFs that had been carried out by D'Vries et al[20]. Succinic acid organic compound used as a ligand with the metal used is chromium nitrate with a molar ratio of 1:1.

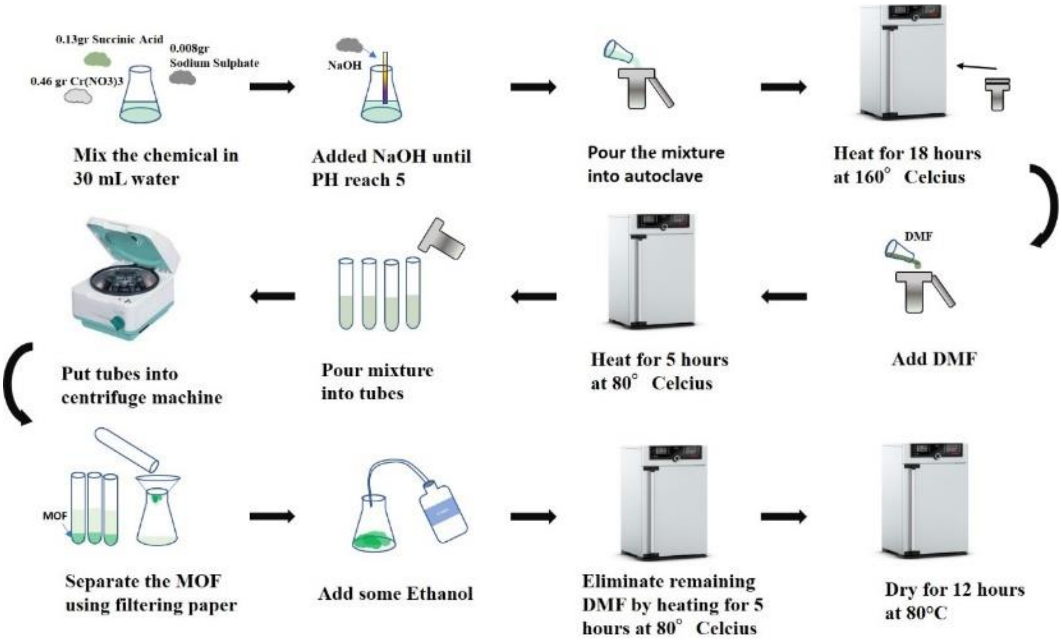


Fig. 1: Synthesis Procedure of Chromium-Succinate Bio-MOFs

The solvent used in the synthesis process affects the size of the MOF. CO_2 molecules adsorbed involve the coordinative vacancies of MOFs[23]. NaOH was used in this synthesis process to increase the pH to 5. Purification method was carried out in two steps to remove succinic acid which does not react with DMF organic solvents and anhydrous ethanol, to obtain better porous Bio-MOFs crystals.

3.2 FTIR Analysis

To identify the functional groups contained in the synthesized Bio-MOFs Chromium-Succinate, FTIR analysis was performed. Fig. 2 shows the IR spectra of Chromium-Succinate. The peak at ~3371 cm^{-1} can be identified as stretching O-H vibrations from water coordination and no peak observed at 1600 cm^{-1} indicates that water adsorption on Bio-MOFs particle did not exist [24]. The broad band at ~1538 cm^{-1} was assigned to as υ_S(OCO), the peak at 1307 cm^{-1} indicates that there was υ_S (OCO) mode[25, 26]. The stretching vibration of the symmetrical carboxylic C=O group was also seen at the peak around 1437 cm^{-1} with medium intensity[27]. Further, the bands at 1108 and 985 cm^{-1} were assigned to asymmetric and symmetric C-C stretching vibrations respectively[28]. The bands at 649 and 592 cm^{-1} were assigned as the bending and vibrations of COO^- in FT-IR spectrum. The peaks that have been described have been in accordance with a study conducted by Bernini et al. by designing Holmium-Succinate MOFs[29]. It means that the MOF that has been synthesized contained the chemical functionalities of the succinic acid ligand. Thus, MOF have been successfully formed.

3.3 Surface Area and Porosity

The specific surface area, pore volume, and diameter of the Bio-MOFs chromium-succinate were calculated using Surface Area Analyzer (SAA) with the Multipoint BET (Brunauer Emmett Teller) method of N_2 adsorption/desorption isotherms at 77.4 K. The calculated surface area obtained is 233 m^2/g.

