PREPARATION AND CHARACTERISTICS OF MIL-53 METAL-ORGANIC FRAMEWORK MATERIAL WITH Al/Fe-BIMETALLIC COMPONENT

Huynh Tuan Anh[1,2], Nguyen Huu Nghi[2], and Pham Dinh Du[3*]
[1]*My Quy High School, Dong Thap province*
[2]*Chemical Analysis Center, Dong Thap University*
[3]*Institute of Applied Technology, Thu Dau Mot University*
[*]*Corresponding author: dupd@tdmu.edu.vn*

Article history
Received: 20/04/2021; Received in revised form: 16/06/2021; Accepted: 12/07/2021

Abstract

In this study, iron doped MIL-53(Al) metal-organic framework material (denoted as Fe/MIL-53(Al)) was prepared by hydrothermal method. The obtained materials were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetry analysis (TG), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), and N_2 *adsorption/desorption isotherms. The influence of iron content on the structure of MIL-53(Al) and treated temperature of Fe/MIL-53(Al) were investigated. The results showed that the obtained Fe/MIL-53(Al) synthesized at mole ratio of Fe/Al = 1/9, still maintains many structural properties of the MIL-53 material, and the iron element was evenly distributed over the entire area of the material. The treatment at 280°C had almost no effect on the metal-organic framework structure of the material. The pore of the material was cleared at the treated temperature of 350°C; therefore, the specific surface area of the material increased significantly.*

Keywords: *Fe/MIL-53(Al), Metal-organic framework, Bimetallic component, Hydrothermal method.*

ĐIỀU CHẾ VÀ ĐẶC TRƯNG VẬT LIỆU KHUNG HỮU CƠ-KIM LOẠI MIL-53 VỚI THÀNH PHẦN LƯỠNG KIM LOẠI Al/Fe

Huỳnh Tuấn Anh[1,2], Nguyễn Hữu Nghị[2] và Phạm Đình Dũ[3*]
[1]*Trường Trung học phổ thông Mỹ Quý, Đồng Tháp*
[2]*Trung tâm Phân tích hóa học, Trường Đại học Đồng Tháp*
[3]*Viện Phát triển ứng dụng, Trường Đại học Thủ Dầu Một*
[*]*Tác giả liên hệ: dupd@tdmu.edu.vn*

Lịch sử bài báo
Ngày nhận: 20/04/2021; Ngày nhận chỉnh sửa: 16/06/2021; Ngày duyệt đăng: 12/07/2021

Tóm tắt

Trong bài báo này, vật liệu khung hữu cơ-kim loại MIL-53(Al) pha tạp sắt (kí hiệu Fe/MIL-53(Al)) đã được điều chế bằng phương pháp thủy nhiệt. Vật liệu thu được đặc trưng bằng nhiễu xạ tia X (XRD), phổ hồng ngoại biến đổi Fourier (FT-IR), phân tích trọng lượng theo nhiệt độ (TG), hiển vi điện tử quét (SEM), hiển vi điện tử truyền qua (TEM), phổ tán xạ tia X (EDX) và đẳng nhiệt hấp phụ/khử hấp phụ N_2*. Ảnh hưởng của hàm lượng sắt pha tạp đến cấu trúc của MIL-53(Al) và nhiệt độ xử lý Fe/MIL-53(Al) đã được khảo sát. Kết quả cho thấy Fe/MIL-53(Al) thu được khi tổng hợp ở tỉ lệ mol Fe/Al = 1/9 vẫn còn duy trì nhiều đặc trưng cấu trúc của vật liệu MIL-53 và nguyên tố sắt được phân bố đều trên toàn bộ diện tích của vật liệu. Việc xử lý ở 280°C hầu như không ảnh hưởng đến cấu trúc khung hữu cơ-kim loại của vật liệu. Khi xử lý vật liệu ở 350°C, các mao quản của vật liệu được khai thông, do đó, diện tích bề mặt riêng của vật liệu tăng lên đáng kể.*

Từ khóa: *Fe/MIL-53(Al), khung hữu cơ-kim loại, thành phần lưỡng kim loại, phương pháp thủy nhiệt.*

DOI: https://doi.org/10.52714/dthu.10.5.2021.894

Cite: Huynh Tuan Anh, Nguyen Huu Nghi, and Pham Dinh Du. (2021). Preparation and characteristics of MIL-53 metal-organic framework material with Al/Fe-bimetallic component. *Dong Thap University Journal of Science, 10*(5), 46-54.

1. Introduction

Metal-Organic Frameworks (MOFs) are porous solid nanomaterials created from metal ions (or inorganic hybrid centers) linked to organic bridges. The existence of organic and inorganic components in the framework can create a synergistic interaction for the adsorption and selection of desired molecules from foreign molecules such as gas separation, gas purification, gas storage, heterogeneous catalysts and drug delivery (Férey, 2008; He *et al.*, 2014; Barea *et al.*, 2014; Hu *et al.*, 2018; Stavila *et al.*, 2014; Khieu *et al.*, 2018; Horcajada *et al.*, 2012).

