

# Synthesis of Aluminum SBA-16 Mesoporous Material Using Ultrasonic Treatment

S. B. Shete<sup>1</sup>, U. D. Joshi<sup>2</sup>

<sup>1</sup>Department of Physics, S.G.B. College, Purna (Jn) – 431 511

<sup>2</sup>Associate Professor, Department of Physics, N.S.B. College, Nanded – 431 601

**Abstract:** Mesoporous molecular sieves in the hexagonal phase (SBA16) are synthesized Tetraethylorthosilicate (TEOS) solutions using Pluronic F127 as template. TEOS as silica source. It is effectively transformed into mesoporous materials depending upon the hydrothermal conditions. It is also found that a high concentration of Na<sup>+</sup> ions is not critical in the formation of SBA16 when prepared under controlled pH of gel, calcinations temperature and calcinations duration conditions. We provide direct evidence of SBA16. Our results resemble that coal combustion byproducts can be utilized for producing mesoporous molecular sieves even if containing significant amounts of impurities. The highest crystalline and well defined phase purity SBA16 is obtained without hydrothermal treatment in short interval of time. X-ray diffraction (XRD) shows that the highly ordered esostructure was maintained even at the high loading of aluminum up to 5.5 (bulk molar ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>). The synthesis of mesoporous Al<sub>2</sub>O<sub>3</sub>-containing SBA-16 composite with a cubic Im3m structure will open new applications for catalysts

**Keywords:** Hydrothermal synthesis; Pluronic 127, Tetraethylorthosilicate (TEOS), SBA-16, Si/Al ratio

## 1. 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 neighbours 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 introducing mesopores or macro pores linked to the zeolite micro pores [4]. These materials called Hierarchical 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 preformed ZSM-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 sulphuric acid, which is less corrosive than concentrated.

## 2. Experimental Details

### Material Synthesis:

SBA composite with different concentrations have been prepared under acidic and basic conditions in the presence of triblock copolymer F127 by using TEOS as silica source 1.6gm of F127 was dissolved in 120gm of H<sub>2</sub>O, 5gm of conc. HCL and 7.5gm of butanol under magnetic stirring 1hrs to obtain homogeneous solution at 45<sup>0</sup>C to this solution 12gm of TEOS was added drop wise .The ratio of Si/Al=0.7 were taken. 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<sup>0</sup>C for 24 hrs The

synthesized mesoporous composite was filtered and dried in air. The sample is calcined at  $1.5^{\circ}\text{C}/\text{min}$  at  $550^{\circ}\text{C}$  for 6 hours (Shaodian Shen et al. [10])

### 3. Results and Discussion

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  $1 \text{ \AA}$  (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.

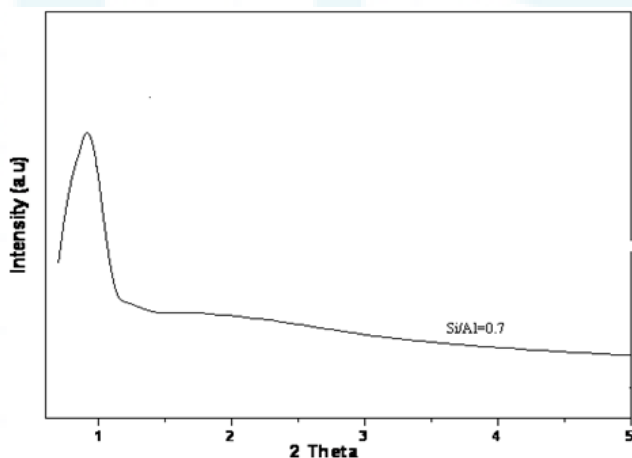


Figure 1: XRD pattern of Al-SBA-16

#### Effect of pH of Synthesis Gel

The pH of reaction mixture of the gel is also plays an important role in synthesis of SBA16 phase. The effect of change of pH of gel shows that, when pH varies from 1.87 to 6.91 the crystalline nature and phase purity improves to highest level. The synthesis was carried out at constant calcinations temperature  $500^{\circ}\text{C}$  for 8 h. The crystallinity reduces when pH of the gel is below 6.91 and above 6.91.

