

Simple Route Synthesis of 3-Cynocoumarin by Knoevengel Condensation of Benzaldehyde with Ethyl Cynoacetate over Si-Al-MCM-41

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ABSTRACT

The objective of the present study is to provide Si-Al-MCM-41 as catalyst for the Knoevengel condensation of benzaldehyde with ethyl cynoacetate. Aluminum was dopped in MCM-41 via ion exchange method and the catalytic performances of the samples were investigated for an efficient, high-yielding, one-pot synthesis of 3-cynocoumarine. The influence of aluminum loading on the basic properties of MCM-41 was also studied.

Keywords : MCM-41, Si-Al-MCM-41, Knoevengel condensation reaction, 3-cynocoumarin, solid base catalyst

I. INTRODUCTION

Porous solid can be defined in wide logic as a solid material, which includes 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 dimensions¹:

Type	Pore Size (nm)
Microporous	< 2
Mesoporous	2-50
Macroporous	> 50

Recognized 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 materials²⁻⁵ are like ordinary porous materials except the pore sizes are in the range of 2-50 nm 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 novel family⁴⁻⁷ of silicate/aluminosilicate mesoporous molecular sieves (M41S) with exceptionally large uniform pore structures^{5,6}.

There was an escalating demand for well-structured mesoporous molecular sieves with pores of uniform diameter. Even if, there exists large number of different mesoporous materials. Discussion is constrained to silica based mesoporous molecular sieves Si-MCM41 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. nifendipine and nitrendipine derivatives for hypertension drugs).

The reaction involves the condensation of methylene compounds (i.e., R-CH₂-R' or R-CHR'-R'') with ketones or aldehydes⁷.

3-Cyanocoumarins have achieved gigantic importance in recent years as they are required for synthesis of methane dyes.

3-carboxycoumarins, which are used for synthesis of cephalosporins⁴, modified penicillin, oxygen bridged tetrahydropyridones, isourases, etc.

The amide obtained from 3-cyanocoumarines exhibit specific inhibitor of α -chymotrypsin, human leukocytic elastase and polymeric compounds of biological importance.

II. METHODS AND MATERIAL

2.1 Chemicals:

Cetyltrimethyl ammonium bromide (CTAB, Spectrochem), Aqueous ammonia (25 wt. %, Fisher Scientific), Tetraethyl orthosilicate (TEOS, Aldrich), Cesium chloride (loba, chemie), Dimethyl sulfoxide (DMSO, Fisher Scientific), Salicylaldehyde (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.

2.2 Catalyst Synthesis:

The mesoporous silica, MCM 41 was synthesized by hydrothermal method followed by post modification, ion exchange of cesium transition metal ion.

In the typical synthesis, CTAB is dissolved in double distilled water. In this solution a fixed amount of 9.60 g of aqueous ammonia was added. Further 10.3 g of tetraethyl orthosilicate was supplemented bit by bit under vigorous stirring to get white precipitate.

The molar composition of the resultant gel was **1TEOS: 0.152CTAB: 2.8NH₃: 141.2H₂O**.

This gel was stirred for 2 hr in the autoclave at 100°C then after it was filtered and washed several times.

The obtained filtered lump was desiccated at 100°C for 10 hr. In temperature control furnace the obtained power was calcined at 550°C for 4.5 hr at the rate of 1°C/min to drive out the template.

The parent synthesized Si-MCM-41 was transformed to the H⁺ form through NH₄⁺ ion exchange and ensuing calcination. Approximately 4.5 gm of Si-MCM-41 was placed in 100ml of 2.5 wt % NH₄NO₃ aqueous solution.

After being refluxed for 5 hr at 300°C, the solution filtered, the obtained filter cake was dried at 100°C for 10 hr. The NH₄ ion exchanged Si-MCM-41 was calcined in air at 500°C for 5 hr.

The H⁺ form of Si-MCM-41 thus obtained was ion exchanged using aqueous solution of Aluminum chloride. Al⁺⁺⁺ ion exchanged MCM-41 (Si-Al-MCM-41) catalyst were prepared by dissolving Aluminum chloride and H⁺-MCM-41 in double distilled water, which is heated at 100°C for 5 hr.

The solid was filtered and dried overnight at 100°C in air followed by calcination. The three different catalyst were prepared with three different weight percentage such as 2wt% Si-Al-MCM-41, 4wt% Si-Al-MCM-41 and 6wt% Si-Al-MCM-41.

