



## SYNTHESIS OF 3-CYNOCOUMARIN BY KNOEVENGL CONDENSATION OF ANISALDEHYDE WITH ETHYL CYNOACETATE OVER CS-RHA-MCM-48

Jagdish P. Kulkarni<sup>1</sup>, Manish R. Deshpande<sup>1</sup>, Uday D. Joshi<sup>1</sup> and Dr. S.D.Ghan<sup>2</sup>  
<sup>1</sup>Department of Physics and Material Science, N. S. B. College, Nanded (MS), India.  
<sup>2</sup>Yogeshwari Mahavidyalaya, Ambejogai Dist. Beed .

### ABSTRACT

The intention of the at hand study is to make available Cs-RHA-MCM-48 as catalyst for the Knoevengel condensation of Anisaldehyde with ethyl cynoacetate. Cesium was doped in MCM-48 via ion exchange method and the catalytic performances of the samples were investigated for an efficient, high-yielding, one-pot synthesis of 3-cynocoumarin. The influence of cesium loading on the basic properties of MCM-48 was also studied.

**KEYWORDS:** MCM-48, Cs-RHA-MCM-48, Knoevengel condensation reaction, 3-cynocoumarin, solid base catalyst .

### 1. INTRODUCTION:

Porous solid can be defined in broad sense as a solid material, which contains pores, i.e. cavities, channels or interstices, which are deeper than they are wide.

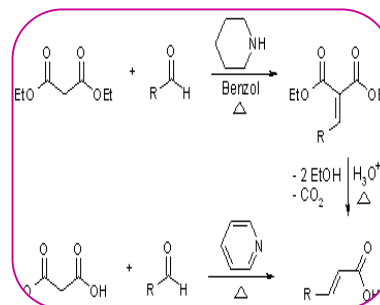
According to IUPAC definition porous materials may be divided into three types based on their pore dimensions<sup>1</sup>:

Type	Pore Size (Å)
Microporous	< 20
Mesoporous	20-500
Macroporous	> 500

Well known microporous materials are zeolites and aluminophosphate molecular sieves which are inorganic composites having a crystalline three-dimensional framework woven with tetrahedral atoms (T-atoms) like aluminium, silicon, phosphorous etc. bridged by oxygen atoms. Mesoporous materials<sup>2,3</sup> are like ordinary porous materials (for example, a sponge) except the pore sizes are in the range of 20-500 Å<sup>0</sup> and generally arranged in a uniform array.

Different types of mesoporous materials have been reported in the literature, such as silicas, pillared clays and other silicates. The synthesis of amorphous silica- alumina in the presence of quaternary salts has also been reported, where the average pore diameter was related to the size of the tetra alkyl ammonium cations.

In 1992 researchers at Mobil Research and Development Corporation reported the synthesis of a new family<sup>4</sup> of silicate/aluminosilicate mesoporous molecular sieves (M41S) with exceptionally large uniform pore structures<sup>5,6</sup>.



There was increasing demand for well-structured mesoporous molecular sieves with pores of uniform diameter. Even though, there exists large number of different mesoporous materials, discussion is restricted to silica based mesoporous molecular sieves Si-RHA-MCM48 work presented in this paper.

The Knoevenagel condensation reaction is an important C–C bond forming reaction commonly used for the production of fine chemical intermediates and products (e.g. coumarin derivatives) as well as pharmaceuticals (e.g. nitrendipine derivatives for hypertension drugs).

The reaction involves the condensation of methylene compounds (i.e., R-CH<sub>2</sub>-R' or R-CHR'-R'') with ketones or aldehydes<sup>7</sup>. 3-Cyanocoumarins have attained enormous importance in recent years as they are required for synthesis of methane dyes. 3- carboxycoumarins, which are used for synthesis of cephalosporins<sup>4</sup>, modified penicillin, oxygen bridged tetrahydropyridones, isourases, etc.

The amide obtained from 3-cyanocoumarines exhibit specific inhibitor of  $\alpha$ -chymotripsin, human leukocytic elastase and polymeric compounds of biological importance.

## 2. METHODS AND MATERIALS:

### 2.1 Chemicals:

Triton-X (Spectrochem), Aqueous ammonia (25 wt. %, Fisher Scientific), Extracted silica from RHA, Cesium chloride (Loba Chemie), Dimethyl sulfoxide (DMSO, Fisher Scientific), Anisaldehyde (Merck), Ethylcynoacetate (ECA, s d fine chemicals) All chemicals were AR grade hence they were used without further purification. Syntheses were carried out at room temperature (293K).

