Scientific Research Publishing

Advances in Chemical Engineering and Science, 2025, 15(4), 69-76
https://www.scirp.org/journal/aces
ISSN Online: 2160-0406
ISSN Print: 2160-0392

Additive-Free Synthesis of Hierarchical Zeolite Y Catalyst from Aloji Kaolin

Rakiya Abdullahi Usman[1,2], Emmanuel Olufemi Osaji[3], Monday Abutu Idakwo[4], Shade Ibiduni Ishola[1], Rasaq Olawale Medupin[1], Eniola Ebenezer Olowofusi[1], Umar A. Saleh[5]

[1]Department of Mechanical Engineering, Federal University, Lokoja, Kogi State, Nigeria
[2]Department of Chemical Engineering, Confluence University of Science and Technology, Osara, Kogi State, Nigeria
[3]Department of Electrical and Electronic Engineering, Federal University, Lokoja, Kogi State, Nigeria
[4]Department of Computer Engineering, Federal University, Lokoja, Kogi State, Nigeria
[5]Centre for Atmospheric Research, National Space Research and Development Agency, Anyigba, Kogi State, Nigeria
Email: *rakiya.usman@fulokoja.edu.ng

How to cite this paper: Usman, R.A., Osaji, E.O., Idakwo, M.A., Ishola, S.I., Medupin, R.O., Olowofusi, E.E. and Saleh, U.A. (2025) Additive-Free Synthesis of Hierarchical Zeolite Y Catalyst from Aloji Kaolin. *Advances in Chemical Engineering and Science*, **15**, 69-76.
https://doi.org/10.4236/aces.2025.154006

Received: February 1, 2025
Accepted: October 12, 2025
Published: October 15, 2025

Abstract

Hierarchical zeolite has multilevel porosity to enable accurate and unhindered diffusion of reactant and product in the zeolite framework. It is an advanced material used to correct the constraint encountered in the conventional zeolite with a micropore system. The development of hierarchical zeolites involves using a mesopore-creating agent to create maximum porosity. This method usually deposits hazards to the environment and requires very high energy to remove them after their synthesis procedure. The additive-free synthesis of hierarchical zeolite is an advanced move to correct the synthesis of hierarchical zeolite Y. The report is on additive-free hierarchical zeolite Y from Aloji kaolin. The synthesized hierarchical zeolite Y has a surface area of 489.09 m^2/g, a pore size of 5.76 nm and can be applied in chemical engineering processes.

