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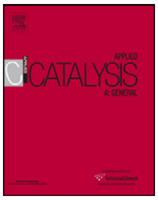

Imidazolium chloride immobilized SBA-15 as a heterogenized organocatalyst for solvent free Knoevenagel condensation using microwave

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Green method

ABSTRACT

Heterogeneous organocatalyst, 1-methyl-3-[(3-triethoxysilyl) propyl] imidazolium chloride [MTESPImCl] immobilized SBA-15 (ILS) was synthesized by co-condensation method using microwave irradiation in which 1-methylimidazole (Im) was modified by organosilane (3-chloropropyl triethoxysilane). The ILS was thoroughly characterized by small angel XRD, N_2 adsorption desorption isotherms, TEM, SEM, TGA and FT-IR. The ILS showed 2D hexagonal short channeled disk type mesostructure which can provide facile to-and-from diffusion of substrates and products with enhanced activity. This heterogenized organocatalyst ILS had been investigated for the Knoevenagel condensation reaction of different aromatic and heteroaromatic aldehyde with ethyl cyanoacetate in solvent free conditions. The catalyst ILS was found to be efficient to catalyze the condensation effectively leading the completion of the reaction within 6 min using single mode microwave irradiation.

1. Introduction

Ionic liquids have achieved great attention as a green solvent [1] in the fields of organic synthesis [2], nanoporous materials' synthesis [3,4], enzyme activation and catalysis [5] because of their unique properties such as non-volatility, non-flammability, polarity, solubility, and high thermal and chemical stabilities [6]. In the field of catalysis, ionic liquids (ILs) play the role of solvents and organocatalysts. In general, organocatalysis uses small organic molecules, composed of C, H, N, O, S and P atoms which play role as active site however, their high cost, and difficulty in recyclability and in the separation of products, cause limitations for their further applications at the industrial scale [7]. To overcome these shortcomings, supporting or immobilizing of organocatalyst ILs onto the solid supports termed as heterogenized IL organocatalysts have become as a green approach in their catalytic applications [8–15].

Since the discovery of ordered mesoporous silicates, a variety of ordered mesoporous materials with high surface area, large pore volume and large pore size have been synthesized using different surfactant templating methods to expand their practical applications in the area of heterogeneous organocatalysis by immobilizing organic functionalities [16,17]. The modified mesoporous materials with various active sites had been extensively investigated in recent decade [18]. The organo-functional modification of mesoporous silica permits to tailor the surface properties, useful for various applications in the heterogeneous catalysis [19]. Generally the synthesis of functionalized mesoporous materials have two approaches: (1) the direct synthesis approach where in a silane containing functional group of ionic liquid was added to the synthetic mixture during the synthesis of mesoporous materials (2) the second approach is by post grafting wherein the organosilane is grafted after synthesis of mesoporous support [20,21].

Among the siliceous supports SBA-15 is promising candidate for the immobilization of organocatalyst due to its high surface area, porosity, uniform pore size distributions, and thermal stability [22]. In recent year our group reported several organic functional groups such as primary and quaternary amine, sulfonic acid, and amino acid (L-proline) functionalized mesoporous silica for organocatalytic applications in various reactions such as Knoevenagel, Henry reaction, Claisen-Schmidt condensation and diethyl malonate addition [23]. SBA-15 supported ionic liquids such as 1-methyl-3-propylimidazolium chloride (MPImCl) and 1-propylpyridinium chloride (PPyCl) ionic liquids have also been used as heterogeneous catalysts providing high yields in Knoevenagel condensation under solvent free conditions; however these are associated with longer reaction times due to conventionally, convective heating over heat baths or electric heating mantles, which have major adverse effect to the environment as well as consumption of energy for heating and cooling [24].

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Over the past few years, the concept of speeding up ionic liquid-bound chemistry by microwave irradiation has created a lot of interest, for both academic as well as industrial communities [25]. In a number of publications, significant rate accelerations and very high loadings for several solid-phase protocols have been reported, with reaction times being reduced in some cases from hours to few minutes. Despite these initial reports, the benefits associated with this new technology have not been rigorously established, since in many cases domestic household microwave ovens have been employed, that do not allow the monitoring of temperature or pressure profiles during irradiation experiments [26]. We have demonstrated here the microwave flash heating, i.e., the very rapid heating of the reaction mixture in combination with high reaction temperatures. The initial studies on the microwave irradiation are reported for its application toward synthetic chemistry and to demonstrate the feasibility of carrying out such transformations in a controlled and reproducible parallel fashion by using dedicated reactor systems [27–30]. In continuation of our earlier studies we here report our recent investigation on microwave mediated morphosynthesis of MTESPImCl immobilized SBA-15 (ILS) as heterogeneous organocatalyst and its potential catalytic applications toward Knoevenagel condensation under solvent free conditions.

2. Experimental

2.1. Materials

Chemicals 1-methylimidazole (99%), 3-chloropropyl triethoxysilane (95%), sodium metasilicate nonahydrate (98%) and P123 (MW 5800) were purchased from Aldrich USA. Hydrochloric acid (37.6%) was purchased from DAE JUNG South Korea. Dichloromethane and ethanol were purchased from Duksan South Korea.