### 2.2 Catalyst Synthesis:

The mesoporous silica, RHA-MCM-48 was synthesized by hydrothermal method followed by post modification, ion exchange of cesium transition metal ion. In the typical synthesis, Triton-x dissolved in double distilled water. In this solution a fixed amount of 9.52 g of aqueous ammonia (25 wt %) was added. Further 10 g of extracted silica from RHA was added pinch wise under vigorous stirring to get white precipitate.

The molar composition of the resultant gel was 1RHA: 0.152Triton-X: 2.8NH<sub>3</sub>: 141.2H<sub>2</sub>O. This gel was stirred for 2 hr in the autoclave at 373K then after it was filtered and washed several times. The obtained filter cake was dried at 373 K for 12 hr. In temperature control furnace the obtained powder was calcined at 823 K for 5 hr at the rate of 1<sup>o</sup>/min to expel the template.

The parent synthesized Si-RHA-MCM-48 was converted to the H<sup>+</sup> form through NH<sub>4</sub><sup>+</sup> ion exchange and subsequent calcination. Approximately 5 gm of Si-RHA-MCM-48 was placed in 100ml of 2.5 wt % NH<sub>4</sub>NO<sub>3</sub> aqueous solution. After being refluxed for 6 hr at 353 K, the solution filtered, the obtained filter cake was dried at 373 K for 12 hr. The NH<sub>4</sub> ion exchanged Si-RHA-MCM-48 was calcined in air at 773 K for 6 hr.

The H<sup>+</sup> form of Si-RHA-MCM-48 thus obtained was ion exchanged using aqueous solution of Cesium chloride. Cesium ion exchanged MCM-48 (Cs-Si-RHA-MCM-48) catalyst were prepared by dissolving cesium chloride and H<sup>+</sup>MCM-48 in double distilled water, which is heated at 353 K for 5 hr.

The solid was filtered and dried overnight at 373 K in air followed by calcination. The three different catalyst were prepared with three different weight percentage viz 1wt% Cs-Si-RHA-MCM-48, 2wt% Cs-Si-RHA-MCM-48 and 3wt% Cs-Si-RHA-MCM-48.

### 2.3 Characterization:

- Power X-ray diffraction: The powder patterns were obtained using Cu K $\alpha$  radiation on a Rigaku diffractometer. The samples were scanned for 2 $\theta$  from 1 to 10<sup>o</sup>
- FT-IR: Fourier transform infra-red spectra were recorded on Bruker ALPHA FT-IR spectrometer.
- BET surface area: Specific BET surface area was calculated using Surface area Analyser Model SAA-2000 for all synthesized samples.

## 2.4 Catalytic reaction:

All the catalytic reactions were carried out in a round bottom flask with a magnetic stirrer immersed in a oil bath. Before the reaction the required quantity of catalyst i. e. Cs-Si-RHA-MCM-48 was heated in the muffle furnace at 373 K for 2 hr so as to evaporate the moisture adsorbed by the catalyst.

In a typical experiment, 9.55 mol (1.16 g) of Anisaldehyde, 9.55 mol (1.01 g) of ethyl cyanoacetate and 30 ml of dimethyl sulphoxide (DMSO) were charged in the round bottom flask. The reaction was maintained at temperatures 353 K under atmospheric pressure.

After attaining the desired reaction temperature, the dried catalyst (0.5 g) was rapidly added into the reactor and the reaction was started. The reactions were carried out for various time durations.

The progress of reaction was monitored by the thin layer chromatography (TLC) on Merck silica plates using ethyl acetate : petroleum ether (1:1) as eluent. TLC was taken after every 10 minutes.

After reaction completion the reaction content were cooled to room temperature by natural convection. Then the catalyst was separated by filtration and washed with distilled water for several times. Later it is kept for drying in air at 373 K.

After separating the catalyst from the reaction content, reaction mixture was poured on the crushed ice, stirred with glass rod for 10 min and filtered to obtain product which was then purified by crystallization with ethanol.

## 3 RESULT AND DISCUSSION:

### 3.1 Charactrization of catalyst:

The XRD patterns of the calcined parent MCM-48, H-MCM-48 and Cs-Si-RHA-MCM-48 samples with different wt.% of Cs (1wt.%, 2wt.% and 3wt.%) respectively are presented in Figure1 (a, b, c, d, e) respectively.

