Research evaluation of some properties of HDX-24 porous metal mechanical frame material

Luong Trung Thien, Le Ngoc Hoan, Nguyen Cao Tuan, Vu Ngoc Toan*

Institute of New Technology, Academy of Military Science and Technology, 17 Hoang Sam, Cau Giay, Hanoi, Vietnam;

*Corresponding author: vntoanchem@gmail.com

Received: 09 Aug. 2024; Revised 12 Oct. 2024; Accepted 12 Nov. 2024; Published 25 Nov. 2024.

DOI: https://doi.org/10.54939/1859-1043.j.mst.99.2024.61-68

ABSTRACT

This paper introduces the results of the research on the fabrication of HDX-24 porous metal-mechanical framework material using 4,4'-Bipyridine-2,6,2',6'-tetracarboxylic acid (H4L). The properties of post-fabrication materials are studied through a number of modern research methods such as Scanning electron microscopy (FE-SEM), BET-specific surface area determination, TGA thermogravimetric analysis, X-ray diffraction spectroscopy (XRD), X-ray energy scattering spectroscopy (EDS), etc. Fourier Transform Infrared Spectroscopy (FT-IR). The results show that HDX-24 material has a specific surface area-BET of 239.06 m^2/g, the adsorption capacity of the material reaches 5.2 mmol/g, the particle size reaches 75-78 mm, and the pore volume is 0.202 cm^3/g.

Keywords: HDX-24 material; MOFs; H4L.

1. INTRODUCTION

Metal-Organic Frameworks (MOFs) have long been known for their diverse structure and flexible adjustments. This is achieved by changing the metal ions and different ligands, which in turn creates structures with adjustable pore sizes and shapes. These pores allow MOFs to absorb, store, and react with molecules ranging from gases and liquids to organic molecules with complex structures. There are several methods for synthesizing MOFs. Hydrothermal and solvothermal synthesis involves high temperature and pressure conditions in aqueous or organic solvents, respectively, to produce well-defined crystalline structures. Gaseous phase synthesis uses gaseous precursors at high temperatures to create MOFs with specific structures or sizes. Precipitation from solution involves dissolving precursors in a solvent and inducing precipitation by altering conditions like pH or concentration, allowing for controlled particle size and shape. Electrochemical synthesis employs electrical current and electrodes to precisely control the formation and structure of MOFs. Self-assembly relies on the spontaneous arrangement of structural components to form MOFs, bypassing traditional methods. Co-crystallization involves using different compounds to create MOFs with unique properties or structures [1].

The structure of HDX-24 is also constructed from metal ions bonded to organic ligands, forming a highly porous crystalline framework [2]. The pores in this structure are not only of exceptional size and shape but also have flexible adjustments, which optimize gas absorption. This outstanding feature gives the HDX-24 a very large surface area, allowing it to absorb and store large amounts of gas in a small volume, increasing efficiency and reducing costs in applications related to gas storage and separation [3]. In addition, with its large specific surface area and porous structure, HDX-24 can increase the efficiency and selectivity of chemical reactions, minimize energy consumption, and enhance the efficiency of production processes [4]. The ability to interact with a wide variety of molecules also gives HDX-24 the potential to be a flexible catalyst that can be adapted to each specific type of reaction [5]. With its outstanding properties and diverse application potentials, HDX-24 not only solves energy and environmental problems but also opens up many new prospects in scientific and industrial research, especially in the field of gas catalysis and storage [6].

This paper introduces some research results on the fabrication and evaluation of properties of HDX-24 porous metal-frame material by 4,4'- Bipyridine-2,6,2',6'-tetracarboxylic acid (H4L) with zinc metal ions.

2. MATERIALS AND METHODS

2.1. Chemicals and equipment

The chemicals used in the experiment include**:**

- 4,4’- Bipyridine -2,6,2’,6’-tetracarboxylic acid (H4L), 97%, Alfachem, China;
- Zinc chloride ($ZnCl_2$), 98%, Xilong Scientific, China;
- 2,6-Lutidine, 98%, Macklin, China;
- Ethanol, 99.98%, Fisher Scientific, USA;
- Diethyl Ether, 99.98%, Fisher Scientific, USA;
- Ultra-pure water, Milli-Q, Merck Millipore, France.

