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Amine-functionalized ionic liquid-based mesoporous organosilica as a highly efficient nanocatalyst for the Knoevenagel condensation†

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A novel amine-functionalized ionic liquid-based periodic mesoporous organosilica (PMO-IL-NH_2) was prepared and characterized and its catalytic performance was investigated in the Knoevenagel reaction. PMO-IL-NH_2 was prepared by simultaneous co-condensation of 3-aminopropyltrimethoxysilane, an ionic liquid and tetramethoxysilane in the presence of a surfactant template under acidic conditions. The material was characterized by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, thermal gravimetric analysis (TGA), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The catalytic application of PMO-IL-NH_2 was then successfully carried out in the Knoevenagel condensation of a variety of different aldehydes with ethyl cyanoacetate under solvent-free conditions at room temperature, giving high to excellent yields of the corresponding products. The catalyst was also recovered and reused several times without a significant decrease in either activity or product selectivity. The TEM image and nitrogen sorption analysis of the recovered catalyst after the fifth reaction cycle confirmed its high stability and durability under the applied reaction conditions.

Introduction

The Knoevenagel reaction is an important process for the formation of carbon–carbon double bonds involving the one-pot condensation of active methylenes with carbonyl compounds followed by a dehydration reaction.[1,2] This has been widely applied for the preparation of a wide range of substituted alkenes and biologically active compounds that are important in natural product synthesis.[1–3] The Knoevenagel reaction has traditionally been performed under homogeneous conditions in the presence of either organic or inorganic base catalysts such as pyridine, piperidine, pyrrolidine, morpholine, triethylamine, KF, K_2CO_3, $NaHCO_3$, K_2HPO_4 and so on.[1,2,4] Moreover, many Lewis acids such as $ZnCl_2$, LiCl, $Mg(ClO_4)_2$, $TiCl_4$, $CuCl_2$, Al_2O_3, $LaCl_3$, $NbCl_5$, *etc.* have also been successfully employed as catalysts for this important condensation reaction.[5,6] However, the aforementioned systems have restrictions including catalyst recovery, product separation, environmental pollution and high reaction temperatures. Therefore, heterogenization of the corresponding catalysts has become a significant tool in order to solve these concerns.[7–11] Along this line, several heterogeneous catalysts based on resins, zeolites, hydrotalcites, heteropolyacids, metal–organic frameworks and organo-functionalized silicas have been introduced for catalyzing the Knoevenagel condensation under heterogeneous conditions.[7–15] In this context, amine-functionalized ordered mesoporous silicas are more attractive due to their high surface area, uniform pore structure, good recoverability and reusability as well as isolated catalytic-amine sites in their channels.[14,15] While these achievements have removed restrictions related to catalyst recovery and product separation, however, in most cases disadvantages such as high catalyst loading, the use of volatile organic solvents and low yield of products are still observed. Therefore, the preparation and development of effective heterogeneous catalyst systems with high efficiency and low loading, while demonstrating excellent reusability features, is still an important challenge in this area.

On the other hand, ordered mesoporous organosilicas (OMOs) with uniform pore sizes larger than 2 nm, large pore volumes, high surface areas and unique surface chemistry play a significant role in the areas of adsorption, catalysis, gas storage, solid phase extraction and so forth.[16–18] Among the different kinds of OMOs, periodic mesoporous organosilicas (PMOs) built from bridged organosilane precursors, $[(RO)_3SiR'Si(OR)_3]$, have attracted tremendous attention because they offer unique properties such as uniform distribution and high loading of organic functional groups in the framework as well as improved thermal and mechanical stability.[19] To date, many PMOs have been prepared using

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different precursors based on alkyl, alkenyl, aryl and heteroaryl groups; however, many of the incorporated organic functional groups are not suitable to be used for catalytic applications.[19,20] A valuable achievement to overcome the aforementioned problem is the creation of bifunctionalized periodic mesoporous organosilicas (BPMOs) combining the unique framework properties with specific active sites.[20,21] In the past few years, several BPMO materials have been prepared and their catalytic applications have been successfully carried out in some important chemical processes.[20–22] More recently, we have also introduced a new class of supported ionic liquid systems based on periodic mesoporous organosilicas composed of an alkylimidazolium ionic liquid framework (PMO-IL).[23] This material has thus far been successfully employed as an efficient support for immobilization and stabilization of Pd nanoparticles in the Suzuki coupling reaction, aerobic oxidation of alcohols and the Heck reaction, for Ru catalysts in aerobic alcohol oxidation, for Au nanoparticles in the synthesis of propargylamines *via* the A3 coupling reaction, as well as for immobilization of tungstate in the oxidation of sulfides and alcohols.[23] As part of our continuing investigation in this area, more recently we prepared and characterized a novel sulfonic acid and ionic liquid-based bifunctional periodic mesoporous organosilica (BPMO-IL-SO_3H) material and studied its catalytic application in the esterification of carboxylic acids and Biginelli reaction.[22] This catalyst exhibited improved catalytic performance compared to the corresponding simple supported sulfonic acids in the described reactions, a feature that was attributed to the presence of imidazolium moieties in the framework of the material. Moreover, the catalyst was recovered and reused several times without a significant decrease in activity and selectivity. In continuation of these studies, herein we wish to disclose the synthesis and characterization of a novel propylamine-functionalized periodic mesoporous organosilica with an ionic liquid framework (PMO-IL-NH_2) and studied its catalytic application in the Knoevenagel condensation of aldehydes with ethyl cyanoacetate (Scheme 1).

