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Research Paper Physics

Basic CS-MCM-41: Synthesis , Characterization and Activity in Synthesis of Methine Dyes as Green Chemistry Approach

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ABSTRACT

The objective of the present study is to provide Cs-MCM-41 as catalyst for the Knoevengel condensation of salicylaldehyde with ethyl cynoacetate. Cesium 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 cesium loading on the basic properties of MCM-41 was also studied.

KEYWORDS : Cs-MCM-41, 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[1]:

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[2,3] are like ordinary porous materials (for example, a sponge) except the pore sizes are in the range of 20-500 A^0 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[4] of silicate/aluminosilicate mesoporous molecular sieves (M41S) with exceptionally large uniform pore structures[5,6]. 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-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 aldehydes[7]. 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 cephalosporins4, modified penicillin, oxygen bridged tetrahydropyridones, isourases, etc. The amide obtained from 3-cyanocoumarines exhibit specific inhibitor of α-chymotripsin, human leukocytic elastase and polymeric compounds of biological importance.

2. Methods and Materials:

2.1 Chemicals:

Cetyltrimethyl ammonium bromide (Spectrochem), Aqueous ammonia (25 wt. %, Fisher Scientific), Tetraethyl orthosilicate (TEOS, Aldrich), Cesium chloride(loba chemie), Dimethyl sulpoxide (DMSO, Fisher Scientific), Salicyaldehyde (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, MCM 41 was synthesized by hydrothermal method followed by post modification, ion exchange of cesium transition metal ion. In the typical synthesis, cetyltrimethyl ammonium bromide 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 tetraethyl orthosilicate was added dropwise under vigorous stirring to get white precipitate . the molar composition of the resultant gel was 1TEOS: 0.152CTAB: 2.8NH_3: 141.2H_2O. This gel was stirrered 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 power was calcined at 823 K for 5 hr at the rate of 1^0/min to expel the template. The synthesized Si-MCM-41 is then converted in its H-form for further modification using batch-ion exchange method to obtain basic material. In view of this H form of the Si-MCM-41 was exchanged using three different aqueous solution of Cesium chloride.. The three different catalyst were prepared with three different weight percentage *viz* 2wt%Cs-MCM-41, 4wt%Cs-MCM-41 and 6wt%Cs-MCM-41.

2.3Characterization:

The synthesized Si-MCM-41 and its modified forms were characterized by different tools to identify phase purity, morphological and structural parameters such as:

- Power X-ray diffraction: The powder patterns were obtained using Cu Kα radiation on a Rigakau diffractometer. The samples were scanned for 2θ from 1 to 100
- FI-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:

Number of attempts have been made to test catalytic activity of Cs-

MCM-41 in Knoevenagel condensation reaction. All the catalytic reactions were carried out in a round bottom flask with a magnetic stirrer immersed in oil bath. The catalyst Cs-MCM-41 was heated in the muffle furnace at 373 K for 2 hr so as to evaporate the moisture before every attempt. In a typical experiment, 9.55 mol (1.16 g) of salicyaldehyde, 9.55 mol (1.01 g) of ethyl cynoacetate 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 and then dried 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-41, H-MCM-41 and Cs-MCM-41 samples with different wt.% of Cs (2wt.%, 4wt.% and 6wt.%) respectively are presented in Figure1 (a, b, c, d, e) respectively.

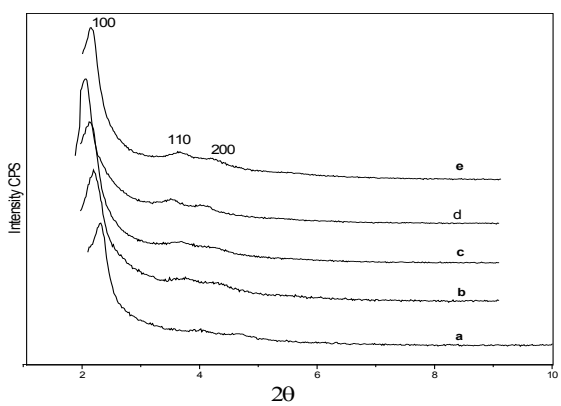


Figure1: Powder XRD Patterns of MCM-41(e), H-MCM-41(d), 2wt%Cs-MCM-41(c), 4wt%Cs-MCM-41(b) and 6wt%Cs-MCM-41(a)

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 Si-MCM-41, H-MCM-41, 2wt%Cs- MCM-41, 4wt%Cs- MCM-41 and 6wt%Cs-MCM-41 samples are given in Table 1. The slight increase in d-spacing and unit cell parameters of Cs-MCM-41 compared to Si-MCM-41 suggests the presence of cesium in the framework.

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 Si-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 Cs^+ percentage. This indicates the structural stability of the parent sample and presence of metal ions in the intra-crystalline voids of the Si-MCM-41.