2.2. Synthesis procedure

The synthesis of 1-methyl-3-[(3-triethoxysilyl) propyl] imidazolium chloride (MTESPImCl) was carried out by reported method [31]. This ionic liquid was synthesized by taking 1-methylimidazole and chloropropyl silane in 1:1 molar ratio by keeping it at 70 °C for 48 h under nitrogen atmosphere. 2.5 g P123 amphilic triblock copolymer ($EO_{20}PO_{70}EO_{20}$) was dissolved in 64 g of water at room temperature followed by addition of 6.835 g of sodium metasilicate and certain amount of MTESPImCl (IL) (IL to SiO_2 molar ratio was 2.5%, 5%, 7.5% and 10%) under vigorous stirring until clear solution is obtained. To this clear mixture 20.25 g of concentrated hydrochloric acid (37%) was added and the final mixture was stirred for 1 h at 40 °C. The resultant solution mixture was transferred to the teflon vessel and aged at 100 °C for 2 h in microwave irradiation (300 W, 100%) under static conditions, Scheme 1. After microwave irradiation the solid products were filtered, washed with distilled water and finally dried at 60 °C. The template was removed by soxhlet extraction using acidic ethanol for 24 h [31,32].

2.3. Sample characterization

The low angle powder X-ray diffraction (XRD) patterns were recorded on a rigaku diffractometer using Cu Kα radiation (λ = 0.154 Å). N_2 adsorption desorption isotherms studies were conducted on a Tri-Star at −196 °C. The surface area was calculated by BET method and the pore parameters were calculated from adsorption branches by BJH methods. Scanning electron microscopy (SEM) images were taken with Hitachi S-4200 at 15–20 kV. Transmission electron microscopy (TEM) images were taken using a Philips CM 200 at 200 kV. The thermogravimetric analysis (TGA) was done by Bruker 2010SA. The Fourier transformation IR (FT-IR) spectra were recorded by Nicolet 5700. The product was analyzed by gas chromatography (GC) (Agilent 6890N, HP-5 capillary column, FID detector) and GC–MS (Agilent technologies, GC6890N, MS5975).

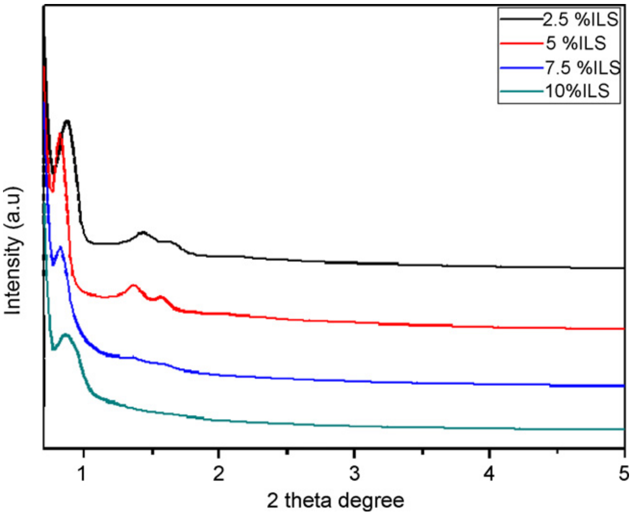


Fig. 1. The powder XRD patterns of 2.5% ILS, 5% ILS, 7.5% ILS and 10% ILS.

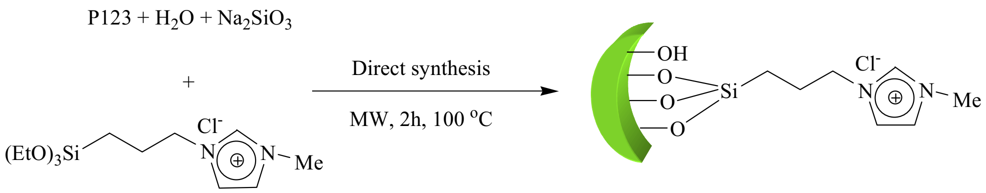
2.4. Knoevenagel condensation reaction

The Knoevenagel condensation reaction was carried out under solvent free conditions at 120 °C using single mode microwave (CEM). In a typical procedure, 1 mmol of aldehyde was added to 1 mmol of the active methylene compound, ethyl cyanoacetate and 10 mg of the catalyst was mixed to the reactant mixture and allowed to react for an appropriate time of 3–6 min at 120 °C under microwave irradiation power 300 W. After completion of the reaction, the reaction mixture was cooled at room temperature and diluted by dichloromethane and then precipitated for quantitative analysis. From the aqueous layer the catalyst was recovered by filtration and dried at 100 °C on an oven for reuse. The reaction product analysis was done by GC and further confirmed by GC–MS.