Among MOFs, MIL-53(M^{III}) (MIL: Materials of Institute Lavoisier; M^{III} = Fe, Al, Cr, Sc, Ga, In...) with the formula $M^{III}(OH)\cdot(O_2C-C_6H_4-CO_2)\cdot H_2O$ has great chemical flexibility and high chemical stability (Naeimi and Faghihian, 2017; Devic *et al.*, 2010; Gordon *et al.*, 2012; Chen *et al.*, 2013). Among the MIL members, MIL-53(Al) is most interested in the "breathing" effect (Loiseau *et al.*, 2004; Trung *et al.*, 2008), and is widely explored in the field of gas storage (Trung *et al.*, 2008) and water treatment (Patil *et al.*, 2011). The characteristic MIL-53(Al) feature is its high thermal stability, reaching up to 500ºC (Patil *et al.*, 2011; Qian *et al.*, 2013).

Most MOFs structures studied in recent years are based on single metal component. Therefore, the MOFs preparation contains a mixture of two or more metals will open up many opportunities for the application of new materials with unique properties (Podkovyrina *et al.*, 2018; Thanh *et al.*, 2018; Rahmani E. and Rahmani M., 2018). Rahmani E. and Rahmani M. (2018) used MIL-53(Al) and MIL-53(Al-Li) as catalysts for the Friedel-Crafts reaction of benzene alkylation. The results showed that both of these catalysts were capable of catalyzing the Friedel-Crafts reaction and were stable after 14 hours of catalysis at 200ºC. In particular, MIL-53(Al-Li) had a higher catalytic efficiency than MIL-53(Al). The MIL-53(Fe) material has interested many scientists (Ai *et al.*, 2014; Vu *et al.*, 2015; Liang *et al.*, 2015; Yilmaz *et al.*, 2016; Pu *et al.*, 2017; Naeimi and Faghihian, 2017; Nguyen *et al.*, 2019; Du *et al.*, 2020). Recently, MIL-53(Fe, Al) has also been successfully prepared by Huang *et al.* (2019) by solvothermal method with N'N-dimethylformamide (DMF) solvent, and applied as an adsorbent for glutathione adsorption from aqueous solution. In addition, these authors have demonstrated that MIL-53(Fe, Al) with bimetallic linkers is not a simple physical mixture of MIL-53(Fe) and MIL-53(Al). This method is synthesized in DMF solvent, so it can lead to secondary pollution. Therefore, environmentally friendly synthetic directions are still attracting a lot of attention of scientists.

In this study, iron doped MIL-53(Al) metal-organic framework material (denoted as Fe/MIL-53(Al)) was prepared by hydrothermal method. The effects of the Fe/Al mole ratio and the treated temperature of the obtained material were investigated.

2. Experiment

The preparation of MIL-53(Al) was carried out according to earlier reports with some modifications (Loiseau *et al.*, 2004; Du *et al.*, 2011). In a typical process, a mixture of 14.685 g aluminum (III) chloride (Merck), 9.13 g terephthalic acid (Acros, denoted as TPA) and 180 mL of distilled water was placed in a Teflon-lined steel autoclave (volume 200 mL) in an oven at 120°C for 3 days. Then, the mixture was cooled to ambient temperature, and filtered to obtain solid product. The solid was washed with distilled water, and dried to obtain MIL-53(Al).

The Fe/MIL-53(Al) material was also prepared according to the same process with the different mole ratio of Fe/Al, including 1/9, 2/8 and 3/7 (the source of iron was used from $FeCl_3\cdot 6H_2O$, Merck). The samples were denoted as Fe-Al(1/9), Fe-Al(2/8) and Fe-Al(3/7), respectively. To remove the non-reactive TPA forms, the as-prepared Fe/MIL-53(Al) was treated at different temperatures, including 280, 350 and 450ºC, for 8 hours.

X-ray diffraction (XRD) patterns were recorded on a VNU-D8 Advance Instrument (Bruker, Germany) under Cu Kα radiation (λ = 1.5406 Å). The thermal behavior of the samples was investigated by using thermal analysis on Labsys TG/dTG SETARAM. The chemical analysis of the sample was examined using Energy-dispersive X-ray spectroscopy (EDX, JEOL JED-2300, Japan) at different sites of the material. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained by using a SEM JMS-5300LV (Japan) and a JEM-2100, respectively. Fourier-transform infrared spectra (FT-IR) were recorded by a Jasco FT/IR–4600 spectrometer (Japan) in the range of 4000–400 cm^{-1}. The N_2 adsorption/desorption isotherms measurement test was performed at 77 K in a Tristar 3000 analyzer, and before setting the dry mass, the samples were degassed at 200°C with N_2 for 5 h.

3. Results and discussion

XRD patterns of MIL-53(Al) and the as-prepared Fe/MIL-53(Al) samples are shown in Figure 1. For MIL-53(Al), there were diffraction peaks at 8.7, 10.2, 15, 17.1, 17.7, 20.4, 21.2, 24.2 and 26.8° (Figure 1a). These peaks are specific to as-prepared MIL-53(Al) (Rallapalli *et al.*, 2010; Rahmani E. and Rahmani M., 2018; Moran *et al.*, 2018; Liu *et al.*, 2019). This proves that the structure of the MIL-53(Al) metal-organic framework material was formed. For as-prepared Fe/MIL-53(Al) samples, the XRD also had these diffraction peaks with low intensity and the intensity decreases gradually with increasing Fe/Al mole ratio from 1/9 to 3/7 (Figure 1b). In addition, The XRD patterns of the samples exhibit diffraction peaks at 17°, 25°, and 27.6° with hight intensity. These are typical peaks of TPA (Figure 1c). This indicates that a large amount of TPA did not react or link weakly on the material surface.

