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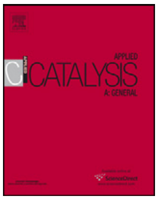

A facile method for synthesis of amine-functionalized mesoporous zirconia and its catalytic evaluation in Knoevenagel condensation

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ABSTRACT

Amine-functionalized mesoporous zirconia was prepared by a co-condensation method using silane (aminopropyltrimethoxysilane, APTES) and zirconium butoxide. The materials were characterized by X-ray diffraction, BET surface area analysis, ^{13}C magic angle spinning-nuclear magnetic resonance (NMR), Fourier-transfer infrared spectroscopy (FTIR), transmittance electron micrography (TEM), and CHN analysis. FTIR and NMR results revealed the successful grafting of organic amines onto the surface of zirconia. The catalytic activities were investigated for liquid phase Knoevenagel condensation of various aromatic aldehydes with diethyl malonate. The catalysts showed excellent yield of products at room temperature in solvent-free condition.

1. Introduction

The past decade has seen significant advances in the synthesis of new periodical mesoporous materials using surfactant micelle-templated method [1]. Many research efforts have focused on the design and preparation of organic functionalized hybrid materials [2]. The success of such investigations will prompt the utilization of these materials in catalysis [3,4], adsorptions [5–10], enzyme immobilizations [11,12], sensor design [13] and drug delivery [14]. Mesoporous materials are interesting supports for organic functional groups due to their high surface areas, uniform and controllable pore sizes, and the periodic orders of their pore packing.

Various literature reports describe methods for functionalizing the interior pore surfaces of mesoporous solids such as MCM-41, SBA-15, and zirconia [15–18]. Two approaches, namely direct synthesis (co-condensation reaction) and post-synthesis (grafting) have been widely investigated for incorporation of functional groups into mesoporous materials. In the post-synthesis grafting process, the organochlorosilanes or organoalkoxysilanes are covalently attached to the surfaces of the mesoporous materials utilizing the surface hydroxyl groups of the supported material [10,19–22]. However, this procedure normally yields low loadings and the distribution of the anchored functionalities cannot be adequately controlled. In the direct synthesis of mesoporous materials, organic silica is an attractive alternative that produces functionalized materials with high loadings and homogeneous surface coverages of the specific functionality. This one-step method involves the co-condensation of siloxane and organosiloxane precursors in the presence of the chosen templating agent [23–26].

Several aminopropyl-functionalized mesostructures have been prepared through direct assembly as well as through grafting reactions of pre-assembled frameworks using aminopropyltrimethoxysilane as the functionalizing agent for some base-catalyzed reactions [27,28]. Up to now, most of the work was on the modification of the small mesopores of MCM-type silica, on HMS-type silica, or SBA-15 mesoporous material. However, Scholz et al. reported methacrylate-functionalized silane on surfaces of zirconia. Zhou et al. reported vinyl group containing ligand functionalized zirconia [29]. Tarafdar and Pramanik reported amine-functionalized on zirconia-silica mixed oxide [30]. However, there are few reports on amine-functionalized zirconia [18]. Luo et al. reported amine-functionalized zirconia obtained by post-synthesis method [18]. However preparation of amine-functionalized zirconia using a direct method has never been reported before. Herein, we report the surface modification of mesoporous zirconia using aminopropyl triethoxy silane (APTES) by a co-condensation method. The catalyst is found robust enough to achieve high catalytic activity towards Knoevenagel condensation reactions.

2. Experimental

2.1. Synthesis of mesoporous zirconia

Mesoporous zirconium (m-ZrO_2) was synthesized by a sol–gel route using zirconium butoxide as the zirconia source and

