



Amine functionalized MCM-41: An active and reusable catalyst for Knoevenagel condensation reaction

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ABSTRACT

This paper reports preparation, characterization of amine modified mesoporous crystalline MCM-41 and its application in Knoevenagel condensation reaction. Amine modified MCM-41 was prepared by co-condensation and post-synthesis methods. The samples were characterized by X-ray powder diffraction, Fourier-transfer infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron micrograph (SEM), ^{29}Si magic-angle spinning (MAS), nuclear magnetic resonance (NMR), diffuse reflectance spectra (DRS), nitrogen adsorption–desorption and CHN analysis. X-ray diffraction patterns indicate that the modified materials retain the standard MCM-41 structure. SEM study exhibits that the arrangement of particles for 12.8% amine modified MCM-41 is well ordered and spherical in nature. CHN analysis supports that complete hydrolysis of ethoxy groups take place in 12.8% amine modified sample. From the NMR study it is confirmed that the surface coverage is 40% in 12.8% amine modified sample. The base catalytic activity of hybrid MCM-41 materials such as amine (post-synthesis and co-condensation methods) and surfactant functionalized materials for condensation reaction between benzaldehyde and diethyl malonate in solvent free, room temperature synthesis of cinnamic acid was evaluated and correlated with the surface and textural properties. Sample containing 12.8 wt% amine loaded by co-condensation method showed highest malonic ester conversion (92%) and selectivity (98%) for cinnamic acid.

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1. Introduction

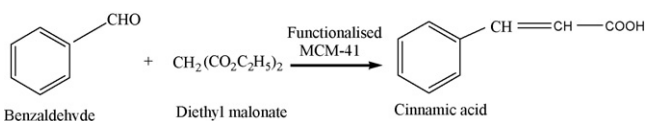
Knoevenagel condensation is one of the well-known reactions in organic chemistry right from the syntheses of small molecules to the elegant intermediates of anti-hypertensive drugs and calcium antagonists [1,2]. It is the condensation of aldehydes with active methylene group compounds, which is catalyzed by basic sites to form C–C bond. Cinnamic acid, its ester and carboxylic functional derivatives, very important components in flavors, perfumes, synthetic indigo and pharmaceuticals, are synthesized by Knoevenagel condensation. Weak bases like primary, secondary, tertiary amine and ammonium salts under homogeneous conditions generally catalyze this reaction [3–6]. The recovery of the conventional catalysts is difficult and their utilization is associated with environmental pollution.

The development of heterogeneous catalysts for special chemical synthesis has become a major area of research. The potential advantage of these materials (simplified recovery and reusability) over homogeneous systems can lead to environmentally benign chemical procedures in academia and industries. The application of

solid acidic and basic catalysts in clean technologies and sustainable chemistry is a “green” alternative for chemical processes. The materials provide high yield and selectivity along with waste reduction, easier catalyst recovery procedures and safer and easier operation methods. Now-a-days among the branches of heterogeneous catalysts, which are likely to be commercialized in near future, ordered mesoporous molecular sieves are the most convenient ones. Silica based mesoporous molecular sieves can be tailored made to acid and basic heterogeneous catalysts. Basicity in Si-MCM-41 molecular sieve is achieved by various ways. One such way is by dispersing with alkali metal oxides [7,8]. The bottleneck in this method is that the high pH used in the impregnation may damage the structure. Another way is by modifying the surfaces with organic compounds, particularly amines by impregnation method [9,10]. In this method, the cationic surfactant present in the pores is removed by calcinations before functionalization. Recently Kubota et al. used MCM-41 molecular sieve as a catalyst in Knoevenagel condensation reaction at room temperature containing its structure-directing organic cation: the cetyltrimethyl ammonium occluded in its pores [11,12]. Martins et al. have proposed that the active sites in this catalyst are the basic siloxy SiO^- anions and the reaction only occurs at the pore mouth [13,14]. In this direction, we have studied the effect of preparation method on the surface characteristics and base catalytic activity of amine functionalized MCM-41.

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Scheme 1. Schematic representation of Knoevenagel condensation reaction between benzaldehyde and malonic ester.

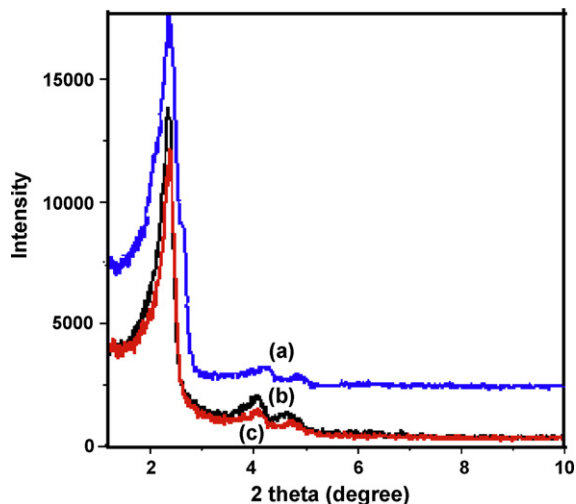


Fig. 1. XRD patterns of MCM-41 (a), MCM-41 (post) (b) and MCM-41 (co) (c).

Herein, we report a comparative study on the physico-chemical properties and base catalytic properties of amine modified MCM-41 (synthesized by both post-synthesis and co-condensation methods) and surfactant functionalized MCM-41. The main objective of the present work is to evaluate the catalytic efficiency of amine modified MCM-41 for the synthesis of cinnamic acid through Knoevenagel condensation reaction. The effects of reaction temperature, catalyst amount and molar ratio of the substrates were also examined to optimize the reaction parameters.

