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A NEW HETEROGENEOUS CATALYST SYNTHESIS USING TRIETHYLAMINE AS TEMPLATE

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ABSTRACT
Mesoporous molecular sieves have been successfully synthesized by a simple and new method using triethylamine (TEA) as a template. The synthesized materials are characterized by using FT-IR, XRD, TGA, BET, and SEM. These characterization techniques are proved the crystalline nature of catalyst and formation of the tetrahedral framework of $AlPO_4$ catalyst. The regular pore dimension and pore volume of the material is tuned through a structure-directing agent and are thermally stable upon calcination. This template is allowed us to prepare a molecular sieve with a pore size of 8.2 nm.

KEYWORDS: mesoporous, molecular sieve, template, triethylamine, thermal stability

1. INTRODUCTION
The development of the methods of preparation of mesoporous material including aluminophosphates (MAP) is among the most intensively developing directions of research in heterogeneous catalysis [i-iv]. The presence of a template in a reaction mixture is a prerequisite for the synthesis of microporous aluminophosphate. Usually, the TEA template produces only microporous materials (0-2 nm). Microporous materials block bulky molecule entry into the pores and it does not apply for a bulky molecular reaction. So there is some necessity for introducing mesoporous (2-50 nm) molecular sieves. The structural type of the resulting microporous or mesoporous material substantially depends on the source material, how the reaction mixture is prepared, the kind of template used and the conditions for hydrothermal synthesis with an autoclave. Nevertheless, some researchers have reported on difficulties in the production of mesoporous type materials with TEA as a template with autoclave [v]. For this reason, alternative routes to synthesize mesoporous aluminophosphates of this structural type are constantly tried, involving structure-directing agents like TEA [vi-vii]. In the present investigation, TEA is used for the preparation of mesoporous aluminophosphate molecular sieve by adopting a simple method without using an autoclave.

2. EXPERIMENTAL PROCEDURE AND CHARACTERIZATION TECHNIQUES

Mesoporous Aluminophosphate is prepared by using Triethylamine as template by a simple synthesis method. 7.8 g of aluminium hydroxide is dissolved in 75 ml of water and 9.39 ml of the template (TEA) added slowly into the solution and stir it for 1h. Phosphoric acid is dissolved with 75 ml of water is added to the above mixture and stirred continuously for 2h to achieve a homogenous mixture. Then the resulting gel is heated and dried on a hot plate at 120ºC in the open air and thoroughly washed with deionized water. The Solid is then filtered, dried, calcinated at 400ºC for 6hr to remove the organic template.

The obtained material is characterized by X-ray diffraction, infrared spectroscopy, thermal analysis, nitrogen adsorption, and SEM for analyzing the structure, framework, thermal stability of the material, pore size and surface area, and surface morphology respectively. XRD is recorded on an analytical XPERT-PRO with a monochromatic beam of Cu Kα (λ= 1.5406Å). Thermal analysis is carried out on Thermal analyst SINT 6300. The SEM analysis is performed by Carl Zeiss EVO 18. The pore size and surface area are measured on Micromeritics, ASAP 2020 V3.00H instrument.

3. RESULT AND DISCUSSION

The XRD patterns of the as-synthesized and calcinated $AlPO_4$ materials are shown in Figures 1 a and b. The 2θ and d–spacing values of the materials are closely matched with the JCPDS file (79-2333) it confirmed that the materials are in a hexagonal structure. The XRD pattern of calcined $AlPO_4$ has a high intense peak at 27.34 with the d-spacing of 3.25 nm which proved the crystalline nature of the material [viii]. FT-IR spectra of as-synthesized and calcinated $AlPO_4$ are shown in figure 1 c and d respectively. FT-IR spectra of as-synthesized $AlPO_4$ show OH stretching frequencies at 3000-3500 cm^{-1} and the C-H stretching bands at 2900-2800 cm^{-1} and C-H deformation bands around 1400cm^{-1} are present in as-synthesized samples. But in calcinated samples these bands are absent. This proved that there is the complete removal of water and template molecules from the as-synthesized samples after calcination. The strong bands around 1100-1200cm^{-1} and bending mode near 400-600 cm^{-1} are attributed to the asymmetric stretching and bending mode of a tetrahedral framework of $AlPO_4$ [ix]. TGA / DTA analysis of as-synthesized $AlPO_4$ sample is shown mainly in three weight loss regions and is shown in Figure 2 a. There is some loss of water molecules from 90-100ºC is due to the loss of physisorbed and chemisorbed water on the surface of the material. Next weight loss is around 290ºC may be recognized to the entire decomposition of the template inside the framework of $AlPO_4$ [x-xi]. Weight loss is absent with the further increase of temperature and the material remains stable up to 800ºC.