The total pore volume of this adsorbent is 0.66 cm^3/g at relative pressure (P/P_0) 0.99. The average diameter of synthesized Chromium Succinate is 16.98 nm. Table 1 shows the surface area comparison of some Bio-MOF that had been synthesized. In addition, the table shows that Chromium-Succinate has a fairly good surface area of another reported Bio-MOF. It is expected that with a good surface area potential, it can adsorb more CO_2 molecules[30].

3.4 Thermal Stability

A property key in MOF adsorbent is thermal stability which is influenced by divalent metal nature[31]. Fig.3 shows the thermogravimetric curves of Chromium-Succinate Bio-MOFs with weight loss ratio with heating process up to 550°C. The decrease in the first stage was at temperature 100°C caused by the evaporation of water molecules from the pores of the adsorbent. Furthermore,

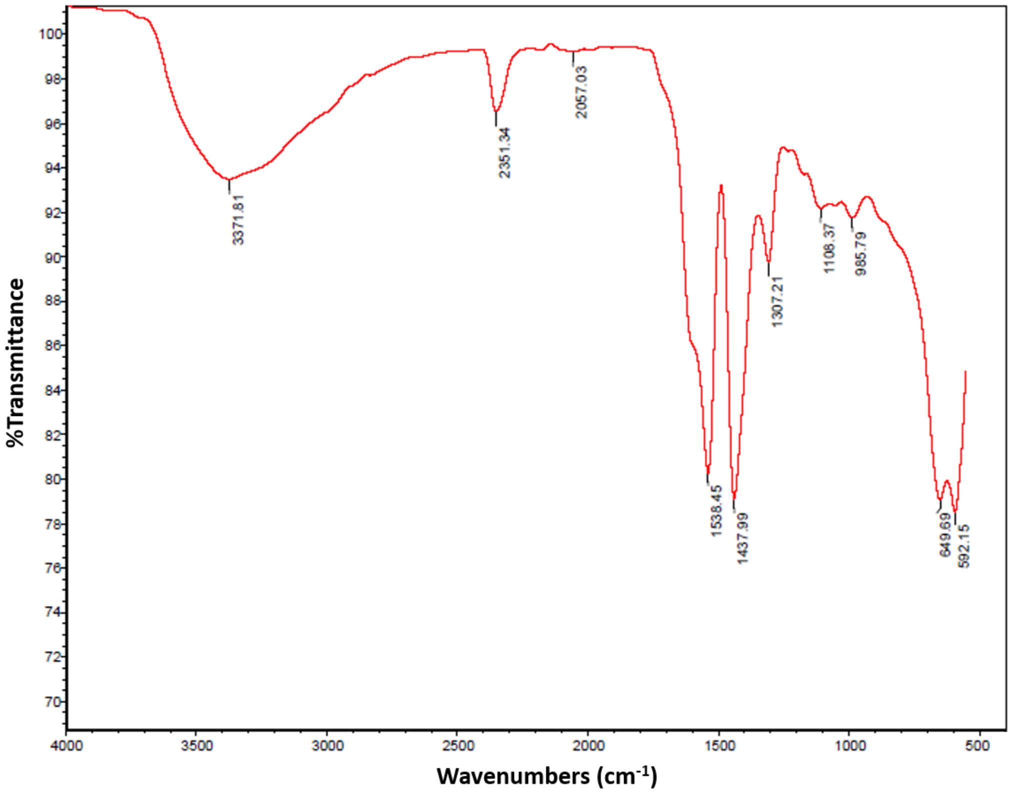


Fig. 2: FTIR spectra of Chromium-Succinate MOFs

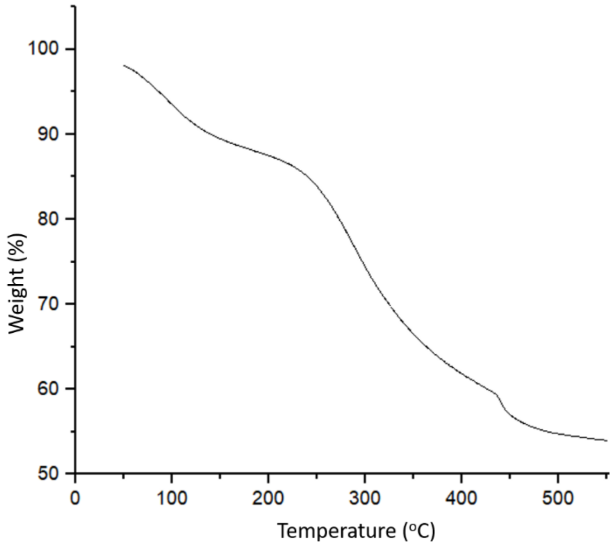


Fig. 3: TG curves of Chromium Succinate synthesized

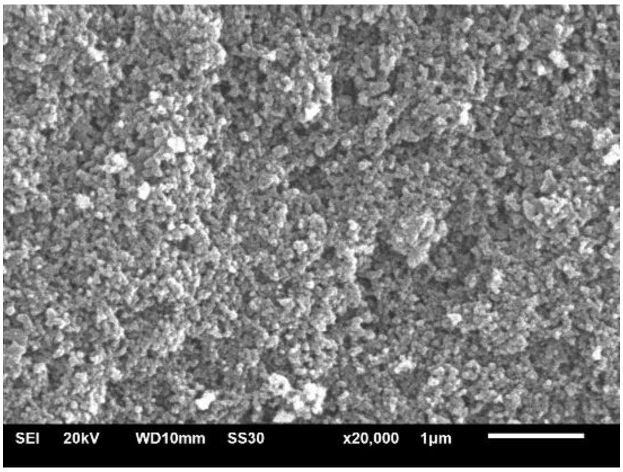
The decrease in mass that occurred at 250°C was due to the evaporation in the MOFs structure. Then, a gradual decline occurred at temperatures above 350°C which indicates residues of the Cr_2O_3 metal.

3.5 Morphological Properties

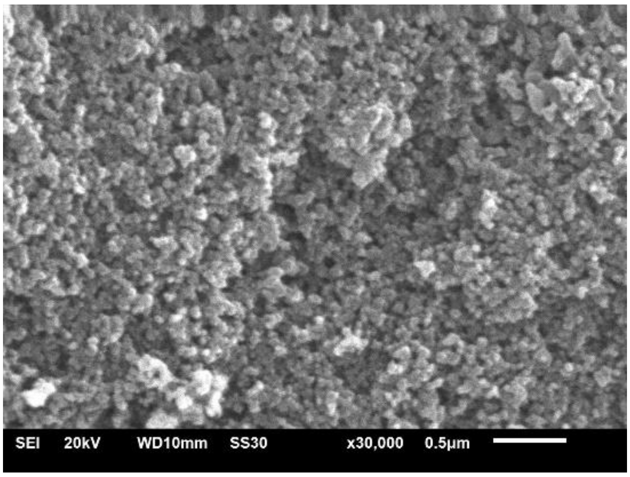