The equipment used in the experiment includes:

- Electric Therm furnace (t_{max}=1500 ^oC), Viet Nam;
- Value Vacuum Machine, China;
- Autoclaver 45 mL, USA;
- A number of other experimental equipment and instruments are available in the laboratory of the Research Room of Toxic Chemical and Radiological Technology, Institute of New Technology.

2.2. Methods

2.2.1. Research on the manufacturing process of HDX-24 porous metal mechanical frame material

Material synthesized by the solvothermal method. Accurately weigh 0.166 g of 4,4′-bipyridine-2,2′,6,6′-tetracarboxylic acid (H4L) and 0.137 g of zinc chloride ($ZnCl_2$) transferred to a 45 mL Autoclaver vessel. A clean, dry measuring tube is used to measure 30 mL of ultrapure water accurately and put it into the reaction vessel. Then, use a micropipette to aspirate and add 220 μL of 2,6-Lutidine to the reaction vessel, stirring the mixture with glass chopsticks for 3-5 minutes at room temperature. Cover the reaction vessel and tighten evenly, chop the screws. Put the reactor into the furnace, heat it at a rate of 1-5 °C/min to 130 °C, and maintain the reaction mixture at this temperature for 6 consecutive days. At the end of the reaction time, shut off and allow the furnace to cool itself to room temperature. Remove the reaction vessel, remove the mixture into a clean, dry glass cup (rinse with ultrapure water 2-3 times with 3-5 mL/time), and filter the solids with a Buchner funnel. Wash the solids obtained with ultrapure water, medical ethanol, and pure diethyl ether (2 times/solvent type, 3-5 mL/time/solvent type). Dry the solids obtained at 60 ^oC for 8 hours continuously, weigh and collect the product into dry, clean glass jars, sealed lids, and affix labels. The amount of substances obtained is 0.1-0.12 g/reaction vessel, and the synthesis efficiency reaches 78.67-80.00%. Do the same with the remaining 02 reaction vessels (each batch of reaction 03 cylinders with a capacity of 45 mL/cylinder).

2.2.2. Evaluation of some properties of HDX-24 material after manufacturing

The surface morphology and particle size of the postsynthetic material were determined by FE-SEM scanning electron microscopy (Hitachi S-4800, Japan). The degradation of components by temperature was studied on the TGA gravimetric thermal analyzer (Netzsch STA-449F5, Germany). Determination of materials' porosity (surface area and capillary distribution) using the BET measurement method on the TriStar II 3020 instrument (Micromeritics, USA). The phase composition and functional groups of the material are determined through XRD spectroscopy on the Panalytical X-ray diffraction spectrometer (Netherlands) and the FT-IR spectroscopy analyzed on the Impact 410 instrument. The structure and chemical composition of the material are shown through EDS measurement results on the Oxford Intrusment instrument (USA). The FE-SEM, TGA, and EDS measurements were conducted at the Institute for Tropical Technology, Vietnam Academy of Science and Technology. The XRD measurement was conducted at the Institute of Chemistry, Vietnam Academy of Science and Technology. The FT-IR measurement was conducted at the Institute of Materials Chemistry, Academy of Military Science and Technology. The BET measurement was conducted at the School of Chemical and Life Sciences, Hanoi University of Science and Technology.

