WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.084
Volume 12, Issue 8, 111-120. Conference Article ISSN 2277– 7105

SYNTHESIS OF MESOPOROUS MOLECULAR SIEVES SBA-16 FROM AGRICULTURAL WASTEMATERIAL AS RICE HUSK ASH

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Article Received on
05 April 2023,
Revised on 26 April 2023,
Accepted on 15 May 2023
DOI: 10.20959/wjpr20238-28153

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ABSTRACT

Rice Husk is the by-product produce during rice milling. Sustainable use of Rice Husk Ash (RHA) and Rice Husk (RH) in Industrial Sector and other fields depends upon its physical and chemical properties. This research contributes holistic approach to the potential use of rice husk towards synthesis of meso-porous material than the traditional uses of husks. It not only reduces the cost of material but also results in the reduction of the environmental greenhouse effects. Attempts have been made to investigate crystallization kinetics of SBA -16. The various synthesis parameters were investigated during crystallization of SBA -16. The activation energy of crystallization kinetics of SBA -16 was calculated using Arrhenius equation and found to be 184.62 kJ / mole in the present system of synthesis.

KEYWORDS: Rice Husk Ash, Sba -16, Pluronic F127, Crystallization Kinetics, Activation Energy.

INTRODUCTION

Harmful wastes are produced annually throughout the world by all industries and their disposal poses major challenges and serious environmental problems. This creates serious health risks, taking into consideration that the large amount of discharged material is expected to increase in the future. In the recent years, there has been a growing interest to find creative ways not only to reduce natural waste and industrial hazard to overcome environmental pollution but also its effective utilization (Beck J.S., *et al.* 1992).

Rice is a primary source of food. Production of rice is almost 1% of the Earth's surface. Globally, approximately 700 million tons of rice (FAO Food Outlook, 2011) is produced

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every year. India is a major rice producing country and annul production of rice husk is approximately 20 million tons (FAO Food Outlook, 2011) For every 100 kg of paddy milled, about 22% of husk is producedeven though some of this husk is converted into end product such as feedstock and adsorbent but most is either dumped as a waste or burnt openly, causing environmental and health problems. Therefore, one of the chief principles of green technology is to utilize the RHA as a raw material or renewable resource for making high value added, versatile materials rather than depleting, as it has high silica content (>90%).

Quite a lot of research groups have taken the advantage of this silica composition and made endeavors in making micro (Boissiere C., *et al* 2001) and mesoporous (Kwon S; *et al* 2013). zeolitic materials synthesized from extracted silica through them. These materials have wide applications as adsorbents, in ion exchange, as molecular sieves, catalystsetc. Compared to conventional microporous zeolites, mesoporous materials possess many advantages such as high surface area, large pore size and an ordered structure ((Kipkemboi P., *et al* 2001). Santa Barbra University discovered new family (SBA-n) of mesoporous materials, among them SBA -16 possesses hexagonal molecular sieves having fairly uniform pores with pore diameter of 20-100Å. They possesses large surface area (more than 900 m^2/g), which is attractive for designing new selective heterogeneous catalyst in production of fine chemicals on large scale.

(Kresge C.T., *et al 1992).*Our research endeavors the use of no-cost raw materials such as agro waste rice husk for our further investigations because it add value; reduce the cost and create effective utilization to protect the environment. (Shaodian Shen, *et al* 2007) It has potential application in synthesis of highly useful porous materials used in water purification technology, as industrial catalyst, supporting materials, exchanger, molecular sieves etc.

MATERIAL AND METHODS

Hydrothermal synthesis of SBA -16 was carried out in hydrothermal reactor at autogenous pressure under stirring conditions. The chemicals used during synthesis were Pluronic F127, Butanol, Hydrochloric acid, Deionized water etc.

The rice husk silica extraction was carried out using acid hydrolysis method. Initially the collected rice husk was washed with deionized water and then dried at 80^0C for 24h. This husk was then treated with 3.0 M HCl acid solution along with heating at 100^0C. This hydrolyzed rice husk was rinsed with distilled water until pH reaches to 7, then it was again

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dried at 100°C for 24 h. Finally, the rice husk was calcined at 800^{0}C for 4h in muffle furnace. The rice husk ash was mixed with 3.75 M NaOH solution and stirred overnight to extract the silicate from the ash. The molar composition of the synthesis gel was as follows.

Molar Ratio

0.91SiO_2:0.0035(F-127): 2.08BuOH: 0.91HCl: 117H_2O

The synthesis of silica SBA-16 was made as following.