2. Experimental

2.1. Sample preparation

2.1.1. Post-synthesis

The parent silica MCM-41 was synthesized by a standard procedure [15]. Two grams of calcined MCM-41 was suspended in 60 ml toluene taken in a round-bottomed flask and then 1.2 ml of organic amine, aminopropyl triethoxy silane (APTES) was added drop wise. Refluxing lasted for 8 h and the resulting solid was recovered by centrifugation. It was washed carefully with ethanol followed by distilled water and then dried at room temperature for 12 h. Further the sample is termed as MCM-41 (post).

Table 1
Surface properties of amine modified MCM-41 samples.

Sample code	Amine content (wt%)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore diameter (\AA)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Micropore volume (cc g^{-1})	Unit-cell parameter (\AA)	Wall thickness (\AA)
MCM-41	0	1380	21.9	1.28	0	42.55	20.65
MCM-41 (post)	12.8	708	21.6	1.04	0.0021	44.36	22.76
2.8MCM-41 (co)	2.80	982	20.9	0.98	0.0020	45.90	25.00
4.2MCM-41 (co)	4.20	990	20.4	0.89	0.0021	46.2	25.8
10.2MCM-41 (co)	10.2	1056	20.2	0.84	0.0019	48.43	28.23
12.8MCM-41 (co)	12.8	1095	20.1	0.78	0.0018	50.02	29.92
14.6MCM-41 (co)	14.6	876	19.8	0.72	0.0017	51.14	31.34
20MCM-41 (co)	20.0	812	19.5	0.67	0.0019	52.68	33.18

2.1.2. Co-condensation

The mixture of cetyltrimethyl ammonium bromide (CTAB, 0.5 g, 5.49 mmol), 2 M of NaOH (aq) (7 ml, 14 mmol), and H_2O (480 g, 26.67 mmol) was heated at 80°C for 30 min at a pH of 12.4. To this clear solution, tetra ethyl ortho silicate (TEOS, 9.34 g, 44.8 mmol) and APTES (1.03 g, 5.75 mmol) were added sequentially and rapidly. Following the addition, a white precipitation was observed after 3 min of stirring. The reaction temperature was maintained at 80°C for 2 h. The products were isolated by a hot filtration, washed with sufficient amount of water followed by methanol and dried under vacuum. For acid extraction, the as-obtained materials (1 g) were treated with a mixture of ethanol (100 ml) and concentrated HCl (1 ml, 38% in weight) at 80°C for 6 h. The resulting (surfactant removed) solid products were filtered and washed with ethanol, and then dried at 60°C . By varying the amount of amine from 0.293 to 2.1 ml, various wt% of amine modified MCM-41 were obtained. Herein after, the samples are named: xMCM-41 (co) (where x = wt% of amine which varies from 2.8 to 20) [16].

2.2. Physico-chemical characterizations

The BET surface area, average pore diameter, mesopore distribution, total and micropore volume were determined by multipoint N_2 adsorption-desorption method at liquid N_2 temperature (77 K) by an ASAP 2020 (Micromeritics). Prior to analyses, all the samples were degassed at 200°C and 10^{-4} Torr pressure for 2 h to evacuate the physically adsorbed moisture.

The low angle X-ray diffractograms were recorded on a Philips PW 1710 powder diffractometer using Ni filtered $\text{CuK}\alpha$ in the 2θ range of $0-10^\circ$.

The FTIR spectra were recorded using JASCO FTIR-5300 in KBr matrix in the range of $4000-400 \text{ cm}^{-1}$.

The scanning electron microscopic figures of MCM-41 (co) samples were recorded using Hitachi S3400N.

TG-DTA was carried out in static air using a Shimadzu DT-40 thermal analyzer in the temperature range $30-1000^\circ\text{C}$ at a heating rate of $10^\circ\text{C min}^{-1}$.

^{29}Si MAS NMR spectra were recorded on AV300 NMR spectrometer.

UV-vis DRS spectra were recorded in VARIAN CARY 100 Conc (model-EL08013244) UV-vis spectrophotometer.

CHN analysis was carried out in a CHNS (O) analyzer (model: FLASH EA 1112 series).

2.3. Catalytic reaction

Knoevenagel condensation reaction of benzaldehyde with diethyl malonate to form cinnamic acid was carried out in a glass batch reactor fitted with a condenser. About 10 mmol of benzaldehyde (1.01 ml), 10 mmol of malonic ester (1.51 ml) and 0.025 g catalyst taken in the reactor were stirred at room temperature in a silicon oil bath. After 24 h of reaction, 50 ml of methanol was

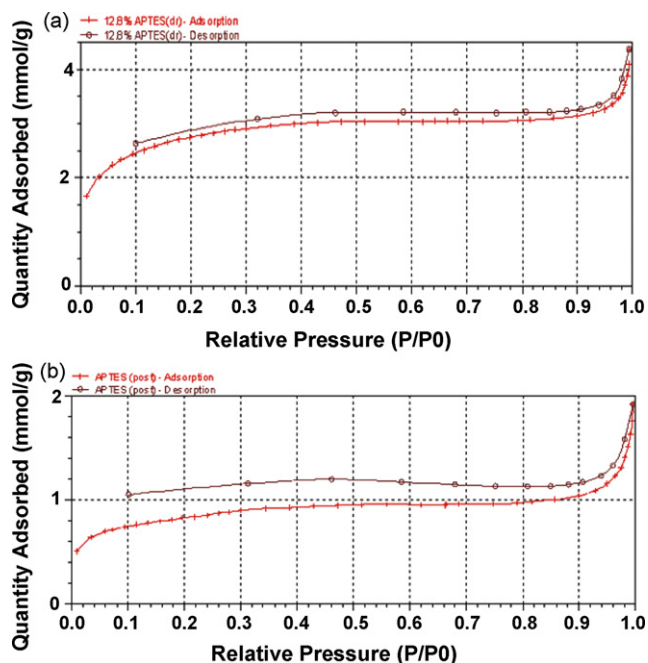


Fig. 2. N_2 adsorption–desorption isotherms of MCM-41 (post) (a) and MCM-41 (co) (b).

added in order to solubilize all the organic compounds (again stirred for 10 min) (Scheme 1). The catalyst was recovered by centrifugation for reuse and the reaction mixture was analyzed off-line by Shimadzu gas chromatography (GC-2010).