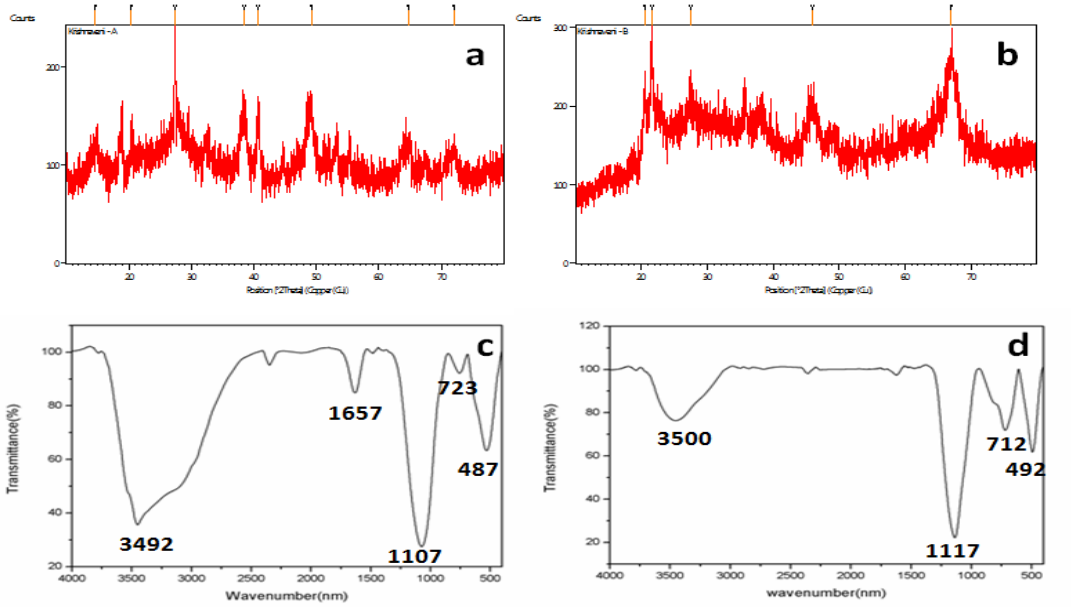

Figure 1 a, b, c, d Wide angle XRD and FTIR Spectra of as-synthesized and calcinated $AlPO_4$

The surface area, pore size, and pore volume are measured by the single point N_2 adsorption-desorption method (Figure 2 b). The surface area and pore size of $AlPO_4$ are 209.93 m^2/g and 8.8 nm. The important achievement is that TEA produces mesopore. It may be due to the simple method of synthesis without an autoclave. The morphology of the synthesized materials of $AlPO_4$ is shown in Figure 2 c. The $AlPO_4$ materials exhibit significantly crystalline morphology [xii-xiii]. This material displays a bulky morphology with a deformed structure.