Keywords

Hierarchical Zeolites, Additive Free, Mesopores, Aloji Kaolin

1. Introduction

Zeolites are essential materials in catalysis, separation, and ion exchange processes. It is particularly important in industrial processes. The applicability of zeolites is linked to their exceptional flexibility as solids whose structure and surface properties can be tuned to suit a particular purpose. They are valid in water softening [1], removal of heavy metal from the soil [2], odor control [3], and petrochemical industries. Generally, zeolites are synthesized from sodium aluminosilicate gel formed from various silica and alumina sources by hydrothermal treatment. However, the source of synthetic aluminosilicate reagents for preparing synthetic zeolites has higher cost implications and generates environmental waste [4] [5]. They are costly because of the high technology involved in their production. However, they have the advantage of having minimum impurities. The search for a cheap source of silica and alumina for the synthesis of zeolite motivated most researchers to use different geological materials and industrial wastes like coal fly ash [6] [7] and kaolin [8] [9]. The use of kaolin in synthesizing zeolite has continued to interest researchers over the years due to its easy accessibility, low impurities, and environmental friendliness. The application of these catalysts depends mainly on their micropores which possess some constraints to bulky reactants and products. However, the small pore sizes restrict molecular diffusion and mass transport within zeolite crystals and prohibit large molecules from accessing the intra-crystalline active sites [10]. Consequently, slow diffusion often limits adsorption processes and catalytic reactions, and zeolites cannot catalyze reactions involving large molecules [11] [12]. Developing hierarchical zeolites with qualities such as long lifetime, high catalytic performance, postponed coking, and deactivation will reduce the constrain observed in the conventional zeolite catalyst. Traditional synthesis strategies of hierarchical zeolites via post-treatment or directing synthesis with mesoporous templates are characterized by high energy consumption and substantial use of expensive and environmentally unfriendly organic templates. A new green synthesis approach has emerged to effectively synthesize hierarchical zeolites that involve self-pillaring, steaming, seed assistance, and kinetic control of crystallization parameters [13]. These additive-free synthesis routes of hierarchical zeolite are ones in which the morphology modifying agent (mesoporogen) is avoided [14]. The additive-free route has industrial importance in zeolite catalysts for catalytic applications. The introduction of mesoporosity in zeolite Y is affected by the following factors: reduction of crystallization temperature, the precursor's molar concentration, and the solvent's quantity (water). The control of the nucleation and crystal growth of precursor gel by varying the crystallization parameters forms hierarchical zeolites without external templating agents [15]-[17]. The nucleation and growth of the synthesis precursor are controlled by adjusting of crystallization parameters. Adjusting the Si/Al ratio from 1.1 to 1.9 through a hydrothermal process synthesizes hierarchical zeolite Y without additives. The crystallization of the zeolite in the Teflon stainless steel autoclave at a temperature of 100˚C for 24 h. The synthesized zeolite Y has a micropore of 0.74 nm and a mesopore of 10 nm [18]. The synthesis precursors of hierarchical zeolite Y with the molar concentration of Al_2O_3: 4.9 - 12 Na_2O: 3.6 - 14 SiO_2: 214 - 300 H_2O were ice-bathed for 1 h. aged at room temperature for 24 h and crystallized at 60˚C for 48 h [19]. Preparing the synthesis gel at 0˚C using an ice bath is a promising way to synthesize sub-micron-sized zeolite Y particles. An additive-free hierarchical zeolite Y with a molar concentration of Al_2O_3: 13.6 - 36 Na_2O: 3 - 8 SiO_2: 545.5 - 1440 H_2O. The precursor was aged at 50˚C for 5 h and crystallized at 60˚C for 24 hours. They used 60˚C as their second temperature step and claimed that at 50˚C, their reaction mixture stayed amorphous. The synthesized zeolite has a pore volume of 0.26 cm^3/g and a surface area of 544 m^2/g [20]. In another research, a synthesized hierarchical zeolite Y with a molar concentration of Al_3O_2: 10 - 18.3 Na_2O: 10 - 22 SiO_2 and 815 H_2O was synthesized with the precursor gel aged at room temperature for 2 hours, crystallized at 70˚C for 24 hours, and obtained a hierarchical zeolite with a pore volume of 0.33 m^3/g. [21]. The focus of the research is the development of additive free hierarchical zeolite Y from kaolin.

2. Materials and Methods

Aloji kaolin, Sodium Hydroxides pellets, Sodium metasilicate powder, distilled water, Ammonium Sulphate.

The kaolin was sourced from Aloji in Ofu Local Government Area of Kogi State. The kaolin was beneficiated by the sedimentation method and calcined at 650˚C for 3 hours to obtain metakaolin. Some sodium hydroxide pellets of mass 20.8 grams were dissolved in 32 grams of distilled water. 39.36 grams of sodium metasilicate and a gram of metakaolin were added to the solution to form aluminosilicate gel. The mixtures were homogeneously stirred for complete dissolution. The aging of the aluminosilicate gel was conducted for 10 hours at 50˚C. This was crystallized in a Teflon-line stainless steel autoclave at 100˚C for 9 hours. The washing of the crystallized zeolite was conducted using deionized water to a pH of 9 and dried in the oven at 100˚C for 8 hours. The mesoporous zeolite Y was protonated by ion exchange with 10 ml of 1.0 M NH_2SO_4 solution by soaking it for 24 hours. The synthesized hierarchical zeolite Y was filtered, dried in the oven at 100˚C for 3 hours, and calcined at 550˚C for 2 hours. XRD, SEM, and BET were used to characterize the synthesized zeolite.

