



Cooperative catalysis: Condensation-aromatization for synthesis of 2-(4-nitrophenyl)-1H-benzimidazole by silica immobilized Brønsted-Lewis acidic ionic liquid (Si-BLAIL)

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ABSTRACT

Herein, pleasing the advantageous of both Brønsted and Lewis acidic site of Si-BLAIL the condensation-aromatization reaction has been carried out. The striking distinctiveness of work is optimum reaction condition, easy work-up, high yield, catalyst recyclability, non-inertness of reaction flask, simple catalyst loading method. The decreases in the amount of catalyst and reaction time shows good to high (71%–93%) yield suggests about the involvement of some interesting mechanism such as cooperative catalysis. The mechanism has been hypothesized as, the Si-BLAIL increase the efficiency of condensation reaction possibly by providing the proton in 2-position of cationic imidazolium ring of BLAIL through the hydrogen bond interaction with carbonyl group and nucleophilic activation during aromatization by hydrogen bond acceptor ability of Lewis adduct anion of BLAIL. The catalyst Si-BLAIL shows massive affirm for industrial applications. The Si-BLAIL has identified as the best acid catalyst for 2-(4-nitrophenyl) benzimidazole synthesis with additional benefits of cooperative catalysis.

1. Introduction

The acid catalyzed synthesis are generally preferred for production of various chemical, pharmacologically important synthetic derivatives etc. [1–5] For bulk production, from the academic laboratory to a chemical industry large number of acid catalyst has been used [1]. The conventional mineral acids provides effectual surface area hence it shows privileged catalytic activity but its use allied with several downsides such as, difficulty in product isolation, corrosion of equipments, acidic waste that hazardous to the environment. Solid acids catalysts are environmental and non-volatile but they have an inadequacy such as high molecular weight to active site ratio, severe reaction condition, matrix coupled acidic sites, longer reaction time and fast deactivation [1,2]. Hence, the researcher takes huge efforts for development of new acidic catalyst. From, the last several decayed the Ionic liquids (ILs) has attracted much attention of researchers due to their unique physical and chemical properties such as favorable solvating power, low vapor pressure, wide liquid range, good conductivity, thermal stability, structural designability etc. [3] Moreover, acidic ionic liquids are well known green solvents and catalysts such as- IL has been used for efficient and reusable green catalyst for biodiesel production

[4], Synthesis of 4-phenacylidene flavene [5], tetrahydropyranlylation of alcohols [6], benzoxanthenones derivatives [7], benzoxazoles, benzthiazoles, benzimidazoles [8], The Brønsted acidic ionic liquid was used for one pot reductive amination of aromatic aldehydes [9]. Such, efficient synthetic utility of acidic IL motivates to its use as heterogeneous catalysis. The ILs is also referred as versatile materials used in chemical manufacture plants [10]. The ILs as a solvent or homogeneous catalyst shows good catalytic activity and high selectivity but the use of ILs as a homogeneous catalyst or solvent has several shortcomings such as extremely difficult disposal of waste materials, expensive disposal operations, due to high viscosity of ILs slow substrate diffusion etc. Therefore, generally the use of ILs as Homogeneous catalyst for industrial bulk scale production is not recommended [11].

The Heterogeneous catalysis gets hold of great attention for large scale production in various chemical industries due to its recyclability, easy separation ability, practical convenience, lower corrosion effect etc. The heterogeneous catalysis has been widely used in the organic synthesis [12] by taking advantageous of cooperative effect of catalyst and solid support [13]. Such synergetic effect increases the catalytic efficiency of the catalyst [14] by the surface modification of the active site in the catalyst [15]. The solid supported ionic liquid take the

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combine advantage of catalytic activity of ILs and solid supports. Hence, immobilization of ILs on solid support with or without covalent bond is more desirable [10]. Supported ILs has been effectively used for several organic reactions such as selective oxidation of alcohols [16], esterification [17], synthesis of methyl caprylate [18], one pot synthesis of 1-amidoalkyl 2-naphthols [19], Heterocyclic synthesis, CO₂ dissolution and fixation [20], polycyclic phenolic compound [21], polyoxy-methylene dimethyl ethers [3], Chemoselective synthesis of dicoumarols and substituted xanthene derivatives [22], hydrolysis of cellulose [23], synthesis of biodiesel, alkylation and oligomerisation [2], fuel oil desulfurization [24] etc. The supported Brønsted and Lewis acidic ionic liquid attracted much attention due to their exceptionally strong acidic characters.