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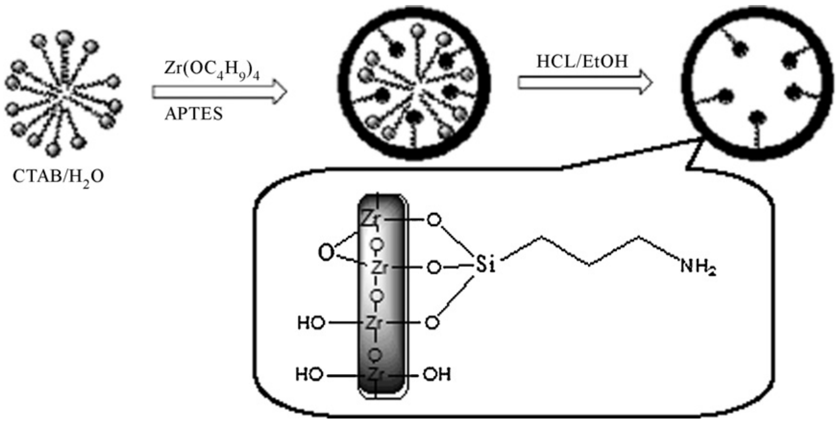
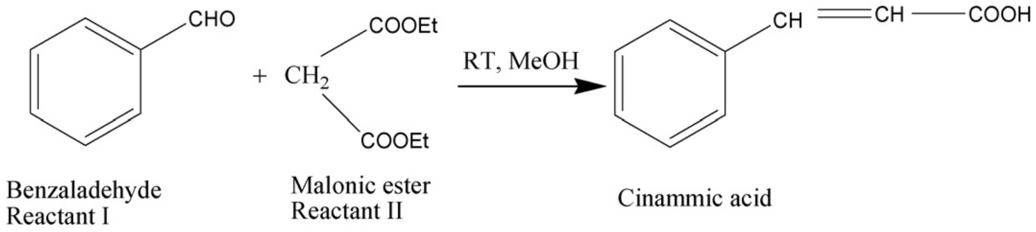


Scheme 1. Schematic presentation of synthesis of amine-functionalized zirconia.



Scheme 2. Schematic presentation of Knoevenagel condensation reaction.

cetyltrimethylammonium bromide (CTMABr) at a pH of 11.5, which was maintained by ammonium hydroxide solution. Acetyl acetone (acac) and ethanol controlled the rate of hydrolysis of zirconium butoxide in water. In a mixture of water (4 mol) and NH_3 (0.03 mol), CTMABr (0.025 mol) was dissolved and stirred for 1 h. Then a mixture of zirconium butoxide (0.1 mol), acetyl acetone (0.05 mol) and ethanol (0.5 mol) was added to the template solution slowly and this mixture was stirred for 3 h. The mixture was then refluxed under stirring for 48 h at 90 °C. The resulting solid was filtered, washed with acetone and dried for 10 h at 100 °C. To remove the surfactant species, finally the samples were heated in air at a ramp rate of 1 °C min^{-1} to 400 °C for 5 h.

2.2. Synthesis of amine-functionalized mesoporous zirconia

The mixture containing cetyltrimethyl ammonium bromide, 2 M of NaOH (aq) and H_2O was heated at 80 °C for 30 min at a pH of 12. To this clear solution, zirconium butoxide and APTES 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 a 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 0.586 to 2.1 ml, one could obtain various wt% of amine modified m-ZrO_2. Hereinafter, the samples are named: xm-ZrO_2 (co) (where x = wt% of amine which varies from 4.2 to 14.8) (Scheme 1).

2.3. Physico-chemical characterization

The BET surface area and pore size distribution were determined by multipoint N_2 adsorption–desorption method at liquid

Table 1
Surface properties of amine modified m-ZrO2 samples.

Catalyst	Surface area ($m^2 g^{-1}$)	Pore volume (cm^3/g)	Pore diameter (Å)
m-ZrO_2	156	0.25	32
4.2 m-ZrO_2	150	0.22	30
10.2 m-ZrO_2	125	0.20	29
12.8 m-ZrO_2	107	0.19	27
14.6 m-ZrO_2	97	0.19	21

