ISSN: 1410-8917
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 25 (8) (2022): 286–291

Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Synthesis of MCM-41 Silica Mesoporous Modified with Zn Metal

Samriani, Muhammad Zakir [a,*], Paulina Taba [a], Nursiah La Nafie [a], Iin Indriani [a]

[a] Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Hasanuddin, Makassar, Indonesia

*Corresponding author: muh.zakir@science.unhas.ac.id

https://doi.org/10.14710/jksa.25.8.286-291

Article Info

Article history:

Received: 14th June 2022
Revised: 3rd August 2022
Accepted: 9th September 2022
Online: 30th September 2022

Keywords:
Synthesis; MCM-41; Silica Mesoporous; Modified; Impregnation; Zn metal

Abstract

MCM-41 and Zn-MCM-41 were successfully synthesized using hydrothermal and impregnation methods. The synthesized silica mesoporous was confirmed by characterizing the material using XRD, SEM-EDS, and BET-BJH analyses. XRD results showed three main peaks at angles of 2θ = 2.40° (100), 3.87° (200), and 4.49° (210), which are characteristics of mesoporous materials with hexagonal structures. SEM analysis showed that the surface morphology of Zn-modified MCM-41 formed aggregates of smaller particles. The EDS results showed that the amount of Zn in MCM-41 was 1.25%. Modification with Zn metal also affected the surface area and porosity of MCM-41, where the surface area, pore volume, and pore diameter decreased. Based on the adsorption-desorption analysis of N2 gas, both materials exhibit a type IV isotherm typical for mesoporous materials with an H1 hysteresis loop.

1. Introduction

Researchers have become interested in porous materials due to their wide application. Suitable porous materials open new perspectives in applying catalysts for environmental pollutants and adsorption fields. Porous materials contain pores or cavities. The part of the material framework is often called the matrix or frame [1].

Porous materials are characterized by their porosity. Based on the pore size, porous materials are classified into three types: micropores less than 2 nm, mesopores with a size of 2–50 nm, and macropores more than 50 nm [2]. Among the three ranges of porous materials, mesoporous materials are of considerable interest because they have a regular arrangement of uniform pore openings, large surface area (~100 $m^2\ g^{-1}$), and pore volume (~1 $cm^3\ g^{-1}$).

In the early 1990s, scientists synthesized a mesoporous silica material called the M41S group. The term M41S is used to classify various types of MCM (Mobil Composition of Matter). Types from this group include MCM-41, MCM-48, and MCM-50 [3]. MCM-41 (Mobil Composition of Matter No.41) is the type most studied because it has a regular hexagonal structure, large specific surface area, good thermal stability, and is easy to obtain compared to other types of M41S [4, 5].

Although MCM-41 has a large surface area, pore volume, and designable chemical composition, MCM-41 does not have photocatalytic activity. The Si and O atoms of MCM-41 are not sensitive to UV-Vis light [1]. As for the adsorption application, the silanol group, which is the active group in MCM-41, is estimated to be a weak group for adsorption [6]. Therefore, MCM-41 must be modified to improve the material's properties to become a potential material, especially as a catalyst and adsorbent.

Modification of MCM-41 will affect the acidity, pore size, hydrophobicity, and stability of the material [7]. Modification of mesoporous silica can be done in various ways. Several studies related to modifications include functionalization by organosilanes [8, 9], polymer impregnation [10, 11] and metal incorporation or impregnation [12, 13, 14].

The large surface area, porosity, and amorphous structure of MCM-41 allow the impregnation of transition metals into the MCM-41 framework [15]. Based on that reason, in this study, the modification of MCM-41 was executed by impregnation of Zn metal. Zn is an essential heavy metal that tends to be harmless. The added Zn is expected to fit into the MCM-41 framework without changing the mesoporous hexagonal structure of the material. This study aimed to determine the characteristics of MCM-41 and Zn-MCM-41.

2. Methodology

This research was performed in the following steps: synthesis, modification, and characterization of MCM-41 and Zn-MCM-41. The following are research materials, tools, and procedures.