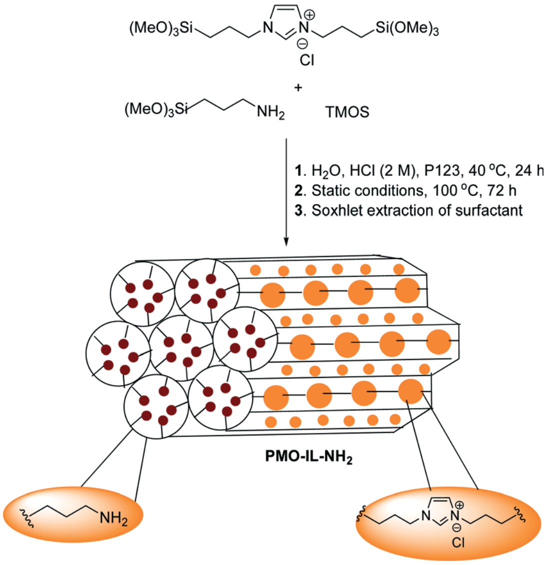
Results and discussion

An amine-functionalized ionic liquid-based periodic mesoporous organosilica (PMO-IL-NH_2) was prepared by the simultaneous hydrolysis and condensation of tetramethoxysilane (TMOS), 1,3-bis(trimethoxysilylpropyl)imidazolium chloride and 3-aminopropyltrimethoxysilane in the presence of Pluronic P123 under acidic conditions (Scheme 1). The PMO-IL-NH_2 nanomaterial was then characterized using several techniques such as thermal gravimetric analysis (TGA), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD).

Transmission electron microscopy (TEM) and PXRD analyses of PMO-IL-NH_2 were performed to get insight into the structural features of the material. The powder X-ray diffraction (PXRD) pattern of the catalyst demonstrated typical d_{100} and d_{110} reflections in the low-angle diffraction region of $2\theta < 2°$, which can be assigned to the two-dimensional hexagonal symmetry (*P6mm*) lattice (Fig. 1). The presence of a d_{100} peak with high intensity excellently confirms the good structural regularity of the material.

The TEM image also showed that PMO-IL-NH_2 features a highly ordered mesoporous structure, which is parallel to the long axis of the uniform rods (Fig. 2). This observation is in good agreement with the results of PXRD analysis and also fits well with the two-dimensional hexagonal mesostructures.

Scanning electron microscopy (SEM) analysis was also performed to study the morphology of the material (Fig. 3). This image clearly showed the presence of uniform and



Scheme 1 Preparation of the PMO-IL-NH_2 nanocatalyst.

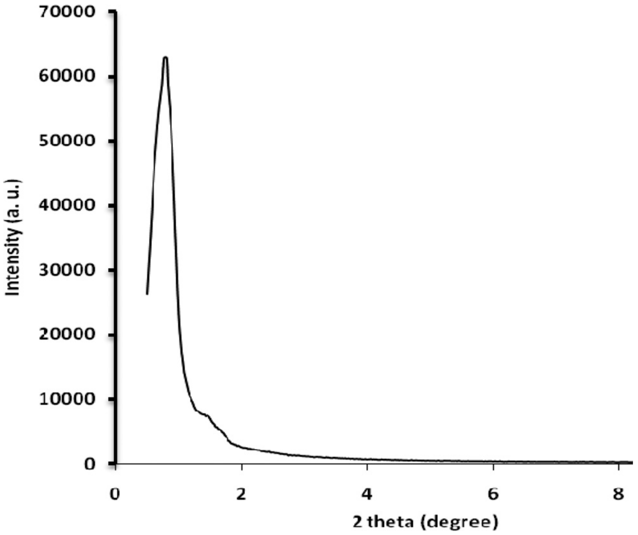


Fig. 1 Powder X-ray diffraction (PXRD) pattern of the PMO-IL-NH_2 nanocatalyst.