2.3 Characterization:

- BET surface area: Specific BET surface area was calculated using Surface area Analyser Model SAA-2000 for all synthesized samples.
- FI-IR: Fourier transform infra-red spectra were recorded on Bruker ALPHA FT-IR spectrometer.
- c) Power X-ray diffraction: The powder patterns were obtained using Cu K α radiation on a Rigakau diffractometer. The samples were scanned for 2 θ from 1 to 10 $^{\circ}$

2.4 Catalytic reaction:

All the catalytic reactions were carried out in a RBF with a magnetic stirrer immersed in a oil bath. Before the reaction, the required quantity of catalyst i. e. Si-Al-MCM-41 was heated in the muffle furnace at 100°C for 2 hr so as to evaporate the moisture adsorbed by the catalyst.

In a typical experiment, 9.50 mol of Benzaldehyde, 9.50 mol of ethyl cyanoacetate (ECA) and 30 ml of dimethyl sulphoxide (DMSO) were charged in the RBF.

The reaction was maintained at temperatures 100°C under atmospheric pressure. After attaining the desired reaction temperature, 0.5 g of dried catalyst was rapidly added in the reactor and the reaction was started.

The reactions were carried out for diverse time durations. The progress of reaction was examined 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 followed by drying in air at 100°C.

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.

III. RESULTS AND DISCUSSION

3.1 Characterization of catalyst:

The XRD patterns of the calcined parent MCM-41, H-MCM-41 and Si-Al-MCM-41 samples with different wt.% of Al (2wt.%, 4wt.% and 6wt.%) respectively are presented in Figure1 (a, b, c, d, e) respectively.

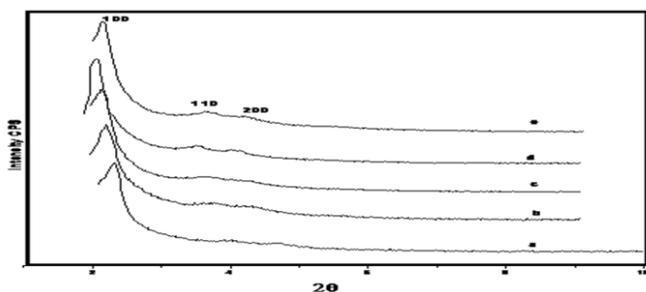


Figure1: Powder XRD Patterns of MCM-41, H-MCM-41, 2wt% Si-Al-MCM-41, 4wt% Si-Al-MCM-41 and 6wt% Si-Al-MCM-41

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-41, H-MCM-41, 2wt% Si-Al-MCM-41, 4wt% Si-Al-MCM-41 and 6wt% Si-Al-MCM-41 samples are given in Table 1.

The slight increase in d-spacing and unit cell parameters of Si-Al-MCM-41 compared to MCM-41 suggests the presence of Aluminum in the framework.

The increase in unit cell parameter on Al incorporation is probably due to the replacement of shorter Si-O bonds by longer Al-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 Al-O-Al bond angle due to Al incorporation, causing a distortion in the long range ordering of the hexagonal mesoporous structure.

Figure 1 illustrate that in all the modified forms MCM-41 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 Al⁺⁺⁺ percentage. This indicates the structural stability of the parent sample and presence of metal ions in the intra-crystalline voids of the MCM-41.

The percent crystallinity of the samples is drawn with the amount of metal ion percent in them. However, if the 'Al' metal ion concentration in MCM-41 was 6wt%, it was 98.3% and then gradually decreased for 4wt% and 2wt% as 90.8% and 84.2% respectively.

The BET surface areas, average pore diameters calculated from N₂-sorption isotherms of MCM-41 and Si-Al-MCM-41 are presented in Table 1.

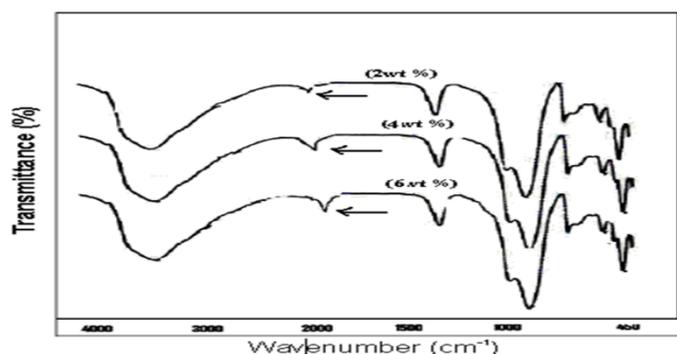


Figure 2: FT-IR of Si-Al-MCM-41

The mid-infrared region from 400-1300 cm^{-1} contains vibrations due to the framework structure of zeolites. Similarly, mesoporous molecular sieves also show series of bands that are characteristics of the SiO_4 tetrahedral unit and its modification by introduction of metal ions.

