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Synthesis of Mobil Crystalline Material Using Rice Husk

Tejas Babaria[1], Anurag Singhania[2], Stuti Khaitan[3], Tejaswi[4], P L Muralidhara[5], Jagadish H Patil[6]

Student, Chemical Engineering, R.V. College of Engineering, Bangalore, Karnataka, India [1]

Student, Chemical Engineering, R.V. College of Engineering, Bangalore, Karnataka, India [2]

Student, Chemical Engineering, R.V. College of Engineering, Bangalore, Karnataka, India [3]

Student, Chemical Engineering, R.V. College of Engineering, Bangalore, Karnataka, India [4]

Professor, Chemical Engineering, R.V. College of Engineering, Bangalore, Karnataka, India[5]

Professor, Chemical Engineering, R.V. College of Engineering, Bangalore, Karnataka, India[6]

Abstract: Mobil crystalline material is a unique material that has propertiesof high surface area, narrow pore size distribution, high thermal stability and has wide applications in the areas of nanoscience, catalysis, environmental engineering, and adsorption and drug delivery. The present work explores to synthesizemobil crystalline material economically using free and abundantly availablerice husk as silica source and cetyltrimethyl ammonium bromide as surfactant. The product was characterized by Fourier Transform Infrared Spectroscopy (1073.91 cm^{-1}), Nitrogen adsorption-desorption technique (2181.7 cm^2/gm), pore size (27 nm) and X-ray diffraction technique (2.6^{o}of 2θ value). The characterizations reveal the product synthesized was agood mobil crystalline material that has mesoporous molecular sieve with good adsorbing capacity.

Keywords: Mobil crystalline material, Cetyltrimethyl ammonium bromide, Rice husk, Nitrogen adsorption-desorption, X-ray diffraction.

I. INTRODUCTION

Mobil Crystalline Material(MCM) is a mesoporous silicate molecular sieve which was discovered in 1992 [1],[2]. Mesoporous materials have particle size in the range of 2 nm to 50 nm. MCM is an allotrope of silicaand hasunique properties like high surface area, narrow pore size distribution, and highthermal stabilityand high hydrophobicity. MCM has been a focus for several research areas like nanoscience [3], catalysis [4], environmental engineering [5], adsorption [6] and drug delivery [7]. Yang et al. [8] introduced a rapid method for the synthesis of highly ordered mesoporous material by using silica gel as silica source. Due to high silica content in rice husk, it has become a source of preparation for a number of silicon compounds [9]. In the present work, MCM was synthesized using freely and abundantly available rice husk as a silica source and cetyltrimethyl ammonium bromide as a templating agent.The mesoporous silicate was obtained after the removal of template by calcination.Synthesis conditions such as silica source, templating agent, pH, composition of the reaction mixture and temperature determine the characteristics of the porous structure [10]-[14]. The present work focuses on effect of pHon the yield of MCM synthesis. Characterization of the porous MCM was carried out using three independent techniques namely,Fourier Transform Infrared Spectroscopy (FT-IR), nitrogen adsorption-desorption, pore size and X-Ray diffraction (XRD)[15].

II. EXPERIMENTAL METHOD

A. Materials

Cetyl Trimethyl Ammonium Bromide (CTAB), silica gel, double distilled water, ammonium hydroxide, hydrochloric acid, sodium hydroxidepurchased from Industrial and Laboratory equipment company, Bangalore India. Rice husk was procured from K R Market, Bangalore India. All the chemicals were used without further purification.

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B. Analytical methods

The XRD patterns were recorded on a Philips PW 1710 automated powder diffractometer using a graphite monochromator-filtered Cu Kα radiation (R = 0.15406 nm), at a generator tension of 40 kV and generator current of 20 mA. XRD patterns for the siliceous MCMwere recorded in the range $1.5^o < 2\theta < 10^o$ using a step size of 0.02^o and 1 s per step, i.e., at a scan speed of 0.02^o/s.