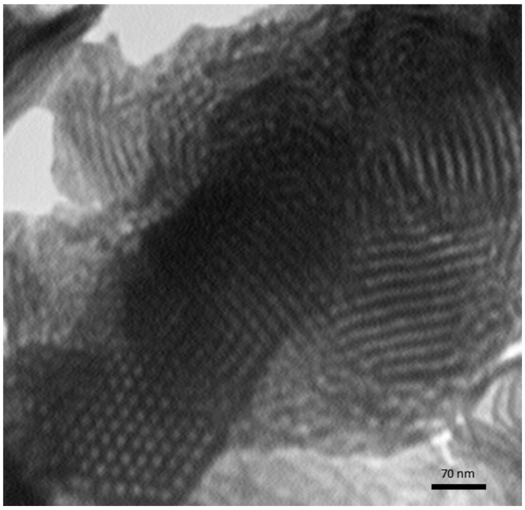


Fig. 2 TEM image of the PMO-IL-NH_2 nanocatalyst.

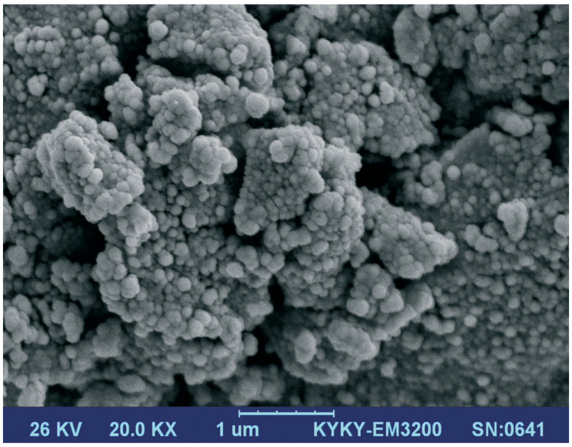


Fig. 3 SEM image of the PMO-IL-NH_2 nanocatalyst.

regular spherical particles with a diameter of 1 micrometer. Thermal gravimetric analysis (TGA) was carried out to investigate the thermal stability of the material (Fig. 4). The thermogravimetric (TG) and derivative thermogravimetric (DTG) diagrams exhibited a weight loss of about 4.6% at temperatures below 100 °C corresponding to the removal of physically adsorbed water and alcoholic solvents. The second weight loss of 2.75% at 100–270 °C corresponding to the elimination of the Pluronic P123 surfactant residue which remained after the surfactant extraction stage. The final and main weight loss of 21.94% at 270–800 °C corresponding to the decomposition and elimination of the ionic liquid and propylamine functional groups from the material framework. These data strongly verify the high thermal stability of the material.

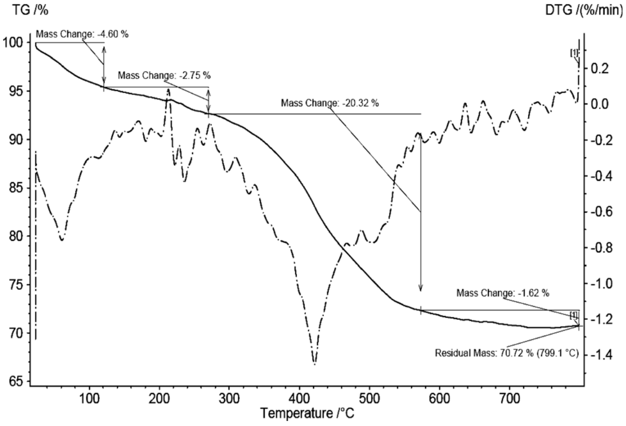
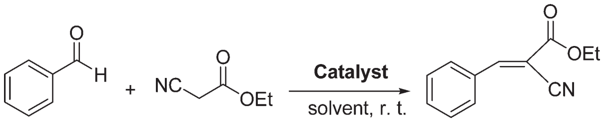


Fig. 4 TG and DTG diagrams of the PMO-IL-NH_2 nanocatalyst.