3. RESULTS AND DISCUSSION

3.1. Surface morphology and particle size of HDX-24 material

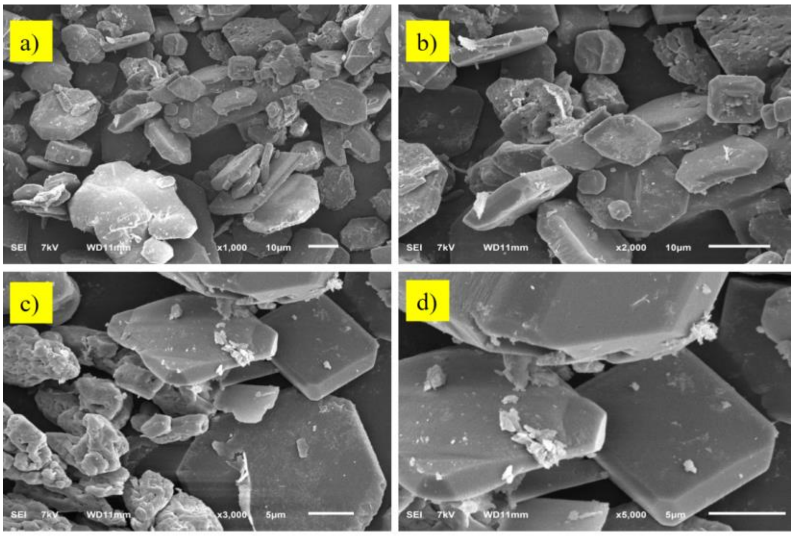

Figure 1. *FE-SEM image of HDX-24 material sample.*

The results of determining the surface morphology and particle size of the post-synthetic material are determined by the FE-SEM scanning electron microscope shown in figure 1. The results show that Materials exist in the form of particles, all of which have polyhedral shapes with clear edges and angles, indicating the crystallinity of the material. Particles vary in size, from a few micrometers to several tens of micrometers. In terms of surface structure, the particles have a relatively smooth surface, but there are also some particles that show the presence of smaller crystals or debris adhering to the surface, especially evident in figures (c) and (d). This may be due to the synthesis process or due to the unfinished crystals in the sample. In terms of uniformity, observe that the particles in figures (c) and (d) tend to be uniform. Figures (c) and (d) show the appearance of some small particles adhering to the surface of the larger particles, possibly subcrystals that have not yet had a complete crystal organization. In addition, it can be seen that there is no clear connection between the particles; they seem to be separated from each other. This can affect the conductive properties or mechanical properties of the material.

Overall, FE-SEM images show that HDX-24 material has a clear crystal structure, but there are still heterogeneities in particle size and the appearance of fragments, impurities, or crystals that are forming and are not finished.

3.2. Determine the structure of HDX-24 materials

3.2.1. Results of infrared spectrum analysis

The results of the infrared spectrum analysis of HDX-24 material sample are shown in figure 2 below:

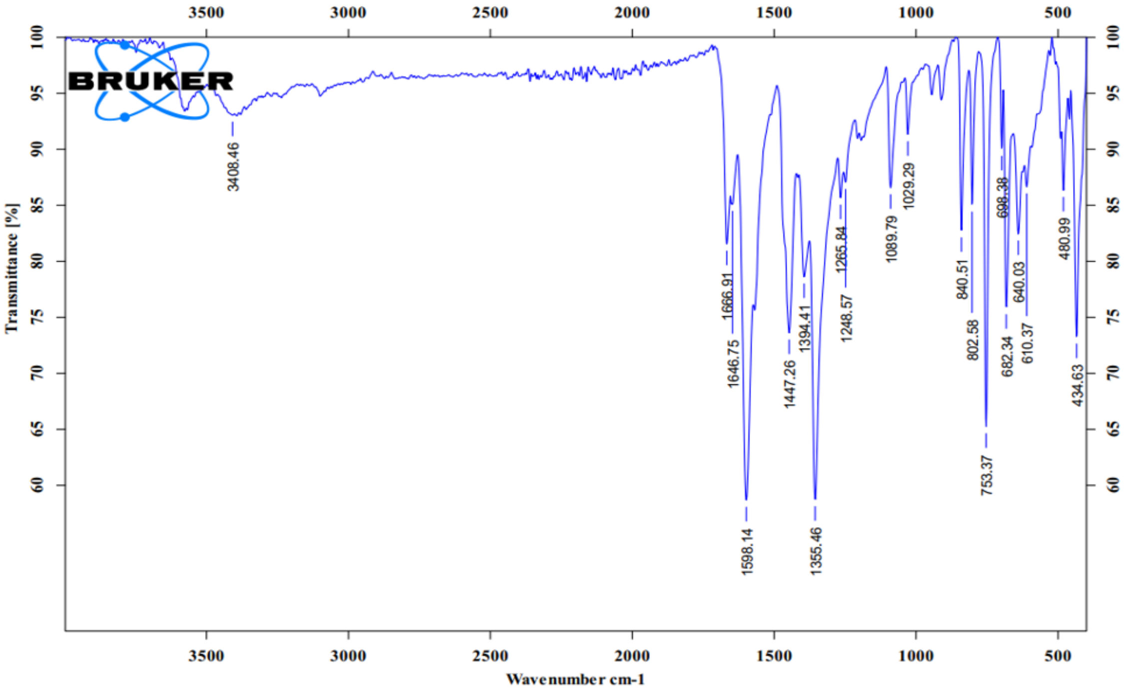

Figure 2. *IR spectrum of HDX-24 material.*

From the results of the infrared spectrum (IR) analysis of HDX-24 material, some comments can be made as follows:

Regarding the identification of functional groups: The broad spectral band around the 3406.66 cm^{-1} region can be related to and characterize the valence vibration of the -OH group, which often appears in free water or hydroxyl groups. This may indicate the presence of -OH groups on the surface or in the structure of the synthesized material. The strong vibration band at 1647.25 cm^{-1} characterizes the valence vibration of the C=O (carbonyl) group in carboxylate bonds. The spectral band at about 1447.78 cm^{-1} characterizes the C=C stretching vibration in the aromatic ring, showing aromatic organic structures in the HDX-24 material. The region from 1200 cm^{-1} to 1000 cm^{-1}

(with pronounced bands at 1029.10, 1090.88, and 1212.94 cm^{-1}) characterizes the oscillations of the C-O bond, which usually occur in ester or ether compounds. The peak oscillations at 766.37 cm^{-1} and 683.73 cm^{-1} characterize the extraplanar oscillations of C-H in aromatic rings.

Structurally: The FT-IR spectrum shows the presence of many organic and inorganic functional groups, including carboxylate groups, aromatic rings, and possibly metal bonds. This is consistent with the structural characteristics of metal-mechanical framework materials (MOFs), which are usually a combination of organic bonds and metal ions.

Characterization: The presence of sharp peaks in the IR spectrum and the results on SEM images show that HDX-24 has a clear crystal structure, with the specific appearance of characteristic functional groups.

3.2.2. Results of X-ray diffraction spectrum analysis

The results of X-ray diffraction (XRD) spectrum analysis are presented in figure 3 below.