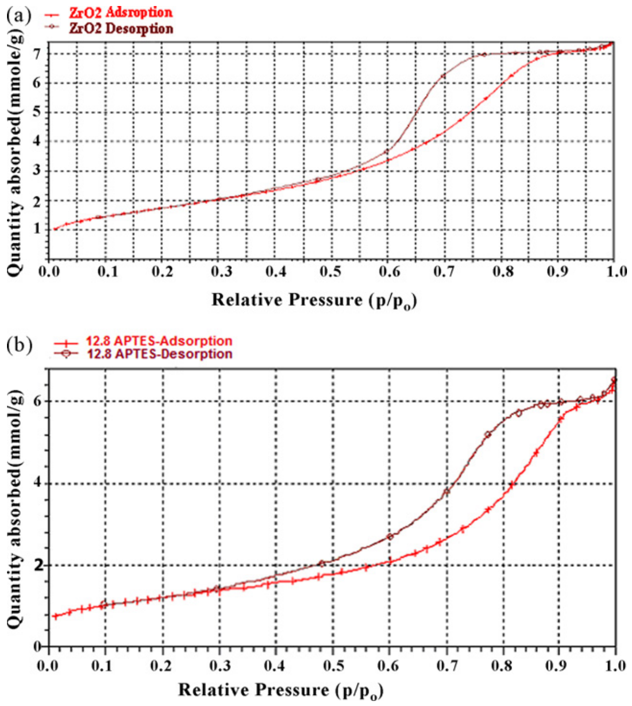


Fig. 1. N_2 adsorption–desorption isotherms of m-ZrO_2 (a) and 12.8% amine-functionalized m-ZrO_2 (b).

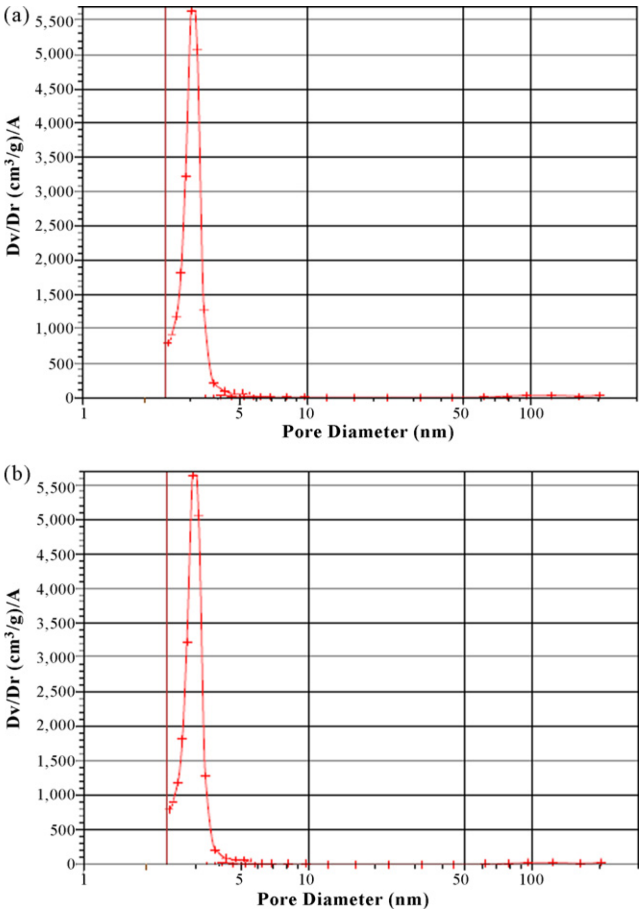


Fig. 2. BJH pore size distribution curves of m-ZrO_2 (a) and 12.8% amine-functionalized m-ZrO_2 (b).

N_2 temperature (−196 °C) by a Sorptomatic 1990 (ThermoQuest, Italy). Prior to analyses, all the samples were degassed at 200 °C and 10^{-4} Torr pressure for 2 h to evacuate the physisorbed moisture. The low-angle X-ray diffractograms were recorded on a Philips PW 1710 powder diffractometer using Ni filtered CuKα in the 2θ range of 0–10 °C. The FTIR spectra were recorded using JASCO FTIR-5300 in KBr matrix in the range of 4000–400 cm^{-1}. The scanning electron microscopic figures of functionalized zirconia samples were recorded using a Hitachi S3400N. CHN analysis was carried out in a CHNS (O) analyzer (model: FLASH EA 1112 series). ^{13}C MAS NMR spectra were recorded on an AV300 NMR spectrometer. TG–DTA was carried out in static air using a Shimadzu DT-40 thermal analyzer in the temperature range 30–1000 °C at a heating rate of 10 °C min^{-1}.