Solution of 2.5 g of Pluronic F127 (Sigma Aldrich) in a mixture of 120 g of distilled water, 5 g of concentrated HCl (37%) and 7.5 g of butanol was first prepared. After one hour stirring at 45 °C, 12 g of RHA 4.5g were added and the mixture stirred for further 24h.The ultrasonic treatment is given at 45 min. The step was followed by a hydrothermal treatment of 24 h at 100°C in Teflon coated stainless steel autoclave. Drying of the as synthesized sample was performed at room temperature overnight part of the dry sample was calcined under air flow by increasing the temperature 1.5°C per minute up to550°C and maintaining it at this temperature for 6 h sample hereafter named calc-SBA-16. (Carniato Fabio., *et al*., 2012).

The samples were synthesized at 60^{0}C, 70^{0}C, 80^{0}C and 90^{0}C and are nominated as RHA-SBA-16 (60, 70, 80 and 90) respectively. After the crystallization, the solids were filtered, washed with deionized water and dried at 100^{0}C for 2h. The products were finally calcined at 550^{0}C for 4.5hrs in air and has been evaluated by X-ray diffraction, N_2 sorption studies etc.

Characterization: To elucidate the structural features, morphology (Lettow JS., *et al* 2000)pore architecture, thermal stability, (Van der Voort P., *et al* 2002) adsorptive (Zhao D., *et al* (1998) and catalytic behaviorurface areaetc: the synthesized samples are characterized by techniques such as XRD, N_2-sorption, FTIR, etc.

RESULTS AND DISCUSSION

I) XRD-studies

$$\% \text{ Crystallinity} = \frac{\text{Sum of the peak heights of unknown material} \times 100}{\text{Sum of peak heights of standard material}}$$

Fig.1 shows the XRD patterns of the samples calcined at 450, 500, 550, 600 and 650^{0}C designated as RHA-SBA-16 (450, 500, 550, 600 and 650) respectively. As shown in the Fig.1RHA-SBA-16 (450), the XRD pattern obtained for the sample calcined at calcinations

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temperature 450^{0}C, the only reflection at (110) plane is more intense, it suggests that the material does not possess the well defined hexagonal arrays even after the calcination.

The diffractograms gained for the samples as increase in their calcination temperature from 500 to 650^{0}C shows three weak peaksalong with single most intense peak with (110) reflection at 2θ value 1.12^0. The d_{110}value is shifted to a higher value up to 600^{0}C Fig. 1 RHA-SBA-16 (500, 550, and 600). In the low 2-theta region of 1^0–10^0, the XRD pattern at 550^{0}C exhibits all prominent diffraction peaks which could be indexed as (110), (200) (210) and etc. reflections, respectively. This is characteristics of long range ordered hexagonal array of parallel silica tubes in RHA-SBA-16mesoporous phase. Therefore, the sample calcined at 550^{0}C can be treated as 100 % crystalline sample. As calcinations temperature in advance increased above 600^{0}C, a considerable decline in the intensity of (110) peak and d_{110} value shifted to the somewhat inferior value indicates condensation of the silanol groups in the pore walls. This can direct to the reorganization of silica walls of RHA-SBA-16 accordingly decreasing the crystallinity very immaterially. Even though at 600^{0}C, the long range order of hexagonal array and textural morphology is still preserved. This resembles that synthesized sample of RHA-SBA-16 is thermally unwavering up to 600^{0}C as accounted.

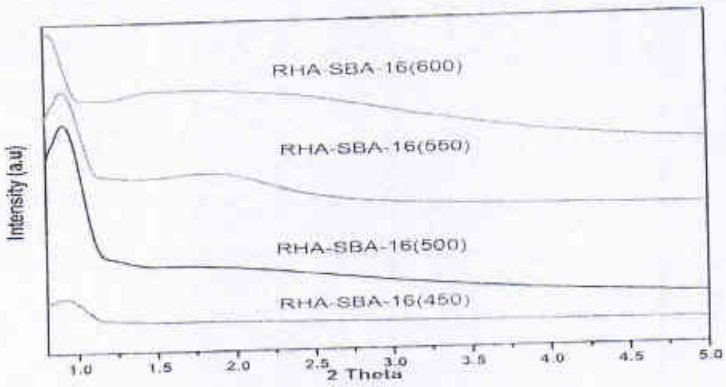

Fig. 1: (C) XRD patterns of calcined samples of RHA-SBA-16 (450, 500, 550, and 600) at various temperatures.

