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Design and Development of Amine Functionalized Mesoporous Cubic Silica Particles: A Recyclable Catalyst for Knoevenagel Condensation

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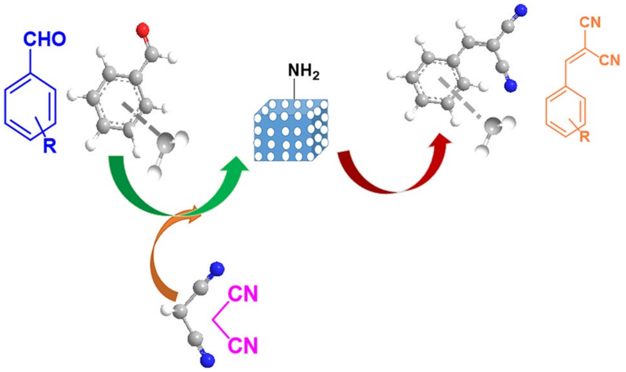
Abstract

The amine functionalized cubic mesoporous silica nanoparticles ($cSiO_2$-NH_2) were successfully synthesized through biphasic stratification approach. The synthesized material was characterised by various spectroscopic and physicochemical techniques; such as, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscope, transmission electron microscope and Brunauer–Emmett–Teller surface area. The mesoporous cubic silica nanomaterial (SiO_2-NH_2) was utilized as recyclable catalyst for liquid phase Knoevenagel condensation reaction. The catalyst could be easily recovered by simple methods like, filtration and centrifugation and be reused for multiple catalytic cycles without any noticeable effect on its activity.

Graphic Abstract



Keywords Heterogeneous catalysis < Catalysis · Mesoporous · Cubic SiO_2

1 Introduction

Industrialisation and globalization has brought various challenges that include large scale production of chemical compounds for variety of purposes. In order to meet the ever increasing requirement, scientific community needs to develop clean, sustainable and economically efficient methods. Globally, most of chemical processes and more than half of the chemical products are produced by catalysis based synthesis. Homogenous catalysts have been widely utilized for a range of synthetic reactions. Although these are more efficient than their heterogeneous counterparts but do have some limitations. The major drawback associated with heterogeneous catalysts is tedious task of separation from reaction mixtures which results in contamination of products [1]. Homogenous catalysts could not be reused for further catalytic cycles and hence these are not considered economically viable [1]. In order to overcome the limitations associated with homogenous catalysts, heterogenization happens

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to be the most viable alternative. Although heterogeneous catalysts have less active sites as compared to homogenous catalysts but these can be easily recovered from the reaction mixtures and then be reused for multiple catalytic cycles, which makes these environment friendly and economically more efficient. Various heterogeneous catalytic systems have been developed and reported in past years [2, 3], still there are problems such as, high catalyst loading, ambient reaction conditions etc. that need to be addressed. Therefore, the required demands could be furnished by utilizing properties of both homogenous and heterogonous catalysts by heterogenization of homogenous catalyst. In the last couple of years' scientific community has designed and developed various heterogeneous catalytic systems by utilizing various solid support materials such as Fe_3O_4, silica based materials and nano carbon based materials [4–11] and utilized these in various fields like catalysis, energy production, sensing etc. [12–17]. Various silica based materials with different morphologies such as spherical, cubic, tubular, fibrous, mesoporous, dendritic, 2D sheets have been utilized to heterogenize the homogenous catalysts. These materials have high specific surface area and are thermally and chemically stable and consist of surface OH groups hence could be easily functionalized with silylating agents [18, 19]. Over the period of time various reports has been published where different type of organic moieties have been immobilized over the surface of silica through covalent bond and utilized as catalyst for various organic transformations. The silica based material can be easily fished out from reaction mixture by simple centrifugation and filtration and could be utilized in further catalytic cycles.

Silica based materials having spherical structure with either mesoporous or dendritic morphology have been extensively utilized for various applications such as sensing, energy production and storage, catalysis, environment remediation, pharmaceutical industry, drug delivery etc [20–30].