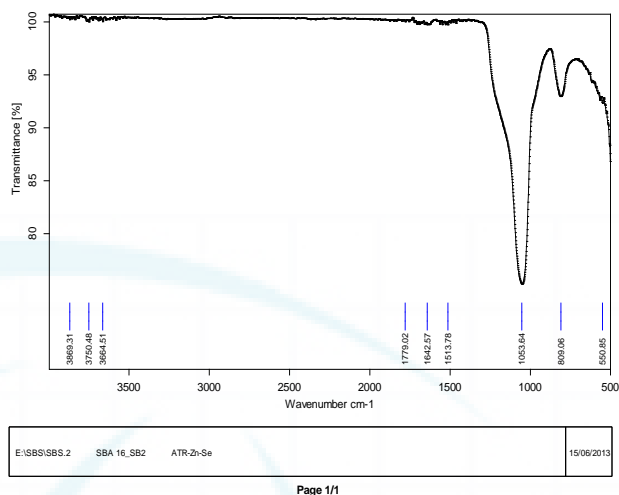


Figure 2: XRD Patterns of Al-SBA16 at different pH of synthesis gel

The XRD data further analyzed to calculate  $I/I_0$ , Unit Cell parameters  $a_0$ , percent crystallinity. The hexagonal unit cell parameter  $a_0$  in the calcined sample increased with pH of synthesis gel value. Therefore it is observed from presented data in the table 4 that pH of gel solution at 6.91 gives good results. The variation of pH of gel plays an important role in the formation of SBA16 the X-RD data further analyzed to calculate  $I/I_0$ , The tabulated data shows that as calcinations time duration increases, percent crystallinity also increases up to 4.3 h then after decreases for the synthesis system under the study. During the change in calcinations time duration pH of the gel was kept constant at 6.9 and calcinations temperature at  $550^{\circ}\text{C}$ .

The FT-IR spectra of as synthesized from TEOS are shown in Fig. 2. From FT-IR spectra, the absorption bands around  $2921$  and  $2851 \text{ cm}^{-1}$  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  $3392.65 \text{ cm}^{-1}$  as observed due to surface silanols and O-H stretching frequency of adsorbed water molecule. Moreover the peaks in the range of  $1500-1600 \text{ cm}^{-1}$  are because of the deformation mode of surface hydroxyl group. A peak at  $1070.63 \text{ cm}^{-1}$  and  $964.44 \text{ cm}^{-1}$  corresponds to the asymmetric and symmetric Si-O groups, respectively. The peaks in the range  $1010-1079 \text{ cm}^{-1}$  are assigned to M-O-M bonding, the bands from  $960$  to  $990 \text{ cm}^{-1}$  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.

### 4. Conclusions

Based upon the experimental study it was concluded that pure and ordered SBA16 material could be successfully synthesized from TEOS at room temperature during 24 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 TEOS the well ordered mesoporous material SBA16 can be synthesized at  $550^{\circ}\text{C}$  for 6 hrs. Keeping pH of gel 6.91. The maximum calculated surface area amounts

to 1801 m<sup>2</sup>/g for the SBA16 materials keeping pH of gel 6.91, calcination time about 6 h. at 550<sup>o</sup>C.