2.1. Materials and Equipment

The materials were Ludox HS40 (39.5 wt % SiO_2, 0.4 wt % Na_2O and 60.1 wt % H_2O, Du Pont) as silica source, cetyltrimethylammonium chloride (CTAC, Sigma Aldrich) as a surfactant, zinc nitrate ($Zn(NO_3)_2.6H_2O$) (Merck) as the source of Zn, sodium hydroxide (NaOH) (Merck), acetic acid (CH_3COOH) (Merck), sodium chloride (NaCl) (Merck), ammonia (NH_3) (Merck), hydrochloric acid (HCl) (Merck), distilled water and Whatman filter paper no. 42.

The equipment used in this study consisted of an analytical balance (Ohaus and Toledo), water bath (Advantec, TBS271SA), hot plate stirrer (Ceramag-Midi), oven (Vacucell), furnace (Nabertherm L3/11/B4), funnel Buchner, vacuum pump, XRD (Shimadzu 7000), SEM-EDS (Jeol JCM-6000plus), surface area and pore analyzer (Micromeritics TriStar II 3020).

2.2. Experiment

The mesoporous silica MCM-41 synthesis method used in this research was hydrothermal, based on research conducted by Taba [2]. Initially, sodium silicate solution was prepared by mixing 46.9 g of 1 M NaOH with 14.3 g of Ludox HS40 and then heating the mixture at 80℃ while stirring for two hours. The following step involved mixing 0.29 g of 28% NH_3 with 20 g of 25% CTAC solution in a polypropylene vial. The sodium silicate solution was cooled to room temperature and then added dropwise to the surfactant mixture in a polypropylene vial while stirring rapidly for 1 hour. The gel mixture was then heated at 97℃ for 24 hours. The pH of the mixture was adjusted to 10 by adding acetic acid (30%) while stirring vigorously at room temperature and adding 2.74 g of NaCl to increase hydrothermal stability [16]. After adjusting the pH, the mixture was reheated at 97℃ for 24 hours. The pH adjustment and heating process were repeated twice. The MCM-41 crystals formed were then filtered, repeatedly rinsed with distilled water until the pH was neutral and dried in an oven at 97°C.

Modification of MCM-41 was executed by impregnation method based on the procedure of Hachemaoui *et al.* [14], by weighing 5 g of MCM-41 with surfactant and mixing it with 100 mL of zinc nitrate solution ($Zn(NO_3)_2.6H_2O$ for 2 hours at room temperature. The resulting powder was washed with distilled water until the pH was neutral and filtered and then dried in an oven at 97°C. The next step was the removal of surfactants which was taken by calcining using a furnace at a temperature of 550°C for 5 hours.

The final powder obtained was characterized by XRD to determine the structure of the material formed, SEM-EDS to determine the morphology and elements or minerals that compose mesoporous silica materials, and then BET-BJH method to determine the surface area and porosity of the material.

3. Results and Discussion

In this research, the synthesis method used was hydrothermal, which during the synthesis used a single-phase reaction or heterogeneous phase in aqueous media at a temperature larger than 25℃ and pressure of more than 100 kPa to produce crystals from the solution. One of the advantages of the hydrothermal method over other types of crystal growth is its ability to make the phase unstable at its melting point [1]. The results obtained were then modified by the wet impregnation method, which is the simplest method. In this method, the amount of metal precursor added exceeds the pore volume of MCM-41. The final product obtained from the synthesis and modification process was white powder MCM-41 and Zn-MCM-41. In order to determine the characteristics of the synthesized material, characterization was executed using X-Ray diffraction (XRD) instruments, Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS), and porosity analysis using the BET-BJH method.

3.1. XRD Analysis

Characterization using XRD provides information about a material's structure with a characteristic diffraction pattern. The diffractograms of MCM-41 and Zn-MCM-41 synthesized in this study are presented in Figure 1. MCM-41 material has a characteristic peak diffraction pattern at an angle of 2θ between 2–5°. The peaks that appear with reasonably high intensity are at 2θ of 2.40°, 3.87°, and 4.49°. The success of the synthesis was also confirmed by JCPDS data No. 00-049-1712 and obtained almost the same results [17].

Based on the miller index calculation, the crystal planes of the synthesized material are (100), (110), and (200), which are characteristics of mesoporous materials and have a hexagonal structure arrangement [18, 19]. No shift was found at angle 2θ in the Zn-MCM-41 diffractogram, but the intensity of the characteristic peaks decreased. Impregnation of Zn metal into MCM-41 will cause a slight distortion of the pore walls resulting in reduced mesoporous characteristics, but the hexagonal peak characteristics are maintained. This indicates that Zn is likely to enter the MCM-41 framework and retain the hexagonal structure of the material [1, 20].