Cubic mesoporous silica materials have provided an alternative and therefore these materials have been extensively utilised for various applications as sensors, catalysis and in drug delivery [31–34]. The cubic mesoporous silica have large surface area, uniform pore size and chances of pore blocking are minimum as compared to the spherical dendritic silica particles. These cubic silica particles could be an alternate to their spherical counter parts for immobilizing various catalytic active sites to synthesize heterogeneous catalyst. In the last few years some reports have been published where mesoporous cubic silica particles have been utilized for synthesizing heterogeneous catalysts [35]. Different types of basic functionalities were immobilized over the surface of silica nano spheres having different morphologies and utilised them for base catalysed reactions such as Knoevenagel's reaction, Heck reaction, Hantzsch reaction, etc. [36–38]. In continuation of our efforts to design and develop nano structured material for catalysis, [39, 40] we have immobilized amine groups over the surface of porous cubic silica particle having uniform pores and then studied its catalytic properties in Knoevenagel's condensation reaction. In recent years Knoevenagel's reaction has drawn major attention of the researchers because of its industrial applications. Its intermediate are of great importance in various biological [41], therapeutic and pharmacological products [39, 42]. Due to all these advantages of Knoevenagel's reaction various reports have been published where homogenous as well as heterogeneous catalyst were used for this reaction. Among the heterogeneous catalysts silica based mesoporous and dendritic nano spheres were immobilized with basic functionalities to catalyse this reaction. Although the result was satisfactory but due to non-uniform pore size of spherical (mesoporous and dendritic) silica particle pore blocking affected their efficiency when utilized for multiple catalytic reactions. In view of the above base functionalized cubic silica particles with uniform pore size have been anticipated to be the suitable candidates for catalysing these kind of organic reactions. In this work we have utilized base functionalized cubic mesoporous silica particles. The catalyst could be easily recycled by means of filtration and centrifugation and could be utilized for multiple catalytic cycle without any noticeable loss in activity.

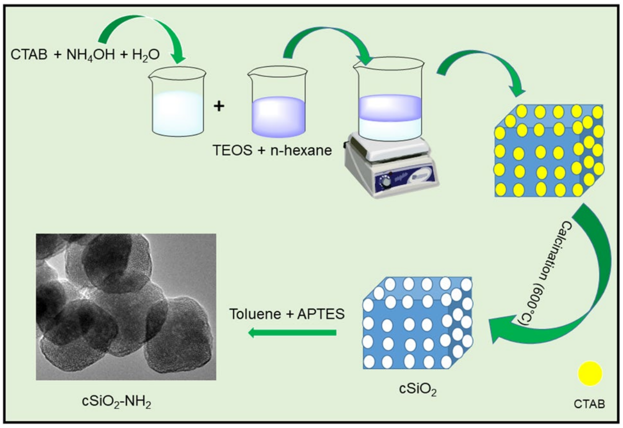
2 Experimental

2.1 Preparation of Mesoporous Cubic Silica Particles ($cSiO_2$)

The synthesis was carried out following the Stöber process [43]. In the typical synthesis (Scheme 1), 2 g of CTAB was taken in 300 mL distilled water. After dissolving CTAB, 14 mL concentrated ammonia water was poured slowly into the CTAB solution, ammonia water added until the formation of clear solution. A separate mixture of n-hexane (40 mL) and TEOS (10 mL) was added to the solution dropwise at magnetic stirrer at 35 °C. After some time (approximately 50 min) a homogenous milky solution appeared, the mixture was kept at stirrer (3000 rpm) for next 12 h. After that the product was collected and washed by ethanol and deionized water for 3–4 times then dried in vacuum oven at 80 °C for 10 h. Finally, the product was calcined in furnace at 600 °C for 6 h. The white solid sample was collected after cooling.

2.2 Preparation of Amine Functionalised Mesoporous Cubic Silica Particles ($cSiO_2$-NH_2)

The synthesised $cSiO_2$ was functionalised with amine groups as depicted in Scheme 1. The synthesized mesoporous cubic



Scheme 1 Synthesis of amine functionalised cubic mesoporous nanoparticles (cSiO$_2$-NH$_2$)

silica particles (200 mg) were mixed with 20 mL anhydrous toluene in 250 mL round bottom flask. The solution was sonicated for 30 min and kept on stirrer for another half hour. Then 0.300 mL of 3-aminopropyltriethoxysilane (APTES) was poured into the mixture. After that the reaction mixture was refluxed at 100 °C in nitrogen atmosphere for 15 h. The NH$_2$ functionalized silica was centrifuged and washed with water and ethanol. Finally, the product was dried overnight in oven at 80 °C.

2.3 Preparation of Knoevenagel Product by Utilising cSiO$_2$-NH$_2$ as Nanocatalyst

Knoevenagel condensation reaction was carried out using an aldehyde and an active methylene compound. In the typical procedure aldehyde (1 mmol) and active methylene compound (1 mmol) were taken in a round shape flask containing 5 mL ethanol and cSiO$_2$-NH$_2$ nanocatalyst (10 mg). The mixture was kept on a magnetic stirrer for appropriate time at room temperature. The reaction was monitored through thin layer chromatography (TLC). After the completion of the reaction, the catalyst was recovered through centrifugation. The product was purified after recrystallization in absolute ethanol. The leaching of catalytic active moieties in the reaction mixture during catalysis was explored by filtration test. Typically, benzaldehyde and malononitrile were used as model substrate for filtration test. After the completion of half of the reaction, the catalyst was separated from reaction mixture through centrifugation and the reaction was allowed to continue without the catalyst to check whether it proceeds or not. Recovery of the catalyst was carried out using simple centrifugation method after the formation of product.