The FT-IR spectra of TPA, MIL-53(Al) and the as-prepared Fe-Al(1/9) sample are shown in Figure 2. For TPA, the absorption peak at 1681 cm^{-1} characterizes the stretching vibration of the C=O group, and the absorption peaks at 1423 and 937 cm^{-1} are attributed to the bending vibration of the O–H of carboxyl groups (COOH), while the absorption peak at 784 cm^{-1} represents the stretching vibration of the C–H bond in the aromatic ring (Liang *et al.*, 2015; Wang *et al.*, 2016). For MIL-53(Al), the absorption peaks at 1601 and 1510 cm^{-1} correspond to the asymmetric stretching vibration of the–COO group, while the absorption peaks at 1438 and 1415 cm^{-1} correspond to the symmetric stretching vibration of the–COO group (Patil *et al.*, 2011; Loiseau *et al.*, 2004; Liu *et al.*, 2019). The absorption peak observed at 1703 cm^{-1} ($\nu_{C=O}$) may be thought to be of free TPA molecules attached inside the pore structures in protonated form ($–CO_2H$) (Loiseau *et al.*, 2004). The absorption peaks in the low wavenumber range of 470–580 cm^{-1} are due to the presence of Al–O in MIL-53(Al) (Liu *et al.*, 2019). The absorption peaks in the 3600-2500 cm^{-1} region are characteristic for free adsorbed water, as well as the stretching vibration of the OH groups in –COOH and the Al–OH fragments (Isaeva *et al.*, 2019). The absorption peak at 3679 cm^{-1} could be assigned the stretching vibration of O–H in hydroxyl groups bridging with Al^{3+} ions in the MIL-53(Al) framework (Isaeva *et al.*, 2019). These values confirm the existence of CO_2^- group coordinated to aluminum inside the material. For Fe-Al(1/9), the characteristic vibration observed on the FT-IR spectra were not different from those of MIL-53(Al). This indicates that the metal-organic framework structure of the MIL-53(Al) material was still formed with iron metal dopping.

The thermal behavior of TPA, MIL-53(Al), and the as-prepared Fe/MIL-53(Al) samples are shown in Figure 3a. For TPA, the TG curve displays two weight losses of 56 and 40% at 412°C and in the temperature range of 400–700°C, corresponding to the decomposition and combustion of TPA. Two weight losses are also observed with the MIL-53(Al) sample. The first one of about 33% in the temperature range of 425–467ºC is probably due to the removal of the formation of TPA bonds on the surface of the material. The second weight loss of about 48% at 607°C is attributed to the decomposition of TPA bridges in the metal-organic framework structure of MIL-53(Al).

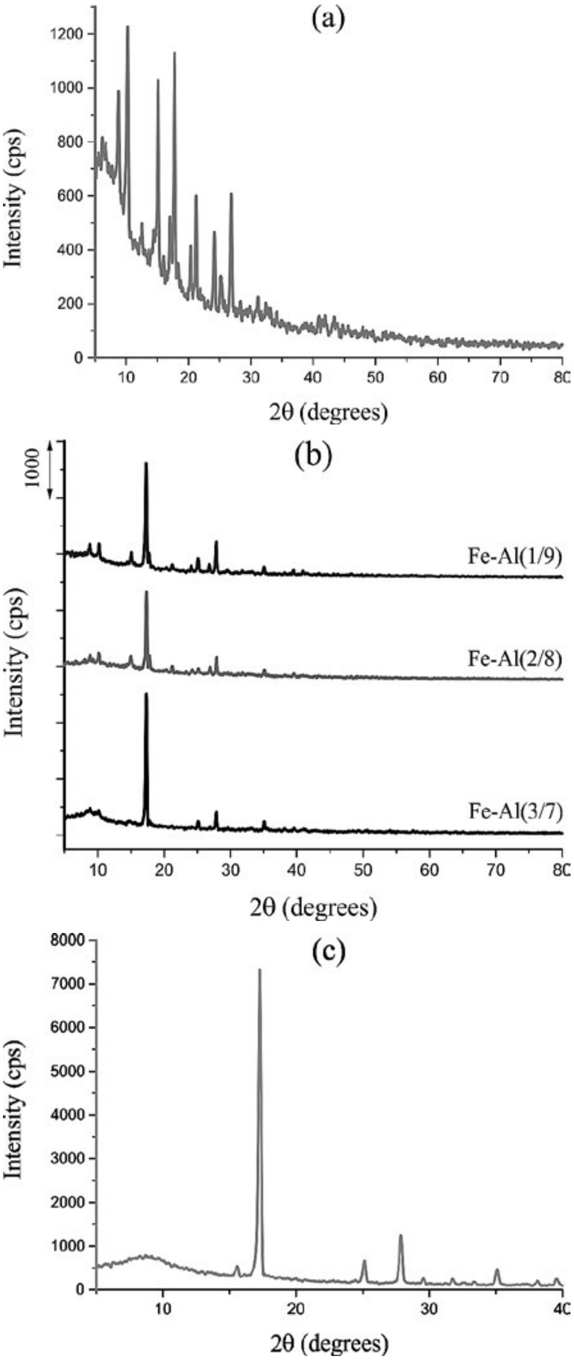

Figure 1. XRD patterns: a) MIL-53(Al); b) as-prepared Fe/MIL-53(Al) samples with different Fe/Al mole ratios; c) TPA (for comparison)