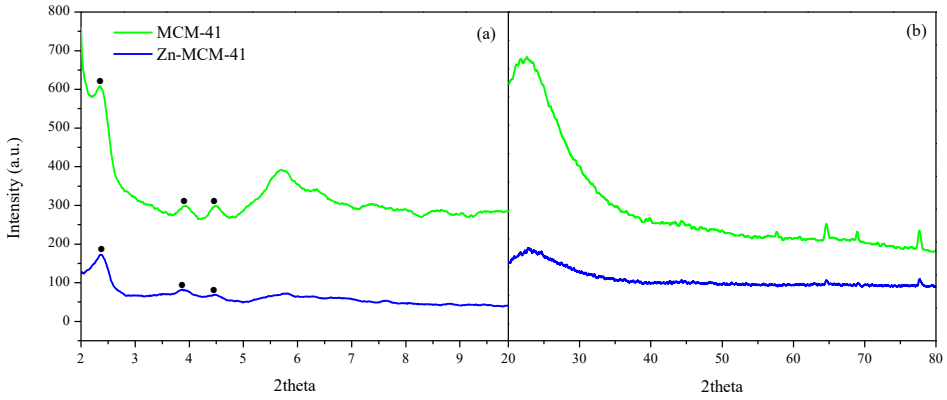

Figure 1. Diffractograms of MCM-41 and Zn-MCM-41 at (a) low angle (b) high angle

The XRD pattern at a larger angle of 2θ in Figure 1 (b) also aimed to determine the presence of Zn metal in MCM-41, which may exist as a finely dispersed oxide form or as particles amorphous in the MCM-41 skeleton. In this study, metal oxide characteristics were not found (36°), indicating that Zn metal ions entered and were evenly dispersed into the MCM-41 framework [21, 22].

3.2. SEM-EDS Analysis

SEM characterization aimed to determine the surface morphology of the synthesized material. SEM images can show the particle shape of mesoporous silica in the form of spheric aggregates with a relatively uniform shape [23]. The results of SEM characterization of the synthesized material are presented in Figure 2.

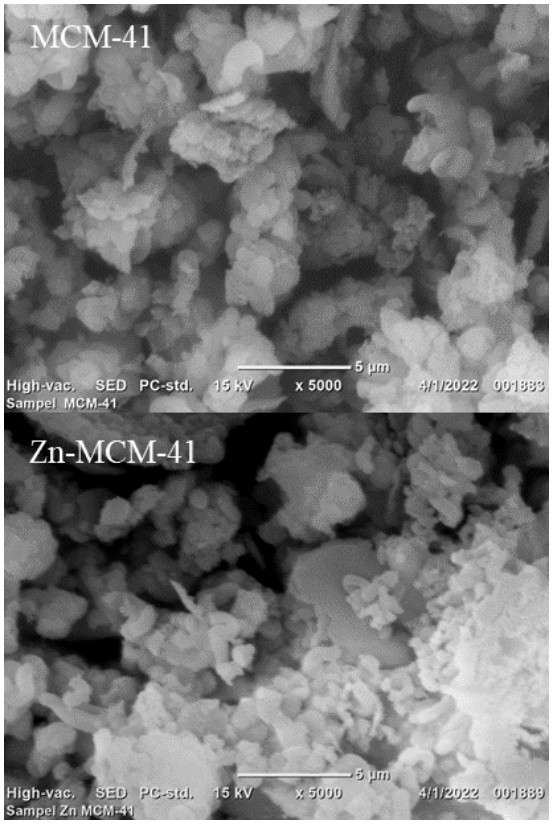

Figure 2. SEM image of MCM-41 and Zn-MCM-41

Figure 2 shows the morphology and surface texture of MCM-41 and Zn-MCM-41 performed at 5000 times magnification. MCM-41 particles tend to aggregate as much as possible with a uniform spherical shape, whereas Zn-MCM-41 particles tend to become stacked aggregates with a smaller size. The same thing was also reported by Admi *et al.* [23] that the Zn ion in the MCM-41 framework influences the form of weak electrostatic repulsion so that the particle size tends to be smaller.