Cooperative catalysis is emerging and most powerful strategy in many organic syntheses. During activation of starting material, Cooperative catalysis significantly increases the selectivity and catalytic activity. The catalyst involves hydrogen bond donor and acceptor moiety that activates both electrophilic and nucleophilic sites of the reaction system. The concept of such cooperative catalysis has been used for several reaction such as Michael addition, Povarov reaction [25], Mannich reaction [26], Biginelli reaction [27] etc. During such catalysis the catalytic efficiency is mainly under control of hydrogen bond interaction between catalyst and reactants. For the reactions involving carbonyl activation, the cation and anion of the ILs can cooperatively activate the reaction centre and 1-butyl-3-methyl-imidazolium based ILs shows prominent activity due to 2-position proton of imidazolium ring with same anion. Furthermore, for imidazolium based ILs, the anion Cl shows high catalytic activity very similar to strong hydrogen bond acceptor ability [25]. Hence the dual acidic ionic liquids with Cl containing anion can be more desirable.

2-nitrophenyl substituted benzimidazole is compounds with tremendous biological importance as it shows antimicrobial, anti-inflammatory, anti-histaminic, antiviral, antitumor, anticancer [28] etc activities. Hence, it is well thought-out that compounds are of multipurpose materials such as sensitive fluorescence sensor for the biomolecules sensing [29]. Furthermore, its derivatives can be possibly used for understanding of structural modification of the biomolecules like julolidine [30] and other fluorophores [31,32]. 2-aryl substituted benzimidazoles are synthesized either alkylation of benzimidazole or by condensation followed by aromatization of Orthophenylenediamne (OPD) with aldehydes. The number of conventional Brønsted and Lewis acid catalysts were used however the synthesis methods have shortcomings such as low yield, expensive and unrecyclable catalyst, cruel reaction conditions etc. Those limitations can be overcomes by using Brønsted and Lewis acidic ILs on the solid supports.

Recently, Thai Nguyen et al has been reported first time the benzimidazole synthesis by BAIL gel [8]. Lewis acid catalyst were reported to be superior for benzimidazole synthesis [33]. The benzimidazoles were effectively synthesized by polymer supported pyridinium chloroaluminate as a heterogeneous Lewis acid catalyst [34]. Liu et al. shown that the Lewis acid site are active centers for dehydrogenation and aromatization of isobutane [35]. Hence, by enchanting an advantageous of cooperative catalysis and efficiency of Lewis acidic site we report herein the use of silica supported Brønsted - Lewis acidic ionic liquid (Si-BLAIL) as a heterogeneous catalyst for benzimidazole synthesis. Interestingly, good to excellent yield, easy product separation, catalyst recovery, optimum reaction condition has been achieved. Herein, we employed the idea of cooperative catalysis of Silica immobilized BLAIL obtained by treating BLAIL with silica gel. The adsorption of BLAIL on the surface of silica gel enhances the catalytic activity. Lewis and Brønsted acidic catalysts are well known for benzimidazole synthesis and the Lewis acidic catalysts are considered as effective catalyst for aromatization. We have identified the cooperative catalytic effect of silica supported Brønsted - Lewis dual acidic ionic liquid for benzimidazole synthesis. The Si-BLAIL shows, the simple catalyst loading method, optimum reaction condition especially- room temperature, free air

medium, minimum reaction time, easy work-up, high yield of the product minimum catalyst leaching with respect to other reported silica supported IL catalyst [8,36,37].