If the calcination temperature is increased up to 650^{0}C and above, the hexagonal phase transforms into the lamellar form which on additional calcination crumples the structure which is reflected as the absence of XRD peaks in RHA-SBA-16 (600) at and above 650^{0}C. Therefore, the above results indicate that calcination temperature plays a noteworthy role to optimize the synthesis condition.

% Crystallinity and Activation Energy

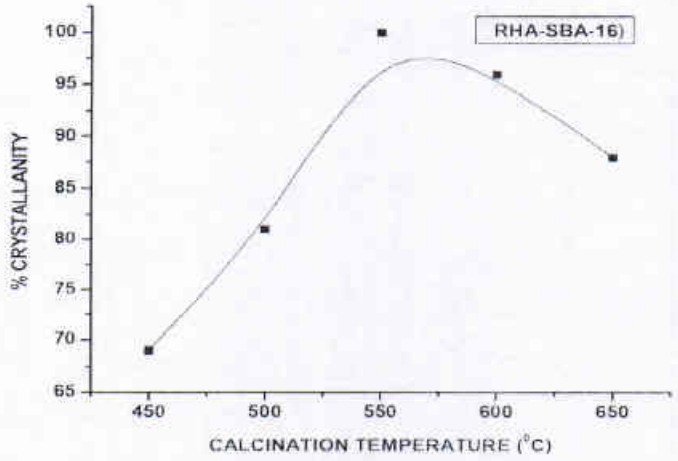

Fig.2: Effect of calcination temperature on crystallization.

Table 1: Effect of calcination temperature on Structural and textural properties of RHA-SBA-16.

Sample	d_{110}	Unit cell parameter	S.A. (m^2/g)	Average pore diameter (Å)	Pore volume (ml/g)	Average Wall thickness (Å)	% Crystal-linity
RHA-SBA-16(450)	22.15	31.90					69
RHA-SBA-16(500)	23.51	33.85	618.21	26.38	0.479	7.47	81
RHA-SBA-16(550)	26.93	38.78	779.70	29.16	0.568	9.62	100
RHA-SBA-16(600)	25.89	37.28	767.13	28.25	0.547	9.03	96
RHA-SBA-16(650)	24.21	34.86	738.22	26.99	0.506	7.87	88

Table 1. Summarizes the values of inter planar spacing (d values) derived from X-ray diffraction pattern for RHA-SBA-16 (100% crystalline) sample. The percent crystallinity of the samples drawn at diverse calcination temperatures in the crystallization kinetics was calculated. The obtained values of % crystallinity were plotted as a function of calcination temperature from which the gradient of crystallization has been evaluated. The percent conversion from amorphous to100% crystalline product of RHA-SBA-16 phase is shown in the Fig. 2. Therefore, this most (100%) crystalline sample was used as a parent sample for further study. The kinetic curve describing the increase in the crystallinity of the crystals with the calcination temperature depends on rate of conversion. It is seen from the Fig.2 that upto 550°C the rate of conversion of amorphous to crystallization of RHA-SBA-16 phase was very acute initially but followed by a subsequent slow down. Therefore, the rate of crystallization decreases as the process approaches to the completion indicated by constancy (100 %) in

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percent crystallization. Using Arrhenius equation to the kinetics of crystallization of RHA-SBA-16, activation energy was reported around 103.74kJ $mole^{-1}$ in the present crystallization scheme.

BET surface area and pore volume of RHA-SBA-16: The samples RHA-SBA-16 (450, 500, 550, 600 and 650) synthesized for 4.5h with different calcinations temperatures have also been characterized further by N2-sorption studies to find BET surface area and the corresponding pore size distribution. The first stage is a linear part almost going through the origin, which is due to monolayer adsorption of nitrogen on the walls of the mesopores ($p/p0 < 0.2$). The second stage is characterized by a steep increase in adsorption (within the relative pressure p/p0 range of 0.2-0.4) due to capillary condensation of N2 in the pore channels. This part shows hysteresis. The p/p_0value at which the inflection starts is related to the diameter of the mesopores. The sharpness in this step indicates the uniformity of the pore size distribution. The third stage in the adsorption isotherm is an almost horizontal part after the relative pressure $p/p_0$of~0.35 and is due to multilayer adsorption on the outer surface of the particles. In addition, a hysteresis loop at relative pressure $p/p_0 > 0.8$ corresponds to a capillary condensation in the inter particle pores .The adsorption-desorption curve obtained for RHA-SBA-16 (550, 600) is shown in the Fig3 these isotherms are of type IVas expected for SBA-16 molecular sieves. The observations regarding N_2-sorption and XRD studies are statistically depicted in Table 1. From which we can conclude that, as the calcination temperature is increased after 550^0C, at the ramp of 1^0C, surface area got reduced by $1.5 m^2/g$. It is probably because of the collapse of gel structure due to the rapid release of water from the pores. Moreover, there is an auxiliary alteration in the average pore diameter and wall thickness. Pores with narrow distribution start forming from 500 ^{0}C and increases as calcination temperature increases. The mean wall thickness of the pores and pore volume increased with calcination temperature from 500^0C to 600^0C. However, there is a slight decrease in wall thickness at the calcination temperature of 600^0C and above. These observations revels the hexagonal phase starts transforming to lamellar phase with lack of specific structural features, which are in well accordance with XRD patterns.