The PMO-IL-NH_2 catalyst was next analyzed by DRIFT spectroscopy in order to get detailed information about the chemical functional moieties of the material (ESI† Fig. S1). The absorption peaks at 700–800 cm^{-1} are attributed to C–Si stretching vibrations. The bands observed at 1095 and 930 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of Si–O–Si bonds.[22,23] The absorption peaks at 1558 cm^{-1} and 1622 cm^{-1} can be assigned, respectively, to C=C and C=N bonds of the imidazolium ring.[22,23] The C–H deformation vibrations, C–H stretching vibrations of propyl groups and unsaturated C–H stretching vibrations are observed, respectively, at 1445, 2927 and 3105 cm^{-1}.[22,23] In addition, the broad signals around 3300 cm^{-1} are assigned to N–H and O–H bonds. N–H bending vibration is also observed at 689 cm^{-1}. The stretching vibration band of C–N is usually observed around 1000–1220 cm^{-1}. However, this peak cannot be resolved due to its overlap with the stretching band of Si–O–Si in the range of 1000–1130 cm^{-1} and that of Si–CH_2–R stretching in the range of 1200–1250 cm^{-1}.[14b] These data are in good agreement with those obtained in TG analysis and strongly confirm the successful incorporation and immobilization of organic groups (ionic liquid and propylamine) in the material network.

After characterization, the catalytic application of PMO-IL-NH_2 was studied in the Knoevenagel condensation of aldehydes with ethyl cyanoacetate under different conditions. In the first step, the effect of solvent and catalyst loading was investigated (Table 1). At the beginning, all reactions were performed at room temperature. The study showed that the reaction was strongly affected by the amount of the catalyst. As can be seen from the data summarized in Table 1, by increasing the catalyst loading, the conversion was significantly increased (entries 1–3) and the best result was obtained in the presence of 0.5 mol% catalyst. The efficiency of the catalyst was also considerably affected by the solvent. While EtOH, CH_3CN, toluene and H_2O resulted in low to moderate yields of products at room temperature, an excellent yield was obtained without employing a solvent under otherwise the same reaction conditions (Table 1, entries 3–7). To show the impact of amine functional groups on the catalytic process, in the next step, the catalytic performance of amine-free PMO-IL was also checked under the same reaction conditions (Table 1, entry 3 *vs.* entry 8). This nanomaterial gave only a low yield (<5%) of the desired product, indicating that the catalytic

Table 1 The effect of solvent and catalyst loading in the Knoevenagel condensation of ethyl cyanoacetate with benzaldehyde[a]



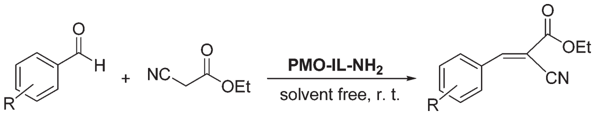
Entry	Catalyst	Catalyst (mol%)	Solvent	Yield[b] (%)
1	PMO-IL-NH_2	0.12	—	18
2	PMO-IL-NH_2	0.25	—	48
3	PMO-IL-NH_2	0.5	—	96
4	PMO-IL-NH_2	0.5	H_2O	40
5	PMO-IL-NH_2	0.5	EtOH	37
6	PMO-IL-NH_2	0.5	CH_3CN	35
7	PMO-IL-NH_2	0.5	Toluene	18
8	PMO-IL	[c]	—	<5
9	SBA-15-Pr-NH_2	0.5	—	37
10	SiO_2-Pr-NH_2	0.5	—	33

[a] Reaction conditions: benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), r.t., 90 min. [b] Isolated yields. [c] The amount of PMO-IL (mg) was the same as that used for PMO-IL-NH_2.

activity mainly originates from the amine functional groups. The efficiency of the catalyst was also compared with those of ionic liquid-free SBA-15-Pr-NH_2 and SiO_2-Pr-NH_2 materials under essentially identical reaction conditions (Table 1, entry 3 *vs.* entries 9 and 10). Interestingly, the results showed that both catalysts had inferior activity as compared with that observed over PMO-IL-NH_2 comprising the same –NH_2 loading. These observations strongly confirm the concomitant key role of ionic liquid moieties in the catalytic process. The effect of ILs may be attributed to their lipophilicity leading to better diffusion of substrates into mesochannels during the reaction. Another advantageous role of ILs is attributed to the effect of the acidic hydrogen of the imidazolium ring (–NCHN–) on the activation of aldehydes during the catalytic process.