The BET (Brunauer, Emmett, Teller) method of calculating specific surface area from an adsorption isotherm is reliable and widely used. Surface area measurements were performed on a Micromeretics ASAP 2010 surface analyzer by adsorbing gaseous N_2 at liquid nitrogen temperature. The samples (0.2-0.3 g) were degassed at 300 ^oC until a vacuum pressure of 2-4 μm Hg was obtained, prior to analysis. A relative pressure range (P/Po) of 0.05-0.25 was used in the analysis.

In FT-IR, the sample was irradiated with a spectrum of infrared radiation. Bonds have specific bond energy associated with them. The irradiated infrared rays of specific wavelengths are deflected according to the bond energy. This helps in identification of chemical bonds in the sample. Also impurities can be identified by this method.

C. Synthesis

1) Preparation of Rice Husk Ash

1 kg of rice husk was first mixed with concentrated hydrochloric acid at 100^0C to leach out all the organic matter from the husk. Rice husk was then washed with water to remove excess acid and then dried for 12 hours at 100^0Cin an oven. The dried rice husk was calcined at 600^0C for 6 hours to obtain 92 gm of rice husk ash.

2) Preparation of MCM from rice husk ash

92 gm of rice husk ash was mixed with excess sodium hydroxide solution and stirred overnight to extract silica from the ash. The solution was crystallized to obtain 59.65 gm of silica. Three reaction mixtures were prepared in three 1000 ml round bottom flasks, in each flask 2.76 gm of CTAB was dissolved in 710ml of Double Distilled Water (DDW) and stirred for 20 minutes then1.68 gm of silica obtained from rice husk ash was added and stirred for 24 hours. Different amounts of ammonium hydroxide solution were added to each flask resulting in three reaction mixtures of pH8.3, 8.6 and 9. The productsobtained from each flask were filtered using a whatman filter paper and filter paper along with residues wasdried in an oven at 100^0C. The dried residues in each casewere calcined at 550^0C to remove the template to obtain three MCMs namely MCM 8.3, MCM 8.6 and MCM 9. The yield in each case were calculated as

$$\%yeild = \frac{weight\ of\ MCM\ obtained}{wieght\ of\ silica\ added} * 100\%$$

The comparison of yield is presented in Table 1:

Table 1: Yield comparison

Type of MCM	% Yield
MCM8.3	60.32
MCM8.6	64.56
MCM9.0	58.21

It can be observed from Table 1 that the pH has significant effect on the yield of MCM. As the pH increases from 8.3 to 8.6, the yield increases, further increase of pH decreases the yield. MCM8.6 had highest yield of 64.56% and was further characterized using analytical methods.

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III. RESULT AND DISCUSSIONS

The MCM8.6 synthesized was characterized using Fourier Transform Infrared Spectroscopy (FT-IR), nitrogen adsorption-desorption, pore size and X-Ray diffraction (XRD)

A. FT-IR Spectroscopy

The results of FT-IR spectroscopy for MCM8.6 are shown in Figure 1. The wavelength associated with Silica-Oxide (Si-O) bond is in the range of 1100-1000 cm^{-1}. It can be observed from the graph the dip lies at wavelength of 1073.91cm^{-1}. This confirms the presence of Si-O bonds in theMCM8.6.

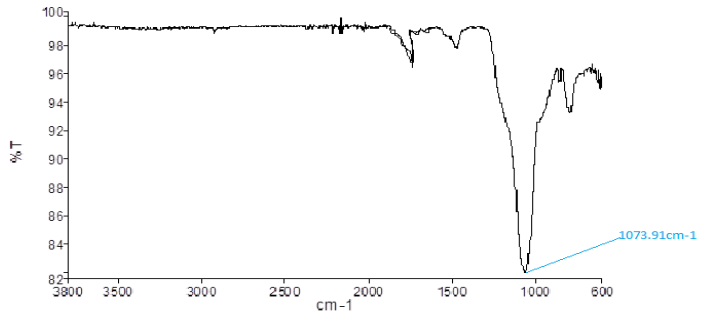

Figure 1FT-IR spectrum of MCM8.6

B. Nitrogensorption-desorption Method

The surface area of MCM8.6 was analysed using Nitrogen sorption-desorption method using Nova Enhanced Date Reduction Software. The summary of the results obtained are given in Figure 2. From the summary sheet, the surface area of the MCM8.6 was found to be 2181.732 m^2/gm.