3. Characterization of the Synthesized Zeolite

The synthesized zeolite was investigated for its crystallinity, morphology, textural structures and porosity by XRD, SEM, and BET analysis. The X-ray diffraction pattern of as-synthesized hierarchical zeolite was recorded on Bruker AXSD8 using nickel-filtered CuKα X-ray radiation at 40 kV and 30 mA. The two-theta degree range was scanned from 5˚ to 90˚ with a scanning rate of 20˚/min. The morphology was examined using a Hitachi SU-8010 scanning electron microscope. Nitrogen isotherms were measured at a nitrogen gas temperature of 77 K as adsorbate to obtain the Brunauaer-Emmett-Teller (BET) surface area adsorption, average pore size, and pore volume of the hierarchical zeolites Y.

4. Results and Discussions

The morphology of refined Aloji kaolin is shown in **Figure 1**. The SEM image of the refined Aloji kaolin shows a platy-like morphology and hexagonal outline and is loosely packed, which are typical of kaolinite clay. It is also a clear indication that the refinement has taken place. The elemental composition of Aloji Kaolin has its Si/Al ratio of approximately 2.

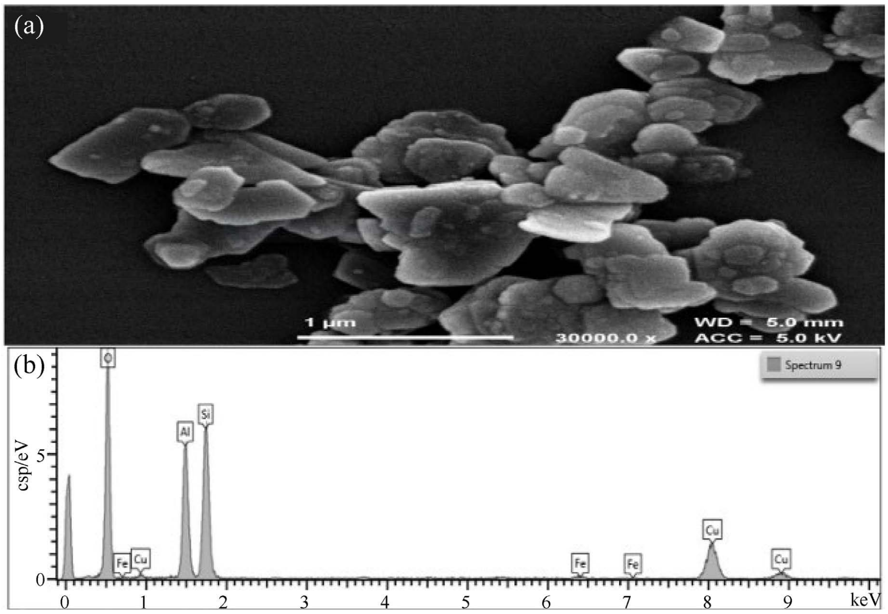

Figure 1. Morphology of refined Aloji kaolin and its EDX.

The kaolin is a poorly crystalline kaolinite mineral with high quartz content. The elemental composition of kaolin has Si/Al ratio approximately I.12.as indicated by the EDX Spectrum. The Aloji kaolin has been adjourned to be a poorly crystalline kaolinite mineral with appreciable quartz content [22].

The synthesized zeolites Y were characterized for phase/morphology identification and structural analysis.

The XRD diffraction pattern shows a characteristic peak at 2θ = 10.13˚, 12.14˚, 14.65˚, and 15.97˚, as the reference ultra-stable hierarchical zeolite Y as shown in Figure 2 (Dekum *et al.*, 2017). The diffraction at 2θ value of 26.65˚ denotes some crystalline phase of quartz, an impurity in synthesizing zeolite with kaolin [23].