Table 1: Physico-chemical properties of MCM-41

Sample Name	d_{100} spacing(nm)	Unit cell parameter a_0 (nm)	Spe. Surface area (m^2g^{-1})	Pore diameter (nm)	Particle size (nm)	% crystalinity
Si-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%Cs-MCM-41	4.01	4.63	949.9	2.22	0.32	84
4wt%Cs-MCM-41	4.02	4.72	1062.4	2.27	0.21	90
6wt%Cs-MCM-41	4.04	4.78	1099.1	2.4	0.26	98

However, if the 'Cs' metal ion concentration in Si-MCM-41 was 6wt%, it was 98% and then gradually decreased for 4wt% and 2wt% as 90% and 84% respectively. The BET surface areas, average pore diameters calculated from N_2-sorption isotherms of MCM-41 and Cs-MCM-41 are also presented in Table 1.

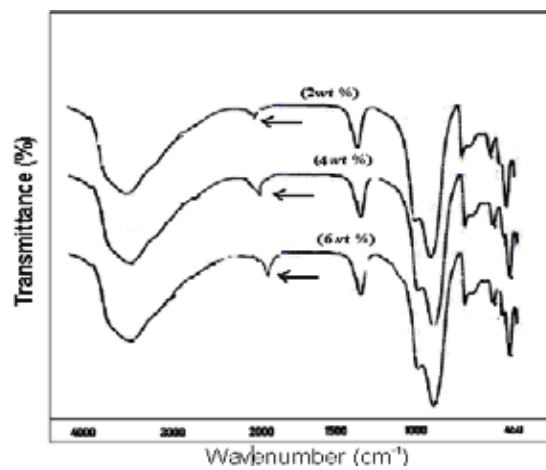


Figure 2: FT-IR of Cs-MCM-41

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 Cs-MCM-41 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^{-1}. FT-IR spectra exhibit a vibrational band at ~ 970 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 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. The Knoevenagel reaction of salicylaldehyde with ethyl cynoacetate (Scheme 1) to form α, ß-unsaturated nitriles (3-cynocoumarine) as a condensation reaction scheme was selected to examine the catalytic performance of the obtained basic forms of MCM-41. Before the reaction the required quantity of catalyst Cs-MCM-41 was heated in the muffle furnace at 373 K for 2 hr so as to evaporate the moisture adsorbed by the catalyst. Pure siliceous Si-MCM-41 treated under the same condition showed no catalytic activity. Fig. 3 gives the dependency of the yields of 3-cynocoumarine on the reaction period over various Cs-MCM-41 materials. There was no side products, only single product 3-cynocoumarine was identified based on TLC analysis. Hence it is proved 100 percent selectivity of the product. The yield of product and TLC analysis data was graphically represented in Figure 3. From figure 3 it is observed that, 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.



Scheme 1: Synthesis of 3-Cyanocumarine

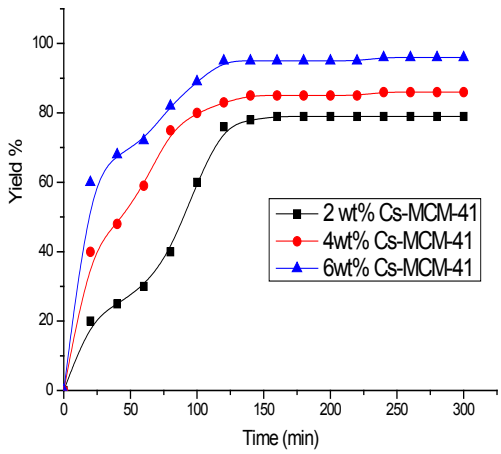
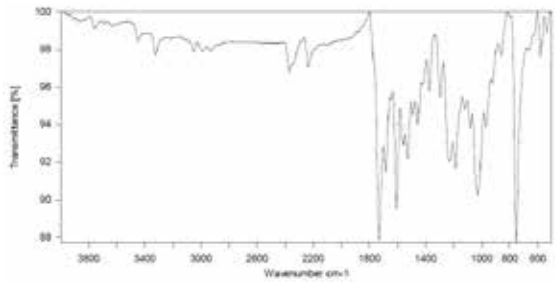


Figure 3: Knoevengel condensation of salicylaldehyde

From figure 3, it is also observed that percentage yield of the product increases from 76 % to 96 % 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 percent yield increases slightly. The product, 3-cynocoumarin was confirmed by FT-IR where the peak at 2231 cm^{-1} corresponds to cyno group and peak at 1781 cm^{-1} corresponds to carboxyl group of the product.



Figjure 4: FT-IR of 3-cynocoumarin

4 Conclusion:

Highly ordered hexagonal Si-MCM-41 and Cs-MCM-41 were synthesized and its catalytic activity was tested for condensation reaction. Here we reported the Knoevengel condensation of salicylaldehyde with ethyl cynoacetate to obtain methine dyes. The synthesis of 3-cynocoumarin *via* Knoevenagel condensation over a recoverable, ordered hexagonal Cs-MCM-41 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 about 96 % . Hence, these findings suggest that Cs–MCM-41 is a good candidate for the reported reaction.

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