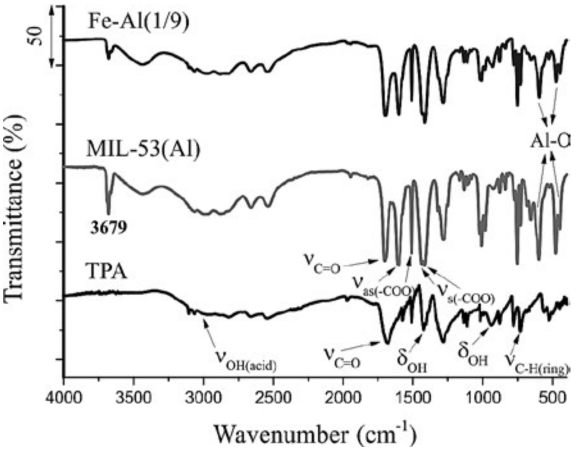

Figure 2. FT-IR spectra of TPA, MIL-53(Al) and Fe-Al(1/9)

For the as-prepared Fe/MIL-53(Al) samples, there are also two weight losses. The first loss of weight occurred at a temperature of 391–430ºC similar to that of TPA, probably due to the decomposition of non-reactive TPA forms (as demonstrated by XRD in Figure 1b). The second weight loss that occurred mainly at 513–522ºC is attributed to the decomposition of bonded TPA forms on the surface and within the framework of the material. It is worth noting that the decomposition of organic components in Fe/MIL-53(Al) occurred at much lower temperatures than in MIL-53(Al). This difference is probably due to the presence of iron components in the framework which may contribute to easier decomposition/ or combustion.

The results of thermal analysis showed that Fe/MIL-53(Al) material is quite stable (only decomposes at temperature above 500ºC). Therefore, to remove the components of non-reactive TPA, Fe-Al(1/9) sample was treated at different temperatures, including 280, 350 and 450ºC, for 8 hours. TG profiles of the heat treated Fe-Al(1/9) samples are shown in Figure 3b.

For the treated sample at 280ºC, the TG curve shows the weight losses occurring in the temperature range of 300-750ºC similar to the as-prepared Fe/MIL-53(Al) samples (Figure 3a). For the treated sample at 350ºC, the TG curve shows that only one loss of weight occurred at 487ºC, this weight loss (about 17%) is probably due to the decomposition (or burning off) of the organic bridges in the material. For the treated sample at 450ºC, the TG curve shows that only one weight loss occurred at 140ºC, which is the desorption of free adsorbed water molecules. This also proves that the organic components were completely eliminated at 450ºC.

XRD patterns of the Fe-Al(1/9) sample treated at different temperatures are shown in Figure 4. For the treated sample at 280ºC (Figure 4a), the diffraction peaks are almost not different from the as-prepared Fe/MIL-53(Al) samples (Figure 1b), but the peaks are sharp and slightly higher intensity. At the treated temperature of 350ºC, the intensity of these peaks decreased significantly and no longer observed when the treated temperature was 450ºC (Figure 4b). These results are completely consistent with those of thermal analysis presented in Figure 3b.

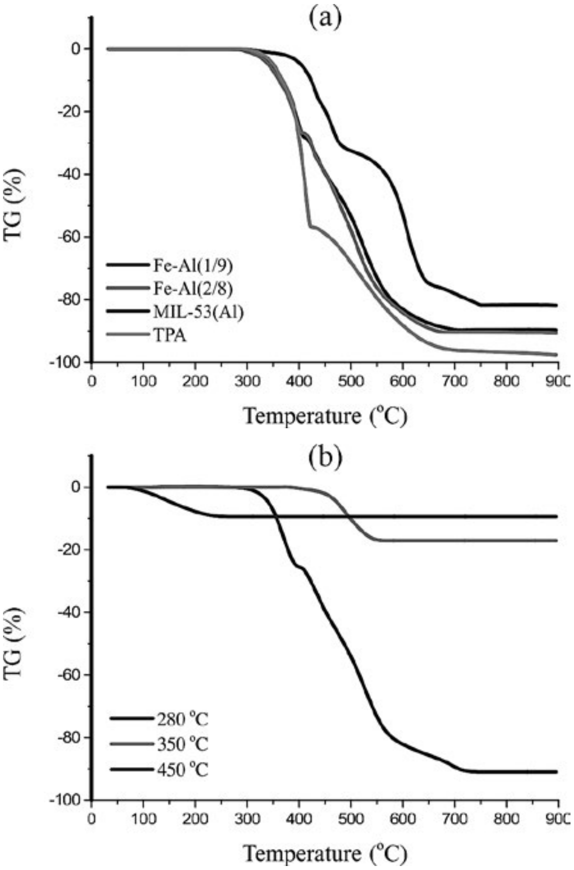

Figure 3. TG profiles: a) TPA, MIL-53(Al), and as-prepared Fe/MIL-53(Al) samples with Fe/Al mole ratio of 1/9 and 2/8 ; b) Fe-Al(1/9) sample treated at different temperatures