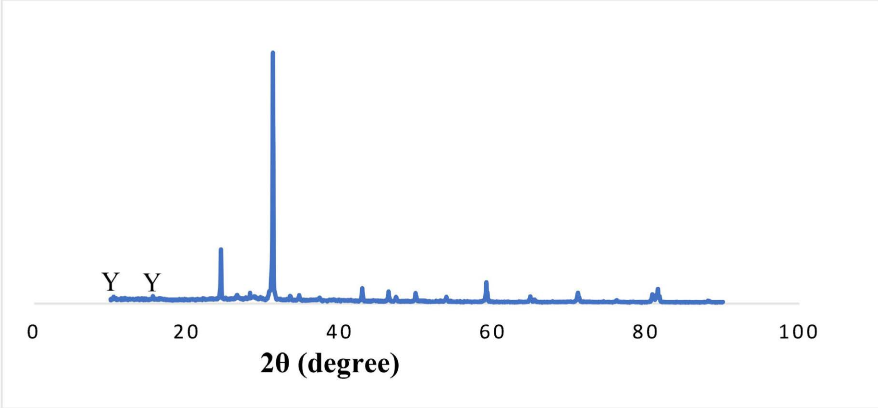

Figure 2. XRD Pattern of hierarchical Zeolite Y.

The SEM, EDX, and the crystallite diameter distribution of the synthesized hierarchical zeolite Y are shown in **Figure 3**. The SEM image of the synthesized zeolite Y shows a plate-like morphology arranged in a cuboctahedral manner of hierarchical zeolites Y. These agree with the work of [17] who obtained a same shaped hierarchical zeolite of high silica layered zeolite Y. The EDX spectra revealed the hierarchical zeolite's elemental composition, showing the presence of Fe, Ti, S, and Na. These elements are the kaolin's impurities and remain as such in the synthesized zeolite. These researchers observed that the zeolite catalyst framework composition (Si/Al ratio) could be tuned from 1 to infinite by altering the hydrothermal synthesis or post-synthetic modifications. The diameter distribution was obtained giving an average crystallite diameter of 219.10 nm.

The BET analysis of the synthesized hierarchical zeolite was conducted, and the following results were obtained. The gas adsorption-desorption isotherm graph was plotted and shown in **Figure 4**. The adsorption isotherm is a type IV and hysteresis of H4 according to IUPAC classification for a porous material. The hysteresis H4 is associated with narrow pores and connected internal voids of irregular shape. The thin hysteresis loop observed at the low-pressure region of p/p˚ of less than 0.2 is evidence of the presence of mesopores. The hysteresis loop at the high-pressure region of p/p˚ greater than 0.2 indicates macro-pores in the synthesized zeolite [24] [25]. The synthesized zeolite Y has a BET surface area of 489.09 m^2/g, pore volume of 0.023178 cm^3/g. The BJH pore size distribution profile of the hierarchical zeolite Y has twenty modes centered at 2.00 nm to 5.00 nm, 10.59 nm, 12.09 nm, and 20.00 nm 30.00 nm, 35.00 nm, 40.00 nm and 90 and average pore size of 50.676 Å or 5.0676 nm, indicating a meso-porosity. The BJH plot for pore size distribution indicated creation of a pore ranging from 2 nm to 90 nm.

