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## RESEARCH ARTICLE

# CONVERSION OF RICE HUSK ASH INTO MESOPOROUS MATERIALS

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### 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<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 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.

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## INTRODUCTION

Rice milling generates a byproduct known 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) cooperative 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:

The synthesis of silica SBA-16 was made following a ternary system based on a previously described method reported in literature.<sup>17</sup> A 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, 4.5 g of RHA were added and the mixture stirred for 24 h. 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 to 550°C and maintaining it at this temperature for 6 h sample hereafter named calc-SBA-16. by Fabio *et al.*, [1] The amorphous SiO<sub>2</sub> component in the R.H.A. was used as Si- source for the synthesis of SBA16

### a) Characterization techniques

#### Powder X-ray diffraction:

X-ray diffraction patterns of the collected RHA and synthesized materials were recorded on a Cu/30 kV/15 mA MiniFlex2 goniometer with a wave length of 1.540 Å<sup>0</sup>.

The powder patterns of synthesized samples were obtained using Cu K $\alpha$  radiation on a Rigakau diffractometer. The samples were scanned for 2 $\theta$  from 1 to 20 $^{\circ}$ .

#### BET surface area:

Specific BET surface area was calculated using Surface area Analyzer Model SAA-2000 for all synthesized samples. P<sup>H</sup> values were measured with a digital pH meter

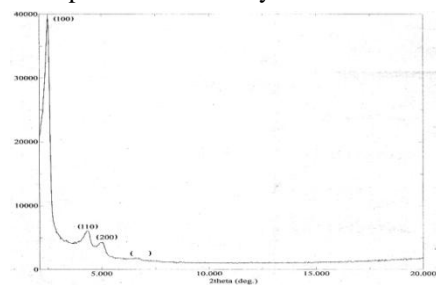
## RESULTS AND DISCUSSION:

### A) XRD of rice husk ash:

The XRD pattern of rice husk Ash (RHA) shown in Fig. 2, 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 2 $^{\circ}$  angles from 1 $^{\circ}$  to 30 $^{\circ}$  as shown in Fig.3. 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<sub>100</sub> 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.



$$d_{100} \text{ value} = 35.3099; \quad 2\theta = 2.500$$

$$\text{Unit cell parameter } a_0 = \frac{2}{\sqrt{3}} d_{100}$$

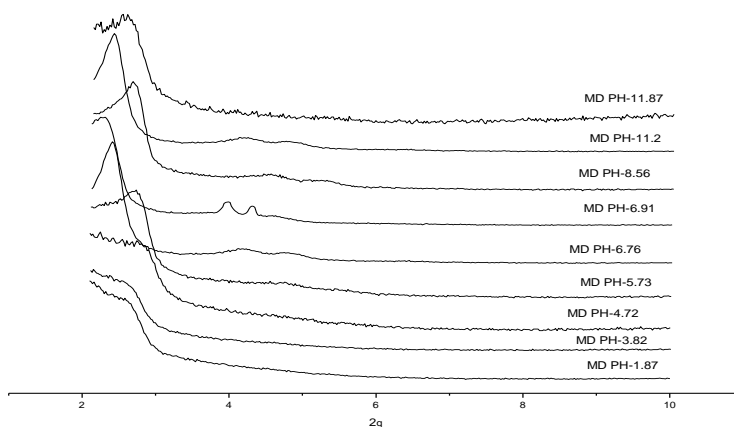
$$a_0 = 40.8$$

$$\text{Intensity (I)} : 14163 \text{ cps} \quad I/I_0 = 1$$

**Fig. 1:** XRD pattern of synthesized material with parameters (pH=6.9) temp. 550°C and calcination time 8 hrs.

### a) 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°C for 8 h. The crystallinity reduces when pH of the gel is below 6.91 and above 6.91.



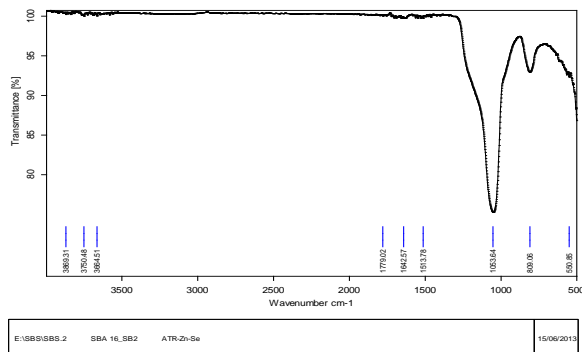
**Fig. 2: XRD Patterns of SBA16 at different pH of synthesis gel.**

The XRD data further analyzed to calculate  $I/I_0$ , 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°C.

### N<sub>2</sub>-ADSORPTION DESORPTION ANALYSIS OF SYNTHESIZED SBA16 MATERIAL:

Nitrogen physisorption probes the textural properties of materials i.e. surface area, pore volume, pore size and pore geometry. At very low relative pressures ( $p/p_0$ ) a very large amount of nitrogen becomes physisorbed which assigns to condensation of nitrogen inside and outside on the surface of SBA16. As the surface area is very high this corresponds monolayer adsorption. Upon monolayer adsorption multilayer of nitrogen starts to developed at higher relative pressures. Also in this case both the external surface area and mesopores contributes to the physisorption process.

### FT-IR ANALYSIS :



### Fig. 3: 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  $\text{cm}^{-1}$  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.

### 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 $^{\circ}$ C for 4 hrs. keeping pH of gel 6.91. The maximum calculated surface area amounts to 1801  $\text{m}^2/\text{g}$  for the SBA16 materials keeping pH of gel 6.91, calcination time about 4 h. at 550 $^{\circ}$ C.

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