3. Results and discussion

3.1. Powder X-ray diffraction pattern

The ionic liquid functionalized SBA-15 were synthesized by co-condensation under microwave irradiation with different ratios of ionic liquid to SiO_2 and small angle X-ray diffraction patterns are recorded (Fig. 1) in order to understand the amount of ionic liquid effecting orderness. The PXRD patterns showed well-resolved peaks with very intense diffraction peaks at $2\theta = 0.8$–0.9 and two ordering peaks at higher degrees, which were indexed to the 1 0 0, 1 1 0, and 2 0 0 planes, characteristic of the long range order and excellent textural uniformity of mesoporous materials with a mesostructure of hexagonal space group symmetry (*p*6*mm*). It was observed that the ratios of ionic liquid to silica affect the intensity of the peaks corresponding to hexagonal orderness (1 1 0 and 2 0 0). The intensity of the order peaks decreased with an increase in the ratios from 2.5% to 10% ILS. It is presumed that the increase in MTESPImCl ratio may lead to minimize the interaction between inorganic silica and organic surfactant due to the hydrophobic nature of organosilane. It is well documented that during cooperative self-assembly such weak interactions decreases the ordering of the hexagonal geometry of the mesostructure [31].



Scheme 1. The synthesis route of ionic liquid functionalized SBA-15.

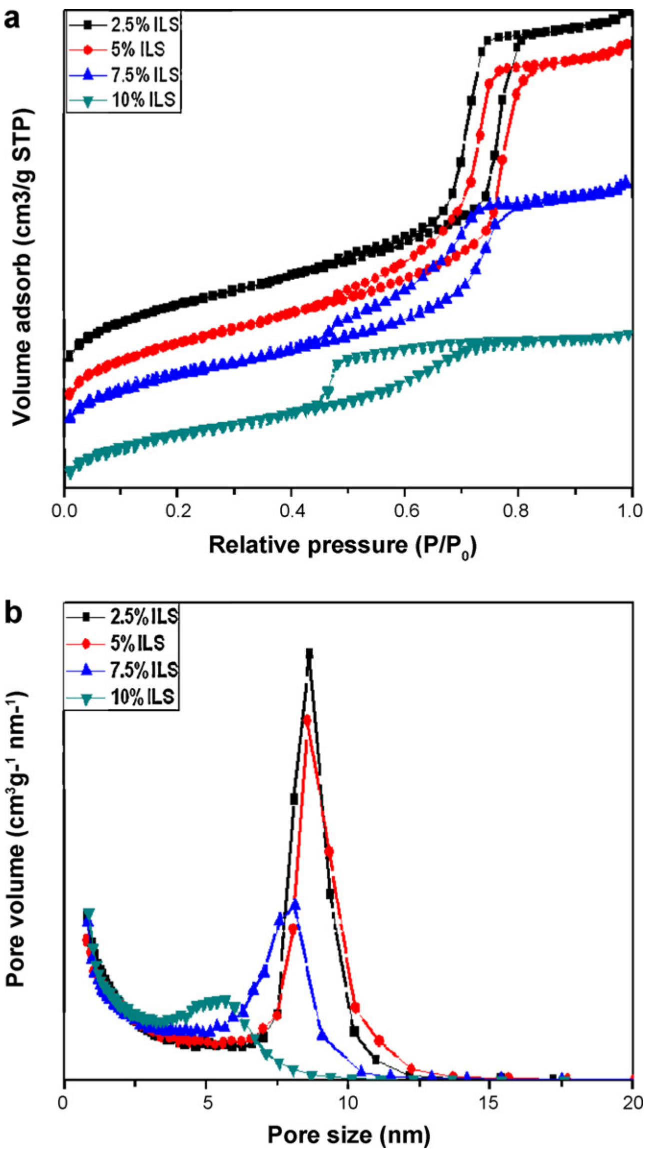


Fig. 2. The N_2 adsorption–desorption isotherms (a) and pore size distributions (b) of 2.5% ILS, 5% ILS, 7.5% ILS, and 10% ILS.

Table 1
Physicochemical properties of the extracted functionalized SBA-15 with ionic liquid concentration in the initial mixture.

Catalysts	S_{BET} (m^2/g)	Total pore volume (m^3/g)	Average pore size (nm)
2.5% ILS	664	0.98	8.6
5% ILS	535	0.91	8.51
7.5% ILS	468	0.64	8.12
10% ILS	418	0.42	5.72

Table 2
The thermogravimetric analysis of ionic liquid functionalized SBA-15.

Catalysts	Weight loss (H_2O, %)	Weight loss (IL, %)	Amount of ILs (mmol/g)
2.5% ILS	5.7	4.4	0.27
5% ILS	5.5	6.7	0.42
7.5% ILS	9.9	12.7	0.78
10% ILS	7.2	15.5	0.95

3.2. N_2 adsorption–desorption analysis

The mesoporous nature of the synthesized samples based upon concentration of organosilane were studied by N_2 adsorption desorption isotherms (Fig. 2). All samples showed type IV isotherms with H1 hysteresis loop being characteristic for highly ordered hexagonal mesostructures with uniform cylindrical channels. All the isotherms presents a sharp adsorption step in the P/P_0 region from 0.4 to 0.8 which implied that the materials possess large pore size with narrow distributions. This was further confirmed by the pore size distributions calculated by Barrett–Joyner–Halenda (BJH) method from the adsorption branches. It is observed that on increasing the IL amount, the BET surface area, pore volume and pore size were decreased due to presence of ionic liquid (Table 1). In the case of 7.5% ILS (Fig. 2a), two steps desorption branches were observed indicating the pore plugging effect. Plugging effect can increase the stability of mesoporous silica and can provide confinement effect which has very superior catalytic activity [33,34].

