



Sustainable Approach Towards the Synthesis of Mesostructured Molecular Sieve from Agricultural Waste.

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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 MCM -41. The various synthesis parameters were investigated during crystallization of MCM-41. The activation energy of crystallization kinetics of MCM-41 was calculated using Arrhenius equation and found to be 184.62 kJ / mole in the present system of synthesis.

Keywords: Rice Husk Ash , MCM-41, Crystallization Kinetics, Activation Energy

1. Introduction Hazardous wastes are generated annually throughout the world by all industries and their disposal poses major challenges and serious environmental problems. This creates serious health risks, taking into account that the 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 utilization¹.

As we know that, Rice is a primary source of food. Its production covers almost 1% of the Earth's surface. Globally, approximately 700 million tons of rice² is produced every year. India is a major rice producing country and annul production of rice husk is approximately 20 million tons³.

For every 100 kg of paddy milled, about 22% of husk is produced². Even 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 micro⁴ and mesoporous⁵ zeolitic materials synthesized from extracted silica through them. These materials have wide applications as adsorbents, in ion exchange, as molecular sieves, catalysts etc. Compared to conventional microporous zeolites, mesoporous materials possess many

advantages such as high surface area, large pore size and an ordered structure^{6,7}.

In 1992, scientist at Mobil Oil Corporation discovered new family (M41S) of mesoporous materials, among them MCM-41 possesses hexagonal molecular sieves having fairly uniform pores with pore diameter of 20-100Å. They possesses large surface area (more than 900m²/g), which is attractive for designing new selective heterogeneous catalyst in production of fine chemicals on large scale.

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. 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.

2. Experimental: Materials and Methods for Synthesis of mesoporous MCM-41 from RHA in alkaline medium:

Hydrothermal synthesis of RHA-MCM-41 was carried out in hydrothermal reactor at autogenous pressure under stirring conditions. The chemicals used during synthesis were Cetyltrimethylammonium bromide (CTAB), Sodium hydroxide, 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 80⁰C for 24h. This husk was then treated with 3.0 M HCl acid solution along with heating at 100⁰C. This hydrolyzed rice husk was rinsed with distilled water until pH reaches to 7, then it was again dried at 100⁰C for 24 h. Finally, the rice husk was calcined at 800⁰C 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. CTAB was dissolved in this solution in a hydrothermal reactor and stirred for 1hr at different synthesis temperatures (80⁰C, 100⁰C and 120⁰C). The molar composition of the synthesis gel was as follows:

1.0SiO₂: 1.09 NaOH: 0.13 CTAB: 50.12H₂O.

The pH value of the mixture was adjusted to 10.2 to obtain a white precipitate by adding 3.0 M HCl solution. The mixture was then heated in microwave oven at 100⁰C for 30min for crystallization. After cooling by the natural convection, the solid was recovered by centrifuge and was dried in oven overnight at 100⁰C. Later, the solid product obtained was calcined at 550⁰C for calcination duration of 6h. After cooling, the samples were characterized for the investigation of optimization. These synthesized samples were designated as RHA-MCM-41 (a, b, c) respectively.

Formation of the materials has been evaluated by X-ray diffraction and N₂ sorption studies. The XRD profiles of RHA and synthesized samples are shown in Fig.1. and Fig.2 respectively and also the data is summarized in Table 1.

3. Characterization:

To elucidate the structural features⁸, morphology⁹, pore architecture¹⁰, thermal stability¹¹, adsorptive¹² and catalytic behavior¹³, surface area¹⁴ etc: the synthesized samples are characterized by techniques such as XRD, N₂-sorption, FTIR, etc.

4. Results and Discussion:

I) XRD-studies:

The XRD scans were recorded from 10⁰-70⁰ with 0.2⁰ step-width and 5.1s counting time for every step. The X-ray diffraction patterns of treated RHA are shown in Fig.1 indicates the presence of quartz (21.31⁰, 25.45⁰ and 41.31⁰ 2θ peaks). From these XRD patterns it can be seen that a broad peak at 2θ = 20⁰ clearly indicates that silica obtained after fusion and burning of rice husk ash was in the amorphous nature.