With the optimized conditions in hand, the scope and limitations of this novel nanocatalyst were next investigated in the Knoevenagel condensation of various aldehydes with ethyl cyanoacetate (Table 2). Notably, all reactions were found to proceed smoothly and the desired products were produced in high to excellent yields without generation of any detectable side products. It is important to mention that according to the NMR results (see the ESI†), only one peak for the alkene proton was observed at a chemical shift of about 8.3 ppm (singlet, 1 H, C=C–H). This is in good agreement with previous studies[5b,24] and corresponds to the alkene group of *E*-products that are more stable isomers successfully confirming the high product selectivity of the catalyst. As presented in Table 2, benzaldehyde was successfully reacted with ethyl cyanoacetate in the presence of 0.5 mol% catalyst to furnish the corresponding coupling product in excellent yield (Table 2, entry 1). Moreover, this novel catalytic system was equally effective with aromatic aldehydes bearing either electron-withdrawing or electron-donating groups and furnished the Knoevenagel products in good to excellent yields (Table 2, entries 2–11). It is important to note that even *ortho*-substituted benzaldehydes, which are known to

Table 2 The Knoevenagel condensation of aldehydes with ethyl cyanoacetate in the presence of the PMO-IL-NH_2 nanocatalyst[a]



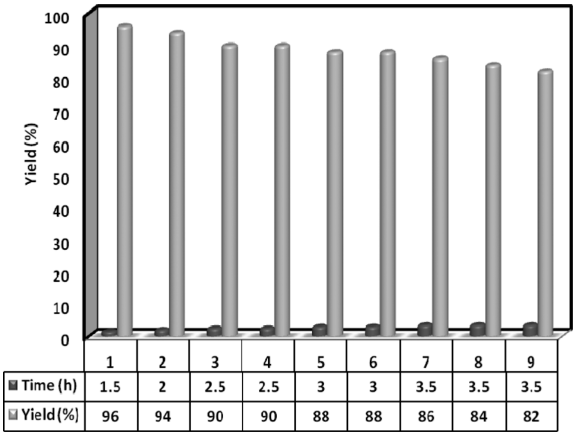
Entry	Aldehyde	Time (min)	Yield[b] (%) [TON]	M. p.
1	PhCHO	90	96 [192]	50–51
2	2-Cl-PhCHO	120	90 [180]	52–54
3	3-Cl-PhCHO	110	93 [186]	160–161
4	4-Cl-PhCHO	100	95 [190]	89–90
5	3-Br-PhCHO	110	93 [186]	105
6	3-NO_2-PhCHO	90	95 [190]	160–162
7	4-NO_2-PhCHO	90	97 [194]	173–174
8	2-Me-PhCHO	120	88 [176]	65–66
9	4-Me-PhCHO	110	93 [186]	95–96
10	4-MeO-PhCHO	110	93 [186]	80–83
11	3-EtO, 4-OH-PhCHO	130	88 [176]	134–136

[a] Reaction conditions: aldehyde (1 mmol), ethyl cyanoacetate (1 mmol), catalyst (0.5 mol%), r.t. [b] Isolated yields.

show lower reactivity in organic transformations due to their steric hindrance, also afforded the respective coupling products in high yield at room temperature (Table 2, entries 2 and 8). These observations strongly confirm the outstanding capability of the PMO-IL-NH_2 nanocatalyst in catalyzing the Knoevenagel condensation of a broad range of aldehydes with active methylene substrates. The advantages of this catalyst may be attributed to the ionic liquid moieties and isolated aminopropyl sites incorporated in the material framework as well as the high surface area of the ordered nanostructured PMO-IL material.

The recoverability and reusability of the catalyst were also investigated in the reaction of benzaldehyde with ethyl cyanoacetate under standard reaction conditions (Fig. 5). To do this, after the reaction was completed, the obtained mixture was filtered and the catalyst was washed thoroughly with ethanol and dried under vacuum at 70 °C. It was then used in the aforementioned reaction under the same conditions as before. Interestingly, the results illustrated that the catalyst could be recovered and reused at least 8 times proving its good durability and recoverability under the applied conditions. It is important to note that the yield and turnover number (TON) decreased by 14 and 28%, respectively, for the regenerated catalyst after 9 cycles (ESI† Table S1). The lower efficiency observed for the recovered mesoporous catalyst can be primarily due to the partial saturation of mesochannels containing catalytic active sites during the reaction process.

Nitrogen adsorption–desorption analysis of the recovered PMO-IL-NH_2 catalyst after the fifth reaction cycle (RPMO-IL-NH_2) showed an isotherm with a typical type IV shape and a distinctive H1-type hysteresis loop at a relative pressure about P/P_0 = 0.5–0.72, which is commonly observed for materials with ordered mesoporous structures (Fig. 6a). It is also important to note that the BET surface area and pore volume of the fresh catalyst decreased from 596 m^2 g^{-1} and 1.12 cm^3 g^{-1} to 438 m^2 g^{-1} and 0.90 cm^3 g^{-1}, respectively, for the recovered catalyst. The BJH calculations also illustrated the presence of a sharp peak with uniform pore size distribution and a mean pore diameter of 7.1 nm for RPMO-IL-NH_2, indicating that the recovered catalyst has very regular mesochannels (Fig. 6b and ESI† Table S2). The highly ordered hexagonally symmetric structure of the recovered aminopropyl-containing PMO-IL was also fully confirmed by the TEM image (Fig. 7 and ESI† Fig. S2). These data are in agreement with each other and strongly confirm the excellent mechanical and structural stability of the desired catalyst under the applied conditions.