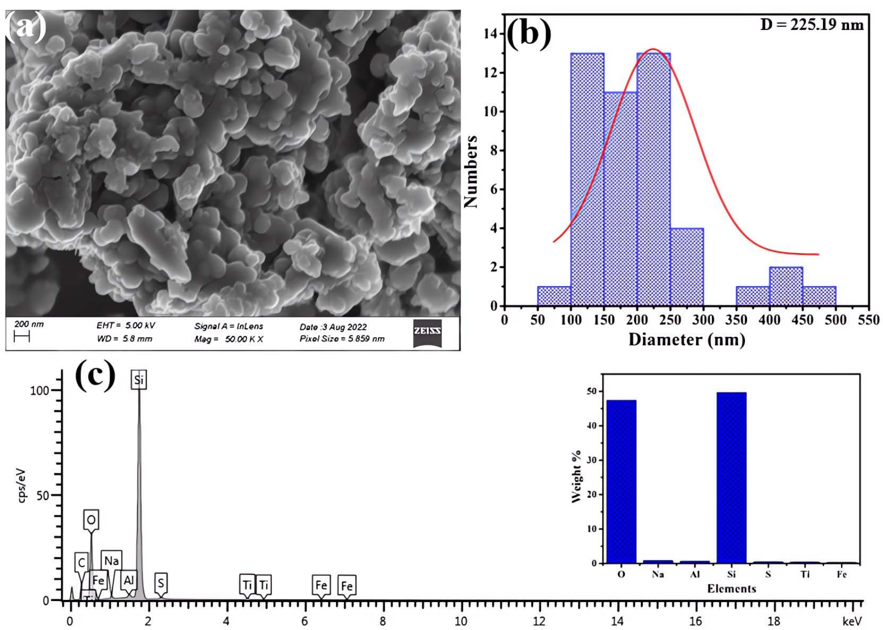

Figure 3. SEM image, crystallite diameter distribution, elemental percentage weight of Hierarchical zeolite Y (c).

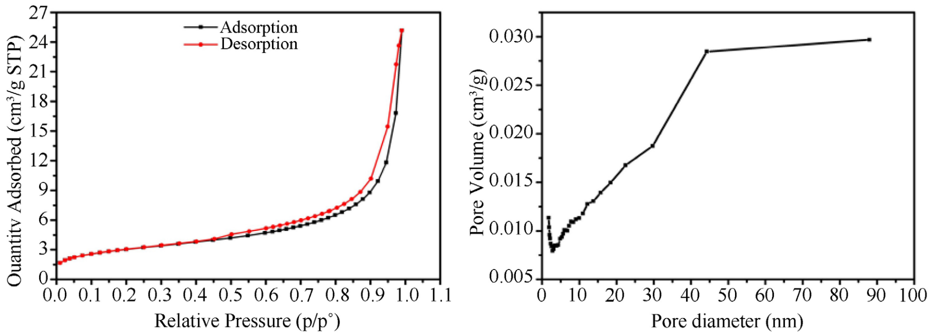

Figure 4. The nitrogen adsorption—desorption isotherm loops of the synthesized hierarchical zeolite Y and BJH pore distribution.

5. Conclusion

Hierarchical zeolite Y was successfully synthesized from Aloji kaolin for the first time by template-free synthesis. This synthesis route is mainly the variation of synthesis parameters such as the crystallization temperature, the ageing time and temperature, the concentration of the reacting aluminosilicate gel and the solvent in the reacting mixtures. The ageing temperature has played a vital role in this additive-free synthesis route. The synthesized zeolite structure and morphology were characterized with BET, XRD, and SEM. A hierarchical zeolite Y with a micro-mesopore was synthesized. The mesopores zeolites Y has an average crystallite diameter of 219.10 nm, a surface area of 489.09 m^2/g, a pore size of 50.676 Å, and a pore volume 0.23178 cm^3/g and can be applied in chemical engineering processes.

Acknowledgements

I humbly wish to acknowledge TETFUND Nigeria for their financial support under the TETFUND Intervention in Research Projects.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Lahnafi, A., Elgamouz, A., Jaber, L., Tijani, N. and Kawde, A. (2023) Naa Zeolite-Clay Composite Membrane Formulation and Its Use as Cost-Effective Water Softener. *Microporous and Mesoporous Materials*, **348**, Article 112339. https://doi.org/10.1016/j.micromeso.2022.112339

[2] Ada, D., Özge, B. and Dr. Sibel, Ö. (2022) Use of Zeolite in the Removal of Surfactants in Gray Waters and Plant Growth. *Chemistry Research Journal*, **7**, 6-19.