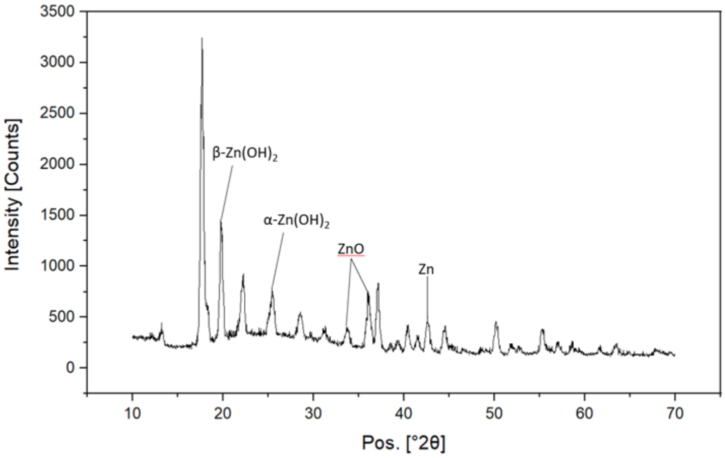

Figure 3. *XRD diagram of HDX-24 material.*

The XRD spectrum of the material appears to peak at various 2θ angles, indicating the presence of different phases in the crystal structure of the post-synthetic material. A strong peak at about 9-12° indicates the clear presence of the β-Zn(OH)$_2$ phase. A few other small peaks of this phase also appear at an angle of about 18-20°. The appearance of peaks at about 21-23°, 24-26° indicates the presence of the α-Zn(OH)$_2$ phase. A peak at about 31-34° suggests the existence of ZnO crystals. The peaks at about 36-39° represent the Zn crystal. These peaks all have relatively different intensities, of which the peak of β-Zn(OH)$_2$ is the strongest, indicating that this phase is mainly present in the material sample. Peaks of α-Zn(OH)$_2$, ZnO, and Zn also appear but with lower intensities, suggesting that they are present only to a lesser extent than β-Zn(OH)$_2$.

3.2.3. X-ray energy scattering spectrum results

The results of X-ray energy scattering spectrum analysis of the material are shown in figure 4 below. The results of the EDS spectral analysis of the HDX-24 material in the image provide some information about the elemental composition of the sample surface. The prominent peak at about 0.3 keV has a mass composition (Wt %) of 44.8%, indicating that carbon accounts for a large proportion of the sample. Peaks at about 1 keV and some other small peaks, with a mass composition of 24.7%, indicate a relatively large content of Zn in the material. Peaking at about 0.5 keV, the mass composition is 24.3 percent, indicating the presence of oxygen in the material. The small peak at about 0.4 keV with a mass composition of 6.2%, suggests the existence of nitrogen in the postsynthetic material. In combination with the previous XRD spectroscopy, EDS spectroscopy provides more information about the sample's chemical composition, helping to identify phases present in the material. The presence of Zn and O consistent with the ZnO and $Zn(OH)_2$ phases has been identified in the XRD spectrum. Carbon and nitrogen can come from organic components in the structure of the metal-mechanical framework, so the material of the synthesis contains good elements Zn, C, O, H exist in crystalline form with uneven particle size.

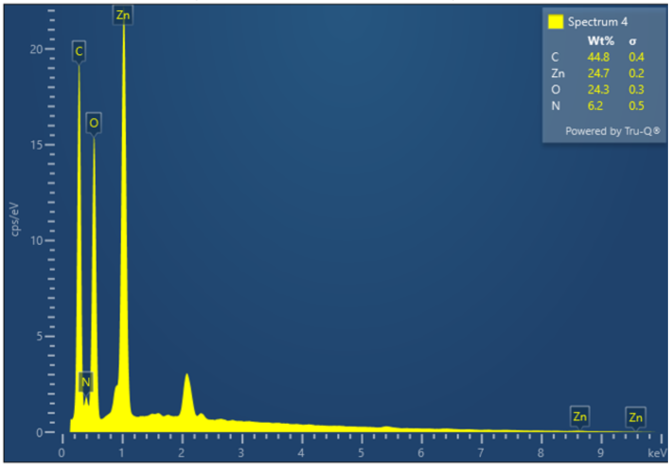

Figure 4. *EDS spectrum of HDX-24 material.*

3.2.4. Specific surface area of the material

The BET measurement results of the synthesized material in figure 5 show the relationship between adsorption capacity and relative pressure.

Isotherm Type IV: The results show that the graph of the shape material is the same as that of isotherm type IV according to the IUPAC classification, which is characteristic of mesopore porous materials (porous materials with an average size of 2-50 nm). This is indicated by a slight slope linear segment in the middle of the graph and a sudden increase in the relatively high-pressure region. The graph has the appearance of a hysteresis loop between adsorption and desorption, which is characteristic of mesoporous materials. Large Specific Surface Area: A high value of adsorption (about 130 cm³/g STP) indicates that the material has a large surface area (239.06 m^2/g), an important characteristic of the MOFs family of materials.