2. Experimental section

2.1. Materials and method

1-Methyl imidazole, 1, 4-Butane sultone, aluminum trichloride, Orthophenylenediamne (OPD), 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, 2-chlorobenzaldehyde, 4-N,N-dimethyl aminobenzaldehyde, anisaldehyde were purchased from Molychem, India all has purity 98–99% and used without any further purification. Silica gel (100–200 mesh) was purchased from lobachemia and 4-methylbenzaldehyde (99%) was purchased from spectrochem and used as received. 0.1g of a Si-BLAIL was dissolved in 25 ml distilled water and stirred for 2h at room temperature and kept in dark for 24 h to settle down the solid residue. After decantation the solution was titrated with 0.025 M NaOH and the conductance was recorded after each addition by using Equitronics conductivity meter (Model EQ 665 EQ 665). FTIR spectra were recorded on FTIR spectrometer- 4600, Jasco, Japan. Morphology was characterized by Thermogravimetric analysis (TGA) using Perkin Elmer STA6000 Instrument and by using SEM analysis. The XRD was recorded on Rigaku miniflex-600 equipment using Cu K α radiation ($\lambda = 0.1540$ nm) operated at 30 kV.

2.2. Synthesis of Brønsted -Lewis acidic ionic liquid (BLAIL)

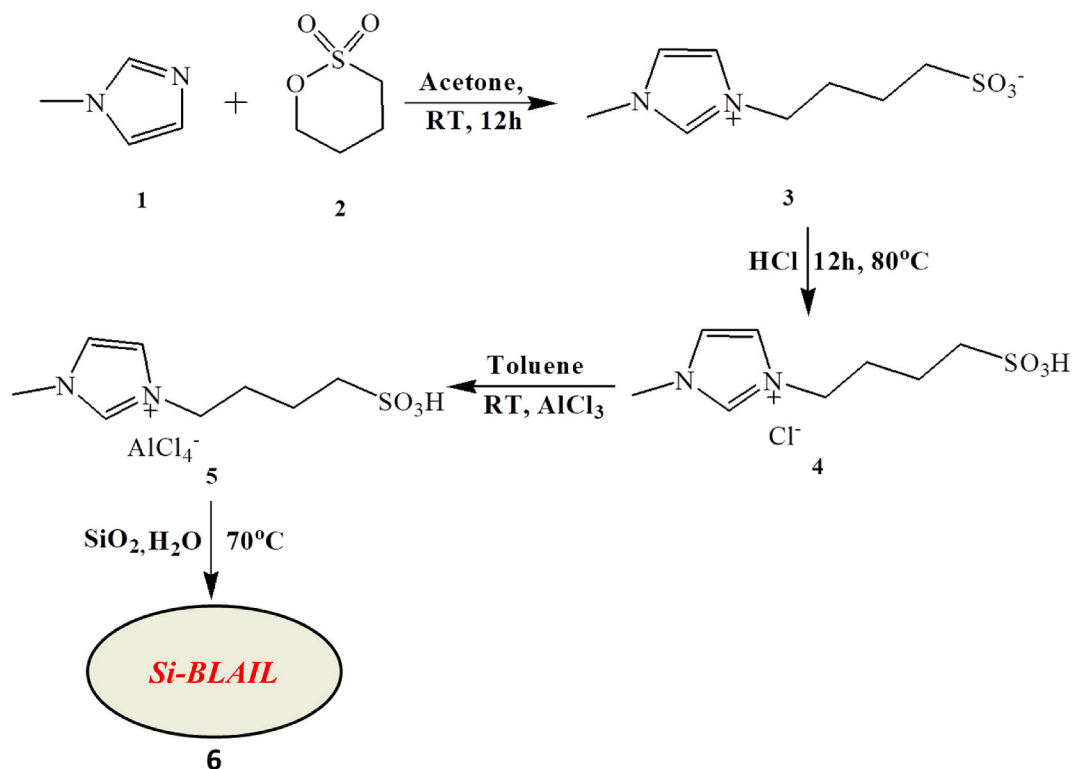
To a vigorously stirred solution of 1-Methyl imidazole (1) (10 mmol) in acetone (25 ml), 1, 4-Butane sultone (2) (11 mmol) was slowly added at room temperature and stirred for 12h. After completion of reaction acetone was decanted and the remaining white solid was separated and was repeatedly washed with diethyl ether to yield pure ionic liquid and dried in vacuum. In the second step ionic liquid (3) was taken in round bottom flask and added equivalent amount of concentrated HCl, then reaction was heated for 24 h at 80 °C. The viscous liquid obtained was dried in oven at 60 °C to give IL (4). This IL (4) was then dissolved in toluene and followed by addition of aluminum trichloride (11 mmol) and stirred it for 24 h at room temperature. Then the solvent was evaporated under vacuum to give the desired BLAIL (5). see the Scheme 1.

