Synthesis and Characterization of High Quality Mesoporous Material SBA-16 with Ultrasonication

S.B.Shete[1]   U.D. Joshi[2]

[1] *Department of Physics, S.G.B. College, Purna (Jn) – 431 511.*
[2.] *AssociateProfessor,DepartmentofPhysics,N.S.B.College,Nanded–431601*

Abstract: *Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and TEOS as silica source. The diameter*
of the spherical particles can be controlled in the range of 0.5–8 μm by varying{Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and TEOS as silica source. The diameter of the spherical particles can be controlled in the range of 0.5 – 8 μm by varying synthesis temperature t 45 °C. A sharp transition from large particle is observed. It is suggested that this morphology transition is due to a change in hydrolysis and condensation rate of the silica source and as a result the assembly of F127 micelles will differ. The SBA-16 samples were characterized using powder
X-ray diffraction (XRD), scanning electron microscopy (SEM),transmissionelectron microscopy (TEM) and Nitrogen adsorption techniques.
Keywords: *SBA-16; Spherical particles; Synthesis temperature; Morphology; F127*

I.   Introduction:

Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and TEOS as silica source. The diameter of the spherical particles can be controlled in the range of 0.5–8 μm by varying .The synthesis of mesoporous materials by a liquid-crystal template mechanism was reported [1, 2] in 1992. The properties of these materials make them attractive for adsorption, catalysis, separation, chemical sensing, optical coating, drug delivery and electronic applications. For practical purposes, the overall morphology of a mesoporous material is a necessary requirement in combination with their internal structure. For instance, in application such as high performance liquid chromatography isometric particles are required [3] and spherical particles are preferably used in chromatography for column packing as irregular particles tend to break down [4]. SBA-16 is a mesoporous material with 3D cubic pore arrangement corresponding to Im3m space group. In this body-centered-cubic structure each mesopores is connected with its eight nearest neighbors to form a multidirectional system of mesoporous network [5]. Due to its large cage, high surface area and high thermal stability, this material appears to be one of the best candidates for catalytic support and packing materials for separation. Using F127 as a surfactant is the common way of synthesizing SBA-16 [6, 7]. However, there are also reports on alternative surfactants such as F108 [8], a blend of P123 and F127 [9]

Micro porous zeolite are widely used as solid acid catalysts, but their applications are intrinsically limited by drawback of zeolite is that the small size of the channels (less than 0.8 nm) and cavities (<1.5 nm) imposes diffusion limitations on reactions that can cause high back pressure on flow systems. Compared to the dimensions of the zeolite micro pores (< 2 nm), mesopores (2-50nm) and macro pores (> 50 nm) permit faster migration of guest molecules in the host frameworks. Since fast mass transfer of the reactants and products to and from the active sites is required for catalysts, the concept of infusing mesopores into zeolite particles has attracted much attention. Recent progress involving this issued to ordered mesoporous materials such as MCM-41, SBA-16 and SBA-15. These mesoporous materials have pore diameters of 3.0 nm– 8.0nm and exhibit catalytic properties for the catalytic conversion of bulky reactants, but unfortunately, when compared with micro porous zeolite, the catalytic activity and hydrothermal stability are relatively low, which can be attributed to the amorphous nature of the mesoporous walls. To overcome this problem, some recent research efforts have been concentrated on introducingmesopores or macro pores linked to the zeolite micro pores [4]. These materials calledHierarchical zeolite materials with combinations of micro/meso/macro pores would further extend the application of zeolite as solid acid. Our aim in this work is to show that ordered mesoporous materials ZSM-5/SBA-15(MAS-9), ZSM-5/ SBA-16 as hierarchical porous solid acid catalysts, which strongly acidic and hydrothermal stable mesoporous aluminosilicates can be synthesized in strongly acidic media by the assembly of preformedZSM-5 zeolite precursors using microwave hydrothermal method. In this study, we have applied the microwave technique to the synthesis of ZSM-5/SBA-15(MAS-9), ZSM-5/SBA-16 using silica source extracted from rice husk ash (RHA) and concentrated sulfuric acid, which is less corrosive than concentrated

hydrochloric acid and also evaluate their catalytic performance for etherification reaction of limonene from waste.

II.   Experimental details:

Material synthesis:

SBA composite with different concentrations have been prepared under acidic conditions in the presence of triblock copolymer F127 by using TEOS as silica source 1.6gm of F127was dissolved in 120gm of H_2O,5gm of conc. HCL and 7.5gm of butanol under magnetic stirring 1hrs to obtain homogeneous solution at 45^0c to this solution 12gm of TEOS was added drop wise .The mixture was stirred for another 24 hours .Ultrasonic treatment is given at power 70 for 30 min Then the solution is taken Teflon coated autoclave and hydrothermal treatment is given to 80^0c for 24 hrs The synthesized mesoporous composite was filtered and dried in air .The sample is calcined at $1.5^oc/$ min .at 550^0c for 6hours (Shaodian Shen et al. [10])

Methods for characterization:

Powder X-ray diffraction (XRD) analysis:

X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials. The method has been traditionally used for phase identification, quantitative analysis and the determination of structure imperfections. In recent years, applications have been extended to new areas, such as the determination of crystal structures and the extraction of 3-dimensional micro structural properties.