	1	2	3	4	5	6	7	8	9
▪ Time (h)	1.5	2	2.5	2.5	3	3	3.5	3.5	3.5
▪ Yield (%)	96	94	90	90	88	88	86	84	82

Fig. 5 Reusability of the PMO-IL-NH_2 nanocatalyst in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

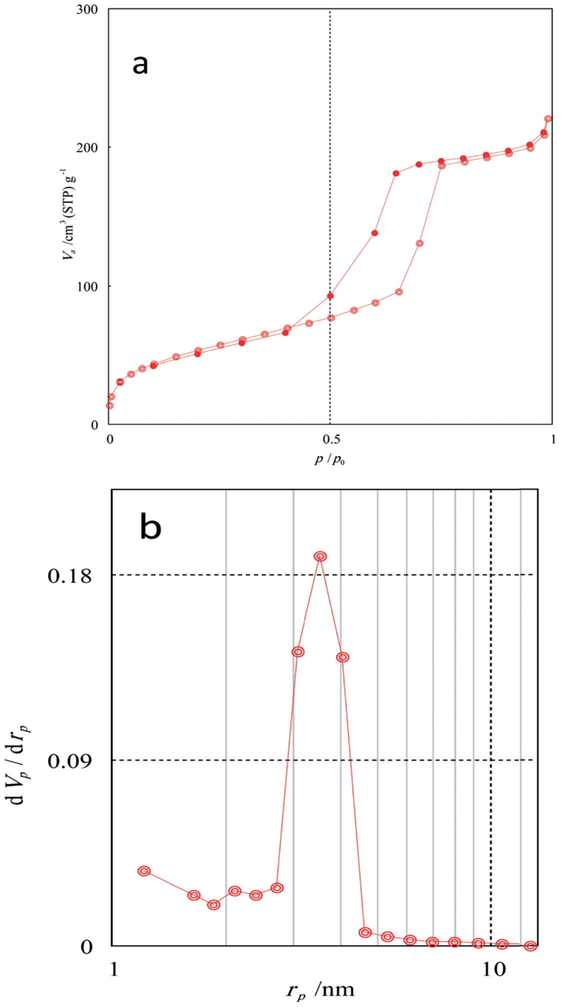


Fig. 6 Nitrogen adsorption–desorption (a) and pore size distribution (b) isotherms of the recovered PMO-IL-NH_2 after the fifth reaction cycle.

In another study, a filtration test was performed in order to investigate whether the catalyst operates in a homogeneous or heterogeneous manner. For this reason, the reaction of benzaldehyde with ethyl cyanoacetate was selected as a model reaction. After 45 minutes, before complete consumption of all substrates, warm EtOH was added into the reaction flask and the obtained mixture was filtered. It was found that a 40% conversion was attained at this stage. The excess EtOH was then removed under reduced pressure from the filtrate and the reaction was allowed to continue at room temperature for another 3 h. In this regard, no considerable reaction progress was observed, indicating that no leaching

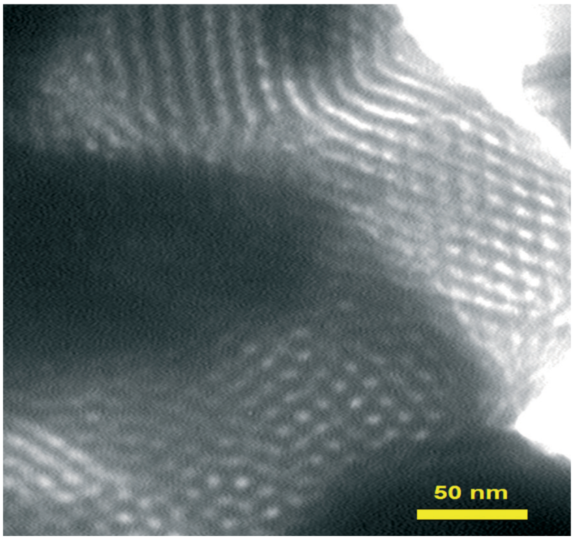


Fig. 7 TEM image of the recovered PMO-IL-NH_2 after the fifth reaction cycle.

of amine functional groups occurred during the reaction and the catalyst most likely worked in a heterogeneous manner.