In the XRD pattern of the calcined RHA-MCM-41 (a), the prominent presence of (100) reflection suggests that this material is likely to possess but not well defined hexagonal arrays after calcination. The maximum contraction is observed in the case of RHA-MCM-41 (a), which may be due to the poorly ordered arrangement of the

mesopores. However, the long range order in hexagonal symmetry is maintained in the calcined forms of RHA-MCM-41 (b, c) which is indicated by the presence of the four or three peaks respectively in their XRD patterns.

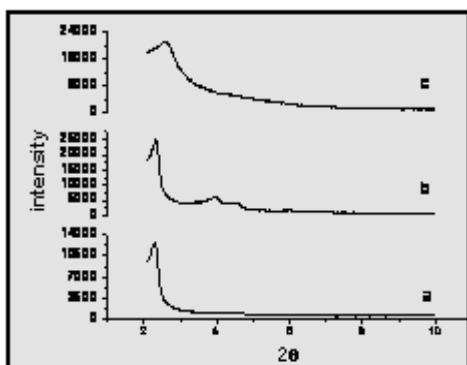
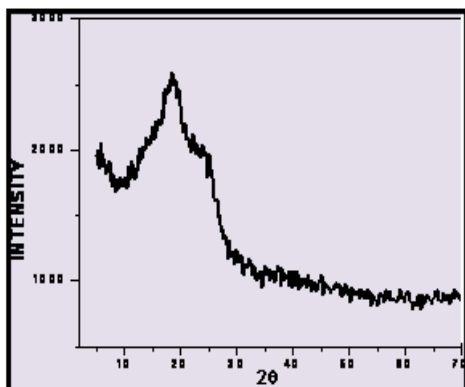


Fig. 1: XRD Pattern of treated RHA

Fig. 2: XRD patterns of calcined samples of RHA-MCM-41 (a, b, c) synthesized at 80, 100 and 120^oC

In calcined sample (b) at 100^oC, the most intense peak with (100) reflection is shifted to higher d_{100} spacing values and afterwards it lowers as in Fig.2-c this is because the calcination causes condensation of internal Si-OH groups giving rise to a contraction of the unit cell . A significant increase in the intensity of this peak in calcined samples b and c indicates that an atomic reorganization occurs during the removal of the surfactant molecules in the calcinations process.

II) FTIR-studies :

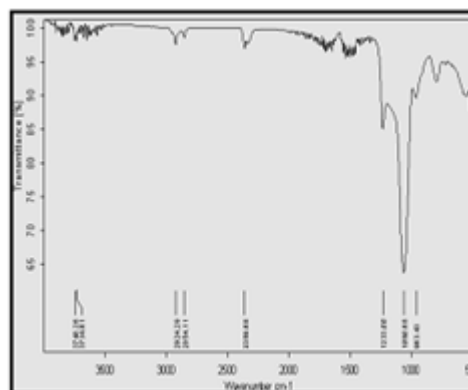
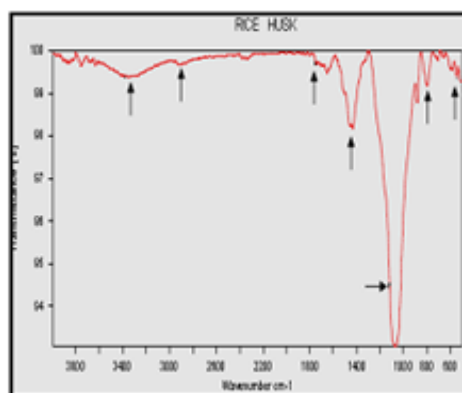


Fig. 3: FTIR spectrum of treated RHA
Fig. 4: FTIR spectrum of RHA-MCM-41 (b)