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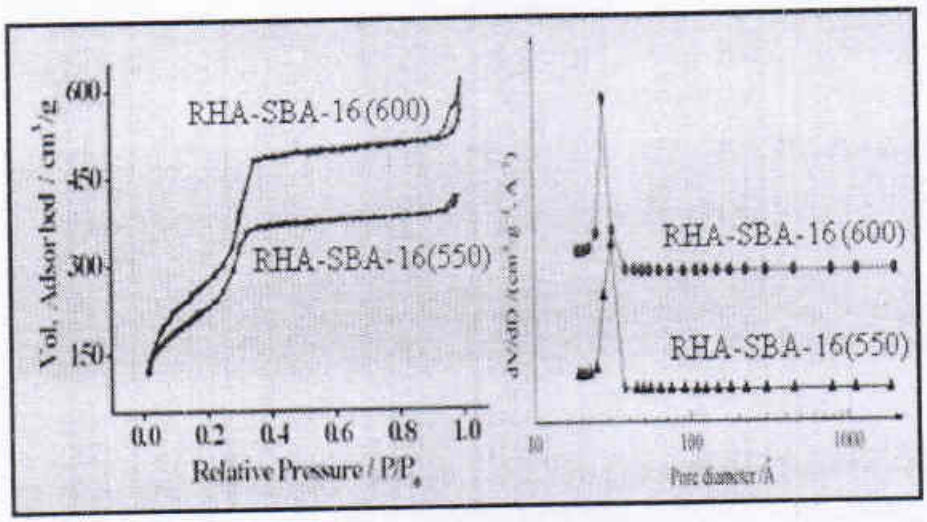

Fig 3: N2 adsorption-desorption isotherms and (B) pore size distribution of (a) RHA-SBA-16 (550^{0}C); (b) RHA-SBA-16 (600^{0}C)

FTIR-studies

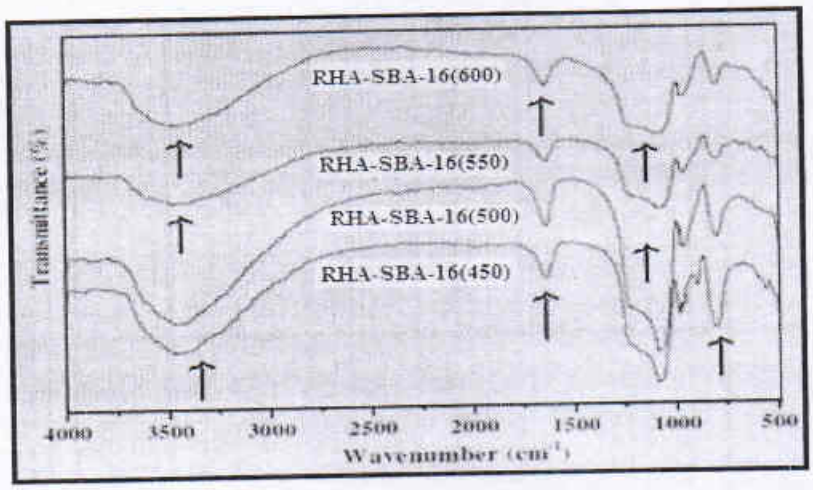

Fig. 4: FTIR spectrum of RHA-SBA-16 (450, 500, 550, 600) calcined from 450-600^{0}C.

The FTIR spectra of RHA-SBA-16 (450, 500, 550, 600) after calcination are illustrated in Fig.4 The broad band around 3476cm^{-1} may be due to surface silanols and adsorbed water molecules which indicating the silica framework is hydrophilic. For calcined RHA-SBA-16, the disappearance of peak at 2922.9 cm^{-1} and 2852.5 cm^{-1} can be concluded that the organic template has been removed completely at 550^{0}C. However, the peak at 3500.1 cm^{-1} is prominently found to be changed due to increase in calcination temperature.