EDS analysis can be implemented to determine the chemical composition and distribution of Zn metal in the MCM-41 [24]. The results of the EDS analysis are shown in Figure 3. The inserted element map image shows the presence and distribution of homogeneous Si, O, and Zn.

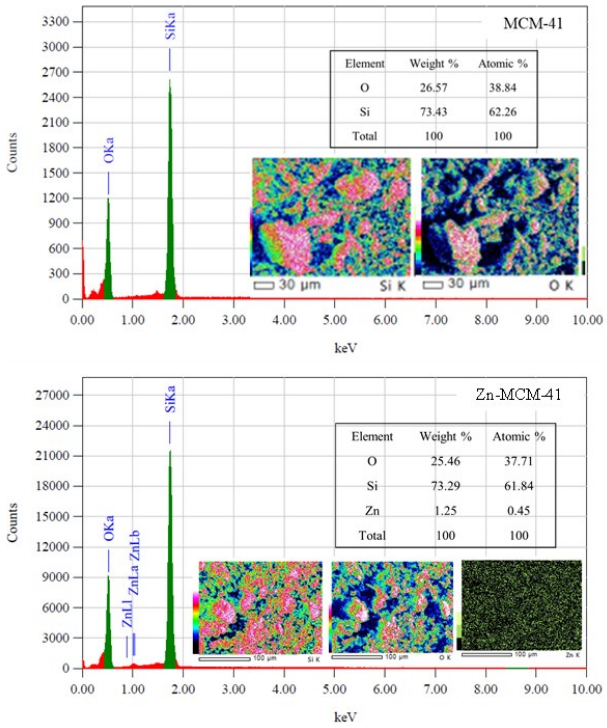

Figure 3. EDS image ofMCM-41 and Zn-MCM-41

In Figure 3, it can be seen that the total mass percent of Zn in MCM-41 is 1.25%. The results also showed that the mass percent and the atomic number of Si MCM-41 decreased in Zn-MCM-41. This indicates that some of the Si atoms were replaced by Zn in the MCM-41 framework. An illustration of the formation of Zn-O bonds in the MCM-41 framework is presented in Figure 4.

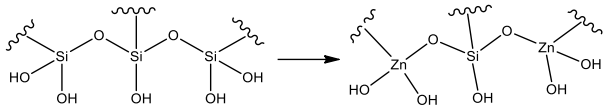

Figure 4. Illustration of the formation of Zn-O bonds in MCM-41

3.3. BET-BJH Analysis

Adsorption-desorption N_2 is a commonly used method for characterizing mesoporous materials. This method provides information on the surface area, pore volume and diameter. The surface area was determined by calculating relative pressure data using the Brunauer-Emmett-Teller (BET) method, and the Barrett-Joyner-Halenda (BJH) method was employed to measure pore volume and diameter[4, 25]. The surface area of BET, volume, and pore diameter of the synthesized MCM-41 and Zn-MCM-41 are presented in Table 1, and the N_2 adsorption-desorption isotherm model is shown in Figure 5.

Table 1. Pore structure data with nitrogen adsorption isotherm

Material	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
MCM-41	920.43	0.80	3.04
Zn-MCM-41	896.04	0.79	2.94

Based on the data in Table 1, it is known that the surface area, pore volume, and pore diameter of MCM-41 decreased after being modified with Zn metal. This is due to the pore blockage in the MCM-41 channel and particle aggregation of the added Zn metal [17].

