ISSN NO. 2320-5407

*Journal homepage: http://www.journalijar.com*

*INTERNATIONAL JOURNAL OF ADVANCED RESEARCH*

**RESEARCH ARTICLE**

# Synthesis Of Titanium SBA-16 mesoporous Material Using Ultrasonic treatment

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

**1** Department of Physics, S.G.B. College, Purna (Jn) – 431 511.

**2**.Associate Professor, Department of Physics, N.S.B. College, Nanded – 431 601

***Manuscript Info***

***Manuscript History:***

Received: 15 July 2014
Final Accepted: 19 August 2014
Published Online: September 2014

***Key words:***
Hydrothermal synthesis; Pluronic 127 , Rice husk ash (R.H.A.), SBA-16, Si/Ti ratio,2MHCL.

***Corresponding Author***

**S.B.Shete[1]**

***Abstract***

Mesoporous molecular sieves in the hexagonal phase (SBA16) are synthesized from rice husk ash (R.H.A.) solutions using Pluronic F127 as template and R.H.A. as silica source. It is found that R.H.A. effectively transformed into mesoporous materials depending upon the hydrothermal conditions. It is also found that a high concentration of $Na^+$ 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 resembles 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 titanium up to5.5 (bulk molar ratio $SiO_2/TiO_2$). The synthesis of mesoporous$TiO_2$-containing SBA-16 composite with a cubicIm3m structure will open new applications for catalysts



## Introduction

Rice milling generates a byproduct know as husk .This surrounds the paddy grain. During milling of paddy about 78 % of weight is received as rice , broken rice and bran .Rest 22 % of the weight of paddy is received as husk . This husk is used as fuel in the rice mills to generate steam for the parboiling process . This husk contains about 75 % organic volatile matter and the balance 25 % of the weight of this husk is converted into ash during the firing process , is known as rice husk ash ( RHA ). This RHA in turn contains around 85 % - 90 % amorphous silica. India is a major rice producing country , and the husk generated during milling is mostly used as a fuel in the boilers for processing paddy , producing energy through direct combustion and / or by gasification . This RHA is a great environment threat causing damage to the land and the surrounding area in which it is dumped. Lots of ways are being thought of for disposing them by making commercial use of this RHA. The synthesis of mesoporous materials by a hydrothermal treatment [1,2,5]. 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 20] and spherical particles are preferably used in chromatography for column packing as irregular particles tend to break down [22]. In this body-centered-cubic structure each mesoporous is connected with its eight nearest neighbors to form a multidirectional system of mesoporous network [23]. 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 [16, 24]. However, there are also reports on alternative surfactants such as F108 [25], a blend of P123 and F127 [26], and other nonionic surfactants [27]. Several studies have been carried out to understand the formation mechanism of this material, for instance, in the framework of the colloidal phase separation mechanism (CPSM) Yu et al. [29] suggested that, the formation process of mesoporous materials involves three stages: (1) operative self-assembly of inorganic/organic composites, (2) Spherical particles of mesoporous silica SBA-16 structure were synthesized at low pH using Pluronic F127 as template and RHA as silica source.

**Experimental details:**

**Material synthesis:**

Ti containing SBA1 composite with different concentrations have been prepared under acidic conditions in the presence of triblock copolymer F127by using RHA as silica source and $Tio_2$ as Titanium source .

1.6gm of F127was dissolved in 40gm of 2MHCL under magnetic stirring to obtain homogeneous solution at $30^0$c to this solution was added Si/Ti molar ratio of 10 after the mixed solution was further vigorously stirred for 30 min. The mixture solution was further stirred for another

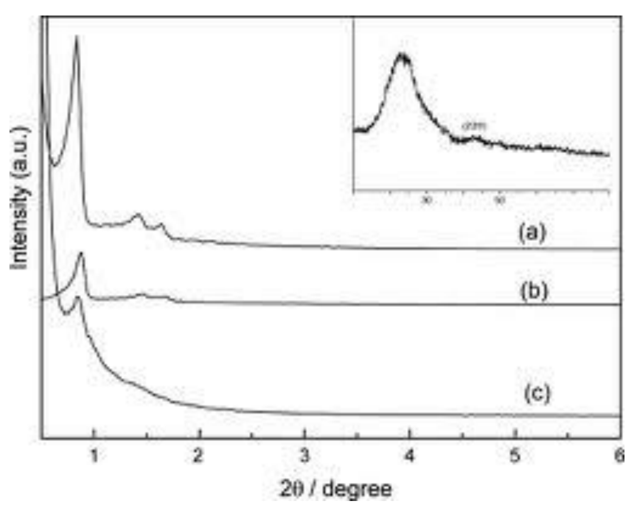
24 hours .Ultrasonic treatment is given at power 70 for 30 min.Then the solution is taken Teflon coated autoclave ande heated at $80^0$c for one day .The synthesized $Sio_2$/ $Tio_2$ mesoporous composite was filtered and dried in air .The sample is calcined at $1.5^o$c/ min.at $550^0$c for 6hours(Shaodian Shen et al. [30] )

## RESULTS AND DISCUSSION:

The XRD pattern of rice husk Ash (RHA) shown in Fig.The different minerals have different unit cell composition, therefore XRD technique allows for qualitative identification of the phases present in the collected mineral. The XRD peak information is important to quantity changes in the composition of Quartz and Mullite reactants that affecting reaction conditions of hydrothermal synthesis of materials and reaction products.