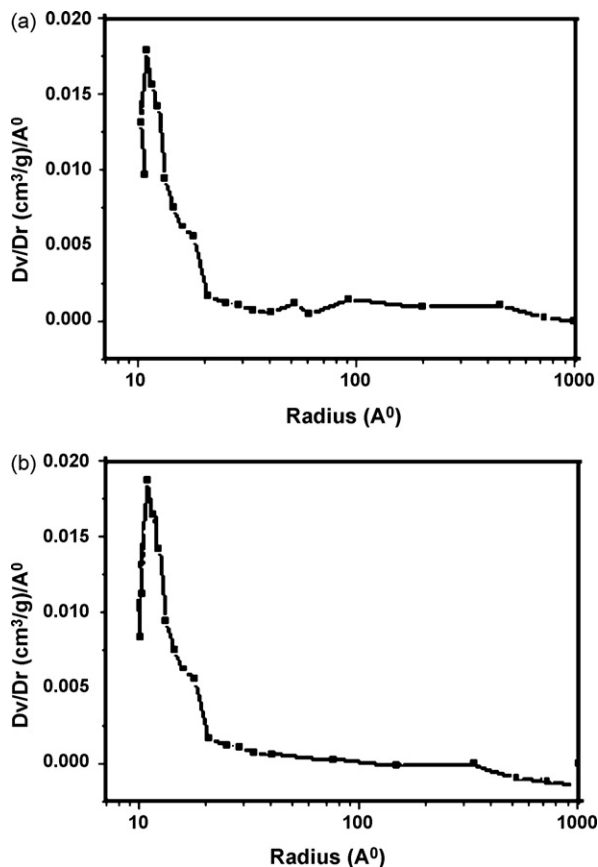


Fig. 3. BJH pore size distribution curves of MCM-41 (post) (a) and MCM-41 (co) (b).

3. Results and discussion

3.1. Characterization

3.1.1. XRD

Powder X-ray diffraction patterns of MCM-41, MCM-41 (post) and MCM-41 (co) samples are shown in Fig. 1. The samples showed a typical mesoporous structure with three sharp peaks corresponding to Miller indices (100), (110) and (200). The prominent peak at 2θ ranging between 2° and 2.5° , corresponds to (100) plane, which is indicative of standard MCM-41. The (100) peak for MCM-41 (co) has stronger intensity than that of parent MCM-41, indicating that the materials became better ordered when APTES was added to the system with TEOS [17]. The size of the mesopore decreased for the samples prepared by post-synthesis method, introduced the inherent disorder but the mesopore structure still remained intact.

3.1.2. Nitrogen adsorption–desorption isotherms

N_2 adsorption–desorption is a common method to characterize mesoporous materials. This method provides information about the specific surface area, average pore diameter and pore volume etc. BET surface area, pore size and pore volume for the synthesized materials are presented in Table 1. MCM-41 (co) has more surface area compared to MCM-41 (post). The distribution of the functional groups on the surface of the pore wall of the materials prepared by post-synthesis method is not uniform and the organic groups are mainly present near the pore mouth. Comparatively the direct synthesis pathway by co-condensation of organic silane precursors controls the resultant materials in a better way. In this method there is more uniform surface coverage of the organic functional groups with fewer blockages of mesopores. Again the surface area of MCM-41 (co) materials decreased with increase in amine

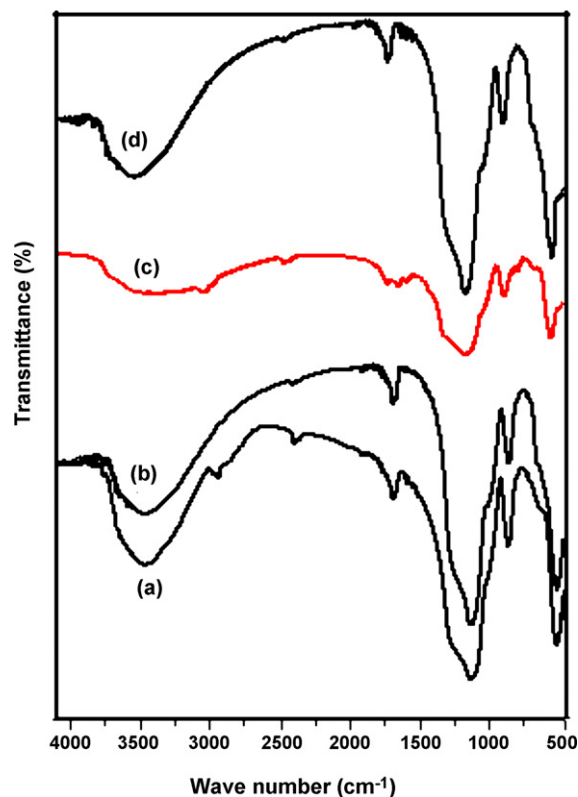


Fig. 4. FT-IR spectra of MCM-41 (heated at 450°C) (a), MCM-41 (heated at 500°C) (b), MCM-41 (as synthesized) (c) and MCM-41 (co) (d).