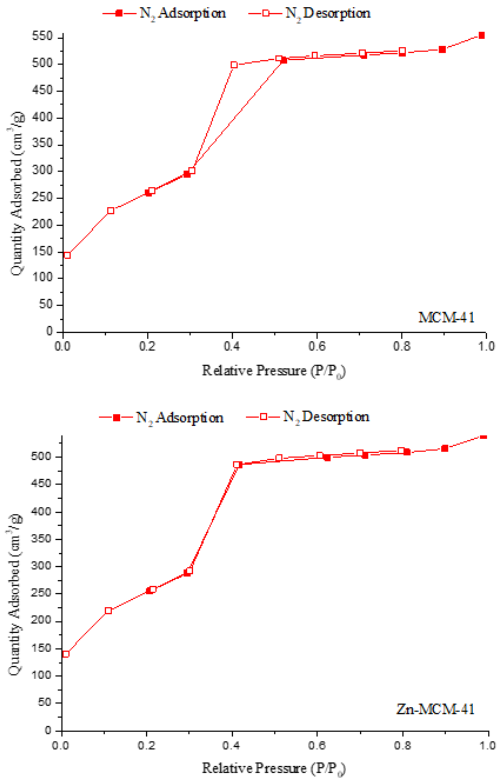

Figure 5. Adsorption-Desorption N_2 of MCM-41 and Zn-MCM-41

Figure 5 shows the nitrogen adsorption-desorption isotherms of the synthesized MCM-41 and Zn-MCM-41, both of which have a type IV isotherm with an H1 hysteresis loop. A similar result was also reported by Boukoussa *et al.* [26]. According to the IUPAC classification, the type of hysteresis loop is reasonably related to a particular characteristic of porous structure [4]. Based on Thommes *et al.* [27] loops in H1 hysteresis are found in adsorbents with a narrow mesoporous range. Minimal network effect and steep and narrow loops are apparent features of pore condensation upon adsorption of N_2 gas. There are three stages in determining the type of adsorption isotherm: the first stage at $P/P_0 < 0.25$ monolayer adsorption occurs on nitrogen gas on the surface material. In the second stage, there was a significant increase in the adsorption volume at $0.25 < P/P_0 < 0.4$, indicating the material's pores filing process. The third stage occurs at a relative pressure >0.4, characterized by a gradual increase in volume with P/P_0 due to multilayer adsorption on the material's surface. A sharp increase at $0.25< P/P_0<0.4$ is characteristic of mesoporous materials [28].

4. Conclusion

Based on the research data, it can be concluded that MCM-41 can be synthesized using the hydrothermal method, and modifications can be made using the Zn metal impregnation method. Modification with Zn metal did not change the hexagonal structure of the MCM-41 mesoporous material. Changes in surface morphology, surface area, pore volume, and pore diameter are caused by ion dispersion and the irregular arrangement of Zn atoms in the MCM-41 framework. The nitrogen gas adsorption-desorption isotherm showed type IV isotherm, a characteristic of mesoporous materials based on the IUPAC classification. Based on the characteristics of the Zn-MCM-41 material obtained, the material can be applied as an adsorbent or catalyst.

References

[1] Dipti Prava Sahoo, Dharitri Rath, Binita Nanda, K. M. Parida, Transition metal/metal oxide modified MCM-41 for pollutant degradation and hydrogen energy production: a review, *RSC Advances*, 5, 102, (2015), 83707-83724 https://doi.org/10.1039/C5RA14555D

[2] Paulina Taba, Adsorption of Water and Benzene Vapour in Mesoporous Materials, *Makara Journal of Science*, 12, 2, (2008), 120-125

[3] Priyanka Solanki, Anjali Patel, Encapsulation of Aspirin into parent and functionalized MCM-41, in vitro release as well as kinetics, *Journal of Porous Materials*, 26, 5, (2019), 1523-1532 https://doi.org/10.1007/s10934-019-00750-w

[4] Jose Arnaldo S. Costa, Roberta A. de Jesus, Danilo O. Santos, Joao F. Mano, Luciane P. C. Romao, Caio M. Paranhos, Recent progresses in the adsorption of organic, inorganic, and gas compounds by MCM-41-based mesoporous materials, *Microporous and Mesoporous Materials*, 291, 109698, (2020), 1-21 https://doi.org/10.1016/j.micromeso.2019.109698

[5] Son Tung Pham, Ba Manh Nguyen, Giang H. Le, Andras Sapi, Suresh Mutyala, Imre Szenti, Zoltan Konya, Tuan A. Vu, Role of Brønsted and Lewis acidic sites in sulfonated Zr-MCM-41 for the catalytic

reaction of cellulose into 5-hydroxymethyl furfural, *Reaction Kinetics, Mechanisms and Catalysis*, 130, 2, (2020), 825-836 https://doi.org/10.1007/s11144-020-01799-4

[6] Saravanan Nagappan, Yubin Jeon, Sung Soo Park, Chang-Sik Ha, Hexadecyltrimethylammonium bromide surfactant-supported silica material for the effective adsorption of metanil yellow dye, *ACS Omega*, 4, 5, (2019), 8548-8558 https://doi.org/10.1021/acsomega.9b00533