X-rays are electromagnetic radiation of wavelength about 1 Å (10 nm), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern, which may be used as a "fingerprint" for its identification. The X-ray crystallography may be used to determine crystal structure, i.e. the atoms arrangement in the crystalline state and inter atomic distance. X-ray diffraction is one of the most important characterization tools used in solid-state chemistry and materials science. It is possible to determine the size and the shape of the unit cell for any crystalline compound using the diffraction of x-ray diffraction studies.
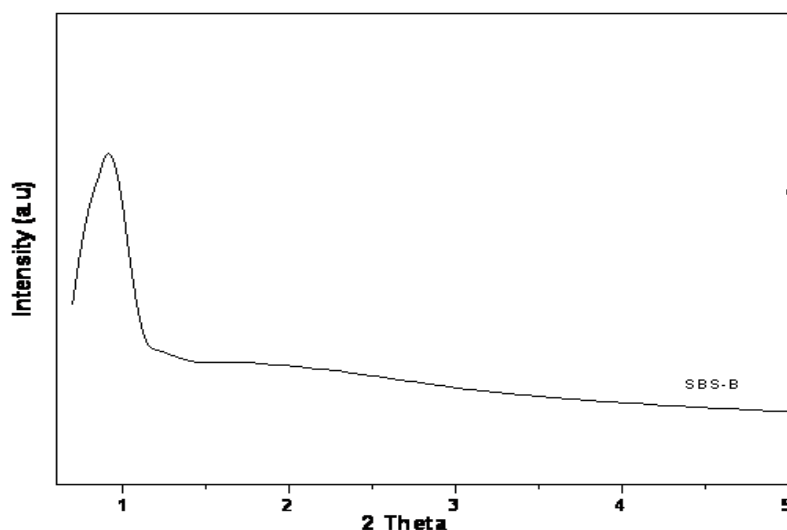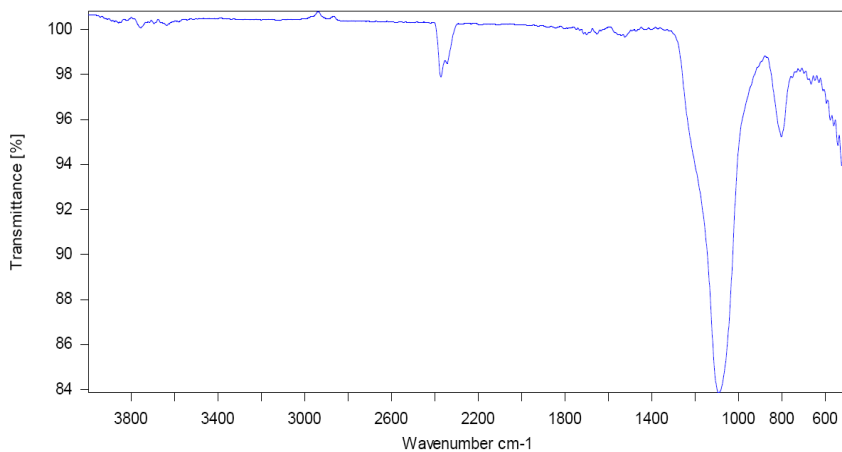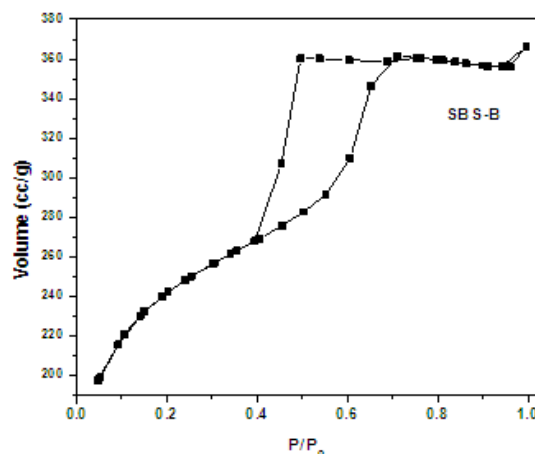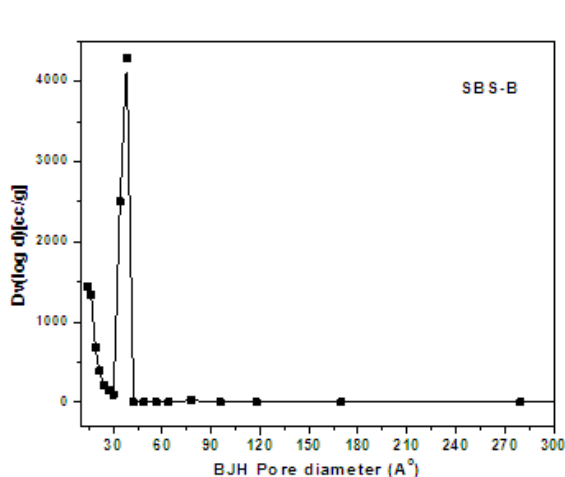