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NOVA Enhanced Data Reduction Software - [c:\docume~1\varada~1\desktop\sio2.dat] - [Multi Point BET (Adsorption)]

File Comms Edit Math Plot Scaling View Window Help

Quantachrome Corporation
NOVA Enhanced Data Reduction Software Ver. 2.13
File Name = c:\docume~1\varada~1\desktop\sio2.dat

Instrument	= NOVA-1000 Ver. 3.70		
User ID	= 02	User Setup	= 14
Comments	=		
Sample ID	= 02	Sample Cell Number	= 11
Sample Weight	= 0.0378 g	Sample Volume	= 0.0143 cc
Sample Density	= 2.6500 g/cc		
Po Type	= User	Po	= 693.41 mm Hg
Adsorbate	= N2	Bath Temperature	= 77.40 deg K
Adsorption Tolerance	= 0.1000 mm Hg	Desorption Tolerance	= 0.1000 mm Hg
Adsorption Equil Time	= 30 sec	Desorption Equil Time	= 30 sec
Adsorption Dwell Time	= 60 sec	Desorption Dwell Time	= 60 sec
Analysis Start Time	= Wed Apr 09 18:19:23 2014	Elapsed Time	= 93.72 Minutes.

Multi Point BET (Adsorption)

P/Po	BET Transform [1/(W[Po/P - 1])]
0.028771	1.904096
0.051577	2.512804
0.093392	3.303811
0.114341	3.619942
0.140776	3.983211
0.182923	4.515790
0.204353	4.768539
0.230091	5.071226
0.272045	5.570347
0.293451	5.831336

= 14.131690
= 1.830478
= 0.991990coefficient
= 8.720220

= 8.2469 m²rea in Cell
= 2181.732 m²/gea

Figure *2* Surface Area of the MCM8.6

C. X-Ray Diffraction Method

The XRD pattern of MCM8.6is shown in Figure 3. Three reflections of silicon dioxide crystals were found at 2θ equal to 2.6°, 4.4° and 5.0° corresponding to hkl reflection planes 100, 110 and 200 respectively. These sharp signals indicated the long-range orders of the uniform hexagonal mesoporous structure. XRD patterns, shows a prominent

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(100) reflection peak and additional higher order peaks in the range $2^o < 2\theta < 7^o$, can provide conclusive evidence about the quality of the synthesized material.

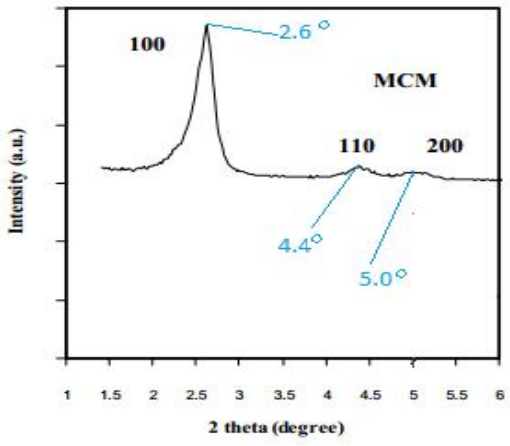

Figure 3 XRD pattern of MCM8.6

D. Barrett-Joyner-Halenda (BJH) Method for Pore Size and Volume Analysis

The pore diameter of MCM8.6 was determined using BJH method with Nova Enhanced Data Reduction Software. Results from this technique is shown in Figure 4. Pore Diameter is found to be 27.01 nm which is the mesoporous scale.

Pore Diameter [Å]	Pore Area [m²/Å/g]	Pore Volume [cc/Å/g] x 10e-3
360.912057	0.018202	0.164232
195.890851	0.295153	1.445444
135.885450	0.909817	3.090771
105.455999	0.851078	2.243781
86.286090	0.813751	1.755384
71.742965	0.813815	1.459638
60.760917	1.231620	1.870859
53.043785	1.866682	2.475397
47.086165	2.617951	3.081752
42.178735	3.704867	3.906665
38.066488	6.510559	6.195853
34.344604	6.542962	5.617886
31.420967	7.885336	6.194122
28.683468	9.795258	7.024049
26.388485	11.978155	7.902134
25.118747	13.511950	8.483081
23.733288	14.815529	8.790531
22.339241	16.234613	9.066723
20.959832	17.802687	9.328533
19.590294	18.975351	9.293318
17.827654	18.631144	8.303740
16.202799	17.392202	7.045059
14.880132	10.166277	3.781889

Total Pore Volume is 0.48154 cc/g for all pores of diameter smaller than 485.126 Å.