3.3. TEM and SEM images analysis

The morphological features of IL immobilized SBA-15 were studied by TEM and SEM (Figs. 3 and 4) respectively. The SEM images of ILS (Fig. 4) indicated a uniform particle size with hexagonal shape for the directly synthesized organosilane modified ionic liquid functionalized SBA-15 under microwave irradiation. The hexagonal shape depended on the different loading amount of ionic liquid functionalized SBA-15. The shapes were changed from prism to platelet like morphologies from 2.5%, 5%, 7.5% and 10% ILS. But the platelet morphology became unclear and particles stacked heavily when the amounts of IL were increased to 10%. Increasing the amount of IL in the initial mixture of SBA-15, also decreased the thickness from 500 nm to 300 nm, which controlled the morphology of ILS and confirmed the formation of short channeled mesoporous silica [31,35].

The TEM images revealed that the short channeled SBA-15 with different loading of IL (Fig. 3) showed the high mesoscopic order. This hybrid material displayed the hexagonal array of well ordered one dimensional pore structure and honeycomb. The TEM images of ILS also indicate the short channels are parallel to the thickness which let to access the molecules easily [36].

3.4. TG analysis

The amount of MTESPImCl in SBA-15 was determined without air flow by the TGA. TGA of ionic liquid functionalized SBA-15 (ILS) is depicted in Fig. 5 and the content of ionic liquid (MTESPImCl) is given Table 2. The first step appeared at <150 °C because of the

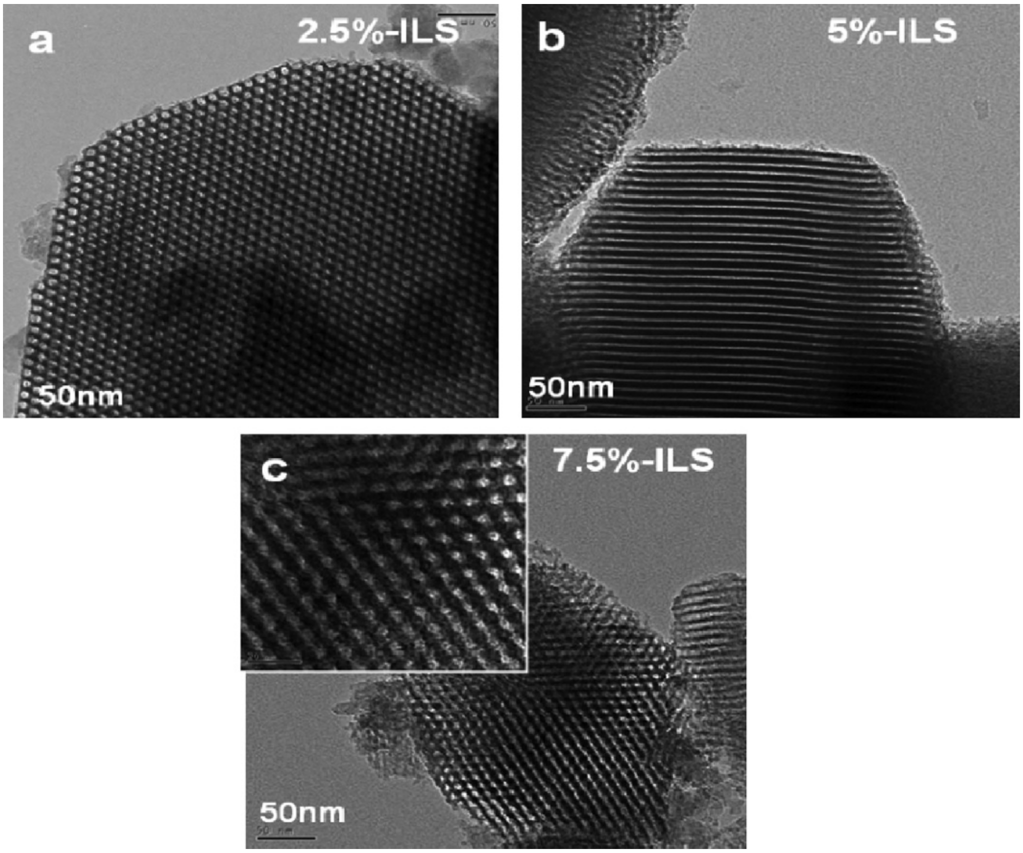


Fig. 3. Transmission electron micrographs of the extracted SBA-15 short channeled mesoporous silica functionalized with different concentrations of MTESPImCl in the initial mixture (a) 2.5% (b) 5% and (c) 7.5%.

loss of water, i.e., adsorbed water on the inner and outer surfaces of ILS. The second step weight loss at 250–500 °C is probably due to the decomposition of the immobilized ionic liquid (MTESPImCl) moieties in SBA-15 (Table 2).