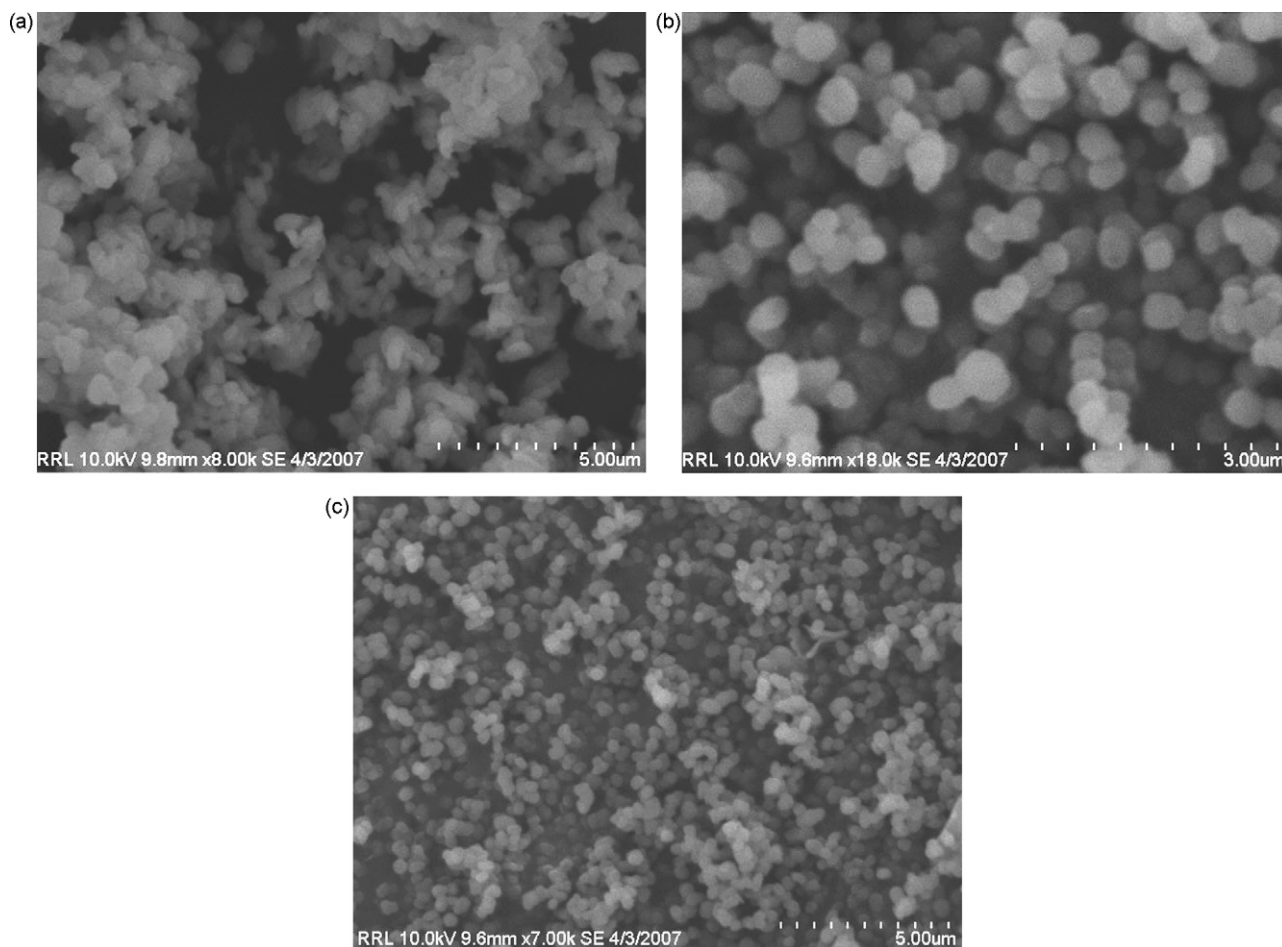


Fig. 5. SEM figures of 4.2% amine modified MCM-41 (a), 12.8% amine modified MCM-41 (post) (b) and (co) (c).

content, which attributes to pore blocking due to overloading of amines. The pore volume and pore diameter of the samples showed the same trend as that of surface area. As shown in Fig. 2a and b all the samples exhibit characteristic type IV isotherms consistent with the presence of cylindrical mesoscale pores. A hysteresis of H_3 type at $P/P_0 > 0.9$ was observed. This is due to N_2 condensation and evaporation with interparticles. Fig. 3 shows the BJH pore size distribution of MCM-41, MCM-41 (co) and MCM-41 (post). From the figure one can see that all the samples possess good mesoporous structural ordering and a narrow pore size distribution.

3.1.3. FT-IR

The FT-IR spectra of as-synthesized and amine modified samples are shown in Fig. 4. The characteristic band at $1080\text{--}1090\text{ cm}^{-1}$ is due to the Si–O stretching in Si–O–Si structure. The absorption band for H–O–H bending vibration in water is at $1620\text{--}1640\text{ cm}^{-1}$. The spectra showed a broad band around $3100\text{--}3600\text{ cm}^{-1}$, which is due to adsorbed water molecules. Presence of N–H bending vibration at 690 cm^{-1} and --NH_2 symmetric bending vibration at 1532 cm^{-1} , absent in neat MCM-41, indicates the successful grafting of organic amine onto the surface. $\text{NH}_2\text{--Si--MCM-41}$ showed the characteristic of asymmetric vibration of the CH_2 groups of the propyl chain of the silylating agent at 2935 cm^{-1} [18]. The FT-IR spectra of the sample (Fig. 4a) heated at 450°C shows the peaks for the surfactant around 2920 and 2851 cm^{-1} corresponding to n–C–H and d–C–H vibrations of the surfactant molecules. But these peaks are absent in the sample heated at 550°C (Fig. 4b).