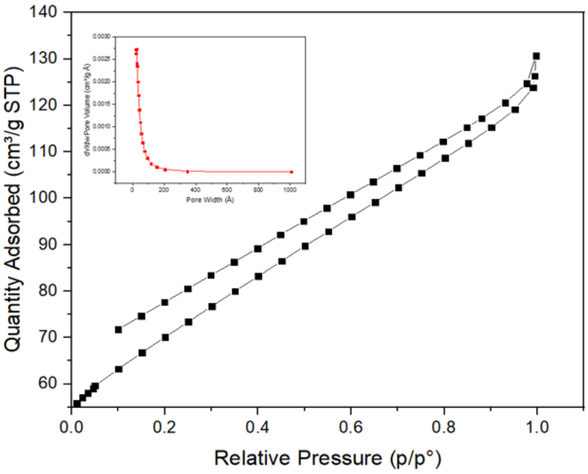

Figure 5. *BET measurement results of HDX-24 material.*

Regarding the pore size distribution: The inset chart shows that the pore size distribution of the post-synthetic material is mainly in the range of 10-20 Å, with some larger porosity, extending to more than 1000 Å. The adsorption capacity of the material reaches 5.2 mmol/g, the particle size reaches 75-78 mm, and the pore volume is 0.202 cm^3/g. These results further demonstrate that the post-synthetic HDX-24 material has high adsorption capacity, large surface area, and wide pore distribution. These characteristics make it very useful in applications such as gas storage, HDX-24 separation, and catalysis.

3.2.5. Thermal resistance of materials

The temperature mass change of the HDX-24 is determined by the TGA thermogravimetric analysis method, the results of which are shown in figure 6. The TGA (Thermogravimetric Analysis) measurement results of the material shown in the graph above include two lines: TG (percentage of mass with temperature) and DTG (rate of mass change with temperature).

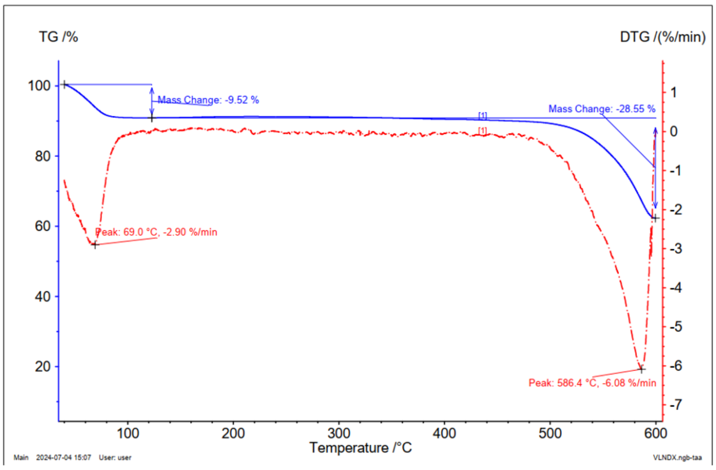

Figure 6. *TGA measurement results of HDX-24 material.*

The TG line (blue) shows that the initial weight of the sample is 100%. There are two main phases of mass reduction: Stage 1: From 0 °C – 150 °C, a 9.52% decrease in volume can be attributed to the evaporation of water. Phase 2: From 150 °C – 500 °C, the sample weight did not change significantly, indicating the strength of the HDX-24 material in this temperature range. Stage 3: From 500 °C – 600 °C, the mass decreases by an additional 28.56%, which may be due to the thermal degradation of organic components or easily degradable compounds in the material.

The DTG line (red) shows the rate of change in mass with temperature. There are two main peaks: The first peak is at 69.0 °C with a mass reduction rate of 2.90%/min, which corresponds to the evaporation phase of water or solvent, as mentioned above. The second peak was at 564.4 °C with a mass reduction rate of -6.08%/min, corresponding to the thermal decomposition phase of the organic components or easily degradable compounds in the sample. The HDX-24 material has two distinct phases of mass reduction, indicating mass loss due to water evaporation and thermal decomposition of the components in the sample. The mass drop occurs in the 150 °C – 600 °C range and tends to increase as heating continues.