[7] Zhuxiu Zhang, Mengnan Hu, Qiumin Mei, Jihai Tang, Zhaoyang Fei, Xian Chen, Qing Liu, Mifen Cui, Xu Qiao, Iron-doped mesoporous silica, Fe-MCM-41, as an active Lewis acid catalyst for acidolysis of benzyl chloride with fatty acid, *Journal of Porous Materials*, 26, 1, (2019), 261-269 https://doi.org/10.1007/s10934-018-0645-9

[8] Qingdong Qin, Jun Ma, Ke Liu, Adsorption of anionic dyes on ammonium-functionalized MCM-41, *Journal of Hazardous Materials*, 162, 1, (2009), 133-139 https://doi.org/10.1016/j.jhazmat.2008.05.016

[9] Aneesh Mathew, Surendran Parambadath, Mary Jenisha Barnabas, Hyun Jin Song, Jae-Sung Kim, Sung Soo Park, Chang-Sik Ha, Rhodamine 6G assisted adsorption of metanil yellow over succinamic acid functionalized MCM-41, *Dyes and Pigments*, 131, (2016), 177-185 https://doi.org/10.1016/j.dyepig.2016.04.007

[10] Bouhadjar Boukoussa, Aboubakr Hakiki, Sarah Moulai, Karim Chikh, Djamal Eddine Kherroub, Larbi Bouhadjar, Djahida Guedal, Khadidja Messaoudi, Fatima Mokhtar, Rachida Hamacha, Adsorption behaviors of cationic and anionic dyes from aqueous solution on nanocomposite polypyrrole/SBA-15, *Journal of Materials Science*, 53, 10, (2018), 7372-7386 https://doi.org/10.1007/s10853-018-2060-7

[11] Zakaria Abid, Aboubakr Hakiki, Bouhadjar Boukoussa, Franck Launay, Hadj Hamaizi, Abdelkader Benguedach, Rachida Hamacha, Preparation of highly hydrophilic PVA/SBA-15 composite materials and their adsorption behavior toward cationic dye: effect of PVA content, *Journal of Materials Science*, 54, 10, (2019), 7679-7691 https://doi.org/10.1007/s10853-019-03415-w

[12] Bingqian Han, Fei Zhang, Zhipeng Feng, Shuyang Liu, Shaojuan Deng, Yan Wang, Yude Wang, A designed Mn_2O_3/MCM-41 nanoporous composite for methylene blue and rhodamine B removal with high efficiency, *Ceramics International*, 40, 6, (2014), 8093-8101 https://doi.org/10.1016/j.ceramint.2013.12.163

[13] Yuehong Shu, Yimin Shao, Xiangyu Wei, Xi Wang, Qiangqiang Sun, Qiuyun Zhang, Laisheng Li, Synthesis and characterization of Ni-MCM-41 for methyl blue adsorption, *Microporous and Mesoporous Materials*, 214, (2015), 88-94 https://doi.org/10.1016/j.micromeso.2015.05.006

[14] Mohammed Hachemaoui, Bouhadjar Boukoussa, Adel Mokhtar, Amel Mekki, Mohammed Beldjilali, Miloud Benaissa, Farouk Zaoui, Aboubakr Hakiki, Wahiba Chaibi, Mohamed Sassi, Dyes adsorption, antifungal and antibacterial properties of metal loaded mesoporous silica: effect of metal and calcination treatment, *Materials Chemistry and Physics*, 256, 123704, (2020), 1-12 https://doi.org/10.1016/j.matchemphys.2020.123704

[15] Jyoti Prakash Dhal, Tapan Dash, Garudadhwaj Hota, Iron oxide impregnated mesoporous MCM-41: synthesis, characterization and adsorption studies, *Journal of Porous Materials*, 27, 1, (2020), 205-216 https://doi.org/10.1007/s10934-019-00803-0

[16] Ryong Ryoo, Chang Hyun Ko, Russell F. Howe, Imaging the distribution of framework aluminum in mesoporous molecular sieve MCM-41, *Chemistry of Materials*, 9, 7, (1997), 1607-1613 https://doi.org/10.1021/cm9700110