3.1.4. SEM

The morphology of the organically functionalized silica materials studied using SEM technique is shown in Fig. 5. The SEM micrographs demonstrated a variety of particle shapes and sizes. The particles for 4.2 wt% loading are somehow worm-like (Fig. 5a). But for 12.8 wt% loading they become spherical. The particles are well ordered and arranged in the best way for 12.8% amine loading (Fig. 5b and c).

3.1.5. TG-DTA

The organic content of the surface modified silica nano-particles, assessed by TGA are shown in Fig. 6a. The weight loss of silica is relatively low due to removal of absorbed water and adventitious hydrocarbon contamination. Amine modified silica showed a higher mass loss indicating APTES was modified onto the silica.

The weight loss below 100°C corresponds to desorption of water molecules. The loss centered at higher temperature should be attributed to desorption of several organic species. The weight loss at 250°C are due to the decomposition of amine anchored to the pore wall. The third stage of weight loss above 500°C is related to surfactant removal in the parent sample. The amine content of the samples is 1.6%, 2.8%, 8.2%, 11.1% and 12% calculated from TGA study.

The differential thermal analysis curves are shown in Fig. 6b. Mainly three peaks are observed in amine modified samples. The first peak around 100°C is due to water loss. The second peak above 300°C may be due to the loss of amine, which is absent in the parent sample. The last peak above 500°C is due to surfactant removal. The middle peak is absent in the parent sample.

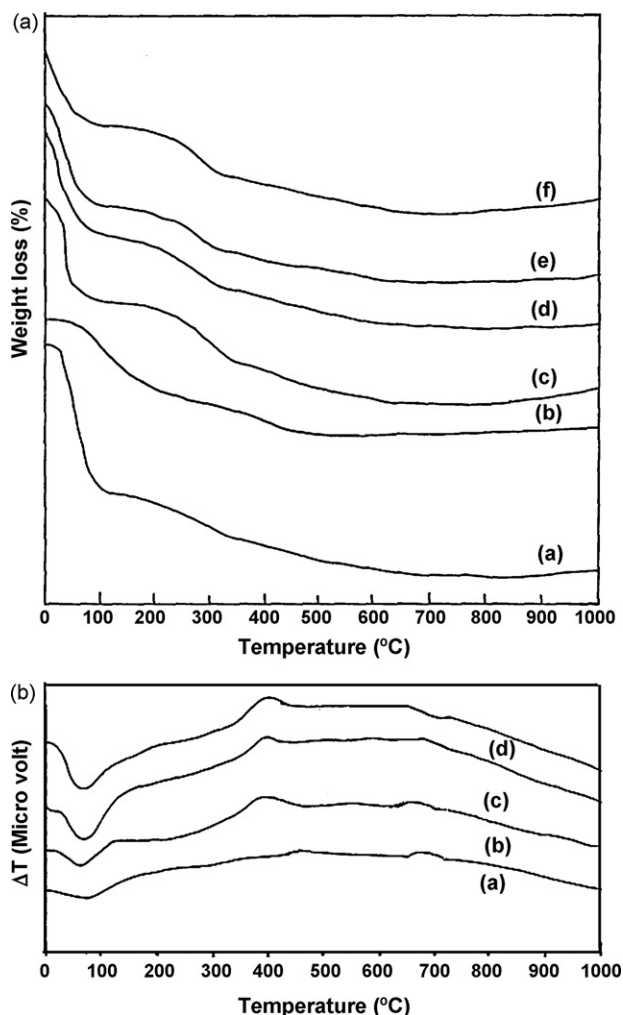


Fig. 6. (a) TGA figures of MCM-41 (a), 2.8 to 20% amine modified MCM-41 (b–f). (b) DTA figures of MCM-41 (a), 2.8, 10.2 and 12.8% amine modified MCM-41 (b–d).

3.1.6. CHN analysis

The percentage of C, H and N were calculated from CHN analysis and the results are given in Table 2. Theoretically, the C/N ratio for complete hydrolysis of ethoxy groups is 3. The C/N ratio for 12.8% amine content is 3.08, which indicates complete hydrolysis of ethoxy groups. The C/N ratio of the samples increases with increase in amine content, it is higher than 3 for samples containing more than 12.8% amine. This may be due to the fact that there is some unhydrolyzed ethoxy groups are present in the sample [19].

3.1.7. ^{29}Si MAS NMR

The NMR spectra of parent MCM-41 and 12.8% amine modified MCM-41 are shown in Fig. 7. Solid-state MAS ^{29}Si NMR experiments with cross polarization (CP) has been found to be a reliable tool to characterize various silicate materials. Si atoms of the trialkoxy silane contribute peaks in the “T” region while those in the

Table 2
CHN elemental analyses and C/N ratio observed.

