

A novel cage type, multifunctional catalyst from natural kaolin

S. Pranav¹, Shifna Ashraf², P. Shanmugam⁴, V.M. Sivakumar⁵, K. Kannan^{3*}

^{1,2,3,4}Department of Chemical Engineering, Kongu Engineering College, Erode, India.

⁵Department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore, India.

*Corresponding author

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Abstract

Cage type catalysts, especially zeolites are very significant in hydrocarbon processing reactions like cracking, isomerization, alkylation, etc. These catalysts when obtained using synthetic sources make the synthesis non-economical. Naturally available clays can serve as a host for the synthesis of such catalysts. Kaolin, as the silica and alumina source, is particularly suitable for the preparation of zeolites due to the high quality and low price. The organic templates are usually used to vary the crystal size and impregnate acid sites on the catalyst. N-propyl amine has been chosen as the template for the synthesis processes. Hydrothermal and ultrasonic methods were performed to determine the effectiveness of each. Hydrothermal synthesis was carried out in a Teflon lined hydrothermal reactor at 100°C for various time intervals. Ultrasonic synthesis was carried out in a bath type ultrasonicator at 30 KHz at 40°C for time spans. The morphology of the obtained catalysts was studied by SEM and XRD analyses. The acid sites concentrations of the catalysts were studied by pyridine adsorbed FTIR analysis and the results were compared. Copyright© 2018 VBRI Press.

Keywords: Cage type catalysts, kaolin, organic template, hydrothermal, ultrasonic synthesis.

Introduction

Cage type catalysts significant in hydrocarbon processes such as cracking, isomerization, alkylation, etc can be synthesized using naturally available clays as precursors. Kaolin, belongs to phyllosilicate, hosts silica and alumina units thereby being suitable for the preparation of aluminosilicates, commonly known as Zeolites. Prior to the venture of zeolites, acid and alkali treated clays were used as catalysts. Zeolites synthesized from commercial silica and alumina is accustomed for catalysis processes, owing to their acidic activity, shape selectivity and thermal stability. An organic template is used in the synthesis of zeolites to alter the chemistry of the silica-alumina colloid to form stable structure with distinct pores and acid sites. ZSM-5, commonly used zeolite has been successfully synthesized from sodium aluminate and fumed silica using various alkyl ammonium hydroxide templates at various concentrations to study the effect of template variations [1]. Effects of various other organic templates, namely 1,6 - hexane diamine, 1-propanamine, etc were studied for synthesis ZSM-5 using aerosol and water glass as silica sources. [2] A brief study on kinetics of organic template based synthesis of ZSM-5 indicates that the activation energy is a paramount factor affecting the characteristics of synthesized zeolites. [3] Synthesis parameters namely crystallization temperature and time are also influential. [4] Other than these factors, properties of template such as dipole moment, ionization potential and geometric configuration of the template are

found to alter the stereo specificity of the synthesized zeolites. [5]

It can be witnessed that zeolites synthesis using synthetic silica and alumina precursors with organic templates as pillaring agents is lucrative. Usage of naturally available clay minerals, especially kaolin for zeolites synthesis using sodium hydroxide is well-known. Experimentation on employing organic templates for the same has not been solicited. The present work targets towards using N-Propylamine as a structure directing agent for synthesis of zeolites from mined raw kaolin. The work also focuses on attempting hydrothermal and ultrasonic methods for the same synthesis.

Experimental setup

Kaolin used for the synthesis was procured from Aashapura Mine Chem Ltd, India. N-propyl amine used as organic template for the synthesis was obtained from Loba Chem, India. Hydrothermal synthesis was carried out at 150°C in a 100 ml Teflon lined stainless steel reactor for 24 hours with template to silica ratio of 1:4. The synthesized catalyst was dried at 110°C for 8 hours and calcined at 600°C for 12 hours. Ultrasonic bath (2 L, 20 KHz) used for ultrasonic transformation was purchased from Arihant marketing Pvt. Ltd., India. The ultrasonic transformation was carried out at 80 °C for 8 hours. The synthesized catalyst was characterized to

compare the physical structure and crystallinity. The synthesized catalyst was dried at 110° C for 8 hours and calcined at 600°C for 12 hours. The Scanning Electron Microscopy (SEM) analysis was carried out using Carl Zeiss Scanning Electron Microscope and the X-Ray Diffraction (XRD) characterization using Bruker D2 Phaser.

Result and discussion

Morphological characterization

The morphology of the catalyst and the extent of the synthesis process was studied using Scanning Electron Microscopy. The SEM image of the hydrothermally synthesized sample is shown in **Fig 1**. The needle type structure on the figure and layer formations indicate the crystallization of amorphous kaolin into pillared structures. But the crystals are found to be non-uniform in size. **Fig. 1** also depicts the SEM image of sample synthesized by ultrasonic transformation. Here the crystals are of grain type with uniform size distribution. This may be due to the cavitation phenomena involved with ultrasonic synthesis. The crystallinity of the samples demonstrates the distinction of cage formation as well as uniformity of molecular arrangements. **Fig. 2** shows the XRD pattern of hydrothermally synthesized sample. The XRD analysis indicates that the sample is found to contain crystallinity of 49.7% which indicates that the synthesized catalyst is semi-crystalline in nature. Miller indices determination of the crystals was performed with the peak and Full Width Half Maximum values. The hkl values for hydrothermally synthesized sample was found to be 220 or 300, implying that the crystal structure is body centered or simple Cubic. **Fig. 3** depicts the XRD pattern of sample synthesized by ultrasonic transformation. The XRD analysis indicates that the synthesized catalyst is found to be semi-crystalline with crystallinity of 52.3%. The Miller Indices values of this sample were found to be 310, revealing that the crystal is body centered cubic or simple cubic. It has to be noted here that the ultrasonic synthesis is more effective for the catalyst synthesis. At low temperature and short time, ultrasonic transformation is capable of synthesizing catalyst with higher degree of crystallinity.