3 Characterization Techniques

Powder X-Ray diffraction of synthesised materials were recorded (using Bruker, D8 Discover, X-ray source Cu, 3 KW) in 2θ range of 5°–60°, the scanning was performed at rate of 2° min^{-1}. Scanning electron microscope (SEM) analysis ware performed (using EVOS Zeiss scanning electron microscope) and images were recorded at different magnifications. Similarly, Transmission Electron Microscope (TEM) was utilized for analysis of morphology and shape of synthesised material (using TALOS Thermo scientific). Fourier transform infrared (FT-IR) spectrum of synthesised material was recorded in the range of 400–4500 cm^{-1} (using Perkin Elmer Spectrum RXI-Mid IR spectrometer). The total surface area and pore dimensions were analysed using BET technique (Quantachrome Instrument ASI-CI-11). TGA (Thermogravimetric analysis) was performed to check the stability of synthesized material.

4 Results and Discussion

The amine functionalized mesoporous cubic silica particles (cSiO$_2$-NH$_2$) were synthesized as depicted in Scheme 1.

Fourier transform infrared spectroscopy (FTIR) has been performed to study the covalent functionalization of amine groups over the surface of mesoporous cubic silica particles. In the FTIR spectra (Fig. 1A) of cSiO$_2$, the peaks appearing at 3375 cm^{-1} and 1085 cm^{-1} could be attributed to Si–OH groups and symmetric stretching vibrations of Si–O–Si bonds respectively. The peaks at 942 cm^{-1} and 810 cm^{-1} could be assigned to Si–O–Si asymmetric stretching and C-Si stretching vibrations, respectively. From the FTIR spectra of cSiO$_2$, it was confirmed that large number of silanol groups are present over the surface of material and could act as linker to anchor catalytic active organic moieties through covalent interaction. After functionalising cSiO$_2$ with APTES, a new peak appeared at 2960 cm^{-1} and it could be attributed to the vibration of alkyl chain of APTES. The FTIR spectra of cSiO$_2$ functioned with APTES confirms that amine groups were successfully anchored over surface of mesoporous cubic silica particles. The amine group over the surface of silica particle was quantified through CHN analysis of prepared material. In the CHN analysis of cSiO$_2$-NH$_2$ weight percent (wt%) of carbon, hydrogen, nitrogen was obtained to be 6.02, 2.13 and 4.25 respectively.

Powder X-ray diffraction (XRD) of cSiO$_2$-NH$_2$ was recorded to examine the structure of synthesised material. In the XRD pattern of cSiO$_2$-NH$_2$, a broad peak appeared between 15° to 35° that could be due to amorphous silica (Figure S1). No specific peak for amine group was observed in XRD patterns of cSiO$_2$-NH$_2$. Small angle powder XRD

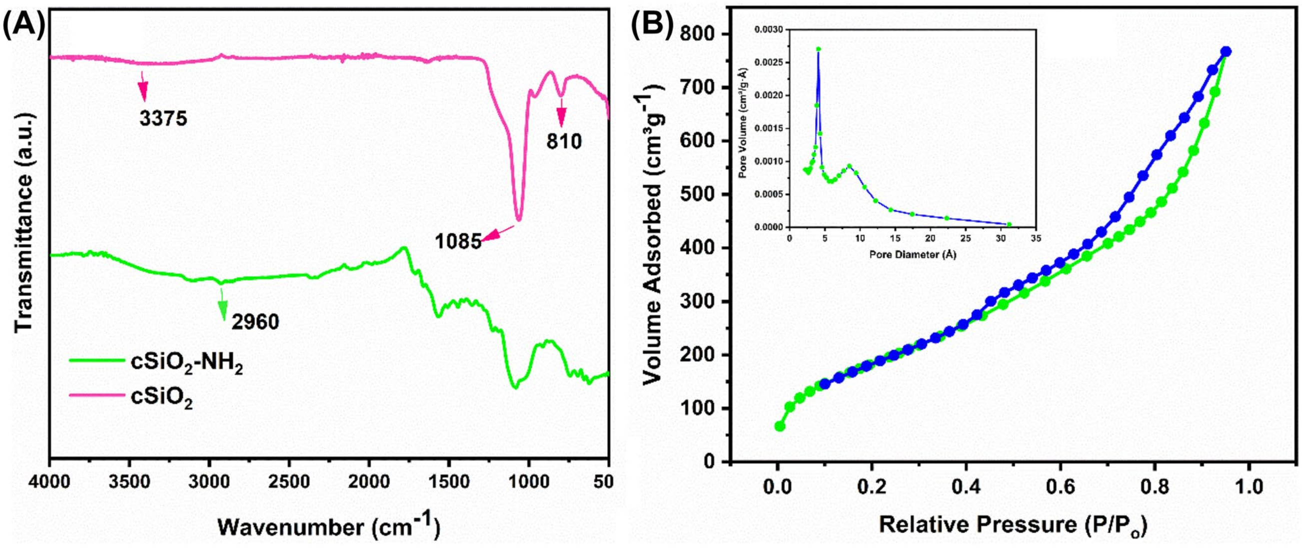


Fig. 1 **A** FTIR image of of $cSiO_2$ and $cSiO_2$-NH_2; **B** BET adsorption–desorption isotherm of $cSiO_2$-NH_2. (Inset) Pore size distribution of $cSiO_2$-NH_2