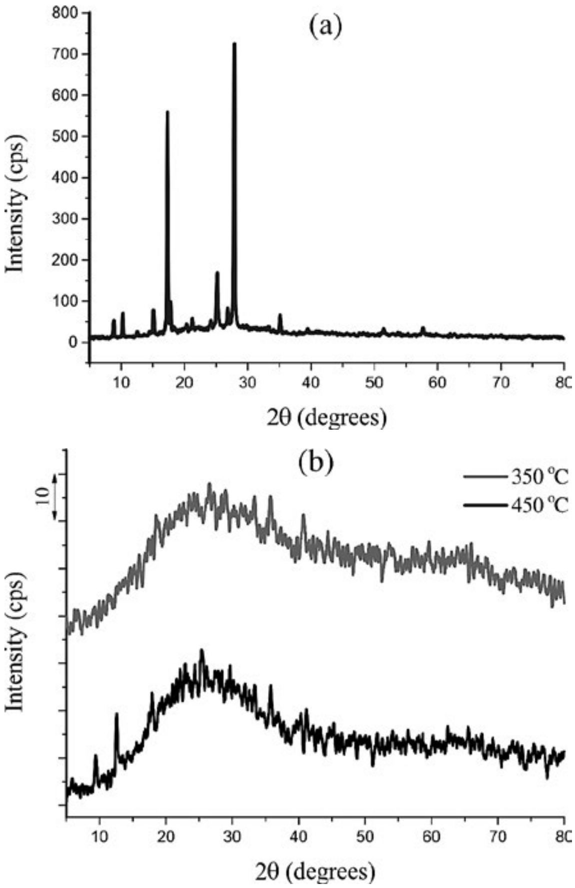

Figure 4. XRD patterns of the Fe-Al(1/9) sample treated by heat at different temperatures: a) 280ºC; b) 350ºC and 450ºC

SEM images of MIL-53(Al) and the Fe-Al(1/9) sample treated at different temperatures are shown in Figure 5. The MIL-53(Al) material consists of plate blocks of varying sizes with a smooth surface (Figure 5a). At the treated temperature of 280ºC (Figure 5b), the resulting material also had block form with smooth surfaces, but larger sizes than that of MIL-53(Al). At the treated temperature of 350ºC and 450ºC (Figures 5c and 5d), the resulting materials consist of smaller blocks and more rough surface than that of MIL-53(Al). The reason for the appearance of these morphologies is probably because the heat treatment fragmented the framework structure of the material and the incomplete decomposition of organic components in the framework, so their surface becomes so rough.

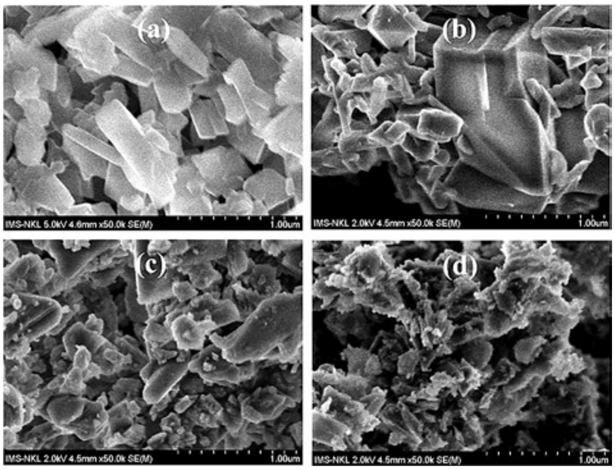

Figure 5. SEM images of MIL-53(Al) (a) and the Fe-Al(1/9) sample treated by heat at different temperatures: b) 280ºC; c) 350ºC; and d) 450ºC

The porosity of the samples was also analyzed by the nitrogen adsorption-desorption method at 77 K and was presented in Figures 6 and Table 1. The results show that MIL-53(Al) and the Fe-Al(1/9) sample treated at 280ºC (Figures 6a and 6b) have a relatively small specific surface area (11.4 and 10.4 m^2/g, respectively). This can be explained by the fact that TPA molecules attached and blocked the pore structures of the material. At high treated temperature (350ºC), the free or bonded TPA molecules on the surface of the material decomposed, the pores of the material were cleared, so the specific surface area of the material increased significantly. The specific surface area of the Fe-Al(1/9) sample treated at 350ºC was 262.8 m^2/g (Figure 6c).

TEM images of MIL-53(Al) and the Fe-Al(1/9) sample treated at 280ºC are presented in Figures 7a and 7b. The results show that their morphology is almost not different, including plate-shaped blocks with different sizes. For the Fe-Al(1/9) sample that was treated at 350ºC (Figure 7c), the TEM image showed the appearance of hollow structures inside the material. These are probably the pore cavities that have been opened up when the material is treated at this temperature. Figure 7c also shows that the metal-organic framework was maintained even though the blocks of the material were broken up under this condition. Many authors have also demonstrated that the metal-organic framework of MIL-53(Al) or MIL-53(Fe, Al) remains stable when heating the material at 330°C for many hours (up to 3 days) (Loiseau *et al.*, 2004; Huang *et al.*, 2019). The fragmentation of the blocks is probably also the cause of its low intensity diffraction peaks on the XRD pattern (Figure 4b).