In the final study, the catalytic efficiency of the PMO-IL-NH_2 nanocatalyst was compared with those of a number of previously reported amine-containing heterogeneous catalysts in the Knoevenagel condensation (Table 3). The results showed that the previously reported catalytic systems have nice activity for the Knoevenagel condensation of a set of different carbonyl compounds with active methylenes; however, in most cases the reaction was performed in organic solvents at temperatures higher than that employed for the present catalyst. Moreover, the recycling properties of the present PMO-IL-NH_2 nanocatalyst were shown to be more or less superior to those of most of the described catalytic systems. These findings significantly confirm the high efficiency of the present catalyst in the base-catalyzed Knoevenagel reaction.

Experimental section

Preparation of the PMO-IL-NH_2 nanocatalyst

The preparation of aminopropyl-containing ionic liquid-based PMO (PMO-IL-NH_2) was achieved by the simultaneous hydrolysis and co-condensation of tetramethoxysilane (TMOS), 1,3-bis(trimethoxysilylpropyl)imidazolium chloride and 3-aminopropyltrimethoxysilane in the presence of Pluronic P123 under acidic conditions.[22b] In a typical procedure, Pluronic P123 (2 g) was added to a solution containing deionised water (11.7 g), HCl (2 M, 50 g) and potassium chloride (12.2 g) while stirring at 40 °C. After complete dissolution of the surfactant, a mixture of tetramethoxysilane (19 mmol), 1,3-bis(trimethoxysilylpropyl)imidazolium chloride (1.8 mmol) and 3-aminopropyltrimethoxysilane (1.5 mmol) was added into the reaction vessel and stirred at the same temperature for 24 h. The mixture was then heated at 100 °C under static conditions for 72 h. After that, the obtained material was filtered, washed with deionised water and dried at room temperature. The removal of the surfactant was achieved by means of a Soxhlet apparatus using ethanol for 48 h. The final material was dried at 70 °C for 12 h and denoted as PMO-IL-NH_2.

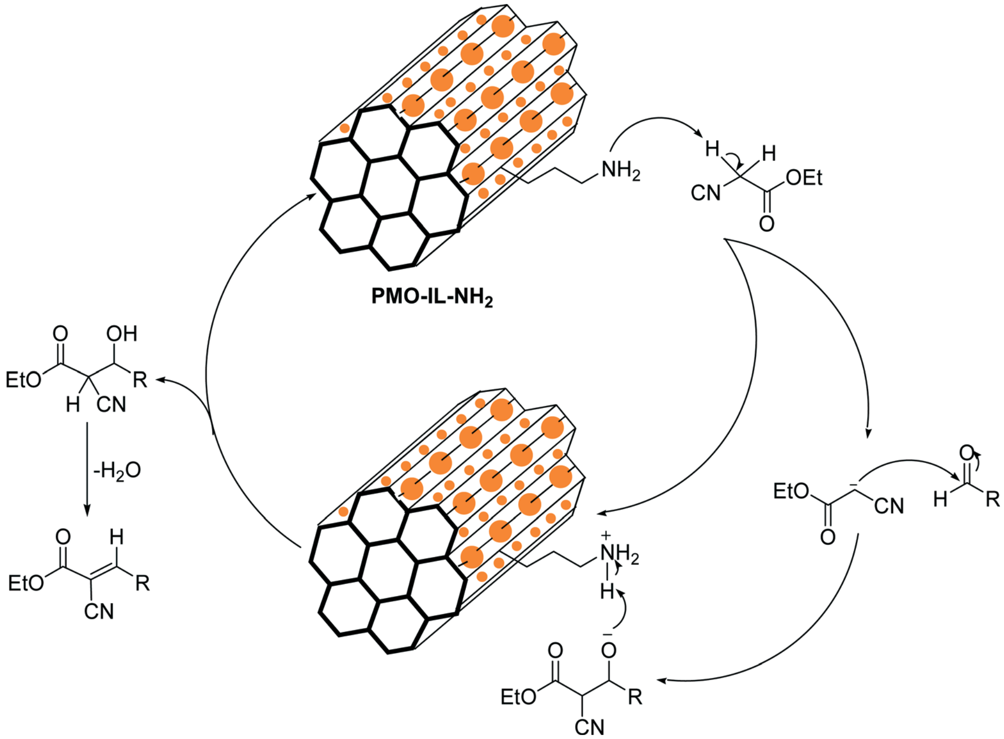
General procedure for the Knoevenagel condensation using the PMO-IL-NH_2 nanocatalyst. An aldehyde (1 mmol), ethyl cyanoacetate (1 mmol) and the catalyst (0.5 mol%)[26] were added into a flask and stirred vigorously at room temperature. The progress of the reaction was monitored *via* TLC. After completion of the reaction, 5 mL of warm ethanol was added to the reaction vessel and the obtained mixture was filtered and completely washed with ethanol. Pure products were obtained after recrystallization in a mixture of hexane/ethanol solvents; otherwise, the residue was isolated by column chromatography on silica.