3.5. FT-IR

The FT-IR spectra of imidazolium based ionic liquid immobilized mesoporous silica SBA-15 is depicted (Fig. 6.) characteristic IR bands at 1380, 978, 798 and 615 cm^{-1} due to the Si–O stretching in Si–O–Si structure. The spectrum displayed vibration peaks at 1634 cm^{-1} and 1508 cm^{-1} which are attributed to C=C and C=N bonds of the aromatic ring of imidazole respectively. The adsorption band around 2978 cm^{-1} assigned to C–H stretching vibration which confirms the presence of propyl groups of ionic liquid.

3.6. Activity test of the catalysts

It is aimed to evaluate the catalytic properties of ILS as an environment friendly base catalyst for typical organic synthetic reaction. The base catalyzed Knoevenagel condensation reaction of aromatic aldehyde and ethyl cyanoacetate (Scheme 2) was investigated in solvent free conditions through single mode microwave. The reaction mixture was cooled at room temperature and diluted by dichloromethane and then precipitated. Product analysis was done by GC and GC–MS for conversion and selectivity. For recycling of the catalyst, the catalyst was recovered from the aqueous layer by filtration and was dried at 100 °C in an oven.

3.6.1. Influence of ionic liquid loading in SBA-15

The condensation reaction between benzaldehyde and ethyl cyanoacetate depicted that with an increase in the loading ratio of ionic liquid to silica, increase in conversion with increase in selectivity was observed (Table 3). The highest conversion was observed in 7.5% ILS (81% conversion and 96% selectivity). The higher conversion with higher selectivity in case of 7.5% ILS may be due to ordered hexagonal short length platelet morphology which allows free flow of reactant and products. The conversions and selectivities associated with 10% ILS were less in comparison with that of 5% and 7.5%

Table 3
The effect of the loading amount of ionic liquid.

Catalyst	Time (min)	Temperature (°C)	[a],[b]Conversion of benzaldehyde %	[b]Selectivity of Ethyl 2-cyano-3-phenylacrylate %
2.5% ILS	3	120	50	45
5% ILS	3	120	63	90
7.5% ILS	3	120	81	96
10% ILS	3	120	60	84
Conventional-SBA-15	3	120	12	99
Blank	3	120	2	–

[a] Reaction conditions: benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), Catalyst weight: 10 mg, Time: 3 min, Temperature: 120 °C.
[b] C analysis.