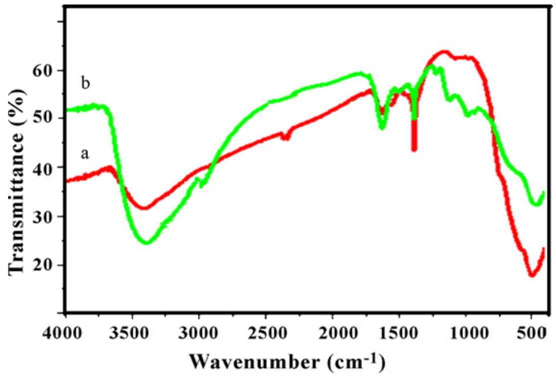


Fig. 4. FTIR spectra of m-ZrO_2 (a) and 12.8% amine-functionalized m-ZrO_2 (b).

2.4. Catalytic reaction

The 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 added in order to soluble all the organic compounds (again stirred for 10 min) (Scheme 2). The catalyst was recovered by centrifugation for reuse and the reaction mixture was analyzed off-line on a Shimadzu gas chromatograph (GC-2010).

3. Results and discussion

3.1. Characterization

The results of nitrogen adsorption–desorption analyses are shown in Table 1. The pure mesoporous zirconia dried at 400 °C

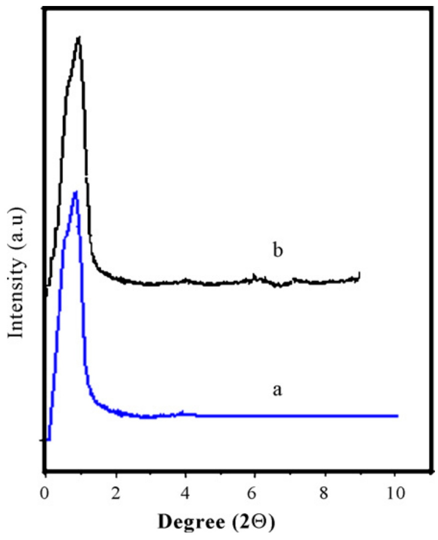


Fig. 3. XRD patterns of m-ZrO_2 (a) and 12.8% amine-functionalized m-ZrO_2 (b).

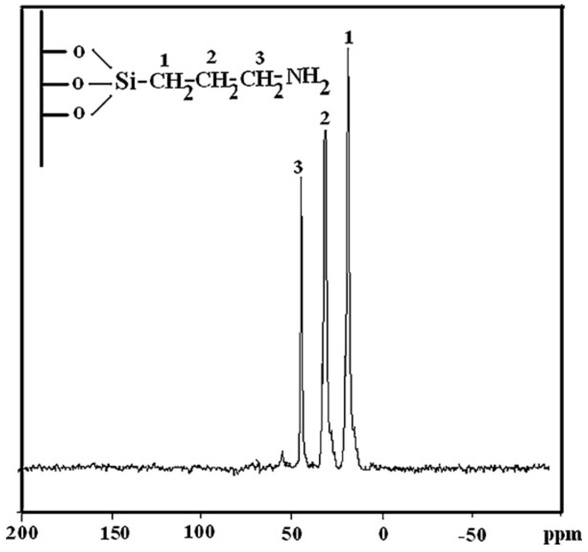


Fig. 5. ^{13}C MAS NMR of 12. 8% amine-functionalized m-ZrO_2.

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

Catalyst	Anime content (wt%)[a]	Anime content (wt%)[b]	Ratio of amine contents (catalyst/gel)	C (wt%)	H (wt%)	N (wt%)	C/N ratio
4.2 m-ZrO_2	4.2	2.9	0.69	3.66	1.36	1.31	2.79
10.2 m-ZrO_2	10.2	8.4	0.82	3.94	1.49	1.38	2.86
12.8 m-ZrO_2	12.8	11.4	0.89	4.54	1.62	1.45	3.13
14.6 m-ZrO_2	14.6	11.8	0.80	5.41	1.25	1.15	4.71

[a] Amine content in the gel.
[b] Amine content in the catalyst found from TGA analysis.

showed a surface area of 156 $m^2 g^{-1}$. But the surface area, pore volume and pore diameter of the amine-functionalized materials decrease compared to those of the parent zirconia due to the anchoring of amine groups.