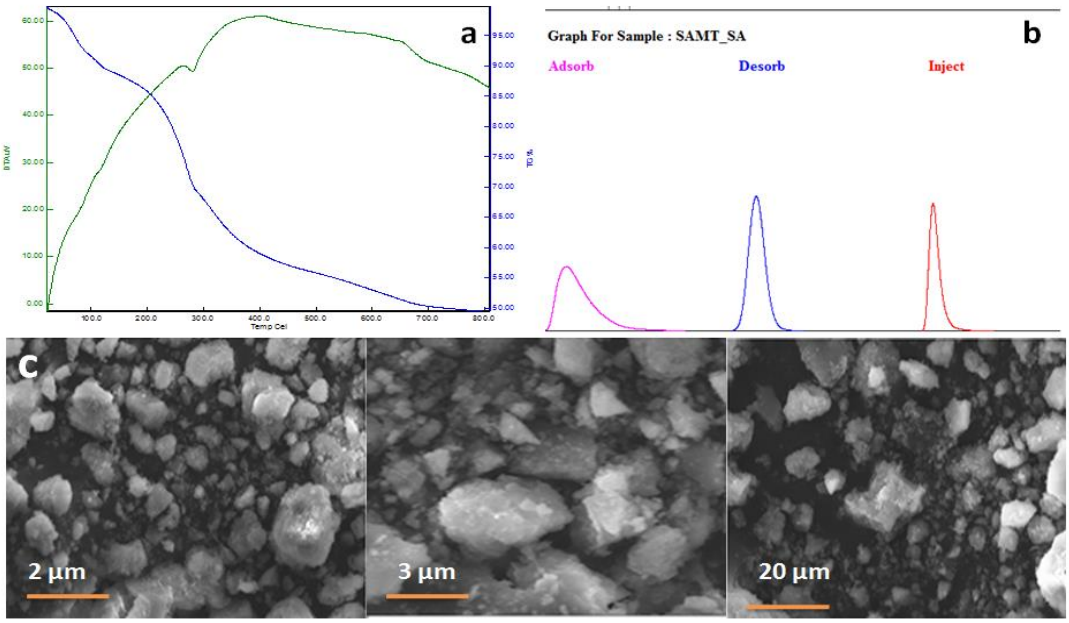

Figure 2 a, b, c TGA & DTA, BET adsorption isotherm curve and SEM micrograph of $AlPO_4$

4. CONCLUSION

It is concluded that the characterization technique confirmed the formation of crystalline mesoporous aluminophosphate (MAP) with an 8 nm pore and high thermal stability (800ºC) by using the triethylamine as a template. This template is less cost-effective. In the present investigation, triethylamine is used for the preparation of mesoporous aluminophosphate molecular sieve by adopting a simple method without using the autoclave.

REFERENCE

i. Sinha, A. K. & Seelan, S. Characterization of SAPO-11 and SAPO-31 synthesized from aqueous and non-aqueous media. **270**, 245–252 (2004).

ii. Abbad, B., Attou, M. & Kessler, H. Synthesis of the silicoaluminophosphate molecular sieve SAPO-31 in the presence of fluoride ions and its characterization. *Microporous Mesoporous Mater.***21**, 13–18 (1998).

iii. Watts, A. E. *et al.* Site Specific Iron Substitution in STA 28, a Large Pore Aluminophosphate Zeotype Prepared by Using 1,10-Phenanthrolines as Framework Bound Templates. *Angew. Chemie* 1–6 (2020) doi:10.1002/ange.202005558.

iv. Wilson, S. T., Lok, B. M., Messina, C. A., Cannan, T. R. & Flanigen, E. M. Aluminophosphate Molecular Sieves : A New Class of. *J. Am. Chem. Soc.***104**, 1146–1147 (1982).

v. Xu, Y., Maddox, P. J. & Couves, J. W. The Synthesis of SAPO-34 and CoSAPO-34 from a. *J. Chem. Soc. Faraday Trans.***86**, 425–429 (1990).

vi. Schwieger, W. *et al.* Hierarchy concepts: Classification and preparation strategies for zeolite containing materials with hierarchical porosity. *Chem. Soc. Rev.***45**, 3353–3376 (2016).

vii. Shcherban, N. D., Ilyin, V. G. & Nauky, P. Preparation , Physicochemical Properties And Functional Characteristics Of Micromesoporous Zeolite Materials. **51**, 331–349 (2016).

viii. Jacobs, J. A. M. and P. A. L. & Weitkamp, P. and J. *Catalysis and zeolites: fundamentals and applications*. (, Springer, Berlin, Heidelbergg, 1999).

ix. Lü, J. M., Ranjit, K. T., Rungrojchaipan, P. & Kevan, L. Synthesis of mesoporous aluminophosphate (AlPO) and investigation of zirconium incorporation into mesoporous AlPOs. *J. Phys. Chem. B***109**, 9284–9293 (2005).

x. Ryczkowski, J., Goworek, J., Gac, W., Pasieczna, S. & Borowiecki, T. Temperature removal of templating agent from MCM-41 silica materials. **434**, 2–8 (2005).

xi. Kannan, C., Muthuraja, K. & Devi, M. R. Hazardous dyes removal from aqueous solution over mesoporous aluminophosphate with textural porosity by adsorption. *J. Hazard. Mater.***244**–**245**, 10–20 (2013).

xii. Betiha, M. A., Menoufy, M. F., Al-sabagh, A. M., Hassan, H. M. A. & Mahmoud, S. A. *Acidic Mesostructured Aluminosilicates Assembled from Economic Acidic Template Characterized by Catalytic Cracking Reactions*. *Microporous And Mesoporous Materials* (Elsevier Inc., 2014). doi:10.1016/j.micromeso.2014.10.043.

xiii. Umegaki, T. *et al.* Control of pore size in shell of hollow silica–alumina composite spheres for hydrolytic dehydrogenation of ammonia borane. *J. Porous Mater.***26**, 611–617 (2019).

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