The X-ray pattern of the synthesized mesoporous silica material is an highly periodic silica phases which is normally reflected by the distinct X-RD signatures at low angles from $1^0$ to $30^0$ as shown in Fig. Sharp signal in XRD spectra indicates the presence of long range order of uniform hexagonal phase in the mesoporous materials. The well defined reflections from [100] plane are a prime characteristics of the hexagonal lattice symmetry of the SBA16 structure.

The observation of three higher angle reflections other than $d_{100}$ indicates that the product is likely to possess the symmetrical hexagonal pore structure typical of SBA16. X-ray diffraction data therefore indicates that the supernatant of the fly ash can be successfully used in the synthesis gel to prepare mesoporous materials




**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 $500^0$C for 8 h. The crystallinit reduces when pH of the gel is below 6.91 and above 6.91.

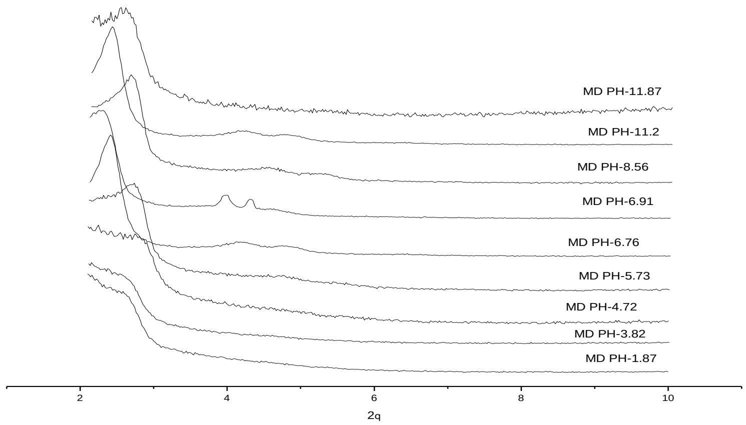
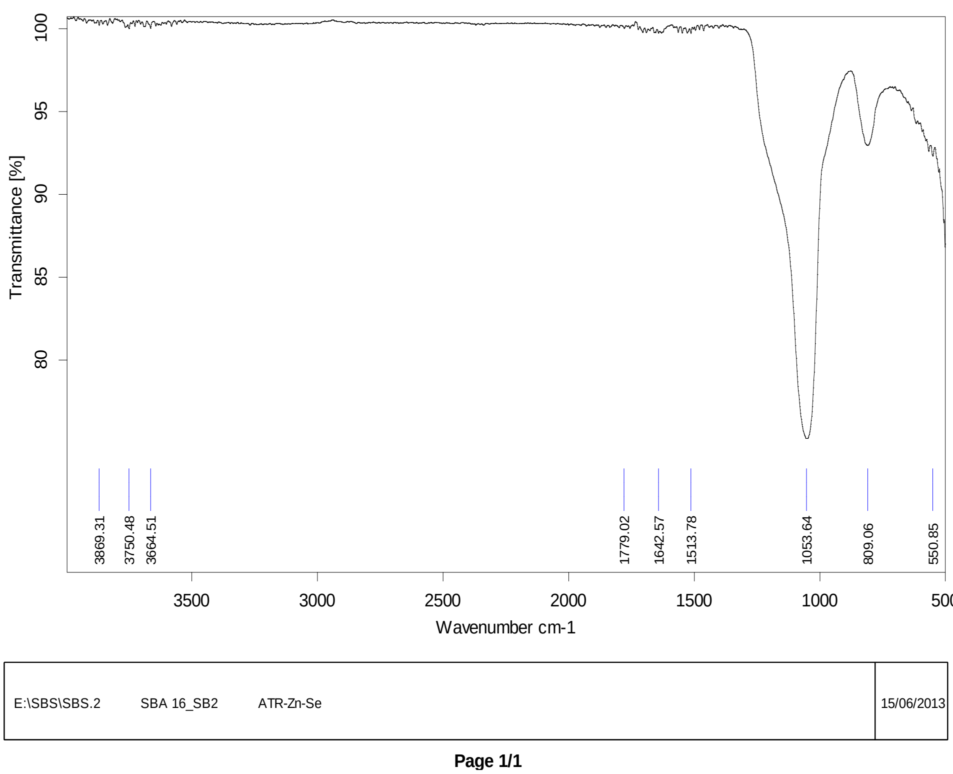



**Fig. 2: XRD Patterns of SBA16 at different pH of synthesis gel.**

The XRD data further analyzed to calculate $I/I_O$, Unit Cell parameters $\mathbf{a_O}$, 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 $I/I_O$, The tabulated data shows that as calcinations time duration increases, percent crystalinity 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 $550^0$C.




**The FT-IR spectra of as synthesized SBA16 from Rice husk ash**

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.

## CONCLUSIONS:

Based upon the experimental study it was concluded that pure and ordered SBA16 material could be successfully synthesized from coal fly ash at room temperature 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 to 1801 $m^2/g$ for the SBA16 materials keeping pH of gel 6.91, calcination time about 4 h. at $550^0C$.

## 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. Colucciaand 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, MicroporousMesoporous Mater., 2004, 68, 21.
19 M.Mesa,L. Sierra, J. Patarinand 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 Spectroscopicand 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. Chmelkaand G. L. Fray, Chem. Mater., 2008, 20, 3745.
30 Shaodian Shen, Yan Deng, Guibo Zhu,Dongsen Mao ;Yuhong Wang , Guishen Wu , Jun Li. XiaoZhen Liu , Guanzhong Lu , Dongyuan Zhao J Mater Sci (2007) 42:7057–7061