Bio-MOFs chromium-succinate synthesized was characterized using SEM to see the morphology of the Particle. Fig.4 shows the results of SEM with magnification of 20,000 and 30,000 times. It shows the smooth surface, agglomerates, and pores of Chromium Succinate. EDX characterization was also carried out to know the composition contained in Bio-MOFs that had been synthesized in this study. The composition of adsorbents characterized by EDX can be seen in Table 2.

Table 2. EDX Result of Chromium-Succinate

Element	Mass%
C	14.75
O	13.23
Na	1.21
Cr	58.11



(a)



(b)

Fig. 4: SEM images of Chromium Succinate at two different magnifications (a) x20,000 (b) x30,000

4. Conclusion

We have synthesized Bio-MOFs chromium-succinate through hydrothermal condition in the temperature condition of 160ºC for 18 hours. It was then characterized for its physical properties using some investigation methods such as FTIR, TGA, SEM, and N_2 adsorption/desorption isotherms. In synthesis process, twice purification was performed to remove unreacted substance in the frameworks of MOFs using DMF and hot ethanol. Specific surface area and pore volume obtained are 233 m^2/g and 0.66 cm^3/g, respectively. The procedure of synthesis of Chromium-Succinate will continue to be optimized to get better porosity and crystallinity. Further, this research could be a starting point in the use of the natural ligand succinic acid in Bio-MOF for CO_2 adsorption.

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