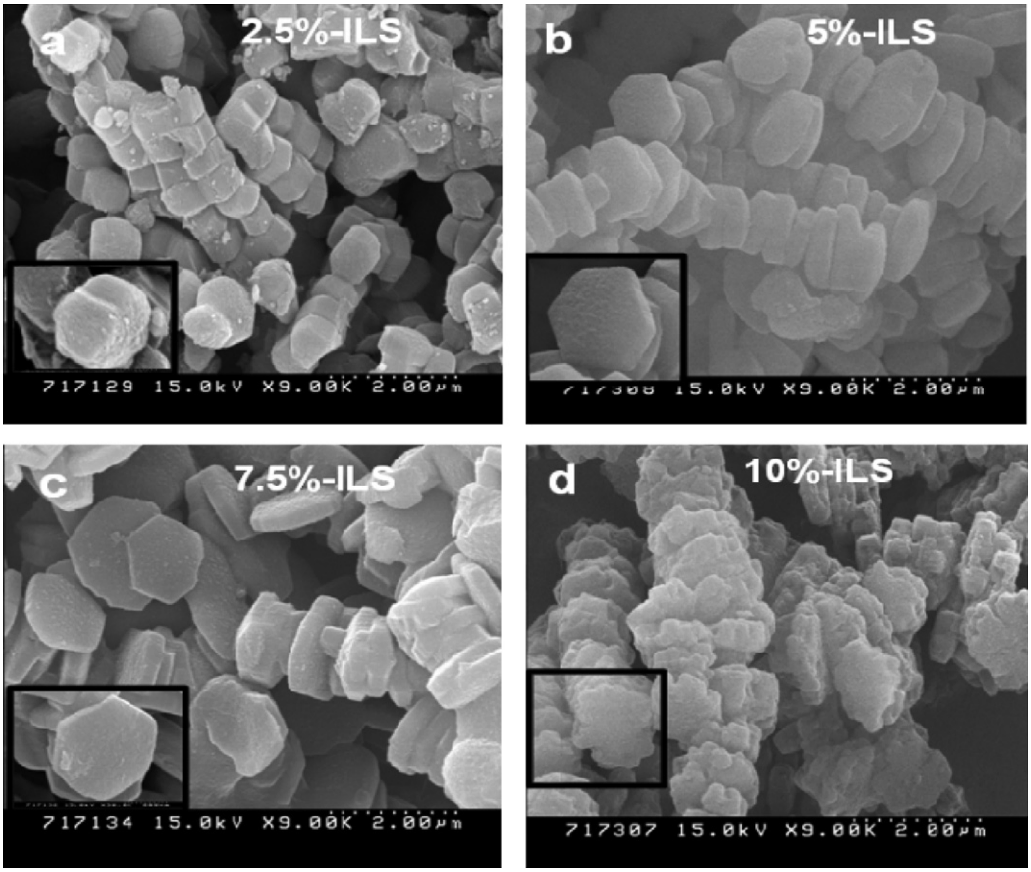


Fig. 4. Scanning electron micrographs of the extracted SBA-15 short channeled mesoporous silica functionalized with different concentrations of MTESPImCl in the initial mixture (a) 2.5% (b) 5% (c) 7.5% and (d) 10%.

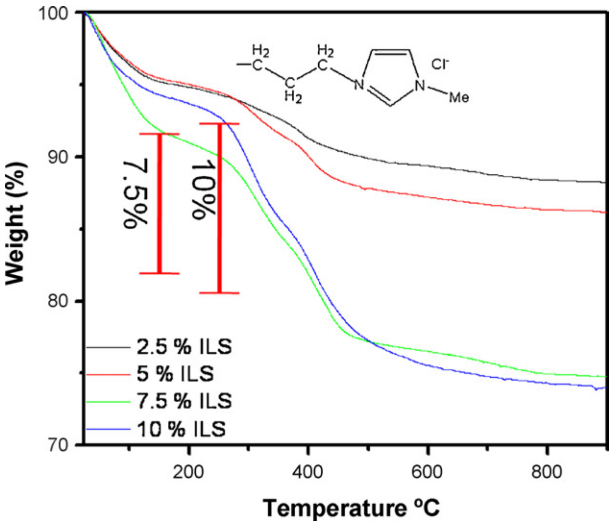


Fig. 5. The thermogravimetric analysis (TGA) of 2.5% ILS, 5% ILS, 7.5% ILS, and 10% ILS.

ILS. This may be due to the destruction of orderness and change in morphology. In order to understand the effect of morphology we have also tested conventional SBA-15 having long channel. The conventional SBA-15 gave 12% conversions with 99% selectivity of ethyl 2-cyano-3-phenylacrylate indicating that morphology of the catalyst also plays an important role. A blank reaction of benzaldehyde and ethyl cyanoacetate conducted under identical reaction condition did not show significant conversion (2%).

Table 4
The effect of reaction temperature.

Catalyst	Temperature (°C)	Time (min)	[a],[b]Conversion of Benzaldehyde %	[b]Selectivity of Ethyl 2-cyano-3-phenylacrylate %
7.5% ILS	30	6	4.8	18
7.5% ILS	60	6	23	70
7.5% ILS	90	6	59	91
7.5% ILS	120	6	97	98

[a] Reaction condition: Benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), catalyst weight: 10 mg, temperature: 30–20 °C, time: 6 min.
[b] GC analysis.

3.6.2. *The effect of reaction temperature*

The effect of reaction temperature on the Knoevenagel condensation was studied in the range of 30–120 °C for a representative substrate, benzaldehyde using 7.5% ILS (Table 4). The rise in tem-

Table 5
The effect of reaction time.

Catalyst	Time (min)	Temperature (°C)	[a],[b]Conversion of Benzaldehyde %	[b]Selectivity of Ethyl 2-cyano-3-phenylacrylate %
7.5% ILS	1.5	120	56	73
7.5% ILS	3	120	81	96
7.5% ILS	4.5	120	78	95
7.5% ILS	6	120	97	98

[a] Reaction conditions: Benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), catalyst weight: 10 mg, time: 3 min, temperature: 120 °C.
[b] GC analysis.

Table 6
Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate catalyzed by ILS (ionic liquid functionalized SBA-15).[a]