2.3. Synthesis of silica supported dual acidic ionic liquid (Si-BLAIL)

Silica gel (100–200 mesh, 10 g) was activated by heating at 100 °C in an oven for 24h. In 50 ml round bottom flask BLA IL (5) (2 g. 41.06 mmol) was dissolved in 10 ml distilled water and heated at 70 °C. The activated silica were added slowly with constant stirring in the hot water and obtained mass (~ 16.6 wt %) is dried in an oven at 100 °C for 48h. The white free flow powder of Si-BLAIL (6) is stored in glass bottle and used without any further activation.

2.4. Procedure for synthesis of 2-aryl benzimidazole

In a 25 ml round bottom flask equipped with magnetic stirrer, Orthophenylenediamne (OPD) (7), (0.200g, 1.85 mmol) and 4-nitrobenzaldehyde (8) (0.279g, 1.85 mmol) was taken with 10 ml absolute ethanol and Si-BLAIL (0.0042g) was added with constant stirring at room temperature. The progress of reaction was monitored periodically by TLC. After completion of a reaction catalyst was separated by adding more ethanol followed by centrifugation and the crude product was precipitated by adding distilled water in ethanol. The crude product was collected by filtration and recrystallized in ethanol to get pure product (9) (0.455g, 1.90 mmol) and formation of product was confirmed by M. P., FT-IR and ¹H-NMR.



Scheme 1. Synthesis of silica gel immobilized dual acidic ionic liquid (Si-BLAIL).

3. Result and discussion

3.1. Characterization of catalyst

Reza et al. has been reported that the structure of silica supported catalyst can be analyzed by different techniques IR, Conductometry, TGA, SEM etc. [17] Hence, the prepared Si-BLAIL was characterized by conductivity measurement, IR, SEM, EDS, DSC, XRD and TGA analysis. The prepared Si-BLAIL catalyst was analyzed for determination of density of acidic group by titrating it with NaOH. The concentration of acid center of the Si-BLAIL has been determined by conductometric titration method. The conductometric titration curve is recorded and shown in Fig. 1. It is quite evident from Fig. 1, that the titration curve is chair shaped which are characteristics of the conductometric titration curve

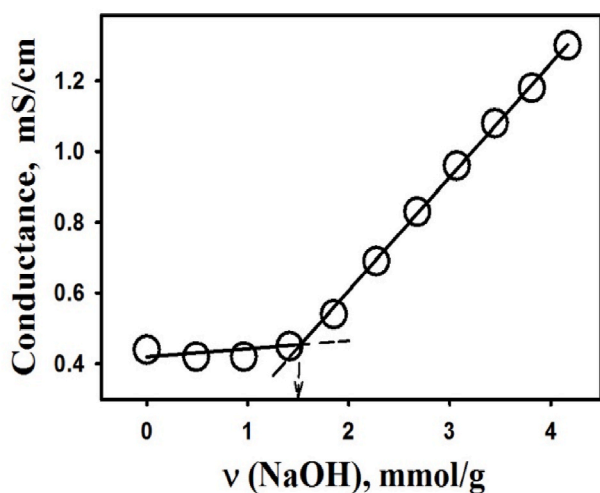


Fig. 1. Conductometric titration Curve of 0.1g of Si-BLAIL with 0.025 M NaOH at room temperature.