[3] Ferreira, A.P., Almeida-Aguiar, C., Costa, S.P.G. and Neves, I.C. (2022) Essential Oils Encapsulated in Zeolite Structures as Delivery Systems (EODS): An Overview. *Molecules*, **27**, Article 8525. https://doi.org/10.3390/molecules27238525

[4] Krisnandi, Y.K., Saragi, I.R., Sihombing, R., Ekananda, R., Sari, I.P., Griffith, B.E., *et al.* (2019) Synthesis and Characterization of Crystalline Nay-Zeolite from Belitung Kaolin as Catalyst for N-Hexadecane Cracking. *Crystals*, **9**, Article 404.

https://doi.org/10.3390/cryst9080404

[5] Zhang, J., Bai, S., Chen, Z., Wang, Y., Dong, L., Zheng, H., *et al.* (2017) Core-Shell Zeolite Y with Ant-Nest Like Hollow Interior Constructed by Amino Acids and Enhanced Catalytic Activity. *Journal of Materials Chemistry. Materials for Energy and Sustainability*, **5**, 20757-20764. https://doi.org/10.1039/c7ta05048h

[6] Wei, F., Guoping, H., Eric, F.M. and Gang, K.L. (2022) Synthesis of Zeolites from Circulated Fluidized Bed Coal Fly Ash. *Inorganic Chemistry Frontiers*, **9**, 1681-1691.

[7] Lin, S., Jiang, X., Zhao, Y. and Yan, J. (2022) Zeolite Greenly Synthesized from Fly Ash and Its Resource Utilization: A Review. *Science of The Total Environment*, **851**, Article 158182. https://doi.org/10.1016/j.scitotenv.2022.158182

[8] Sazali, N. and Harun, Z. (2022) One Shot of the Hydrothermal Route for the Synthesis of Zeolite LTA Using Kaolin. *Journal of Inorganic and Organometallic Polymers and Materials*, **32**, 3508-3520. https://doi.org/10.1007/s10904-022-02369-y

[9] He, Y., Guo, S., Li, S. and Yin, S. (2022) Green and Efficient Synthesis of High-Purity Y Zeolite Using Natural Raw Material-Kaolin Activated by Microwave Heating. *Applied Physics A*, **128**, Article No. 1077. https://doi.org/10.1007/s00339-022-06230-4

[10] Dabbawala, A.A., Ismail, I., Vaithilingam, B.V., Polychronopoulou, K., Singaravel, G., Morin, S., *et al.* (2020) Synthesis of Hierarchical Porous Zeolite-Y for Enhanced CO_2 Capture. *Microporous and Mesoporous Materials*, **303**, Article 110261. https://doi.org/10.1016/j.micromeso.2020.110261

[11] Chen, L., Sun, M., Wang, Z., Yang, W., Xie, Z. and Su, B. (2020) Hierarchically Structured Zeolites: From Design to Application. *Chemical Reviews*, **120**, 11194-11294. https://doi.org/10.1021/acs.chemrev.0c00016

[12] Ji, D., Liu, H., Wang, X., Liu, H., Gao, X., Xu, C., *et al.* (2017) Mesostructured Y Zeolite from Nay with Low Si/Al by One-Step Method Based on Bifunctional Surfactant. *Materials Chemistry and Physics*, **196**, 284-287. https://doi.org/10.1016/j.matchemphys.2017.04.059

[13] Jain, R., Mallette, A.J. and Rimer, J.D. (2021) Controlling Nucleation Pathways in Zeolite Crystallization: Seeding Conceptual Methodologies for Advanced Materials Design. *Journal of the American Chemical Society*, **143**, 21446-21460. https://doi.org/10.1021/jacs.1c11014

[14] Jan-Paul, G., Katharina, K., Bastian, R., Wilhelm, S. and Alexandra, I. (2021) Layer-Like Zeolite X as Catalyst in a Knoevenagel Condensation: The Effect of Different Preparation Pathways and Cation Exchange. *Catalysts*, **11**, Article 474.