Fig.1 XRD pattern of SBA-16

Fig2. FTIR of SBA-16

The FT-IR spectra of as synthesized SBA16 :

The FT-IR spectra of as synthesized from Rice husk ash are shown in Fig. 3. From FT-IR spectra, the absorption bands around 2921 and 2851 cm^{-1} correspond to n-C-H and d-C-H vibrations of the surfactant molecules, such bands disappeared in the calcined sample indicating the total removal of organic material during calcinations. The broad band around 3392.65 cm^{-1} as observed due to surface silanols and O-H stretching frequency of adsorbed water molecule. Moreover the peaks in the range of 1500-1600 cm^{-1} are because of the deformation mode of surface hydroxyl group. A peak at 1070.63 cm^{-1} and 964.44 cm^{-1} corresponds to the asymmetric and symmetric Si-O groups, respectively. The peaks in the range 1010-1079 cm^{-1} are assigned to M-O-M bonding, the bands from 960 to 990 cm^{-1} appeared due to Si-O-M (M=metal ions) vibrations in metal incorporated silanols. The shift in the lattice vibration bands to lower wave numbers is due to the substitution of silicon by other metal ions.

Pore size distribution measurements (PSD):

Quantitative evaluation of the pore structure in porous solids is a crucial aspect of the processes involved in the design and application of materials for adsorption and catalysis. The number, shape and size of the pores present in the material largely determine adsorption behavior of a solid. Development of an equation for calculating the distribution of surface area and pore volume from gas adsorption data on Wheelers dual theory of multi adsorption and capillary condensation. The invention of mercury porosimeter and the Washburn equation to mercury penetration into pores at high pressures has provided a second method of measuring pore size distribution of catalysts and adsorbants with the pore radii ranging from the largest pore down to 15 Å radius which is upper limit of micropore range. Thus the two methods are complementary with each other, nitrogen adsorption being used to obtain the smaller pore size range and mercury penetration being used for the larger pore size range.

Multi point Surface Area: 779.7 m^2/g , Total Pore Volume: 0.5684 cc/g ,
Average Pore Diameter: 29.16 A^o

III.   Conclusions:

Based upon the experimental study it was concluded that pure and ordered SBA16 material could be successfully synthesized by triblock copolymer F127 during 18 hrs of reaction. The parametric variations such as change of calcination temperature, the change of calcination time duration and the change of initial pH value of gel suggested that from RHA the well ordered mesoporous material SBA16 can be synthesized at 550^0C for 4 hrs. keeping pH of gel 6.91. The maximum calculated surface area amounts to779.7 m^2/g for the SBA16 materials keeping pH of gel 6.91, calcination time about 4 h. at 550^0C.

References:

[1].   J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[2].   C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.

[3].   C. Boissiere, M. Kummel, M. Persin, A. Larbot and E. Prouzet, Adv. Funct. Mater. 11 (2001) 129.

[4].   H.B.S. Chan, P.M. Budd, T.D. Naylor, J. Mater. Chem.11 (2001) 951.

[5].   Y. Sakamoto, M. Kaneda, O. Terasaki, D.Y. Zhao, J.M. Kim, G. Stucky, H.J. Shin, R. Ryoo, Nature 408 (2000) 449.

[6].   D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.

[7].   P. van der Voort, M. Benjelloun, E.F. Vansant, J. Phys. Chem. B 106 (2002) 9027.

[8].   P. Kipkemboi, A. Fogden, V. Alfredsson, K. Flodström, Langmuir 17 (2001) 5398.

[9].   T.W. Kim, R. Ryoo, M. Kruk, K. P. Gierszal, M. Jaroniec, S. Kamiya, O. Terasaki, J. Phys. Chem. B, 108 (2004) 11480.

[10].   Shaodian Shen, Yan Deng, Guibo Zhu,Dongsen Mao;Yuhong Wang,GuishenWu , Jun Li.XiaoZhen Liu , Guanzhong Lu , Dongyuan Zhao J Mater Sci (2007) 42:7057–7061