N_2 adsorption–desorption isotherms of the parent zirconia and 12.8% amine-functionalized zirconia samples are shown in Fig. 1a and b. According the IUPAC classification, the N_2 isotherms are of type IV with a typical hysteresis loop of a mesoporous material. The relative pressure (P/P_0) of the inflection points is related to a pore diameter in the mesopores range and the sharpness of the step indicates the uniformity of pore size distribution.

Fig. 2 shows the BJH pore size distribution of zirconia and 12.8% amine-functionalized zirconia. From the figure, one can see that there is a slight decrease in pore diameter of the amine-functionalized sample in comparison to that of parent zirconia and both the samples possess good mesoporous structural ordering and a narrow pore size distribution.

Small angle X-ray diffraction patterns of the mesoporous zirconia and 12.8% amine modified zirconia sample are shown in Fig. 3. The low-angle XRD patterns of zirconia samples demonstrated the mesostructure because there was only one broad peak at around 1° which translates to a spacing of 6.94 nm, calculated from the Bragg Equation, $2d \sin\theta = n\lambda$. The intense and narrow XRD peak of zirconia sample suggested a relatively organized and oriented mesostructure [31]. The XRD pattern of amine-functionalized m-ZrO_2 is similar to that of m-ZrO_2.

The FTIR spectra of mesoporous zirconia and 12.8% amine-functionalized zirconia are presented in Fig. 4a and b. The FTIR spectrum of zirconia shows a broad band in the region of 3410 cm^{-1} due to asymmetric stretching of OH group and two bands at 1621 and 1386 cm^{-1} which are due to bending vibrations of – (H–O–H) – and – (O–H–O) – bonds. The band at 503 cm^{-1} resulted from the existence of both tetragonal and monoclinic zirconia. The spectra at 730 cm^{-1} are attributed to the presence of the Zr–O bond (Fig. 4a). The presences of N–H bending vibration at 690 cm^{-1} and of NH_2 symmetric bending vibration at 1532 cm^{-1} of amine-functionalized ZrO_2 nanoparticles, absent in neat zirconia, indicate the successful grafting of organic amine onto the surface. Two new absorption bands, namely, 800–1200 and 2800–3000 cm^{-1}, are observed on the spectrum of amine-functionalized ZrO_2 nanoparticles, suggesting that APTES has been successfully attached to the ZrO_2 nanoparticles.

The ^{13}C MAS NMR spectra of 12.8% amine modified zirconia sample are shown in Fig. 5. The sharp peak at 11.4 ppm is ascribed to the carbon atom bonded to silicon. The signal at 25.4 ppm corresponds to methylene group carbon and the peak around at 45 ppm can be attributed to methylene group carbon atoms attached to the anime group.

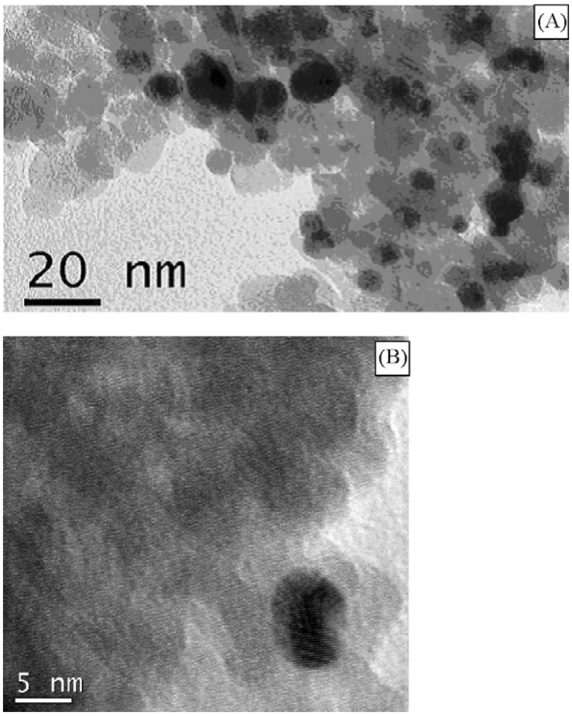


Fig. 6. TEM figures of 12.8% amine-functionalized zirconia.