Average pore diameter is 270.199 Å.

Figure4 Pore Size and Pore Volume from BJH method

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IV. CONCLUSION

Mesoporous silica materials represent a unique class of silica based materials which possess high specific surface area, large pore volume, uniform pore size (between 2-50nm), high hydrothermal stability and rich surface chemistry. MCM has been synthesized using free and abundantly available rice husk as silica source and cetyltrimethyl ammonium bromide as surfactant.at pH values 8.3, 8.6 and 9.0. The yield obtained was highest in the case of MCM 8.6. The product was characterized by Fourier Transform Infrared Spectroscopy (1073.91 cm^{-1}), Nitrogen adsorption-desorption technique (2181.7 cm^2/gm), pore size (27 nm) and X-ray diffraction technique (2.6^{o}of 2θ value). The characterizations reveal the product synthesized was a good mobil crystalline material that has mesoporous molecular sieve with good adsorbing capacity. MCM has a diverse area of application and as a result the synthesis method needs to be modified for the mass production of it can be achieved at competitive rates.

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BIOGRAPHY

Mr. Tejas Babaria is a final year student of R.V. College of Engineering (Autonomous institution under Visvesvaraya Technological University, Belgaum), Bangalore, India. He is pursuing a Bachelor of Engineering degree in Chemical Engineering. His areas of research include nanotechnology, Process Design and renewable energy. He is Team Captain of International Formula SAE-Ashwa Racing with head of finance. He has won technical Paper presentation in IIT Kanpur, India.

Mr. Anurag Singhania is a final year student of R.V. College of Engineering (Autonomous institution under Visvesvaraya Technological University, Belgaum), Bangalore, India. He is pursuing a Bachelor of Engineering degree in Chemical Engineering. His areas of research include nanotechnology and paints.

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Ms. Stuti Khaitan is a final year student of R.V. College of Engineering (Autonomous institution under Visvesvaraya Technological University, Belgaum), Bangalore, India. She is pursuing a Bachelor of Engineering degree in Chemical Engineering. She has won 1st place for Paper presentation in IIT Kanpur, India. She secured 3rd for Paper presentation in Renewable club of RVCE.

Mr. Tejaswi is a final year student of R.V. College of Engineering (Autonomous institution under Visvesvaraya Technological University, Belgaum), Bangalore, India. He is pursuing a Bachelor of Engineering degree in Chemical Engineering. Secured 1st place in an event organised byFOLK Organisation.

Dr. Jagadish H Patil. He obtained BE in Chemical Engineering with III rank to the KUD, India in 1998. Completed M.Tech in CPD from KREC Surathkal in 2000. Completed PhD from VTU, Belgaum in 2013.Major research areas include Biomethanation of Organic waste and Biofuels.He is Associate Professor, department of Chemical Engineering, RVCE, Bangalore. He has 21 International journal publications and 10 International conference presentations. He has delivered talk at IIT Guwahati and many other places on his area of interest. Dr. Jagadish H Patil is Life Member of Indian Institute of Chemical Engineers and member of Indian Society for Technical Education. He is Editorial board member for many International journals and societies.

P L Muralidhara. Born in Gudibande, Karnataka, India on June 03, 1964. Obtained bachelor degree in Chemical Engineering with I class from Bangalore University, India in 1989. Completed M.E in Chemical Engineering from Bangalore University, India in 1998. Major research areas include Lubricant additives. He worked as Lecturer in MVJ College of Engineering, Bangalore from 1994-2007. Latter he joined R V College of Engineering, Bangalore and currently is Assistant professor. He has 17 years of teaching and 5 years research experience. He has presented one paper in an international conference. He has guided many UG projects few were awarded at various competitions.