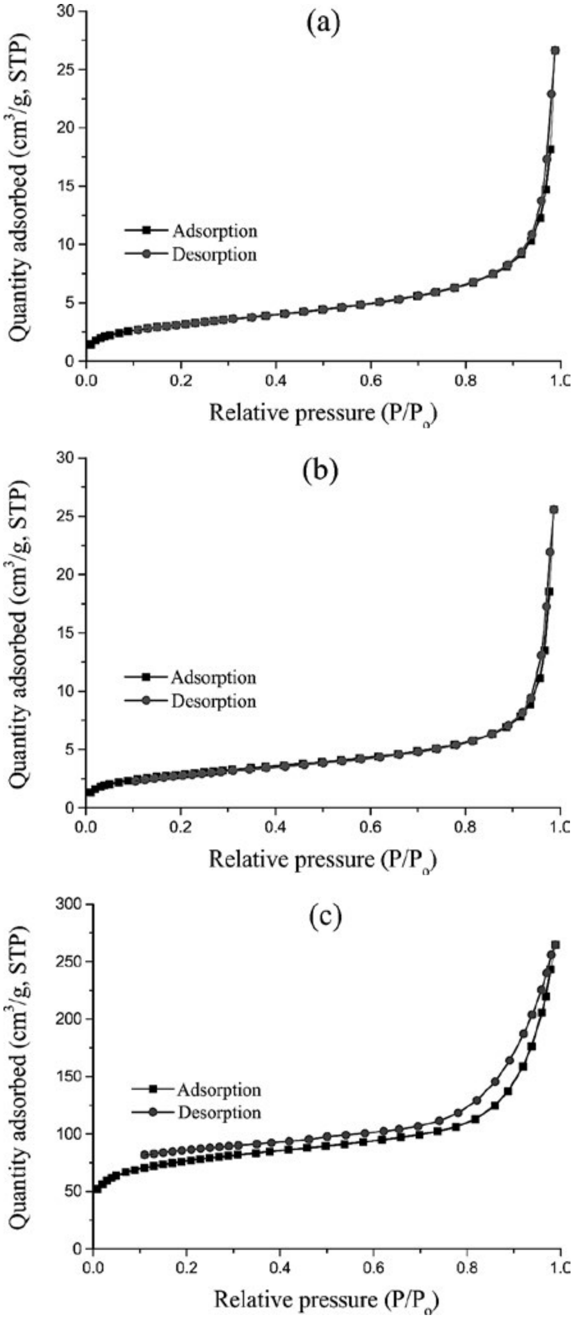

Figure 6. Nitrogen adsorption-desorption isotherms of MIL-53(Al) (a) and the Fe-Al(1/9) sample treated by heat at 280ºC (b) and 350ºC (c)

Table 1. Porous properties of the MIL-53(Al) and Fe-Al(1/9) samples

Sample (treated temperature)	BET surface area, S_{BET} (m^2•g^{-1})	*t*-Plot micropore area (m^2•g^{-1})	*t*-Plot external surface area (m^2•g^{-1})	*t*-Plot micropore volume (cm^3•g^{-1})
MIL-53(Al)	11.4	2.4	9.0	0.000991
Fe-Al(1/9) (280°C)	10.4	3.3	7.1	0.001450
Fe-Al(1/9) (350°C)	262.8	174.7	88.1	0.081475

The distribution of the different elements on the Fe-Al(1/9) sample was also mapped by EDX (Figure 8). The results show that the characteristic elements (C, O, and Al) are evenly distributed over the material's area. Furthermore, the iron map also shows that the iron elements are evenly distributed over the entire area of the material. This indicated that the iron was regularly bonded in the framework of MIL-53(Al) material.

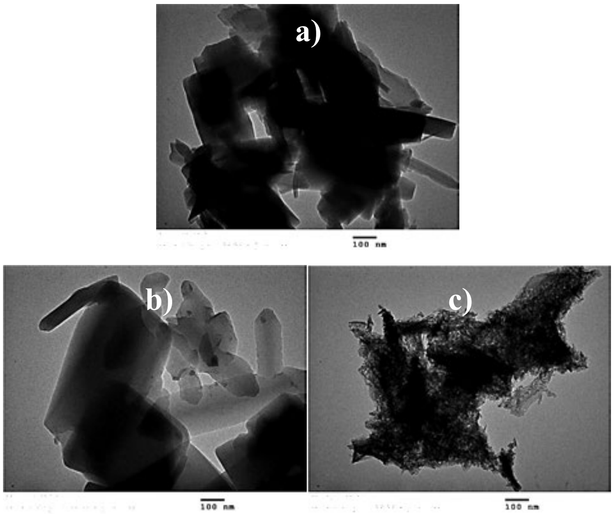

Figure 7. TEM images of MIL-53(Al) (a) and the Fe-Al(1/9) sample treated by heat at 280ºC (b) and 350ºC (c)

4. Conclusions

Iron doped MIL-53(Al) metal-organic framework material was successfully prepared by hydrothermal method. The content of iron doped into the material was suitable at the mole ratio of Fe/Al = 1/9, and the treatment by heat at 280ºC did not affect the structure of the material. The obtained Fe/MIL-53(Al) at treated temperature of 350ºC has a rather large specific surface area (SBET = 262.8 m^2/g) and still maintains a metal-organic framework structure.