Table 2 illustrates the percentage of C, H and N content which was calculated from the CHN analysis. The C:H:N ratio does not remain constant in all the cases, as it depends on several factors such as the degree of functionalization on zirconia surface and the hydrolysis of ethoxy group of APTES. The N content increases with increase in amine content up to 12.8% and thereafter it decreases on further increase of APTES content. This may be due to the introduction of a large amount of APTES in the gel. This results in competition between the APTES units to attach on the zirconia surface. Probably partial hydrolysis of ethoxy group takes place for maximum attachment of APTES. Upon washing, a part of the amine moiety may be

Table 3
Conversion and selectivity of various catalysts towards Knoevenagel condensation reaction.

Catalyst	Conversion %	Selectivity (%)	
		Cinammic acid	Other
m-ZrO_2	5	51	49
4.2 m-ZrO_2	67	77	23
10.2 m-ZrO_2	75	91	7
12.8 m-ZrO_2	89	98	2
14.6 m-ZrO_2	84	99	1
m-ZrO_2 (with surfactant)	54	56	44

Table 4a
Knoevengel condensation of various aldehydes with diethyl malonate under solvent-free condition.

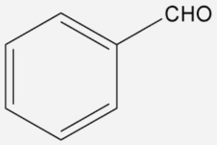
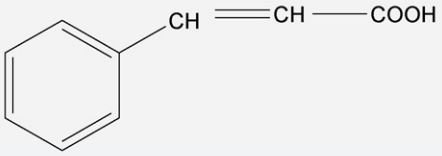
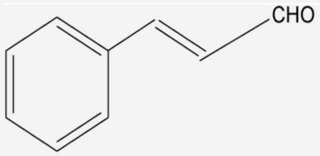
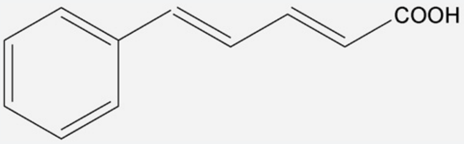
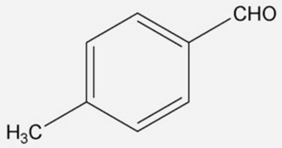
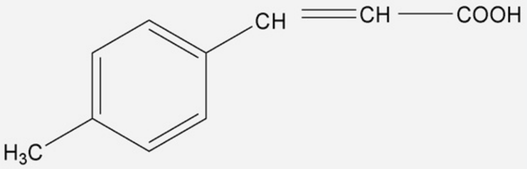
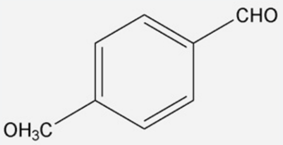
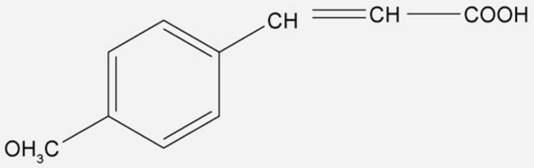
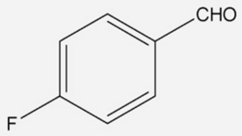
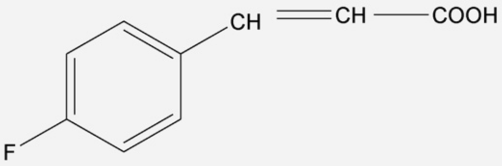
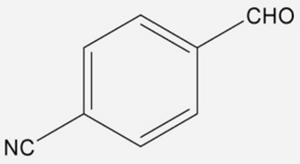
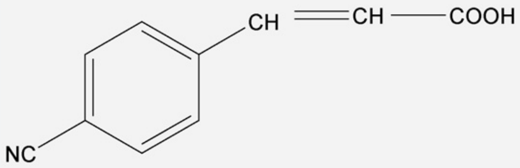
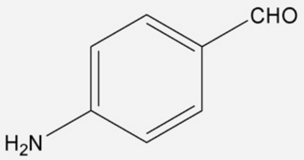
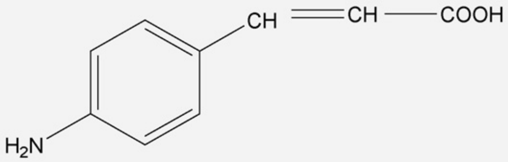
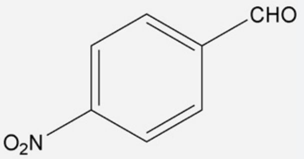
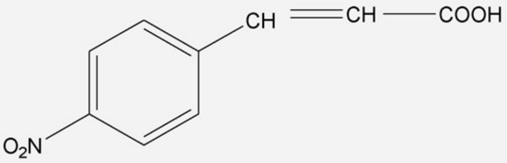
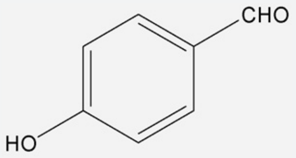
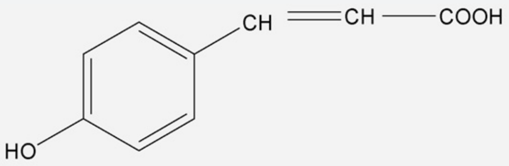
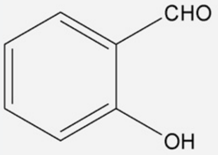
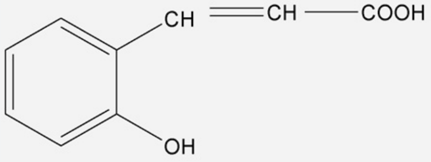
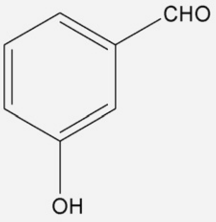
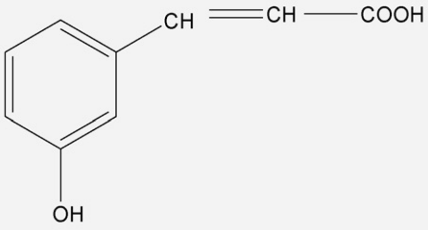
Reactant I (aldehyde)	Product (major)	Conversion (%)	Selectivity (%)	
			Major	Others
		89	98	2
		95	98	2
		80	85	15
		82	86	14
		93	94	6
		97	99	1
		85	90	10
		98	99	1
		83	90	10