## References

- [1] F. Hoffmann, M. Cornelius, J. Morell and M. Froba, *Angew. Chem.Int. Ed.*, 2006, 45, 3216.
- [2] Q. Yang, J. Liu, L. Zhang and C. Li, *J. Mater. Chem.*, 2009, 19, 1945.
- [3] H. Xiong, Y. Zhang, S. Wang, K. Liew and J. Li, *J. Phys. Chem. C*, 2008, 112, 9706.
- [4] W. Zhou, J. M. Thomas, D. S. Shephard, B. F. G. Johnson, D. Ozkaya, T. Maschmeyer, R.G. Bell and Q. Ge, *Science*, 1998, 280, 705.
- [5] B. J. Scott, G. Wirnsberger and G. D. Stucky, *Chem. Mater.*, 2001, 13, 3140.
- [6] X. Gao and S. Nie, *J. Phys. Chem. B*, 2003, 107, 11575.
- [7] B. Lei, B. Li, H. Zhang, L. Zhang and W. Li, *J. Phys. Chem. C*, 2007, 111, 11291.
- [8] J. Feng, H. J. Zhang, C. Y. Peng, J. B. Yu, R. P. Deng, L. N. Sun and X. M. Guo, *Microporous Mesoporous Mater.*, 2008, 113, 402.
- [9] S. Wang, *Microporous Mesoporous Mater.*, 2009, 117, 1.
- [10] M. Vallet-Regi, F. Balas and D. Arcos, *Angew. Chem., Int. Ed.*, 2007, 46, 7548.
- [11] J. Kim, Y. Piao and T. Hyeon, *Chem. Soc. Rev.*, 2009, 38, 372.
- [12] F. Carniato, L. Tei, W. Dastru', L. Marchese and M. Botta, *Chem. Commun.*, 2009, 1246.
- [13] F. Carniato, C. Bisio, G. Paul, G. Gatti, L. Bertinetti, S. Coluccia and L. Marchese, *J. Mater. Chem.*, 2010, 20(26), 5504.
- [14] J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed.*, 1999, 38, 56.
- [15] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, 120, 6024.
- [16] Y. Wan, Y. Shia and D. Zhao, *Chem. Commun.*, 2007, 897.
- [17] F. Kleitz, L. A. Solovyov, G. M. Anilkumar, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2004, 1536.
- [18] Y. K. Hwang, J.-S. Chang, Y.-U. Kwon and S.-E. Park, *Microporous Mesoporous Mater.*, 2004, 68, 21.
- [19] M. Mesa, L. Sierra, J. Patarin and J.-L. Guth, *Solid State Sci.*, 2005, 7, 990.
- [20] D. Li, X. Guan, J. Song, Y. Di, D. Zhang, X. Ge, L. Zhao and F.-S. Xiao, *Colloids Surf., A*, 2006, 272, 194.
- [21] K. Flodstrom, H. Wennerstrom, C. V. Teixeira, H. Amenitsch, M. Linden and V. Alfredsson, *Langmuir*, 2004, 20, 10311.
- [22] T.-W. Kim, R. Ryoo, M. Kruk, K. P. Gierszal, M. Jaroniec, S. Kamiya and O. Terasaki, *J. Phys. Chem. B*, 2004, 108, 11480.
- [23] M. Mesa L. Sierra and J.-L. Guth, *Microporous Mesoporous Mater.*, 2008, 112, 338.
- [24] (a) E. J. van Rossum, H. Forster and H. J. M. de Groot, *J. Magn. Reson.*, 1997, 124, 516; (b) G. Paul, S. Steuernagel and H. Koller, *Chem. Commun.*, 2007, 5194.
- [25] G. Socrates, *Infrared and Raman Characteristic Group Frequencies*. Chichester: Wiley, 2001.
- [26] A. Zecchina, S. Bordiga, G. Spoto, L. Marchese, G. Petrini, G. Leofanti and M. Padovan, *J. Phys. Chem.*, 1992, 96, 4991.
- [27] A. Novak, *Hydrogen Bonding in Solids. Correlation of Spectroscopic and Crystallographic data, from Structure and Bonding*, Vol 18, Springer-Verlag, Berlin-Heidelberg-New York, 1974.
- [28] N. A. Melosh, P. Lipic, F. S. Bates, F. Wudl, G. D. Stucky, G. H. Fredrickson and B. F. Chmelka, *Macromolecules*, 1999, 32, 4332.
- [29] S. Kirmayer, E. Dovgolevsky, M. Kalina, E. Lakin, S. Cadars, J. D. Epping, A. Fernandez-Arteaga, C. Rodriguez-Abreu, B. F. Chmelka and G. L. Fray, *Chem. Mater.*, 2008, 20, 3745.
- [30] Shaodian Shen, Yan Deng, Guibo Zhu, Dongsun Mao; Yuhong Wang, Guishen Wu, Jun Li, XiaoZhen Liu, Guanzhong Lu, Dongyuan Zhao *J Mater Sci* (2007) 42:7057–7061