Conclusion

Thus natural mined kaolin was successfully transformed into cage type catalyst structures using hydrothermal and ultrasonic methods. The SEM analysis of the samples indicated the formation of crystals and ultrasonic methods gave out crystals with uniform crystal sizes. The XRD analysis of the samples indicated transformation of amorphous kaolin via ultrasonic method yielded catalysts with higher degree of crystallinity. Both samples were subjected to water adsorption and were calcined to find the thermal stability of both. The sample synthesized by ultrasonic transformation showed formation of agglomerates. Whereas sample synthesized by

hydrothermal transformation did not agglomerate. This indicates lesser thermal stability of the sample synthesized by ultrasound assistance. The synthesized catalyst has to be compared with commercial zeolites to compare their effectiveness.

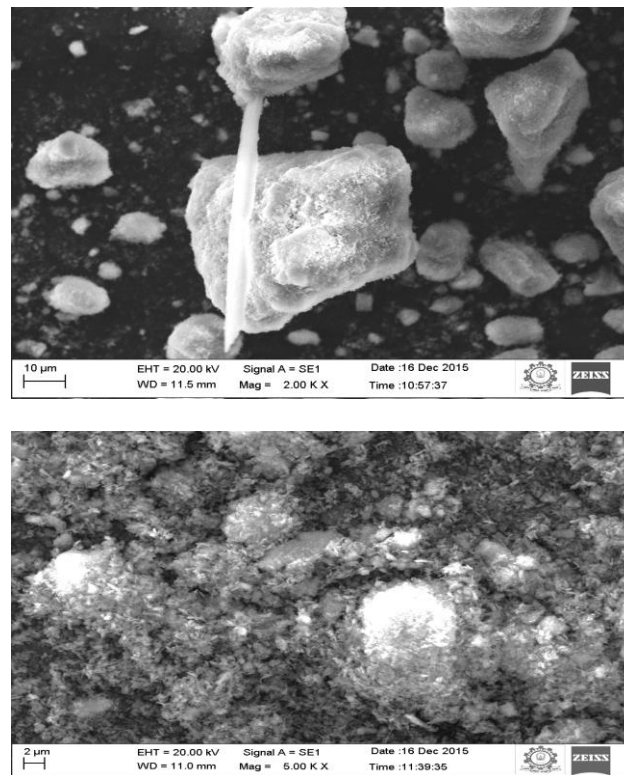


Fig 1. SEM Image of Hydrothermally synthesized and Ultrasonic synthesized sample.

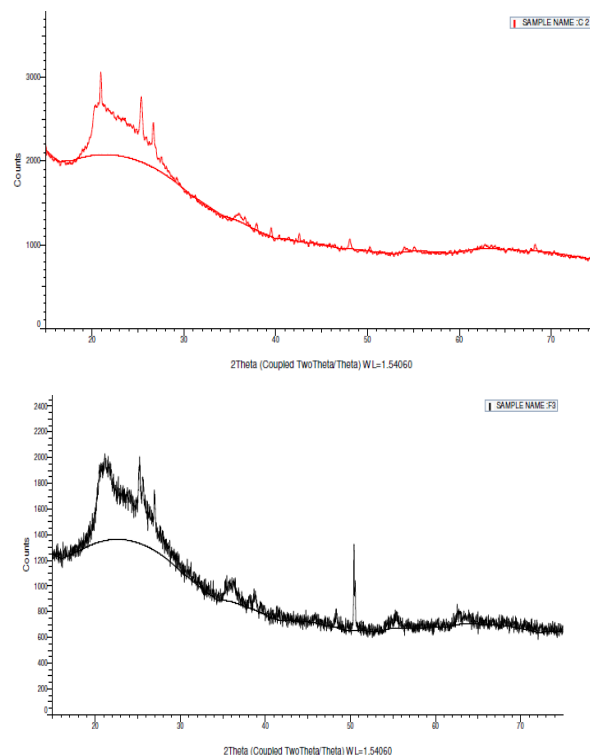


Fig. 2. XRD pattern of Hydrothermally synthesized and Ultrasonic synthesized sample.

References

1. O.A. Fouad.; R.M. Mohamed.; M.S. Hassan.; I.A. Ibrahim.; *Catal. Today.*, 2006, 82–87, 116.
DOI: [10.1016/j.cattod.2006.03.004](https://doi.org/10.1016/j.cattod.2006.03.004)
2. Shiyun Sang.; Fuxiang Chang.; Zhongmin Liu.; Changqing He.; Yanli He.; Lei Xu.; *Catal. Today.*, 2004, 729–734, 93–95
DOI: [10.1016/j.cattod.2004.06.091](https://doi.org/10.1016/j.cattod.2004.06.091)
3. S. MIntova.; V. Valchev.; E. Vulcheva N.; S. Veleva.; *Mat. Res. Bull.*, 1992, 515-522, 27.
DOI: [10.1016/0144-2449\(92\)90086-5](https://doi.org/10.1016/0144-2449(92)90086-5)
4. F.J.Vandergag; J.C.Jansen; H. Van Bekkum B.V.; Amsterdam.; *Appl.Catal.*, **1985**, **261-271**, **17**.
DOI: [0166-9834/85/03.30](https://doi.org/10.1016/0166-9834(85)03.30)
5. S. MIntova.; V. Valchev.; I.Kanev.; *Zeolites.*,**1993**, **305-308**, **13**.
DOI: [10.1016/0144-2449\(93\)90010-Z](https://doi.org/10.1016/0144-2449(93)90010-Z)