pattern of $cSiO_2$-NH_2 was analysed in order to determine mesoporosity of the synthesised material (Figure S2). The reflection plane 2θ at 3° as shown in Figure S2 could clearly indicate the mesoporous structure of the synthesized material.

As reported earlier silica particles either silica nanosphere or cubes shows weight loss of physisorbed water below 150 °C and no weight loss was reported at elevated temperature above 150 °C [35, 39]. In the TG analysis of $cSiO_2$-NH_2, the weight loss below 150 °C could be due to physisorbed water molecules (Fig. 2). The approximately 20% weight loss after 200 °C could be due to the APTES molecules anchored over $cSiO_2$.

The morphology, size and shape of prepared material were analysed by using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM images (Fig. 3D) of $cSiO_2$ could clearly confirm the synthesis of uniformly dispersed mesoporous cubic silica particle. After the immobilization of amine group, no significant change in the shape of cubic silica particle was observed (Fig. 3E, F). It remains in well-defined cubic shape without any aggregation. SEM analysis of prepared material further confirms the cubic morphology of the synthesised silica material, which is uniformly dispersed (Fig. 3A) and remains in cubic shape after anchoring it with organic moieties. SEM images also revealed that after functionalization with amine groups, $cSiO_2$ retains its cubic morphology without any aggregation (Fig. 3B, C). From TEM and SEM analysis of the prepared materials, the average particle size was found in the range of 100–150 nm.

In order to determine surface area, pore diameter and pore volume of the prepared material, BET surface area measurements experiments was performed. The N_2 adsorption–desorption experiment (Fig. 1B) of $cSiO_2$-NH_2 showed type-IV curve indicating the mesoporous nature of prepared material. The BET surface area was found to be 685.63 m^2/g and the average pore diameter and pore volume were found to 6.9 nm and 1.19 cm^3/g respectively. The obtained results indicate that the synthesized $cSiO_2$-NH_2 is highly porous material with high surface area and could be effectively utilized for catalytic purpose where substrate molecules could easily interact with catalytically active moieties.