Fig.3 and Fig.4 shows the IR spectra of rice husk ash and RHA-MCM-41(b) after calcination. A broad band between 3300 cm^{-1} - 3400 cm^{-1} is attributed to surface -OH groups of silanol groups (-Si-OH) and adsorbed water molecules on the surface. The broadness of band indicates the presence of strong hydrogen bonding. In the calcined sample a very small peak in the same range confirms the retention of the silanols group resembling the hydrophilicity of the material. Peak at 2854 cm^{-1} could be assigned to C-H stretching vibration of organic contaminants which may be introduced during sample handling or some hydrocarbon present in rice husk. A broad band ranging from 1070 cm^{-1} to 1170 cm^{-1} due to Si-O-Si asymmetric stretching vibrations of silica is present in uncalcined and calcined rice husk samples. The effect of the higher reaction temperature was a large amount of silanol group. The effect observed for RHA-MCM-41

(b) is noticeable, which is also supported by the XRD analysis and sorption studies of the samples.

III) N₂-Sorption studies

The sample (b) synthesized at temperature 100⁰C have been characterized by N₂-adsorption-desorption isotherms and the corresponding BJH pore size distribution was shown (Fig.5 A, B). According to IUPAC classification, all the isotherms of RHA-MCM-41 are of type IV, which is the characteristic of mesoporous material. The isotherms exhibit three stages. 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 ($p/p_0 < 0.2$). The second stage is characterized by a steep increase in adsorption (within the relative pressure p/p_0 range of 0.2-0.4) due to capillary condensation of N₂ in the pore channels.

The p/p_0 value 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 ~ 0.38 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 capillary condensation in the inter particle pores. The hysteresis loop is found over a wide range of relative pressures, p/p_0 (0.35-1.00). The shape of the hysteresis loop confirms the formation of a lamellar phase. The pore size distribution becomes broader. Thus, the XRD results are confirmed by N₂-adsorption-desorption data. We noted that the surface areas of calcined RHA-MCM-41 samples are increasing with the increase in crystallization temperature up to 100⁰C. The more surface area (933.27m²/g) is an indication of narrow pore size distribution.

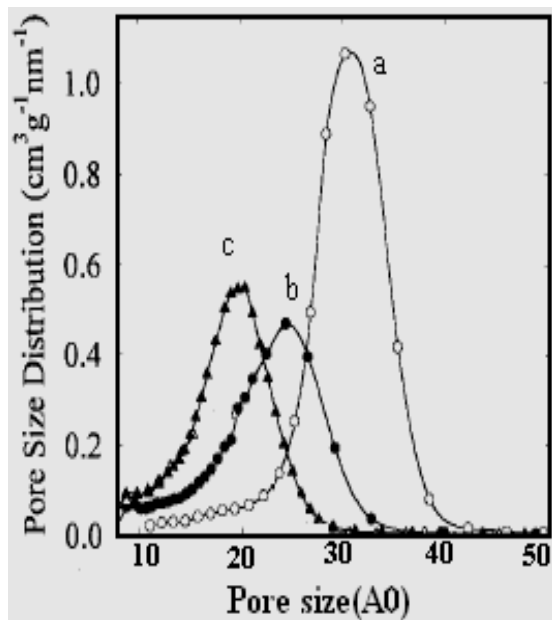


Fig. 5: (A) N₂ adsorption-desorption isotherms and (B) pore size distribution of RHA-MCM-41(a, b, c) synthesized at 80, 100 and 120⁰C