Compounds	C (wt%)	H (wt%)	N (wt%)	C/N ratio
2.8MCM-41 (co)	3.56	1.37	1.31	2.72
4.2MCM-41 (co)	3.94	1.49	1.38	2.86
10.2MCM-41 (co)	4.46	1.62	1.45	3.08
12.8MCM-41 (co)	5.41	1.25	1.10	4.91
14.6MCM-41 (co)	6.84	1.19	1.09	6.23

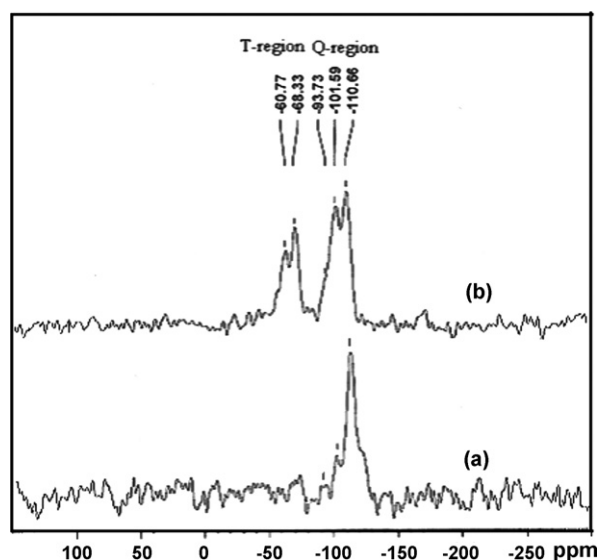


Fig. 7. ^{29}Si MAS NMR of MCM-41 (a) and 12.8% amine modified MCM-41 (b).

“Q” region arise from Si atoms of TEOS. Presence of T² and T³ functionalities confirmed the existence of the covalent linkage between the organic groups and the silica surface. Resonances around –60 and –68 ppm represent silicon atoms in positions [(=SiO)₂Si(OH)R] and [(=SiO)₃SiR], which are denoted as T² and T³ respectively. The resonance lines at –110.56, –101.56 and –93.73 representing Q⁴ [siloxane, (=SiO)₄Si], Q³ [single silanol, (=SiO)₃SiOH] and Q² [geminal silanol, (=SiO)₂Si(OH)₂] are also observed [14].

The (Q² + Q³)/Q⁴ ratio indicates the presence of silanol groups residing on the support surface. This value for amine modified samples is less than that of the parent MCM-41. Hence it indicates that the materials have few residual silanol groups with a greater degree of condensation and hydrothermal stability than that of parent sample.

The surface coverage of the mesopores with organic amine could be estimated as $SC = (T^2 + T^3)/(T^2 + T^3 + Q^2 + Q^3)$ [14]. The surface coverage of 12.8% amine modified sample is calculated as 40%. These results suggested that the organoalkoxy silanes with hydrophobic functional groups could better orient themselves around the water/micelle interface and intercalate these groups

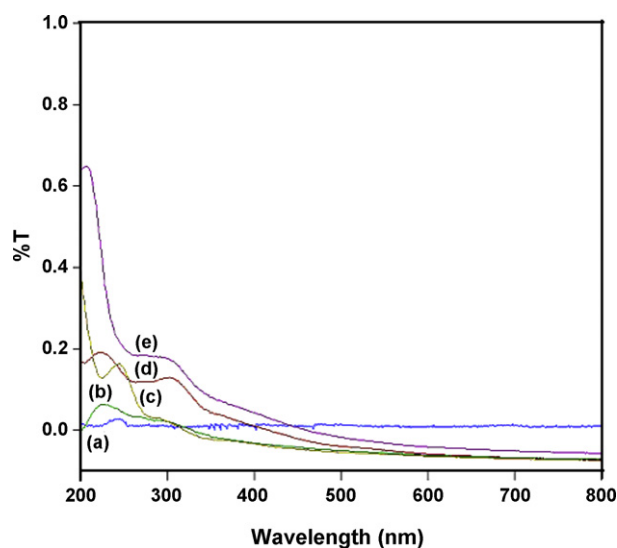


Fig. 8. DRS figures of 2.8% (a), 4.2% (b), 10.2% (d), 12.8% (e) and post (c) amine modified MCM-41 samples.

Table 3
Effect of various catalysts on Knoevenagel condensation reaction.

Catalyst	Conversion (%)	Selectivity (%)		Yield (%)	
		CA	CP	CA	CP
MCM-41 (with surfactant)	56	88	12	49.28	6.72
MCM-41 (post)	70	91	9	63.70	6.30
2.8MCM-41 (co)	78	85	15	66.30	11.70
4.2MCM-41 (co)	82	86	14	70.52	11.48
10.2MCM-41 (co)	85	89	11	75.65	9.35
12.8MCM-41 (co)	92	98	2	90.16	1.84
14.6MCM-41 (co)	81	81	19	65.66	15.34

to the hydrophobic regions of the CTAB micelles during the co-condensation reactions.

3.1.8. Diffuse reflectance spectra

The UV–vis diffuse reflectance spectra of the amine modified samples are shown in Fig. 8. All the samples show an intense peak around 200 nm, which is typical of siliceous materials. There is no significant change in the DRS spectra. This confirms that the bonding type in the silica structure remains intact after amine modification.

3.2. Catalytic activity

The synthesized material (MCM-41) did not show any activity for condensation of benzaldehyde with malonic ester to produce cinnamic acid. The malonic ester conversion is 70% for functionalized MCM-41 synthesized through post-synthesis method. The mate-