The effect observed for RHA-SBA-16 (600) is significant. Since the surface of silica framework is water liking, the stretching mode of H-O-H is observedat 1640.1cm^{-1}. This peak is reduces as calcination temperature increases indicating removal of water molecule.

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Bands observed at 1213.6 cm^{-1} and 1061.9 cm^{-1} are characteristics peaks of asymmetric Si-O-Si stretching. Another characteristics peak is the symmetric Si-O-Si stretching observedat 780.2 cm^{-1}.

V) SEM and TEM-Analysis

SEM images of RHA-SBA-16 (500, 600) are depicted in Fig.5 represents that the particles are nearly in spherical form exclusive of agglomerations. The typical diameter of the particles is moderately same although the calcination temperature is raised from 450^{0}C to 650^{0}C representing an excellent thermal stability. The diameter of spherical particles is found to vary in the range of 2.6A^0 to 9.98A^0, which is consistent with the XRD and N_2sorption data. The SEM photo graph of RHA-SBA-16 at 550^{0}C indicates a good structural morphology.

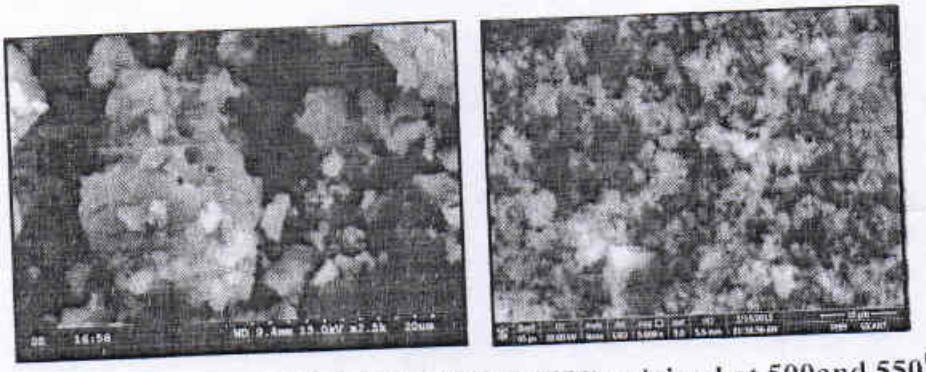

Fig. 5: SEM images of RHA-SBA-16 (500, 550) calcined at 500and 550^{0}C.

TEM-Analysis: Fig. 6 represents the TEM images of RHA-SBA-16synthesized at 80^{0}C and calcined at 550^{0}C. TEM image of the parent RHA-SBA-16samples provided sturdy verification of the retainment of mesoporous structure. The characteristic hexagonal silicate structures shown on TEM, supports the observation made by low angle XRD.

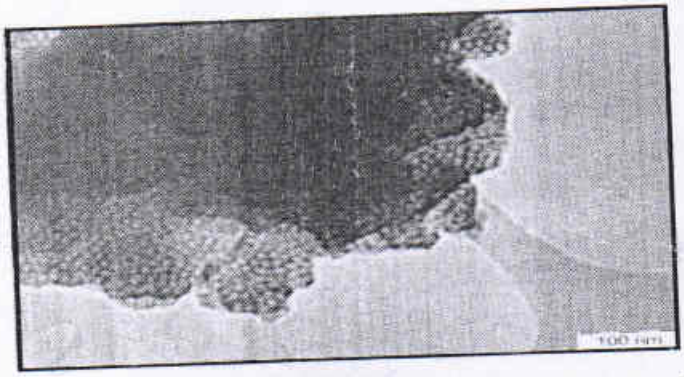

Fig. 6: TEM images of RHA-SBA-16 (550) calcined at 550^{0}C.

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CONCLUSION

The correlation of the work reported by (Carniato Fabio *et al* 2012) is using commercially available chemicals but our research is by using low cost waste material. We got the same result as reported.

All the characterization techniques performed in this study reveals that well ordered mesoporous material of uniform hexagonal array can be synthesized very conveniently and in a very short span of time from an agro waste rice husk ash instead of commercial expensive silica sources. The parametric variation such as change of synthesis temperature helps to optimize the synthesis conditions. The well ordered mesoporous material RHA-SBA-16 can be synthesized at 80^0C for 4.5h keeping pH of gel 6.9 and calcined at 550^0C. The apparent activation energy of conversion of synthesis gel to 100 % crystalline RHA-SBA-16 phase was 184.62kJ/molecalculated by Arrhenius equation.

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