[15] Wang, J., Huang, Y., Pan, Y. and Mi, J. (2016) New Hydrothermal Route for the Synthesis of High Purity Nanoparticles of Zeolite Y from Kaolin and Quartz. *Microporous and Mesoporous Materials*, **232**, 77-85. https://doi.org/10.1016/j.micromeso.2016.06.010

[16] Bai, R., Song, Y., Li, Y. and Yu, J. (2019) Creating Hierarchical Pores in Zeolite Catalysts. *Trends in Chemistry*, **1**, 601-611. https://doi.org/10.1016/j.trechm.2019.05.010

[17] Reiprich, B., Tarach, K.A., Pyra, K., Grzybek, G. and Góra-Marek, K. (2022) High-silica Layer-Like Zeolites Y from Seeding-Free Synthesis and Their Catalytic Performance in Low-Density Polyethylene Cracking. *ACS Applied Materials & Interfaces*, **14**, 6667-6679. https://doi.org/10.1021/acsami.1c21471

[18] Jia, X., Han, L., Ma, Y. and Che, S. (2018) Additive-Free Synthesis of Mesoporous Fau-Type Zeolite with Intergrown Structure. *Science China Materials*, **61**, 1095-1100. https://doi.org/10.1007/s40843-017-9227-y

[19] Khaleel, M., Xu, W., Lesch, D.A. and Tsapatsis, M. (2016) Combining Pre- and Post-

Nucleation Trajectories for the Synthesis of High Fau-Content Faujasite Nanocrystals from Organic-Free Sols. *Chemistry of Materials*, **28**, 4204-4213. https://doi.org/10.1021/acs.chemmater.6b00588

[20] Agata, W., Izabela, N., Natalia, W., Jagoda, C. and Agnieszka, F. (2023) Synthesis and Characterization of Hierarchical Zeolites Modified with Polysaccharides and Its Potential Role as a Platform for Drug Delivery. *Pharmaceutics*, **15**, 535. https://doi.org/10.3390/pharmaceutics15020535

[21] Du, Y., Kong, Q., Gao, Z., Wang, Z., Zheng, J., Qin, B., *et al.* (2018) Flowerlike Hierarchical Y with Dramatically Increased External Surface: A Potential Catalyst Contributing to Improving Precracking for Bulky Reactant Molecules. *Industrial & Engineering Chemistry Research*, **57**, 7395-7403. https://doi.org/10.1021/acs.iecr.8b00751

[22] Jia, X., Khan, W., Wu, Z., Choi, J. and Yip, A.C.K. (2019) Modern Synthesis Strategies for Hierarchical Zeolites: Bottom-Up versus Top-Down Strategies. *Advanced Powder Technology*, **30**, 467-484. https://doi.org/10.1016/j.apt.2018.12.014

[23] Haddaji, Y., Majdoubi, H., Mansouri, S., Tamraoui, Y., Boulif, R., Oumam, M., *et al.* (2021) Effect of Sodium Hexafluorosilicate Addition on the Properties of Metakaolin Based Geopolymers Cured at Ambient Temperature. *Silicon*, **13**, 1441-1451. https://doi.org/10.1007/s12633-020-00536-9

[24] Kaltume, A., Mohamad, A.N. and Paul, T.W. (2017) Aromatic Fuel Oils Produced from the Pyrolysis-Catalysis of Polyethylene Plastic with Metal-Impregnated Zeolite Catalyst. *Journal of the Energy Institute*, **92**, 195-202.

[25] Silva, D.P.S., Santos, A.T., Ribeiro, T.R.S., Solano, J.R.S., Cavalcanti, R.K.B.C., Silva, B.J.B., *et al.* (2021) Monosodium Glutamate-Mediated Hierarchical Porous Formation in LTA Zeolite to Enhance CO_2 Adsorption Performance. *Journal of Sol-Gel Science and Technology*, **100**, 360-372. https://doi.org/10.1007/s10971-021-05644-5