4. CONCLUSIONS

HDX-24 porous metal-frame material is made based on the precursor 4,4'-Bipyridine-2,6,2',6'-tetracarboxylic acid (H4L), which exists in the form of a blue powder, with an unevenly distributed particle size, from a few micrometers to several tens of micrometers. The material has a transparent crystalline structure, with peaks that characterize the oscillations of functional groups in the structure. HDX-24 material has a specific surface area - BET reaches 239.06 m^2/g, the adsorption capacity of the material reaches 5.2 mmol/g, and the particle size reaches 75-78 mm. HDX-24 material has high adsorption capacity, large surface area, and wide pore distribution. This result is used as a basis for the authors to conduct further studies on the possibility of applying HDX-24 material to gas storage, separation, and catalysis.

Acknowledgments: *Thank you for the funding of the project at the Ministry of National Defense level under the Science and Technology between the Institute of New Technology, the Academy of Military Science and Technology and the Department of Military Science.*

REFERENCES

[1]. Jiangnan Li, Xue Han, Xinran Zhang, Alena M. Sheveleva, Yongqiang Cheng, Floriana Tuna, Eric J. L. Mc Innes, "*Capture of nitrogen dioxide and conversion to nitric acid in a porous metal-organic framework*", Nature Chemistry, Vol 11, pp. 1085–1090, (2019).

[2]. Chao Liu, Jing Wang, Jingjing Wan, Chengzhong Yu, *"MOF-on-MOF hybrids: Synthesis and applications"*, Coordination Chemistry Reviews, Vol 432, pp. 1051-1064 (2021).

[3]. Aysha Al Obeidli, Haifa Ben Salah, Mohammed Al Murisi, Rana Sabouni, "*Recent advancements in MOFs synthesis and their green applications* ", International Journal of Hydrogen Energy, Vol 47, pp. 2561-2593, (2022).

[4]. Shunsuke Tanaka, "*Chapter 10 - Mechanochemical synthesis of MOFs*", Metal-Organic Frameworks for Biomedical Applications, Vol 10, pp. 197-222, (2020).

[5]. Chandan Dey, Tanay Kundu, Bishnu P. Biswal, Arijit Mallick, Rahul Banerjee, "*Crystalline metal-organic frameworks (MOFs): synthesis, structure and function*", Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials, Vol 70, pp. 3-10, (2014).

[6]. Wei Chen, Liping Du, Chunsheng Wu, "*Chapter 7 - Hydrothermal synthesis of MOFs*", Metal-Organic Frameworks for Biomedical Applications, Vol 7, pp. 141-157, (2020).

TÓM TẮT

Nghiên cứu chế tạo và đánh giá một số tính chất của vật liệu khung cơ kim dạng xốp HĐX-24

Bài báo giới thiệu kết quả nghiên cứu chế tạo vật liệu khung cơ kim dạng xốp HĐX-24 bằng tác nhân 4,4'- Bipyridine-2,6,2',6'-tetracarboxylic acid (H4L). Đặc tính của vật liệu sau chế tạo được nghiên cứu thông qua một số phương pháp nghiên cứu hiện đại như: Kính hiển vi điện tử quét (FE-SEM), xác định diện tích bề mặt riêng BET, phân tích nhiệt trọng lượng TGA, quang phổ nhiễu xạ tia X (XRD), phổ tán xạ năng lượng tia X (EDS), quang phổ hồng ngoại biến đổi Fourier (FT-IR). Kết quả nghiên cứu cho thấy vật liệu HĐX-24 có diện tích bề mặt riêng-BET đạt 239.06 m^2/g, dung lượng hấp phụ của vật liệu đạt 5,2 mmol/g, kích thước hạt đạt 75-78 mm, thể tích lỗ xốp là 0,202 cm^3/g.

Từ khóa: Vật liệu HĐX-24; Khung cơ kim; H4L.