These XRD patterns showing three prominent reflections which can be assigned to the hexagonal lattice of the meso-porous materials. The 100, 110 and 200 are well resolved. The unit cell parameters  $a_0$  were calculated by the formula:

$$A_0 = (2/\sqrt{3}) \times d_{100}$$

The unit cell parameter and d-spacing of the MCM-48, H-MCM-48, Cs-Si-RHA-MCM-48 (1wt.%, 2wt.% and 3wt.%), samples are given in Table 1. The slight increase in d-spacing and unit cell parameters of Cs-Si-RHA-MCM-48 compared to MCM-48 suggests the presence of cesium in the framework.

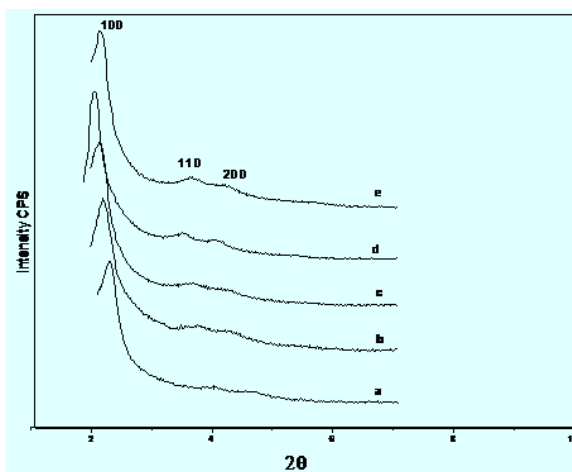


Figure1: Powder XRD Patterns of MCM-48, H-MCM-48, Cs-Si-RHA-MCM-48 (1wt.%, 2wt.% and 3wt.%)

The increase in unit cell parameter on Cs incorporation is probably due to the replacement of shorter Si-O bonds by longer Cs-O bonds in the structure. It is also observed that along with an increase in the unit cell parameter, the (100) diffraction peak becomes broader and less intense with increasing cesium content, probably because of the change of the Cs-O-Cs bond angle due to Cs incorporation, causing a distortion in the long range ordering of the hexagonal mesoporous structure. Figure 1 illustrate that in all the modified forms MCM-48 sample, there are marginal changes in the crystallinity but almost no changes in the phase purity and structural morphology are being observed after modification with different amounts of Cs<sup>+</sup> percentage. This indicates the structural stability of the parent sample and presence of metal ions in the intra-crystalline voids of the MCM-48.

The percent crystallinity of the samples is drawn with the amount of metal ion percent in them. However, if the 'Cs' metal ion concentration in MCM-48 was 3wt%, it was 96.4% and then gradually decreased for 2wt% and 1wt% as 86.8% and 84.3% respectively. The BET surface areas, average pore diameters calculated from N<sub>2</sub>-sorption isotherms of MCM-48 and Cs-Si-RHA-MCM-48 are presented in Table 1.

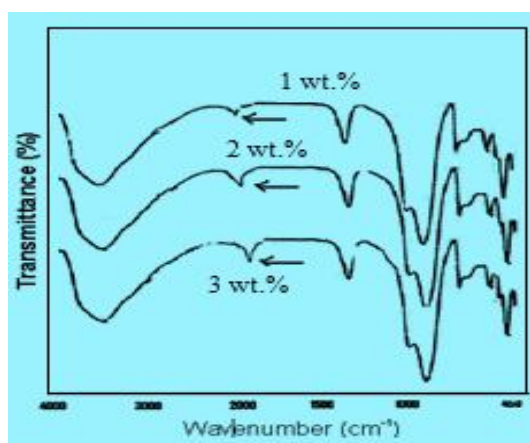


Figure 2: FT-IR of Cs-Si-RHA-MCM-48

The mid-infrared region from 400-1300 cm<sup>-1</sup> contains vibrations due to the framework structure of zeolites. Similarly, mesoporous molecular sieves also show series of bands that are characteristics of the SiO<sub>4</sub> tetrahedral unit and its modification by introduction of metal ions. The FT-IR spectra of lattice vibration of calcined Cs-Si-RHA-MCM-48 are presented in Figure 2.

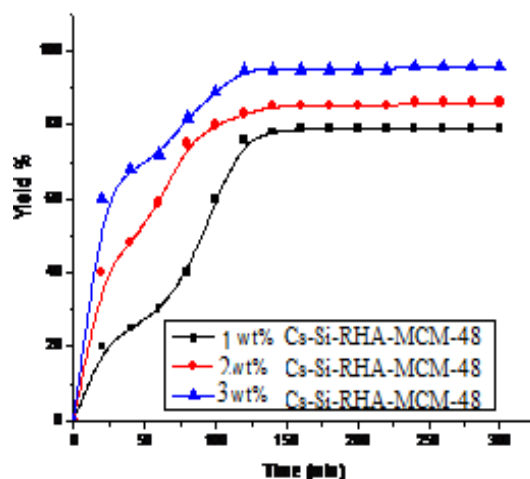
The spectra shows four main absorption bands between the regions 1210-1230, 1045-1080, 790-815 and 440-470 cm<sup>-1</sup>. FT-IR spectra exhibit a vibrational band at ~ 970 cm<sup>-1</sup> which is considered as a proof for the incorporation of the heteroatom into the framework, the intensity of this band marginally increases with increase in the Cs wt %.