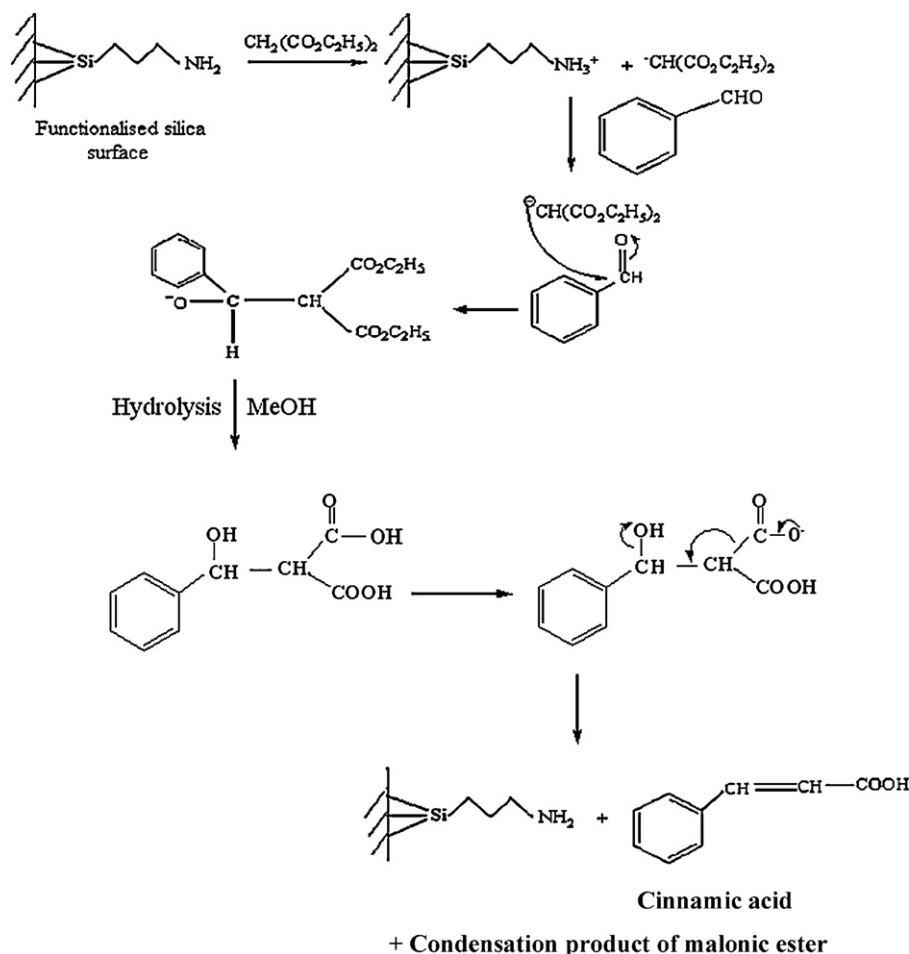
rial prepared by co-condensation method shows drastic increase in conversion. The malonic ester conversion increased from 78% to 92% with increase in amine content from 2.8 to 12.8 wt%. The percentage of conversion decreased with further increase in amine content. The percentage of yield is also highest for 12.8% amine modified sample. The percentages of conversion, selectivity and yield are shown in Table 3.

Knoevenagel condensation is mainly a base catalyzed reaction. The pores of functionalized MCM-41 are occluded by organic amine templates, which provide high activity as a base in mild conditions. The organo silane is more evenly distributed on the silica surface in case of the co-condensation method than that of post-synthesis method. So the former is more efficient as a base catalyst than the latter. The high activity for surfactant containing Si-MCM-41 is due to the presence of alkoxy anions located in the pore cavity. The reactivity trend can be rationalized by the possible mechanism illustrated in Scheme 2. Functionalized silica surface acts as the proton scavenger to generate malonic ester anion, which acts as the attacking reagent. It attacks the carbonyl group of benzaldehyde and in subsequent steps produce cinnamic acid.

Effect of various reaction parameters on the condensation of benzaldehyde with malonic ester were studied using 12.8 wt% amine modified MCM-41 (co) as catalyst.

3.2.1. Effect of temperature

The effect of reaction temperature was studied to establish the importance of activation energy in this reaction. Condensation was performed in the temperature range 20–80 °C using 12.8 wt% amine MCM-41 (co) as catalyst, keeping other parameters fixed (Fig. 9).



Scheme 2. Possible mechanism of Knoevenagel condensation reaction.

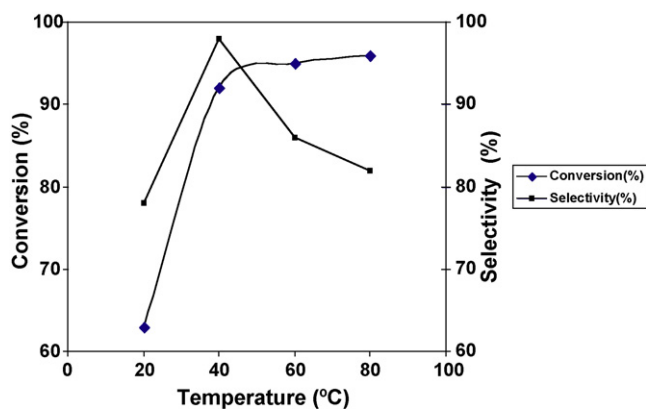


Fig. 9. Influence of temperature on Knoevenagel condensation. Catalyst, 0.025 g; reaction time, 24 h; benzaldehyde:malonic ester = 1.

The increase in percentage of conversion along with the decrease in cinnamic acid selectivity was observed on increasing reaction temperature. At the room temperature the conversion is 92% and cinnamic acid selectivity is 98%. At 50 °C the conversion of malonic ester increases to 95% and the selectivity of cinnamic acid decreases to 86% which further increased to 96% (conversion) and decreased to 82% (selectivity), respectively at 80 °C. With further increase in temperature, the conversion remained constant but the cinnamic acid selectivity decreased due to formation of more condensation products.