The FT-IR spectra of lattice vibration of calcined Si-Al-MCM-41 are presented in Figure 2. The spectra shows four main absorption bands between the regions 1200-1250, 1050-1070, 785-830 and 425-475 cm^{-1} . FT-IR spectra exhibit a vibrational band at $\sim 980 \text{ cm}^{-1}$ 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 Al 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 Benzaldehyde with ethyl cyanoacetate (Route 1) to form α,β -unsaturated nitriles (3-cynocoumarin) as a condensation reaction to examine the catalytic performance of the obtained materials. Before the reaction the required quantity of catalyst i. e. Si-Al-MCM-41 was heated in the muffle furnace at 100°C for 2 hr so as to evaporate the moisture adsorbed by the catalyst.

Pure siliceous MCM-41 treated under the same condition showed no catalytic activity. Fig. 3 gives the dependency of the yields of 3-cynocoumarin on the reaction period over various Si-Al-MCM-41 materials.

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.

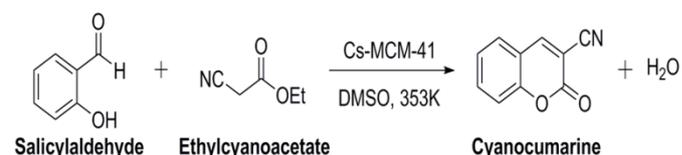


Figure 3: Knoevenagel condensation of salicylaldehyde

Route 1: Synthesis of 3-Cyanocoumarin

From figure 2, it is observed that percentage yield of the product increases from 78 % to 98 % with increase in cesium weight percent in parent MCM-41, 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 2240 cm^{-1} corresponds to cyano-group and peak at 1790 cm^{-1} corresponds to carboxyl group of the product.

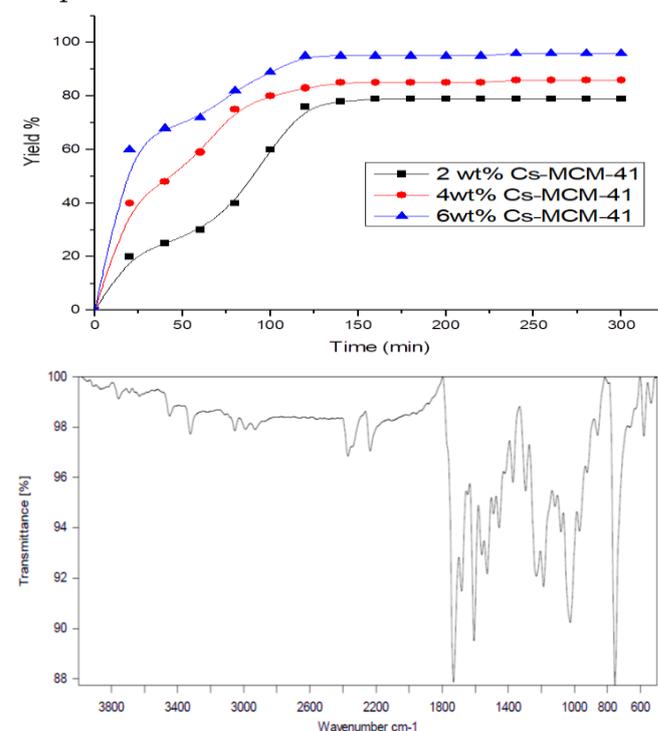


Figure 4: FT-IR of 3-cynocoumarin

IV. CONCLUSION

Highly ordered hexagonal MCM-41 and Si-Al-MCM-41 were synthesized. The synthesis of 3-cynocoumarin *via* Knoevenagel condensation over a recoverable, ordered hexagonal Si-Al-MCM-41 solid base catalyst, is reported within a short period of time

i.e. 150 min and at lower temperature *i.e.* 100°C in liquid phase.

This method produces substituted coumarins in very high yields (98%) These findings suggest that Si-Al-MCM-41 is a good candidate for the Knoevenagel condensation of salicylaldehyde with ethyl cynoacetate.

Table 1: Physico-chemical properties of MCM-41

Sample Name	d ₁₀₀ spacing(nm)	Unit cell parameter a ₀ (nm)	Spe. Surface area (m ² g ⁻¹)	Pore diameter (nm)	Particle size (nm)	% crystallinity
MCM-41	3.80	4.32	1034.0	2.7	0.21	100
H-MCM-41	3.84	4.39	1057.8	2.76	0.20	99
2wt% Si-Al-MCM-41	4.01	4.63	949.9	2.22	0.32	84
4wt% Si-Al-MCM-41	4.02	4.72	1062.4	2.27	0.21	90
6wt% Si-Al-MCM-41	4.04	4.78	1099.1	2.4	0.26	98

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