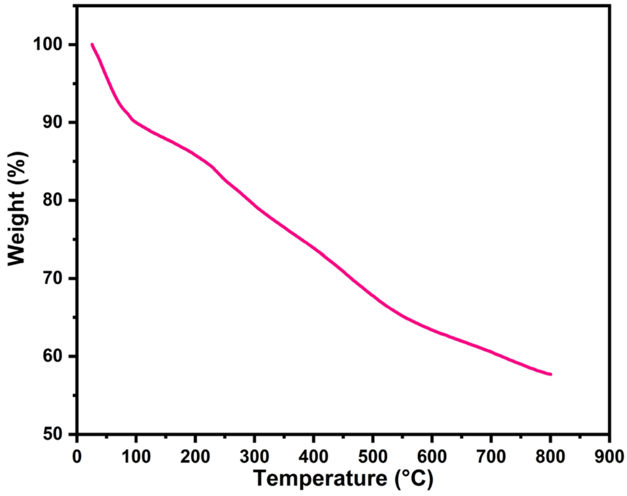


Fig. 2 Thermogravimetric analysis of $cSiO_2$-NH_2

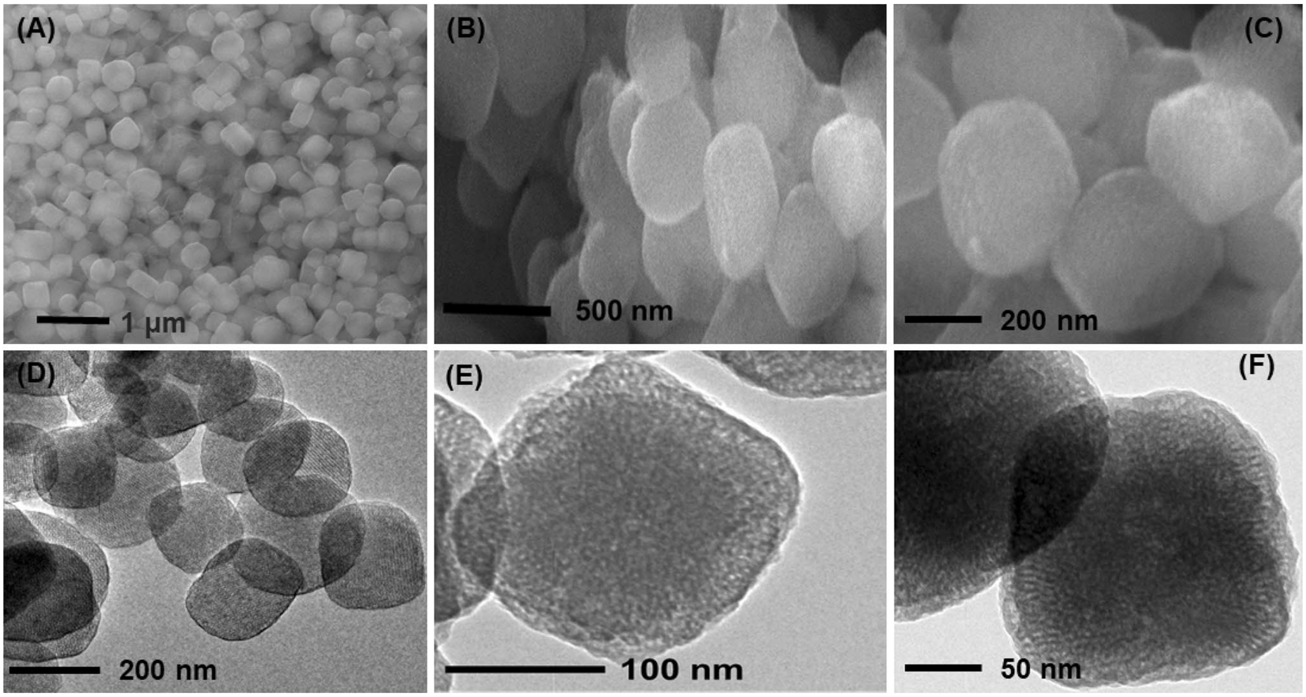
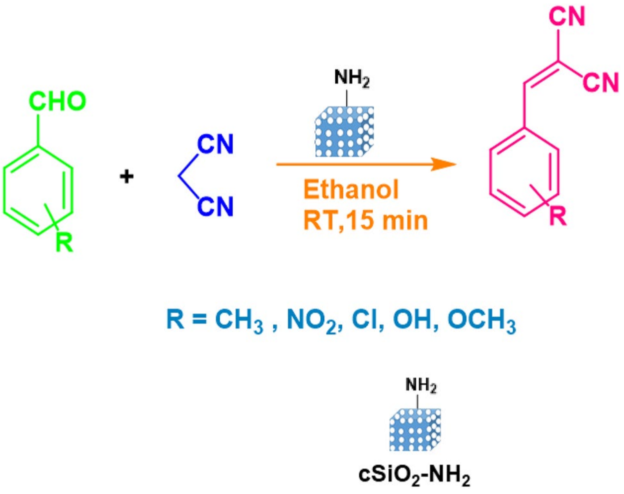


Fig. 3 **A** SEM image of $cSiO_2$; **B**, **C** SEM image of $cSiO_2$-NH_2; **D** TEM image of $cSiO_2$ and **E**, **F** TEM image of $cSiO_2$-NH_2



Scheme 2 Utilization of $cSiO_2$-NH_2 in Knoevenagel condensation reaction

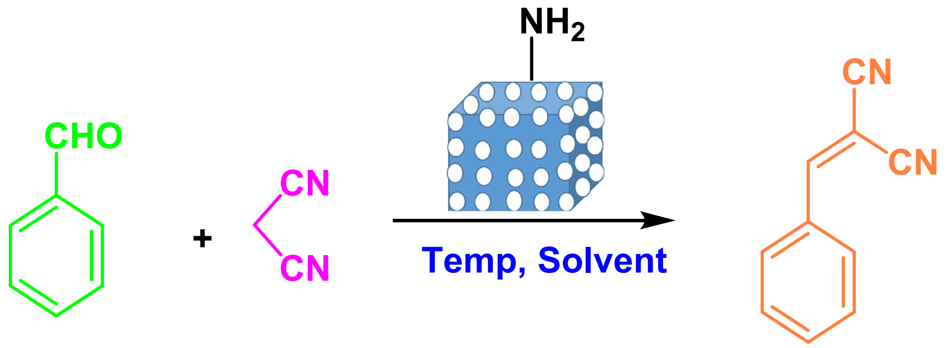
4.1 Catalytic Activity

The $cSiO_2$-NH_2 has been assessed as solid base catalyst in solvent phase Knoevenagel condensation reaction (Scheme 2). In this reaction, aldehyde was taken along with compounds bearing active methylene group under optimized conditions.