General procedure for the recovery of the PMO-IL-NH_2 nanocatalyst in the Knoevenagel reaction. For this purpose, in a flask containing benzaldehyde (1 mmol) and ethyl cyanoacetate (1 mmol), 0.5 mol% PMO-IL-NH_2 catalyst was added

Table 3 Comparative study of the efficiency of the PMO-IL-NH_2 nanocatalyst with that of previously reported catalytic systems in the Knoevenagel condensation[a]

Catalyst	Conditions	Recycling times	Ref.
CsNaX-NH_2 zeolite	Solvent-free, 180 min, 90 °C	—[b]	8*c*
Am-IL-SBA-15	H_2O, 1 h, RT	9	11*c*
AP-MCM-41	Toluene, 2 h, RT	3	13*c*
AP-SBA-1	Toluene, 6 h, RT	—[b]	13*c*
ZrO_2-Pr-NH_2	Solvent-free, RT, time (no reported)	3	14*c*
NH_2-MSNS	H_2O, decane (100 : 1), 15 min, MW, 100 °C	8	14*f*
SBA-15-Pr-NH_2	Cyclohexane, 1 h, 82 °C	—[b]	25*a*
APS-MIL-101(Cr)	Cyclohexane, 80 °C, 19 h	—[b]	25*b*
ED-MIL-101(Cr)	Cyclohexane, 19 h, 80 °C	3	25*b*
NH_2-MIL-101(Cr)	Toluene, 2 h, 60 °C	—[b]	25*c*
NH_2-MIL-101(Al)	Toluene, 4 h, 40 °C	Several times[b]	25*d*
PMO-IL-NH_2	Solvent-free, 90 min, RT	8	This work

[a] Abbreviations: AM: aminopropyl; APS: aminopropyl silica; ZrO_2-Pr-NH_2: propylamine-functionalized mesoporous zirconia; MIL-101(Cr): $[Cr_3(F,OH)(H_2O)_2O(bdc)_3]$; ED: ethylenediamine; NH_2-MSNS: amine-functionalized mesoporous silica nanospheres; Am-IL-SBA-15: aminopropyl-ionic liquid-SBA-15. [b] The recycling times were not reported.



Scheme 2 Proposed mechanism for the Knoevenagel condensation using the PMO-IL-NH_2 nanocatalyst.

and the mixture was magnetically stirred at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, warm ethanol (5 mL) was added and the obtained solution was filtered and washed with ethanol. The recovered catalyst was then reused under the same conditions as those in the first run at least 8 times and gave the corresponding Knoevenagel product in high yield and selectivity.

Although the exact reaction pathway for the present base-catalyzed Knoevenagel condensation is not clear to us, a proposed plausible mechanism for the reaction of different aldehydes with ethyl cyanoacetate is presented in Scheme 2. In this context, the amine group of PMO-IL-NH_2 is thought to pick up one acidic proton from the active methylene group of ethyl cyanoacetate to produce the corresponding enolate. Then, the nucleophilic attack of this anion at the carbonyl carbon followed by re-capture of the proton from the protonated catalyst would result in the formation of the corresponding β-hydroxyl compound and regenerated catalyst. Finally, the Knoevenagel products can be obtained *via* the dehydration of β-hydroxyl compounds.

Conclusions

In conclusion, a new amine-containing ionic liquid-based ordered mesoporous organosilica (PMO-IL-NH_2) nanocatalyst was prepared and characterized and its application was successfully developed in the Knoevenagel condensation. The PXRD analysis and TEM image of the PMO-IL-NH_2 nanocatalyst demonstrated a highly uniform mesostructure with two-dimensional symmetry for the material. The IR and TG analyses also confirmed the excellent stability of the incorporated ionic liquid and aminopropyl groups in the material network. The PMO-IL-NH_2 nanocatalyst was successfully applied to C=C bond formation through the Knoevenagel reaction of aldehydes with ethyl cyanoacetate and gave the corresponding products in high to excellent yields and selectivities. The catalyst was easily recovered and reused several times without a significant decrease in efficiency. Some other advantages of the present study are solvent-free media, short reaction times, mild reaction conditions, high yield of products as well as high activity, stability and durability of the catalyst under the applied reaction conditions. Due to the remarkable properties of this catalytic system, some of its applications in other chemical processes are under way in our laboratories.

Acknowledgements

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