# A Green and Efficient Route for Knoevenagel Condensation Over Rice Husk Based MCM-41

M. R. Deshpande[1], C.V.Rode[2], U.D.Joshi[1]
[1]Netaji SubhashChandra Bose College, Nanded
[2]National Chemical Laboratory Pune
e-mail: joshiud@yahoo.com, +919850826030,Fax: +912462244486

## Abstract

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. We report eco-friendly synthesis of mesoporous molecular sieve MCM-41as a member of M41S family using rice husk plentily available as an agro-waste. This contributes ro the green synthesis of MCM-41 at a cheaper production cost. Synthesised material (denoted as RH-MCM-41) was charecterised by powder XRD, FT-IR,$N_2$ physisorption, TGA-DTA and SEM to understand the effect of silica source on physico-chemical propoerties. RH-MCM-41 having basic characteristics was efficiently used to catalyze Knoevenagel condensation reaction between aldehyde and malonitrile.

***Keywords:*** Rice Husk, MCM-41, Knoevengel condensation, silica, aromatic aldehyde,

## 1. Introduction

Rise husk is a residue produced during milling of paddy (Oryza sativa). Approximately 22% weight of paddy is obtained as husk which after burning produces about 25 % rice husk ash (RHA). India is a major rice producing country and annul production of rice husk ash is approximately 20 million tons [1].Due to low content moisture, 8-10 % rice husk is commonly used as a biomass fuel [2-4].Even though rice husk is an agricultural residue, it is not recommended as cattle feed since its cellulose and other sugar contents are low. Due its high silica (>90%) content, it can be a renewable resource for making high value, versatile mesoporous material like MCM-41[5,6]. This paper reports the synthesis strategy of MCM-41 from rice husk ash, its characterization and evaluation as base catalyst for Knoevenagel condensation reaction.

## 2. Materials and Methods

Cetyl-tri-methyl-ammonium bromide (CTAB), sodium hydroxide and conc. hydrochloric acid were purchased from SD fine chemicals, India.

The acid pretreated (2.0 M HCl at 100˚C) rice husk was washed with water to remove the excess acid on the surface and dried in oven overnight at 100˚C. This was then calcined at 750˚C in air for 4h to obtain the extracted silica from RHA. Silica extracted from RHA was first fused with 3M NaOH solution and was stirred for 2h to extract the silicate from the ash. A clear solution of CTAB prepared in water was then slowly transferred into silicate supernatant solution and kept under stirring for 2h. The reaction gel mixture had the molar composition of 1.0 $SiO_2$:3.0NaOH:0.25CTAB:180 $H_2O$. The pH value of the gel was then adjusted to 8.5 by adding 3.0M HCl solution. This homogeneous gel was heated under autogenous pressure at 80˚C for 2h in a teflon coated autoclave. After cooling, the solid product was filtered and washed repeatedly by de-ionized water. The solid thus obtained was then dried in a muffle furnace at 100˚C and calcined at 550˚C for 4.5h. This sample was named as RH-MCM-41 which was evaluated for Knoevenagel condensation reaction.

Knoevenagel condensation reaction was performed using 1g (0.00943 moles) of benzaldehyde, 1g (0.00885 moles) of ethyl cyanoacetate and 30 ml of DMSO (solvent) in a glass reactor equipped with a magnetic stirrer at the desired reaction temperatures. After attaining the desired temperature, 2 g of the catalyst was added and the reaction was started. The liquid samples were periodically withdrawn (every 2 h.) and analyzed on GC using 2025 Shimadzu model equipped with RTX-5 capillary column. The other conditions of analysis were:Injector (split) temperature: 250 $^{O}$C; FID temperature: 250 $^{O}$C Column final temperature: 220 $^{O}$C, ($N_2$) carrier gas flow rate: 30 ml/*min* Inlet Pressure ($N_2$) :30 psig, Split ratio: 1: 100. IR was recorded using Brucker-ATR ZnSe spectrophotometer in transmission mode. Powder X-ray diffraction patterns of the materials were recorded on Rigaku MiniFlex2 model with a monochromated Cu Kα radiation in the angular range from 1.8° to 10° (2θ) with a scanning speed of 0.03° $s^{-1}$. FT-IR spectra of the RHA and synthesized materials RH-MCM-41 were recorded on a FT-IR spectrometer (ATR eco ZnSe) using dry KBr pallet as a standard reference in the range of 500-4000$cm^{-1}$. BET surface area was measured using Surface area Analyzer Model SAA-2000. Chemical composition of rice husk ash was estimated on a dry basis by gravimetry in conjunction with atomic adsorption spectrometer (Shimadzu AA 6200). TGA-DTA characteristics of the synthesized sample were taken on DTG-60H detector.