for weak acid with strong base. Due to presence of heavy ions in the suspension of Si-BLAIL catalyst, the small change in conductance was observed up to equivalent point. Once the equivalence point is reached then hydroxonium ion goes to increase in the suspension solution and hence conductance increases [38]. The concentration of acid group on the surface of catalyst was found to be $\sim 1.5 \pm 0.05$ mmol/g Such reasonable loading of acid on the surface of silica suggest the adsorption of BLAIL (5) on the surface of Si. The XRD pattern of Si-BLAIL show peak at $2\theta = 22^\circ$ as supported silica only. The XRD data shows that, the nature of the silica support preserves after immobilization of BLAIL [39,40]. (cf. Fig. S3).

3.1.1. Infra-red spectral characterization

The FT-IR spectra of BLAIL, Si and Si-BLAIL have been recorded and the results are shown in Fig. 2. The FTIR spectrum of silica gel has characteristics absorption band in at 3454 cm^{-1} (O-H, Si-O-H stretching), 1633 cm^{-1} (bending vibration of adsorbed water), 1090 cm^{-1} 800 cm^{-1} (Si-O stretching). Reza et. all has been reported that on immobilization of IL on Si-gel surface the spectral characteristics of Si-gel change [17]. Due to immobilization of BLAIL on Si the absorption bands of silica are shifted. It is evident from Fig. 2 that, the Si-IL shows strong absorbance at 3465 cm^{-1} due to Si-OH bond stretching vibration and the water absorbed by the silica gel. The peak at 1563 cm^{-1} and 1644 cm^{-1} correspond to C=N and C=C vibrations of imidazole ring. The band centered at 2958 cm^{-1} and 1455 cm^{-1} are due to C-H stretching and ring deformation of imidazole and long hydrocarbon chain. The strong absorption peak at 1092 cm^{-1} is because of stretching mode of vibration of Si-O-Si bond in the silica. The band at 1168 cm^{-1} is assigned to Si=O stretching vibration. Such spectral changes in the FTIR of Si-BLIL further confirm immobilization of BLAIL on the surface of Si. The presence of two strong peaks at 1092 cm^{-1} & 1168 cm^{-1} further assigned to S = O stretching vibration of SO_3H group of Brønsted acidic site. [41–43]. The S = O stretching vibration in Si-BLAIL suggest the existence of Brønsted acidic site in the catalyst.

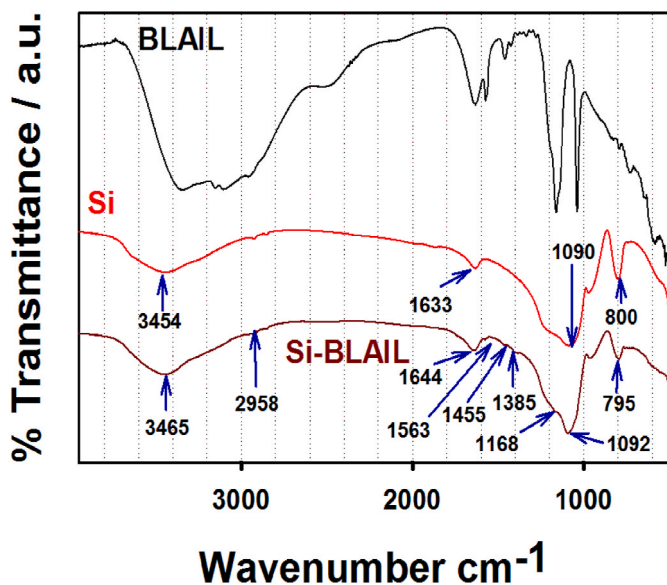


Fig. 2. Fourier Transform Infra-red (FT-IR) spectra of BLAIL neat (solid), silica gel (dashed) and Si-BLAIL (dotted) with KBr pellet. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.1.2. Scanning electron microscopy (SEM)