Initially, different reaction parameters were optimized through condensation of benzaldehyde and malononitrile as a sample reaction. Different type of solvent such as water, ethanol, DCM and THF were used to perform this reaction. The result obtained (Table 1) shows that maximum yield of the product was obtained when ethanol is used as solvent. Although a good result was obtained when water was used as solvent but at the elevated temperature as compared to ethanol.

Furthermore, both $cSiO_2$ and $cSiO_2$-NH_2 were utilized for Knoevenegel reaction. It was observed that the reaction proceeds only with $cSiO_2$-NH_2, which indicates that amine groups are necessary to catalyse this type of reaction. The amount of catalyst was also optimized and is presented in Table 2. Different amounts of catalyst i.e. $cSiO_2$-NH_2 were utilized and it was observed that the maximum yield of product was obtained when 10 mg of catalyst was used (Table 2, entry 2). After optimization of various reaction parameters, $cSiO_2$-NH_2 was utilized as catalyst for Knoevenegel reaction with different substrate of aldehyde and malononitrile (Table 3). Aldehyde having both electron and electron donating groups were utilized to check the efficiency of catalyst. In all the cases good to excellent yield of product was obtained. The excellent catalytic ability of catalyst could be due to mesoporous cubic morphology of the catalyst. The large surface area and pore diameter can easily facilitate the interaction of reactants with catalytic active amine sites without any pore blocking. The yield obtained for ortho substituted aromatic aldehydes was less and it could be due to steric hindrance at the reaction site.

Table 1 Optimization of the solvent for Knoevenagel reaction

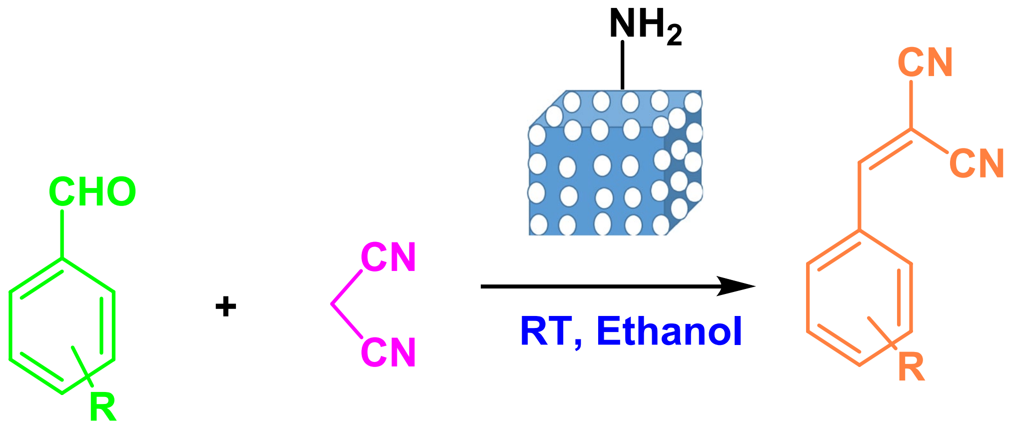


S. no	Catalyst	Solvent	Temperature (℃)	Time (min)	Isolated yield[a] (%)
1	$cSiO_2$-NH_2	Ethanol	RT	15	95
2	$cSiO_2$-NH_2	H_2O	40	15	80
3	$cSiO_2$-NH_2	DCM	50	30	60
4	$cSiO_2$-NH_2	THF	50	30	40

Reaction parameters: Aldehyde (1 mmol), Active methylene compound (1 mmol), catalyst (10 mg), RT

[a] Isolated yield

Table 2 Optimization of catalyst and catalyst amount for Knoevenagel reaction

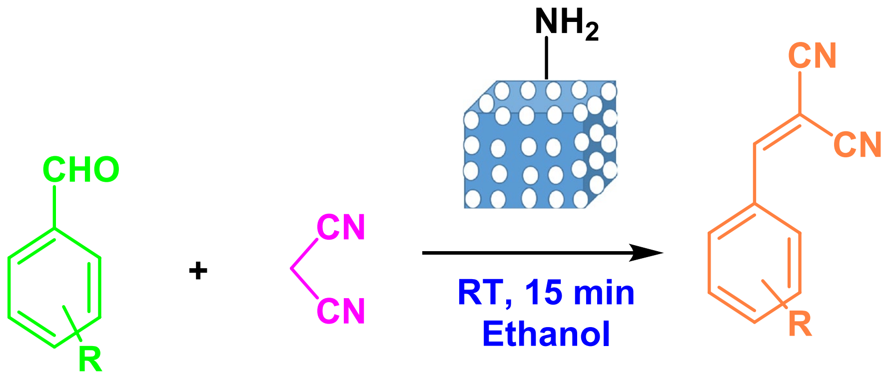


S. no	Catalyst	Catalyst amount (mg)	Isolated yield[a] %
1	$cSiO_2$-NH_2	5	80
2	$cSiO_2$-NH_2	10	95
3	$cSiO_2$-NH_2	20	95
4	$cSiO_2$	25	