## 3. Results and Discussion

### 3.1. Characterization

Chemical analysis of the rice husk ash confirmed its major constituent as $SiO_2$ (90 – 95 %) necessary for the synthesis of mesoporous materials. The crystallinity of MCM-41 synthesized from rice husk ash was from the corresponding XRD patterns of RHA and RH-MCM-41 as shown in Fig.s 1 (a) and (b). A broad peak at 2θ = 20° clearly indicated that silica obtained after fusion and burning of rice husk ash was in the amorphous while the peaks at 2θ = $2.4^0$, $4.0^0$, $4.4^0$ and $6.0^0$ indexed as (100), (110), (200) and (210) reflections, respectively, were the characteristics of long range ordered hexagonal MCM-41 mesophase of which the corresponding lattice parameter $a_o$ = 47.31Åfor peak at 2θ = $2.4^o$. The specific BET surface area of as-synthesized sample was 677.162 m$^2$/g which significantly increased to 901.361 m$^2$/g after calcination. FTIR spectra of RH-MCM-41 before and after calcination showed the peak at 552.7cm$^{-1}$ which was characteristic of Si-O-Si bending while, that observed at 789cm$^{-1}$ was due to the symmetric Si-O-Si stretching. The bands observed at 1240.8 cm$^{-1}$ and 1083.4 cm$^{-1}$ were the characteristics of asymmetric Si-O-Si stretching and the broad band around 3604cm$^{-1}$ was due to surface silanols and adsorbed water molecules which indicate that the silica framework is hydrophillic. The disappearance of peaks at 2930.4cm$^{-1}$ and 2858.1cm$^{-1}$ after calcination confirmed the complete removal of the organic template at $550^0$C [7].

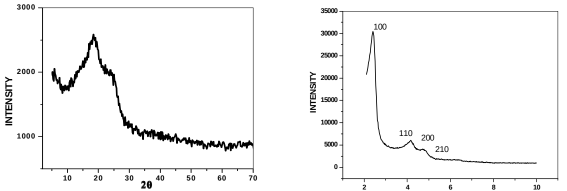


Fig.1. XRD of (a) RHA, (b) RH-MCM-41

Scanning Electron Microscope (SEM) micrograph of the silicon extracted from the Rice Husk Ash (RHA) in Fig. 2, shows agglomerated particles varying in sizes confirming their tendency to cluster together. Fig. 2 (b) exhibited the agglomerated particles with the uniform size in a range of 0.3-0.5 μm and shapes of the particales are like a silik cocoon with random arrangment.

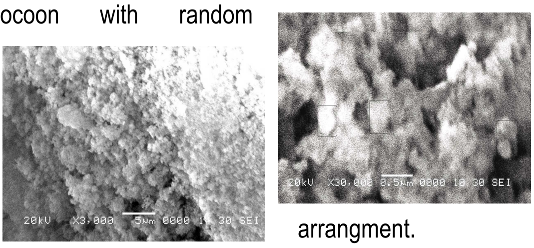
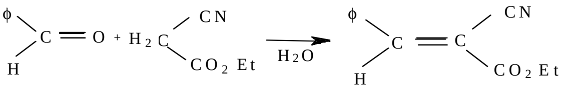


Fig. 2. SEM of a) Silica from RHA b)Calcined RH-MCM - 41

TG and DTG thermograms were scanned in a temperature range of 300 to 1273 K which showed a smooth weight loss due to desorption of water, starting from 310 K to 450 K. The total weight loss was 22 % up to 1273 K. There was almost no weight loss after 823K indicating that surfactant had been removed completely after calcination. This also indicates that the sample was thermally stable up to 1273 K.