[17] Sahar Dehghani, Mohammad Haghighi, Neda Vardast, Structural/texture evolution of CaO/MCM-41 nanocatalyst by doping various amounts of cerium for active and stable catalyst: biodiesel production from waste vegetable cooking oil, *International Journal of Energy Research*, 43, 8, (2019), 3779-3793 https://doi.org/10.1002/er.4539

[18] Soenandar Milian Tompunu Tengker, Iip Izul Falah, Sintesis dan karakterisasi material mesopori MCM-41 menggunakan TMAOH dan garam anorganik K2SO4, *Fullerene Journal of Chemistry*, 2, 2, (2017), 61-65 https://doi.org/10.37033/fjc.v2i2.10

[19] Nastaran Hazrati, Ali Akbar Miran Beigi, Majid Abdouss, Amir Vahid, One-step synthesis of zinc-encapsulated MCM-41 as H_2S adsorbent and optimization of adsorption parameters, *Analytical Methods in Environmental Chemistry Journal*, 3, 02, (2020), 74-81 https://doi.org/10.24200/amecj.v3.i02.104

[20] Nur Hasanah, Sutarno Sutarno, Eko Sri Kunarti, Characteristic Study of the MCM-41 Modified with Zn by Direct Synthesis, *JKPK (Jurnal Kimia dan Pendidikan Kimia)*, 3, 3, (2018), 183-192 https://doi.org/10.20961/jkpk.v3i3.22808

[21] Xiaojuan Liu, Dezhi Yi, Yuanyuan Cui, Li Shi, Xuan Meng, Adsorption desulfurization and weak competitive behavior from 1-hexene over cesium-exchanged Y zeolites (CsY), *Journal of Energy Chemistry*, 27, 1, (2018), 271-277 https://doi.org/10.1016/j.jechem.2017.04.006

[22] Xiaoqin Guo, Lei Bao, Liping Chang, Weiren Bao, Junjie Liao, Influence of modifications on the deep desulfurization behavior of NaY and Na13X zeolites in gasoline, *Environmental Science and Pollution Research*, 26, 13, (2019), 13138-13146 https://doi.org/10.1007/s11356-019-04824-9

[23] Admi Admi, Fitria Ramadhani, Syukri Syukri, Sintesis dan Karakterisasi Enkapsulat Katalis Nikel (II) pada Silika Mesopori Modifikasi, *Jurnal Riset Kimia*, 11, 2, (2020), 89-96 https://doi.org/10.25077/jrk.v11i2.356

[24] Yu-Hua Guo, Guo-Xiang Pan, Min-Hong Xu, Tao Wu, Yong-Ya Wang, Synthesis and adsorption desulfurization performance of modified mesoporous silica materials M-MCM-41 (M= Fe, Co, Zn), *Clays and Clay Minerals*, 67, 4, (2019), 325-333 https://doi.org/10.1007/s42860-019-00030-3

[25] M. M. Rahman, M. A. B. M. Aznan, A. M. Yusof, R. H. Ansary, M. J. Siddiqi, S. Yusan, Synthesis and Characterization of Functionalized Se-MCM-41 a New Drug Carrier Mesopore Composite, *Oriental Journal of Chemistry*, 33, 2, (2017), 611-621 http://dx.doi.org/10.13005/ojc/330208

[26] Bouhadjar Boukoussa, Zahira Kibou, Zakaria Abid, Rachida Ouargli, Noureddine Choukchou-Braham, Didier Villemin, Abdelkader Bengueddach, Rachida Hamacha, Key factor affecting the basicity of mesoporous silicas MCM-41: effect of surfactant extraction time and Si/Al ratio, *Chemical Papers*, 72, 2, (2018), 289-299
https://doi.org/10.1007/s11696-017-0279-4

[27] Matthias Thommes, Katsumi Kaneko, Alexander V. Neimark, James P. Olivier, Francisco Rodriguez-Reinoso, Jean Rouquerol, Kenneth S. W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure and Applied Chemistry*, 87, 9-10, (2015), 1051-1069
https://doi.org/10.1515/pac-2014-1117

[28] Soenandar Milian Tompunu Tengker, Jenny Kumajas, Karakterisasi material mesopori Ni/MCM-41 dan pengaruh penambahan logam nikel terhadap tingkat keasaman material, *Fullerene Journal of Chemistry*, 4, 2, (2019), 61-65
https://doi.org/10.37033/fjc.v4i2.83