Reaction parameters: Aldehyde (1 mmol), Active methylene compound (1 mmol), RT, Ethanol: 5 mL

[a] Isolated yield

Table 3 SiO_2-NH_2 catalysed Knoevenagel condensation



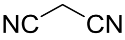
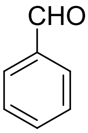
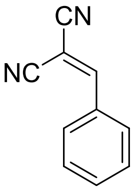
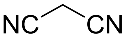
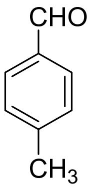
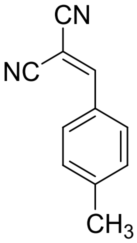
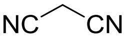
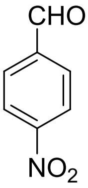
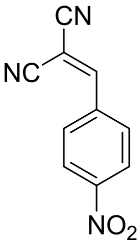
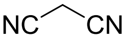
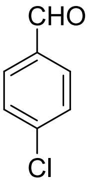
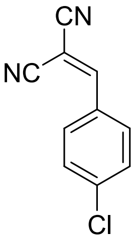
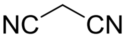
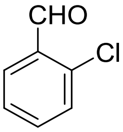
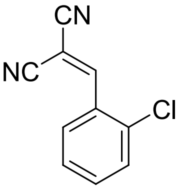
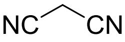
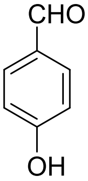
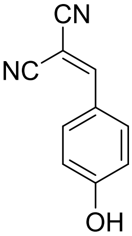
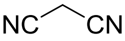
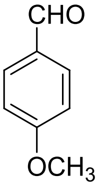
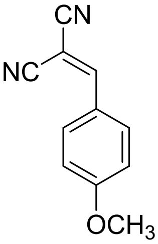
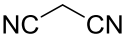
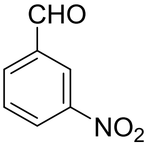
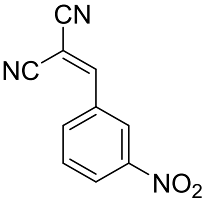
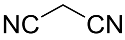
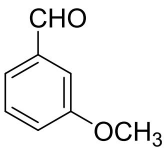
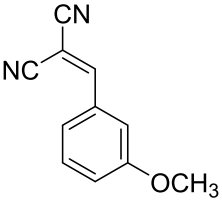
S. no	Substrate	Aldehyde	Product	Time (min)	Isolated yield[b] %	TON/TOF
1				15	95	62/248
2				15	96	63/252
3				5	99	65/780
4				10	95	62/372

Table 3 (continued)

S. no	Substrate	Aldehyde	Product	Time (min)	Isolated yield^b %	TON/TOF
5				20	91	59/180
6				15	94	61/248
7				12	92	60/300
8				10	94	61/372
9				12	95	62/310

Reaction parameters: Aldehyde (1 mmol), Active methylene compound (1 mmol), catalyst (10 mg), Room temperature, Ethanol: 05 mL. ^{b}Isolated Yield, Turnover number (TON) = Yeild (%)/ Catalyst (mol %), Turnover frequency (TOF) = TON per hour

Finally, filtration test was carried out in order to check the leaching of catalytic active moieties in the reaction mixture during catalysis. Benzaldehyde and malononitrile were used as model substrate for filtration test. The catalyst was separated during the course of reaction from the reaction mixture through centrifugation and the reaction was allowed to continue without the catalyst. It was observed that reaction could not progress further without the catalyst, which confirms the strong binding of amine group with mesoporous cubic silica particle as its leaching was not detected in reaction mixture.

The recyclability of the catalyst has been examined with benzaldehyde and malononitrile as a model reaction. After completion of reaction, the catalyst was filtered out from the reaction mixture, minutely washed with ethanol and dried under vacuum at 60 ℃. The separated catalyst was further tested for its activity in the consecutive catalytic cycle. We observed that the catalyst remains active till the 5th catalytic cycle with negligible loss in its activity (Fig. 4).

The catalytic efficiency of $cSiO_2$-NH_2 was compared with some of the earlier reported heterogeneous catalyst

(Table 4). Some of the reports suggest that alongside heterogeneous catalyst elevated temperature was utilized for the synthesis of Knoevenagel product. [44, 45] In the other reported heterogeneous catalyst although the amount of catalyst is comparatively lesser but the reaction time was longer for the synthesis of Knoevenagel product as compared to cSiO_2-NH_2. From the comparative study presented in Table 4 our prepared catalyst i.e. cSiO_2-NH_2 shows more efficient activity for the synthesis of Knoevenagel product when compared with other reported heterogeneous counterpart in terms of lesser reaction time, minimum use of catalyst amount and reaction at room temperature.