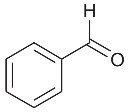
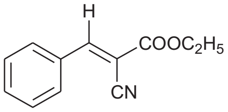
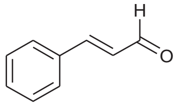
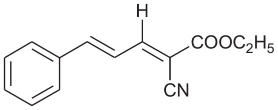
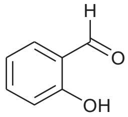
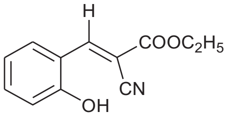
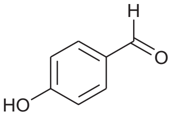
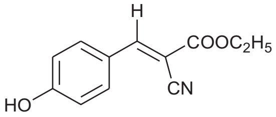
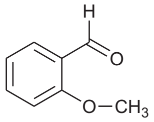
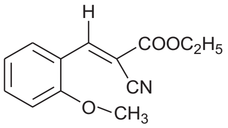
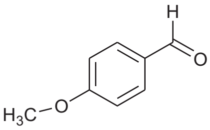
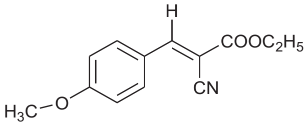
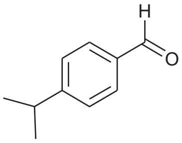
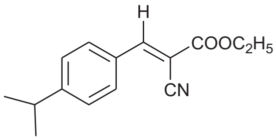
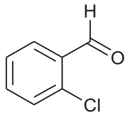
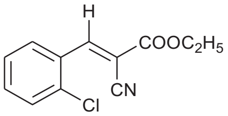
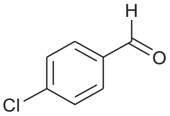
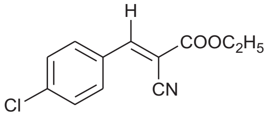
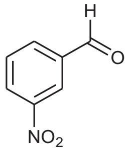
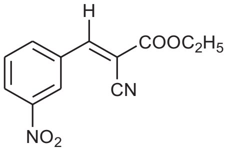
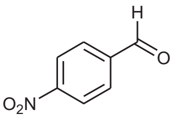
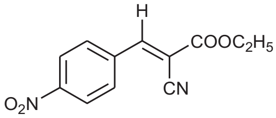
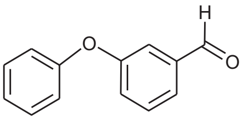
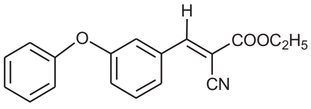
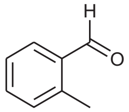
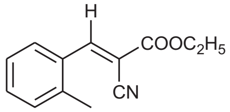
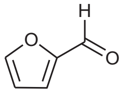
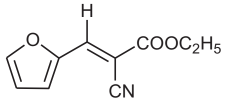
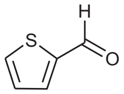
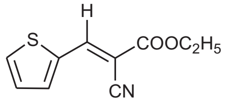
Entry	Substrate	Product	Time (min)	[a],[b]Conversion %	[b]Selectivity %
1			6	97	99
2			3	83	99
3			6	98	99
4			3	91	99
5			3	97	92
6			3	82	87
7			6	89	99
8			3	90	86
9			3	80	99
10			3	99	98
11			3	99	99
12			1.5	96	70

Table 6 (*Continued*)

Entry	Substrate	Product	Time (min)	[a],[b]Conversion %	[b]Selectivity %
13			3	92	91
14			3	94	99
15			3	73	99

[a] Reaction conditions: aldehyde (1 mmol), ethyl cyanoacetate (1 mmol), Catalyst weight: 10 mg, Temperature: 120 °C.

[b] GC and GC–MS analysis.

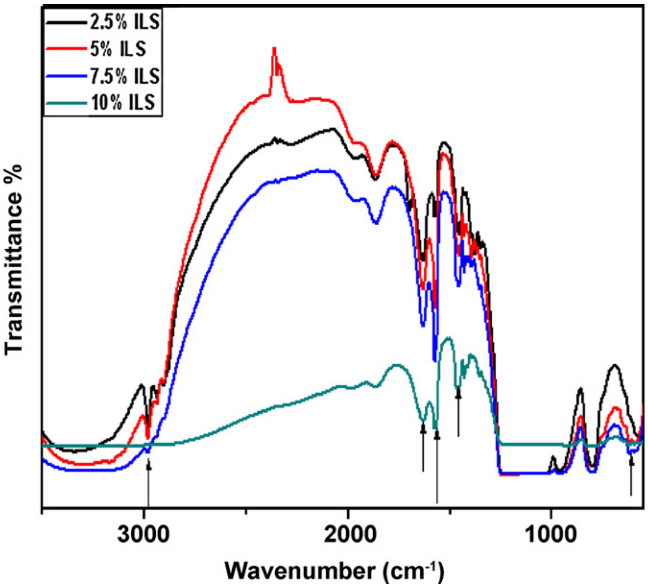
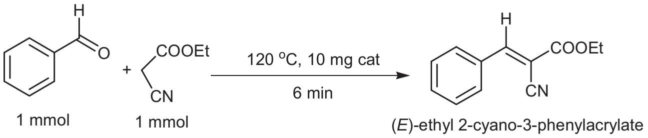


Fig. 6. The FT-IR spectra of ionic liquid functionalized SBA-15 with different concentrations 2.5% ILS, 5% ILS, 7.5% ILS and 10% ILS.



Scheme 2. Knoevenagel condensation catalyzed by ILS.

perature was found to be highly effective for the performance of the catalyst for enhancing both conversion and selectivity. At lower temperature 30 °C, the conversion of benzaldehyde was 4.8% with 18% selectivity. There was regular increase in conversion of benzaldehyde upto 97% and selectivity of ethyl 2-cyano-3-phenylacrylate upto 98% with 6 min using microwave. The higher temperature favored the formation of ethyl 2-cyano-3-phenyacrylate with subsequent condensation of benzadehyde.