### 3.2 Catalysis reaction:

The Knoevenagel condensation is of great importance to the synthetic chemists in the construction of new C-C bonds. Here we choose the Knoevenagel reaction of Anisaldehyde with ethyl cyanoacetate (Scheme 1) to form  $\alpha,\beta$ -unsaturated nitriles (3-cynocoumarine) as a condensation reaction to examine the catalytic performance of the obtained materials.

Before the reaction the required quantity of catalyst i. e. Cs-Si-RHA-MCM-48 was heated in the muffle furnace at 373 K for 2 hr so as to evaporate the moisture adsorbed by the catalyst. Pure siliceous MCM-48 treated under the same condition showed no catalytic activity.

No other side products except the 3-cynocoumarin were detected in the products based on TLC analysis. All the catalysts showed rapid reaction rates in the first 150 min, after this the yields of the product only increased slightly. This might be due to the deactivation of the catalysts by adsorption of formed water.



From figure 2, it is observed that percentage yield of the product increases from 76 % to 96 % with increase in cesium weight percent in parent MCM-48, it is may be due to increase in the basic site. Reaction was completed in almost 150 min beyond that % yield increases slightly. The product, 3-cynocoumarin was confirmed by FT-IR where the peak at  $2231\text{ cm}^{-1}$  corresponds to cyano group and peak at  $1781\text{ cm}^{-1}$  corresponds to carboxyl group of the product.

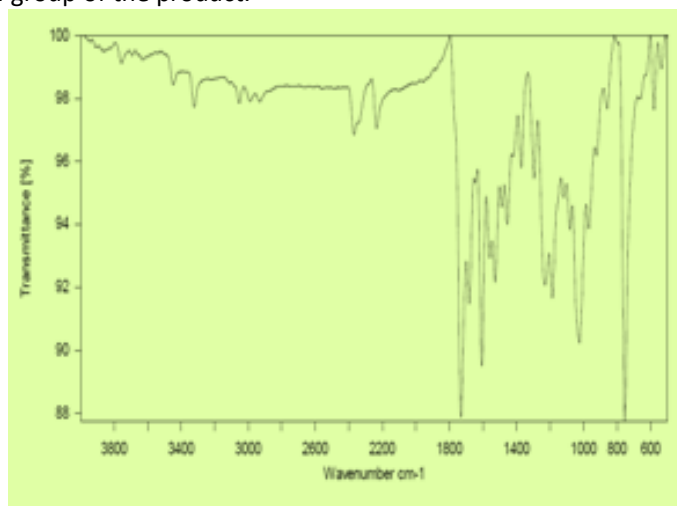


Figure 3: FT-IR of 3-cynocoumarin

Table 1: Physico-chemical properties of MCM-48

Sample Name	$d_{100}$ spacing(nm)	Unit cell parameter $a_0$ (nm)	Spe. Surface area ( $\text{m}^2\text{g}^{-1}$ )	Pore diameter (nm)	Particle size (nm)	% crystallinity
MCM-48	3.80	4.32	1034.0	2.7	0.21	100
H-MCM-48	3.84	4.39	1057.8	2.76	0.20	99
1wt% Cs-Si-RHA-MCM-48	4.01	4.63	949.9	2.22	0.32	84

2wt% Cs-Si-RHA-MCM-48	4.02	4.72	1062.4	2.27	0.21	90
3wt% Cs-Si-RHA-MCM-48	4.04	4.78	1099.1	2.4	0.26	98

#### 4 CONCLUSION:

Highly ordered hexagonal MCM-48 and Cs-Si-RHA-MCM-48 are synthesized. The synthesis of 3-cynocoumarin *via* Knoevenagel condensation over a recoverable ordered hexagonal Cs-Si-RHA-MCM-48 solid base catalyst, is reported within a short period of time *i.e.* 150 min and at lower temperature *i.e.* 353 K in liquid phase.

This method produces substituted coumarins in very high yields (96%) These findings suggest that Cs-Si-RHA-MCM-48 is a good candidate for the Knoevenagel condensation of salicylaldehyde with ethyl cyanoacetate.

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