The SEM images of Si, Si-BLAIL and four times reused Si-BLAIL has been recorded, compiled as reported in literature [44,45] and shown in Fig. 3. Fig. 3A and B, 3C demonstrate that, the dimension of silica is approximately unchanged after immobilization of BLAIL and reused four times. The unaffected particle size of Si indicates the mechanical permanence of Si during the immobilization processes. The inset of Fig. 3B shows that, the surface morphology of Si-BLAIL has small aggregate type shell. These aggregate type layer is not observed for Si only (inset of Fig. 3A) hence, the aggregate type shell formation is due to immobilization of BLAIL. Such changes in the surface morphology of silica due to immobilization of IL was reported earlier [3]. The

formation of such aggregate type shell in Si-BLAIL confirms the immobilization of BLAIL on the surface of silica. Fig. 3C show the particle size and surface morphology of Si-BLAIL recycled four times almost remains constant. The EDS spectrum of Si-BLAIL and four times reused Si-BLAIL shows the presence of S, Cl, Al and O elements further suggest the presence of both Brønsted and Lewis acidic sites. (cf. Fig. S2).

3.1.3. Thermogravimetric analysis (TGA)

The thermogravimetric analysis of Si and Si-BLAIL has been carried out and presented in Fig. 4. Fig. 4 reveals that, the activated silica dose not shows any significant peak in the TGA. Additionally, the silica shows approximately 8% of weight loss as the nature of Si is hygroscopic that is responsible for such peak in TG curve and such weight loss has been reported for silica [46]. The observed weight loss is expected due to removal of absorbed water with dehydroxylation of silica surface.

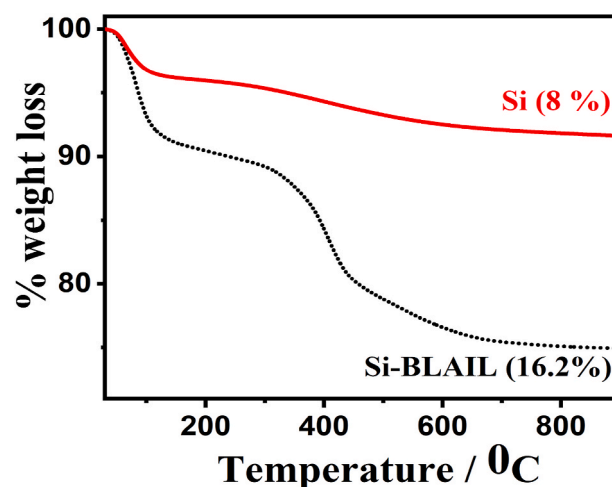


Fig. 4. The TG curve of Silica gel (solid line) and Si-BLAIL (dotted line). Samples were dried in a hot air oven at 80 °C for 30 min before recording the spectra.