Table 4a (*Continued*)

Reactant I (aldehyde)	Product (major)	Conversion (%)	Selectivity (%)	
			Major	Others
		83	88	12
		87	90	10

leached out due to lack of strong binding. Theoretically, the C/N ratio for complete hydrolysis of ethoxy groups is 3. The C/N ratio increases with increase in amine content of the sample. It is 4.7 for samples containing more than 14.6% amine which may be due to the presence of some unhydrolyzed ethoxy groups in the sample [32]. The ratio of amine in each catalyst to the corresponding ratio in the gel is incorporated in Table 2.

The extent of amine functionalization on the surface of zirconia samples is calculated from TGA and the results are presented in Table 2. The amine content is found to be 2.9%, 8.4%, 11.4% and 11.8% for the samples with *x* values of 4.2, 10.2, 12.8 and 14.6, respectively.

The TEM image (Fig. 6) also proved that the zirconia possessed a worm-like framework, which was very similar to that of the MSU silica [33]. As can be seen from the figure, the pore system is well connected and is open to the surface, which is advantageous for catalysis applications. Additionally, the pore size is very uniform and the average pore diameters are 3–5 nm, which in line with the N_2-adsorption analysis results.

3.2. Catalytic activity towards Knoevenagel condensation

Liquid phase Knoevenagel condensation of benzaldehyde and diethyl malonate was carried out over zirconia and amine-functionalized zirconia. The yields of cinnamic acid over various catalysts are presented in Table 3.

In the case of unpromoted zirconia, the conversion was only 5%, whereas the amine-functionalized zirconia sample shows significant conversion, which clearly signifies the involvement of amine

Table 4b
Effect of various active methylene groups towards Knoevengel condensation.