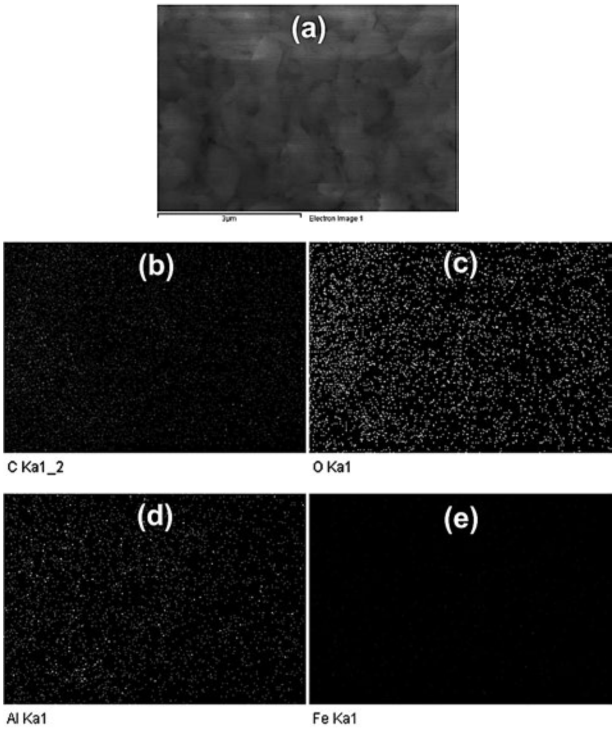

Figure 8. Elemental mapping of the Fe-Al(1/9) sample: a) Bright field image; b) Mapping of carbon; c) Mapping of oxygen; d) Mapping of aluminum; and e) Mapping of iron

References

Ai, L., Zhang, C., Li, L., Jiang, J. (2014). Iron terephthalate metal-organic framework: Revealing the effective activation of hydrogen peroxide for the degradation of organic dye under visible light irradiation. *Applied Catalysis B: Environmental*, (148-149), 191-200.

Barea, E., Montoro, C., Navarro, J. A. R. (2014). Toxic gas removal – metal-organic frameworks for the capture and degradation of toxic gases and vapours. *Chem. Soc. Rev.*, (43), 5419-5430.

Chen, I., Mowat, J. P. S., Jimenez, D. F., Morrison,

C. A., Thompson, S. P., Wright, P. A., and Düren, T. (2013). Elucidating the Breathing of the Metal-Organic Framework MIL-53(Sc) with ab Initio Molecular Dynamics Simulations and in Situ X-ray Powder Diffraction Experiments. *J. Am. Chem. Soc.*, (135), 15763-15773.

Devic, T., Horcajada, P., Serre, C., Salles, F., Maurin, G., Moulin, B., Heurtaux, D., Clet, G., Vimont, A., Grenèche, J. M., Ouay, B. L., Moreau, F., Magnier, E., Filinchuk, Y., Marrot, J., Lavalley, J. C., Daturi, M., and Férey, G. (2010). Functionalization in Flexible Porous Solids: Effects on the Pore Opening and the HostGuest Interactions. *J. Am. Chem. Soc.*, (132), 1127-1136.

Du, J. J., Yuan, Y. P., Sun, J. X., Peng, F. M., Jiang, X., Qiu, L. G., Xie, A. J., Shen, Y. H., Zhu, J. F. (2011). New photocatalysts based on MIL-53 metal-organic frameworks for the decolorization of methylene blue dye. *Journal of Hazardous Materials*, (190), 945-951.

Du, P. D., Danh, H. T., Hoai, P. N., Thanh, N. M., Nguyen, V. T., and Khieu, D. Q. (2020). Heterogeneous UV/Fenton-Like Degradation of Methyl Orange Using Iron Terephthalate MIL-53 Catalyst. *Journal of Chemistry, (Volume 2020)*, Article ID 1474357, 13 pages.

Férey, G. (2008). Hybrid porous solids: past, present, future. *Chem. Soc. Rev.*, (37), 191-214.

Gordon, J., Kazemian, H., Rohani, S. (2012). Rapid and efficient crystallization of MIL-53(Fe) by ultrasound and microwave irradiation. *Micropor. Mesopor. Mat.*, (162), 36-43.

He, Y., Zhou, W., Qian, G., Chen, B. (2014). Methane storage in metal-organic frameworks. Chem. Soc. Rev., (43), 5657-5678.

Horcajada, P., Gref, R., Baati, T., Allan, P. K., Maurin, G., Couveur, P., Férey, G., Morris, R. E., Serre, C. (2012). Metal-Organic Frameworks in Biomedicine. *Chem. Rev.*, (112), 1232-1268.

Hu, M., Lou, H., Yan, X., Hu, X., Feng. R., Zhou M. (2018). In-situ frabrication of ZIF-8 decorated layered double oxides oxides for adsorption and photocatalytic degradation of methylene blue. *Micropor. Mesopor. Mat.*, (271), 68-72.

Huang, D., Liu, Y., Liu, Y., Liu, Y., Di, D., Wang, H., Yang, W. (2019). Preparation of metal-organic frameworks with bimetallic linkers and corresponding properties. *New J. Chem.*, (43), 7243-7250.

Isaeva, V. I., Vedenyapina, M. D., Kulaishin, S. A., Lobova, A. A., Chernyshev, V. V., Kapustin, G. I., Tkachenko, O. P., Vergun, V. V., Arkhipov, D. A., Nissenbaum, V. D., and Kustuv, L. M. (2019). Adsorption of 2,4-dichlorophenoxyacetic acid in an aqueous medium on nanoscale MIL-53(Al) type materials. *Dalton Trans.*, (48), 15091-15104.

Khieu, D. Q., Thanh, M. T., Thien, T. V., Phong, N. H., Van, D. H., Du, P. D. and Hung, N. P. (2018). Synthesis And Voltammetric Determination Of Pb(II) Using A Zif-8 Based Electrode. *Journal of Chemistry*, 2018, Article ID 5395106, 12 pages.

Liang, R., Jing, F., Shen, L., Qin, N., and Wu, L. (2015). MIL-53(Fe) as a highly efficient bifunctional photocatalyst for the simultaneous reduction of Cr(VI) and oxidation of dyes. *Journal of Hazardous Materials*, (287), 364-372.