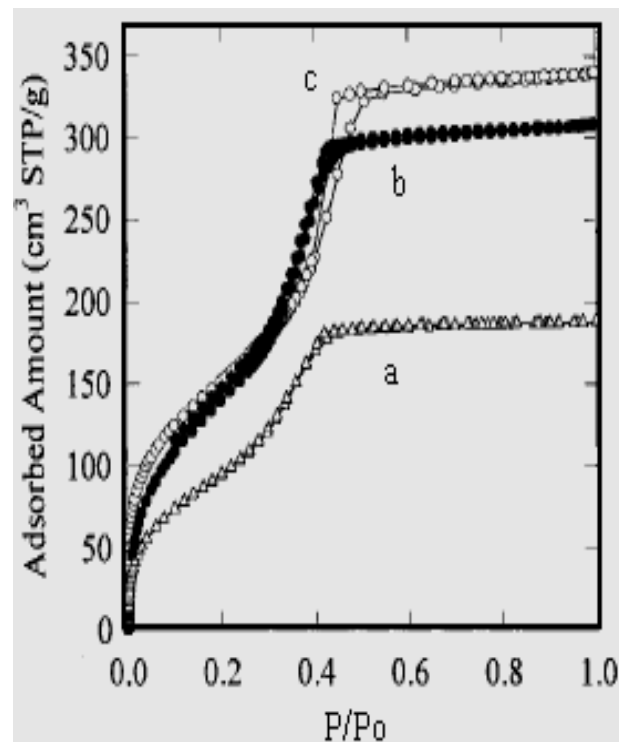


Table.1: Data obtained from XRD and N₂-sorption studies

Sample name	d ₁₀₀	Unit cell parameter	S.A. (m ² /g)	Average pore diameter (Å)	Pore volume (ml/g)	Average wall thickness (Å)	% Crystallinity
RHA-MCM-41 (a)	33.81	39.22	571.35	31.27	0.382	7.95	71
RHA-MCM-41 (b)	36.28	42.06	933.27	28.63	0.491	14.43	100
RHA-MCM-41 (c)	35.82	41.55	761.38	30.02	0.452	11.53	96

5. Study of Kinetics of

The percent crystallinity of the samples drawn at different synthesis

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

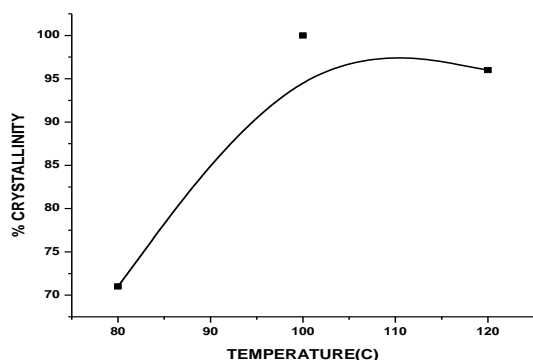


Fig.6 Kinetics of crystallization of RHA-MCM-41

The obtained values of % crystallinity were further plotted as a function of temperature from which the gradient of crystallization has been evaluated. The percent conversion from amorphous to 100 % crystalline product of RHA-MCM-41 phase is shown in the Fig.6 indicates that the rate of conversion of amorphous to crystallization of RHA-MCM-41 phase was initially slow and then it is increased sharply followed by subsequent slow down. Therefore, the rate of crystallization decreases as the process approaches to the completion indicated by constancy (100 %) in percent crystallization.

Crystallization of RHA-MCM-41:

temperatures in the crystallization kinetics was obtained by the following relation.

Sum of peak heights of standard material

The apparent activation energy for conversion was estimated from the slope of linear plot of $\ln K$ vs. $(1/T)$ by applying the Arrhenius equation $d \ln K/d (1/T) = E_{ac}/RT$, Where, K is the rate of conversion, E_{ac} is the energy of crystallization/ conversion, R is the gas constant. The apparent activation energy of conversion of silicate gel to 100 % crystalline RHA-MCM-41 phase was calculated and found to be 184.62 kJ/mole in the present crystallization system.

6. Conclusion:

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 CFA-MCM-41 can be synthesized at 100^oC for 6h keeping pH of gel 10.2 and calcined at 550^oC. The apparent activation energy of conversion of synthesis gel to 100 % crystalline CFA-MCM-41 phase was 184.62kJ/mole calculated by Arrhenius equation.



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