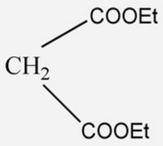
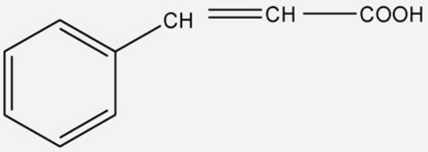
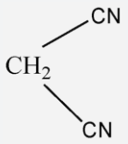
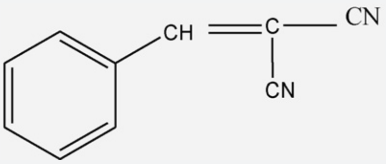
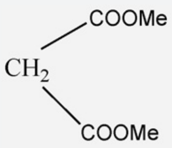
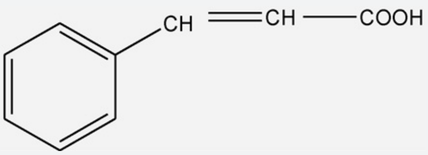
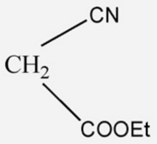
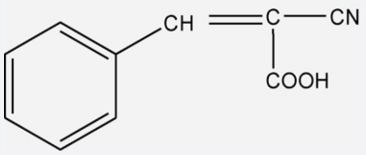
Reactant II (activated methylene group)	Product (major)	Conversion (%)	Selectivity (%)	
			Major	Others
		89	98	2
		95	99	1
		80	89	11
		92	95	5

Table 5
Knoevenagel condensation over 12.8% amine-functionalized zirconia and comparison of the data with other reported methods.

Catalyst used	Conversion (%)	Temperature (°C)	Reference
12.8% amine-functionalized zirconia	89	RT	[This method]
Amine-functionalized SBA-1	98	105	[34]
Amine-functionalized MCM-41	81	RT	[35]
Functionalized γ-Fe_2O_3	50	50	[36]

group in the reaction. With increase in amine content the selectivity of cinammic acid increases up to 12.8%, then it decreases with further increase in amine content.

The Knoevenagel condensation reaction mechanisms on amine-functionalized zirconia catalysts are described by the reaction, where the catalyst activity is mainly due to the structural basicity of the amine group. The reaction is initiated when a benzaldehyde molecule reacts with a surface amine to form an amine compound. The addition of diethyl malonate and the subsequent molecular rearrangement produces the final reaction product and water molecules. In the reaction, the grafted organic amine acts as a Bronsted base.

Several organic substituents on aldehydes including 3-phenyl, prop-2-enal were subjected to the Knoevenagel condensation using 12.8% amine-functionalized zirconia as catalyst and the results are summarized in Table 4a. The presence of electron withdrawing substituents (nitro group, −CN and halo group) on the aromatic ring substantially increases the conversion while in case of electron donating group (–CH_3, –OCH_3, –NH_2, etc.) the conversion decreased. In the cases of electron withdrawing groups the possibility of attack of the carbanion (generated from the active methylene group) at the carbonyl carbon is enhanced compared to that of electron donating groups.

Several active methylene compounds were subjected to Knoevenagel condensation using 12.8% amine-functionalized zirconia as catalyst; the results are summarized in Table 4b. Those substituents having more electron withdrawing nature stabilize the carbanion (due to resonance) compared to those having electron donating nature. So malononitrile shows the highest conversion among all the substrates. Table 5 presents a comparative feature between the performances of 12.8% amine-functionalized zirconia with other reported catalysts for Knoevenagel condensation reaction.

3.3. *Reusability of the catalyst*

Reusability of the catalyst was investigated by carrying out repeated runs on the same batch of the used 12.8% amine-functionalized zirconia as catalyst towards Knoevenagel condensation of benzaldehyde and diethyl malonate. The catalyst 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 decreased by 3% in the regenerated sample after three cycles.

4. Conclusions

a. The amine-functionalized zirconia exhibits excellent catalytic activity for Knoevenagel condensation of aldehydes with diethyl malonate under solvent-free conditions.
b. FTIR and NMR results revealed the successful grafting of organic amines onto the surface of zirconia.
c. Among all the catalyst, the 12.8 wt% amine-functionalized zirconia showed the highest yield (89%) of cinnamic acid.
d. The reusability test exhibits the good recycling capacity of the functionalized material.

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