3.2.2. Effect of catalyst amount

The variation of catalytic activity with the amount of catalyst is shown in Fig. 10. It is not of practical interest to use a large amount of catalyst. Again the removal of high molecular weight adsorbed products from the catalyst is quite expensive too. It is observed that with increasing the amount of catalyst from 0.015 to 0.025 g, the product conversion increases from 70% to 92%. With excess amount of catalyst, the conversion obviously increased, because of the availability of more basic sites, which favors the dispersion of more active species. With further increase in catalyst amount the percentage of conversion remains nearly the same.

3.2.3. Effect of benzaldehyde to malonic ester molar ratio

Benzaldehyde to malonic ester molar ratio plays an important role for the selectivity of cinnamic acid. The cinnamic acid formation and selectivity increased with increase in the benzaldehyde to malonic ester molar ratio from 0.25 to 1 (Fig. 11). With further increase in molar ratio it decreased sharply. The low selectivity of cinnamic acid at lower concentration of benzaldehyde may be due to self-condensation of malonic ester. The selectivity of condensation product of malonic ester was observed to decrease with

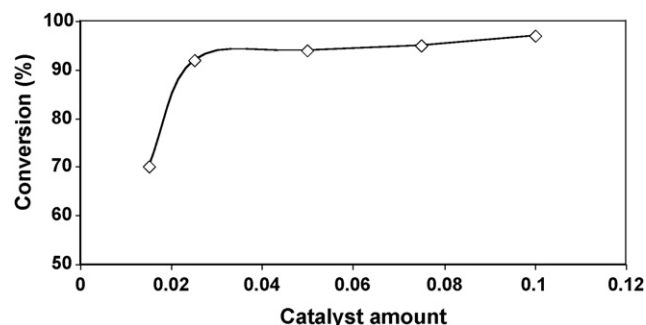


Fig. 10. Influence of catalyst amount on Knoevenagel condensation. Reaction time, 24 h; room temperature; benzaldehyde:malonic ester = 1.

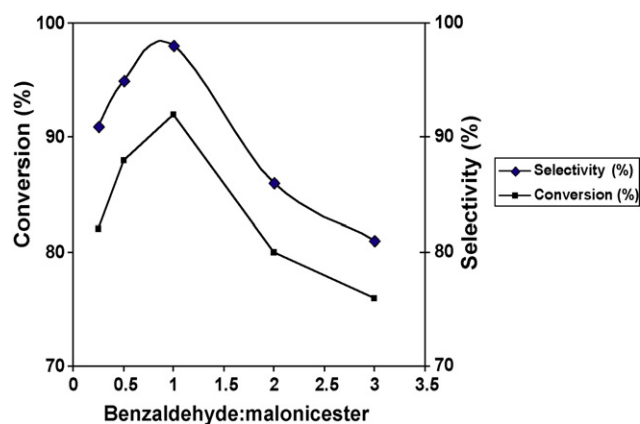


Fig. 11. Influence of benzaldehyde:malonic ester molar ratio on Knoevenagel condensation. Catalyst, 0.025 g; reaction time, 24 h; room temperature.

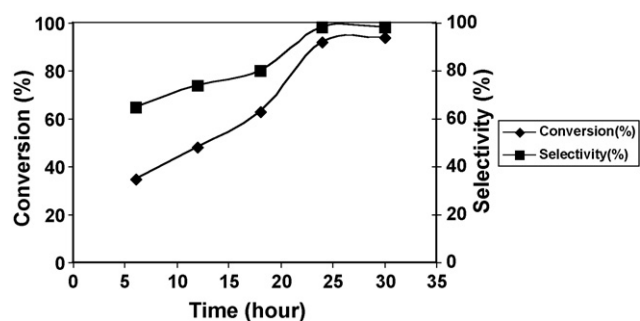


Fig. 12. Influence of reaction time on Knoevenagel condensation. Catalyst, 0.025 g; room temperature; benzaldehyde:malonic ester = 1.

increase in benzaldehyde to ester ratio. This indicates that the self-condensation of malonic ester is faster than that of benzaldehyde with malonic ester at higher concentration of ester (lower benzaldehyde to ester ratio). With increase in molar ratio the ester concentration decreases hence the condensation product gets suppressed.

3.2.4. Effect of time

The variation of product conversion and selectivity with time were studied and the results are given in Fig. 12. The reaction products were collected time-to-time and analyzed by GC. The percentage of conversion of benzaldehyde and selectivity of cinnamic acid increased with increase in reaction time. The product collected after 6 h gave 35% conversion and 65% selectivity. There is a sharp increase in both the values with time. At 24 h the conversion reached 92% with 98% selectivity. The conversion and selectivity values show no appreciable change with further rise in reaction time.

3.3. Reusability of the catalyst

The reusability of the catalyst was studied taking 12.8 wt% amine modified MCM-41 (co) in recycling experiments. In order to regenerate the catalyst, it was separated by centrifugation after the reaction, washed several times with distilled water, dried and used in the reaction with a fresh reaction mixture. The yield decrease by 4% in the regenerated sample after three cycles.

4. Conclusions

Amine functionalized MCM-41 was prepared by post-synthesis and co-condensation method and their physicochemical proper-

ties were investigated. The d-spacing, unit-cell parameters and wall thickness increase with increasing amine content in MCM-41. Surface area, pore diameter and pore volume decrease with increase in amine content. FT-IR and NMR studies confirmed that the amine retains within the framework of silica. Amine modified MCM-41 can be used as reusable heterogeneous solid base catalyst for Knoevenagel condensation reaction at room temperature under solvent free condition. About 12.8 wt% amine modified MCM-41 (co) showed highest malonic ester conversion (92%) and cinnamic acid selectivity (98%). So amine functionalized MCM-41, prepared by co-condensation method is found to be a superior base catalyst compared to post-synthesis and surface directing agent-modified samples. The functionalized materials can be reused several times.

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