*3.2. Activity testing*

The above prepared RH-MCM 41 catalyst was tested for the Knoevenagel condensation rection of aromatic aldehydes such as benzaldehyde and salicylaldehyde and molecules containing activated methylene group e.g. ethyl cyano acetate to give the corresponding $\alpha,\beta$ unsaturated nitrile in presence of RH-MCM-41, as shown below.



$$\phi(H)C{=}O + H_2C(CN)(CO_2Et) \xrightarrow[H_2O]{} \phi(H)C{=}C(CN)(CO_2Et)$$

The reaction was catalyzed by the basic sites of RH-MCM-41, which were associated with the framework oxygen bearing negative charge of the lattice and consequently the density of negative charge on a given oxygen(Lewis basicity). Being a solid catalyst, not only proton-abstracting capacity of RH-MCM-41 but its specific (BET) surface area, pore diameter and type of cationic surfactant also substantially influence its activity. We have also studied the effect of other reaction parameters like catalyst loading, the reaction time and temperature from process optimization point of view. The loading of RH-MCM-41 catalyst in the reaction blend was varied from 0.5 g to 3.0 g in the steps of 0.5 g.The effect of duration on reaction was examined for various timings of 8 h,10 h and 12 h. Reaction was carried out at different temperatures i.e.$75^0$C,$85^0$C and $95^0$C.

The gas chromatographic analysis of reaction product obtained from Knoevengeal condensation between benzaldehyde and ethyl cyano acetate gave the highest conversion of 96.9% for 2g loading of RH-MCM-41 at $95^0$C after 8 h of the reaction. However for the Knoevengeal condensation between salicylaldehyde and ethyl cyano acetate, we have achieved almost complete conversion for the same experimental parameters indicating the effect of substituent on the aromatic aldehyde.

FT-IR spectra of the reaction products showed diagnostic bands in the 2206-2225 cm$^{-1}$ range attributable to the stretching vibration of the C≡N group. The spectra also showed the bands in the 1440-1665 and 2933-3021 cm$^{-1}$ ranges which are assigned to C=C and C-H group stretching frequencies, respectively.

## 4. Conclusion

This study concludes that rice husk extracted silica is an inexpensive, active and renewable raw material as compared to the conventional expensive resource for the synthesis of MCM-41. The synthesised RH-MCM-41 was thoroughly characterized possessing the basic sites due to whhich it exhibited high activity and selectivity for Knoevenagel condensation of aromatic aledehydes and cyano esters to give the corresponding $\alpha,\beta$ unsaturated nitriles.

## 5. References

[1] “Rice husk ash market styudy”, BronzeoakLtd.,UK2003

[2] L.P. Hunt, J.P. Dismukes, J.A. Amick, Rice hull as a raw material forproducing silicon, J. Electrochem. Soc. 131 (1984) 1683–1686.

[3] H. Halimaton, N.M.M. Mohd, E. Salasiah, L. Endang, R. Zainab, 29Si MAS NMR, XRD and FESEM studies of rice husk silica for the synthesis of zeolites, J. Non-Cryst. Solids 211 (1997) 126–131.

[4] N. Yalcin, V. Sevinc, Studies on silica obtained from rice husk,Ceramic Int. 27 (2001) 219–224

[5] J.S. Beck, C. Vertuli, W.J. Roth, C.T. Kresge, Family of mesoporous molecular sieves prepared with liquid crystal templates, J. Am. Chem. Soc. 114 (1992) 10834–10843.

[6] N. Grisdanurak, S. Chiarakorn, J. Wittayakun, Utilization of mesoporous molecular sieve synthesized from natural source rice husk silica to chlorinated volatile organic compounds (CVOCS) adsorption, Korean J. Cem. Eng. 20 (2003) 950–955.
[7]Kalapathy U., Protor A. and Shultz J., “A simple method for production of pure silica from rice hull ash”, Bioresource Technology, Vol. 73, (2000), pp 257-264.