Liu, J. F., Mu, J. C., Qin, R. X., Ji, S. F. (2019). Pd nanoparticles immobilized on MIL-53(Al) as highly effective bifunctional catalysts for oxidation of liquid methanol to methyl formate. *Petroleum Science*, (16), 901-911.

Loiseau, T., Serre, C., Huguenard, C., Fink, G., Taulelle, F., Henry, M., Bataille, T., and Férey, G. (2004). A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration. *Chem. Eur. J.*, (10), 1373-1382.

Moran, C. M., Joshi, J. N., Marti, R. M., Hayes, S. E., and Walton, K. S. (2018). Structured Growth of Metal-Organic Framework MIL-53(Al) from Solid Alumium Carbide Precursor. *J. Am. Chem. Soc.*, (140, 29), 9148-9153.

Naeimi, S., Faghihian, H. (2017). Application of novel metal organic framework, MIL-53(Fe) and its magnetic hybrid; for removal of pharmaceutical pollutant, doxycycline from aqueous solutions. *Environmental Toxicology and Pharmacology*, (53), 121-132.

Nguyen, D. T. C., Le, H. T. N., Do, T. S., Pham, V. T., Tran, D. L., Ho, V. T. T., Tran, T. V., Nguyen, D. C., Nguyen, T. D., Bach, L. G., Ha, H. K. B., and Doan, V. T. (2019). Metal-Organic Framework MIL-53(Fe) as an Adsorbent for Ibuprofen Drug Removal from Aqueous Solutions: Response Surface Modeling and Optimization. *Journal of Chemistry*, (2019), Article ID 5602957, 11 pages.

Patil, D. V., Rallapalli, P. B. S., Dangi, G. P., Tayade, R. J., Somani, R. S., and Bajaj, H. C. (2011). MIL-53(Al): An Efficient Adsorbent for the Removal of Nitrobenzene from Aqueous Solutions. *Ind. Eng. Chem. Res.*, (50), 10516-10524.

Podkovyrina, Y., Butova, V., Bulanova, E., Budnyk, A., Kremennaya, M., Soldatov, A., Lamberti, C. (2018). Characterization of local atomic structure in Co/Zn based ZIFs by XAFS. *Journal of Physics: Conf. Series*, 987, 012-031.

Pu, M., Ma, Y., Wan, J., Wang, J., Brusseau, M. L. (2017). Activation performance and mechanism of a novel heterogeneous persulfate catalyst: Metal Organic Framework MIL-53(Fe) with FeII/FeIII mixed-valence coordinative unsaturated iron center. *Catal. Sci. Technol.*, 7(5), 1129-1140.

Qian, X., Yadian, B., Wu, R., Long, Y., Zhou, K., Zhu, B., Huang, Y. (2013). Structure stability of metal-organic framework MIL-53 (Al) in aqueous solutions. *International Journal of Hydrogen Energy*, (38), 16710-16715.

Rahmani, E., and Rahmani, M. (2018). Al-based MIL-53 Metal Organic Framework (MOF) as the New Catalyst for Friedel-Crafts Alkylation of Benzene. *Ind. Eng. Chem. Res.*, (57, 1), 169-178.

Rallapalli, P., Patil, D., Prasanth, K. P., Somani, R. S., Jasra, R. V., Bajaj, H. C. (2010). An alternative activation method for the enhancement of methane storage capacity of nanoporous aluminium terephthalate, MIL-53(Al). *J. Porous Mater.*, (17), 523-528.

Stavila, V., Talin, A. A., Allendorf, M. D. (2014). MOF-based electronic and optoelectronic devices. *Chem. Soc. Rev.*, (43), 5994-6010.

Thanh, M. T., Thien, T. V., Du, P. D., Hung, N. P., Khieu, D. Q. (2018). Iron doped zeolitic imidazolate framework (Fe-ZIF-8): synthesis and photocatalytic degradation of RDB dye in Fe-ZIF-8. *J. Porous Mater.*, (25), 857-869.

Trung, T. K., Trens, P., Tanchoux, N., Bourrelly, S., Llewellyn, P. L., Serna, S. L., Serre, C., Loiseau, T., Fajula, F., and Férey, G. (2008). Hydrogen Adsorption in the Flexible Metal Organic Frameworks MIL-53(Al, Cr). *J. Am. Chem. Soc.*, (130), 16926-16932.

Vu, T. A., Le, G. H., Dao, C. D., Dang, L. Q., Nguyen, K. T., Nguyen, Q. K., Dang, P. T., Tran, H. T. K., Duong, Q. T., Nguyen, T. V. and Lee, G. D. (2015). Arsenic removal from aqueous solutions by adsorption using novel MIL-53(Fe) as a highly efficient adsorbent. *RSC Adv.*, (5), 5261-5268.

Wang, Y., Kretschmer, K., Zhang, J., Mondal, A. K., Guo, X. and Wang, G. (2016). Organic sodium terephthalate@graphene hybrid anode materials for sodium-ion batteries. *RSC Advance*s, (6), 57098-57102.

Yilmaz, E., Sert, E., Atalay, F. S. (2016). Synthesis, characterization of a metal organic framework: MIL-53 (Fe) and adsorption mechanisms of methyl red onto MIL-53 (Fe). *Journal of the Taiwan Institute of Chemical Engineers*, (65), 323-330.