4.2 Proposed Mechanism for the Knoevenagel Condensation Reaction

A probable mechanism has been proposed for the activity of cSiO_2-NH_2 on the basis of the existing mechanism for this reaction (Fig. 5). In the first step the amine group (NH_2) of the catalyst extracts a proton of active methylene compound, which can lead to the generation of negative charge on this compound. In the second step the negatively charged species acts as the nucleophile and could attack on carbonyl carbon which results in the synthesis of *β*-hydroxyl compounds and the catalyst could be regenerated. In the final step *β*-hydroxyl compound results in the formation of the product by eliminating a water molecule [39, 46].

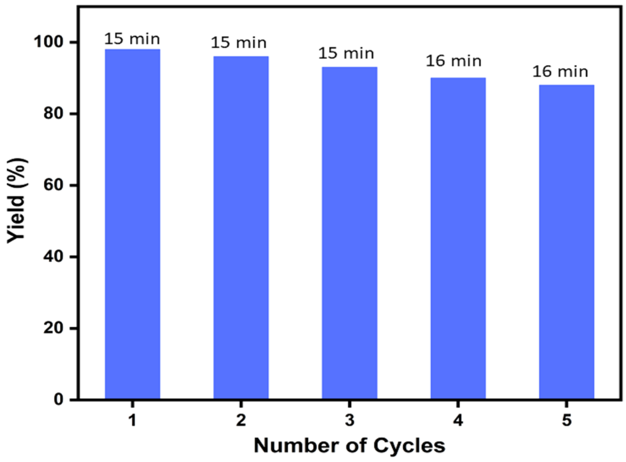


Fig. 4 Recyclability test of cSiO_2-NH_2 for for Knoevenagel condensation reaction

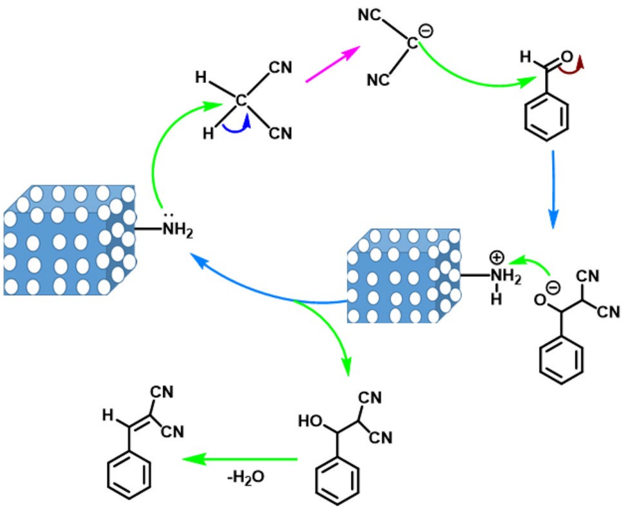


Fig. 5 Proposed mechanism for Knoevenagel condensation reaction

5 Conclusion

In the present work, the cSiO_2-NH_2 mesoporous cubic silica particles have been synthesised following the biphasic approach. The amine groups were uniformly anchored over the surface of mesoporous cubic silica particles through covalent interaction. The synthesised material was characterized by using various techniques such as, FTIR, SEM, TEM, X-ray diffraction, BET and CHN analysis. Due to high surface area and larger pore diameter, the material was employed as recyclable catalyst for Knoevenagel reaction. The use of the reported nanocatalyst has been advantageous in two ways. One is its easy separation from the reaction mixture and the other being its reuse for multiple catalytic cycles. This makes it also a cost effective process causing less environmental hazards.

Table 4 Comparison of catalytic efficiency of cSiO_2-NH_2 with earlier reported nanocatalysts for Knoevenagel condensation reaction

S. no	Catalyst	Amount of catalyst	Time	Temperature (℃)	Solvent	References
1	Chol-MSMs	50 mg	2 h	60 ℃	Ethanol	[44]
2	Fe_3O_4@SiO_2@ CuO–Fe_2O_3	30 mg	40 min	70 ℃	Water	[45]
3	PMO-IL-NH_2	0.5 mol%	90 min	RT	Solvent free	[46]
4	MSiO_2–NH_2	20 mg	5 h	RT	Ethanol	[47]
5	cSiO_2–NH_2	1.53 mol% (10 mg)	15 min	RT	Ethanol	This study

6 Supporting Information

Powder XRD of cSiO_2-NH_2, proton and carbon NMR of various products.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10562-021-03749-8.

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Declarations

Conflict of interest The authors declare no competing financial interest.

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