3.6.3. The effect of reaction time

The influence of reaction time over conversion and selectivity was also studied (Table 5). The conversion of benzaldehyde (79%) was found to be significant even with very short irradiation 1.5 min. It is presumed that the strong basic sites offered by modified imidazolium chloride groups and the rapid heating of reaction mixture by the microwave could directly activate the reactants to form products. As the reaction time increased (1.5–6 min), the conversion of benzaldehyde increased upto 97% (Table 5) 6 min was found to be the best considerable time for higher conversion and higher selectivity under the employed reaction conditions.

The study of Knoevenagel condensation reaction was then extended to the several substituted aromatic and heteroaromatic aldehydes using the ILS catalyst through microwave irradiation. All the reactions occurred in solvent free conditions within 6 min and gave α, β-unsaturated carbonyl compounds with selectivities in range of 90–99% (Table 6). The Knoevenagel condensation of aromatic aldehydes with both electron-withdrawing groups (such as nitro $-NO_2$) (entries 8–11) and electron-donating groups (such as hydroxyl (–OH), methoxy ($-OCH_3$)) (entries 3–7), gave higher conversions (≥80%) with short time of 3–6 min with good selectivity. The heteroaromatic aldehyde like furfural, thiophenaldehyde also provided appreciable conversions with 99% selectivity within 1.5–3 min.

3.6.4. Reusability studies of ILS

Reusability of the catalyst was tested by carrying out repeated runs of the reaction of benzaldehyde using the catalyst, 7.5% ILS. After each cycle the catalyst was filtered, washed with methylene chloride and dried at 100 °C and then reused for the successive cycles. The reusability studies (Table 7) revealed that the catalyst could recycle without any significant loss in its activity and selectivity.

3.6.5. Plausible mechanism

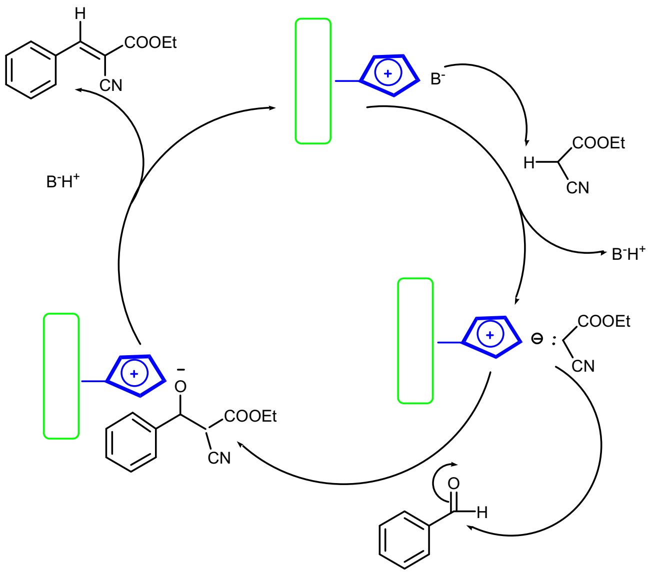
Based on the above experimental results and with reference to previous report [37], the following mechanism for ILS catalyzed

Table 7
The reusability test of 7.5% ILS.

Catalyst	Test	Time (min)	[a],[b]Conversion of Benzaldehyde %	[b]Selectivity of Ethyl 2-cyano-3-phenylacrylate %
7.5% ILS	fresh	6	97	98
7.5% ILS	1 reuse	6	98	98
7.5% ILS	2 reuse	6	96	94

[a] Reaction condition: benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), temperature: 120 °C, time: 6 min.

[b] GC analysis.



Scheme 3. Representative mechanism for the Knoevenagel condensation reaction over ILS through microwave irradiation.

Knoevenagel condensation is proposed in Scheme 3. The solid supported ionic liquid with base character Cl^- (B^-) abstracts a proton from the active methylene group of ethyl cyanoacetate leading to formation of carbanion. The formed carbanion of ethyl cyanoacetate makes nucleophilic attack to the carbonyl carbon atom of aromatic aldehydes, followed by loss of water molecule to form α, β-unsaturated carbonyl compound.

4. Conclusions

In the present study ordered organo functionalized SBA-15 (ILS) were synthesized by the co-condensations of MTESPImCl ionic liquid and sodium metasilicate was carried out in the presence of amphilic triblock co-polymer (P123) as a structure directing agent under the acidic conditions. The morphologies of prepared samples were hexagonal short channeled with platelet type instead of fibrous. The high loading ratio of ionic liquid to silica led to decrease the ordered hexagonal mesoporousity of ILS. The performance of the catalyst depended on loading ratio of the ionic liquid to silica. ILS catalyst of 7.5% loading showed the optimum catalytic activity for Knoevenagel condensation under the employed reaction conditions. The catalyst has wide substrate scope from substituted aromatic to heteroaromatic aldehydes within short reaction times of 6 min in solvent free conditions. The reaction methodology of this heterogenized organocatalyst was elegant, fast and efficient. Further this protocol avoided the use of expensive, harsh chemicals, and leads to high yields of products with very fast reaction time in solvent free media. The catalyst can be easily recovered and reused without loss of its catalytic activity and selectivity.

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