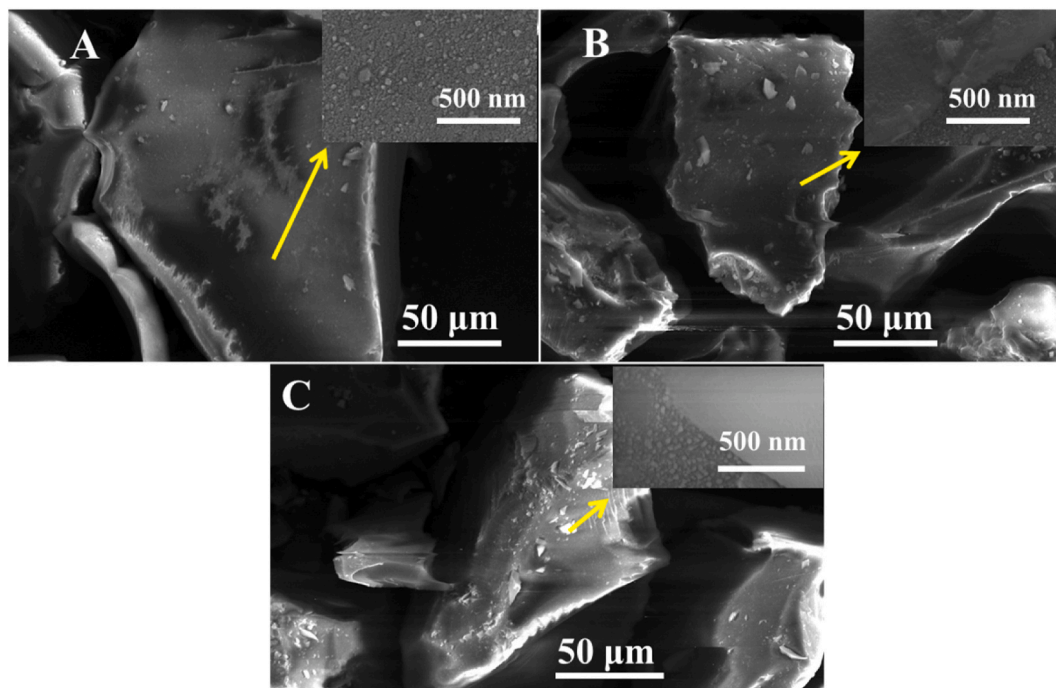


Fig. 3. The SEM images of Silica (A), Si-BLAIL (B), and (C) after four times reused Si-BLAIL catalyst.

Furthermore, it is also evident from Fig. 4 that the Si-BLIL shows weight loss in two stages, the first stage of weight loss over the range of 52 °C–148 °C, slightly higher than Si can be due to desorption of absorbed water which remains associated with Si after immobilization of BLAIL with silica by using water as a solvent. The thermal decomposition of Si-BLAIL shows the second step weight loss of approximately 16.2% over the temperature range 148 °C to 700 °C which can be due to degradation of bounded BLAIL. The removal of BLAIL from the surface of Si was further supported by the DSC curve (cf. Fig. S1). At a temperature higher than 700 °C the constancy in the weight indicates the presence of only Si. The loading of BLAIL on the surface of silica in weight percent can also be determined by analyzing the TG curve [17]. The detail analysis of TG curve shows that loading of BLAIL on Si is 16.18%, that matches very well with the weight percent determined by the calculations.

3.2. Application to synthesis of 2-aryl substituted benzimidazole

The Thai Nguyen et al. reported the synthesis of benzimidazole using BAIL gel as a catalyst [8]. They were not getting any product formation below 100 °C under solvent free condition and time required for completion of reaction was minimum of 5 h. The Lewis or Brønsted acid centers are known for the condensation and formation of Schiff base of acetaldehyde [47]. P. Sarma et al. and A. Khazaei et al. has been reported that, synthesis of benzimidazole at room temperature is also feasible by the use of high-valent oxidoiron (IV) as an intermediate in presence of FeCl₃ and air [48,49]. The dehydrogenation and aromatization of isobutene by Lewis acid as active centers were reported by Liu et al. [35]. The presence of H-bonds in ILs as a catalyst reduce the energy barrier of the reaction with stabilization of transition state [50] Furthermore, Hong Bo Wang et al. shown that the Mannich reaction can be catalyzed by mesoporous silica supported Brønsted-Lewis dual acidic ionic liquid with mild reaction condition, excellent yield and good reusability of the catalyst by the cooperative catalysis methodology [26]. Hence, our expectation is that it is possible to synthesize the benzimidazole derivatives at ambient temperature in suitable solvent with minimizing the reaction time. To check the possibility of such synthesis we have tested catalytic efficiency of Si-BLAIL for synthesis of benzimidazole.

The BLAIL was synthesized by the method as described earlier, characterized by the various techniques and tested for their catalytic efficiency as a heterogeneous catalyst for the synthesis of 2-aryl benzimidazole. Firstly, we have compared the catalytic activity of number of traditional Brønsted and Lewis acid catalyst towards synthesis of 2-aryl benzimidazole that reported in the literature and presented in Table 1. It has been observed from Table 1 that, the velocity of a reaction enhances drastically with maximizing the greener approach towards the synthesis of 2-aryl substituted benzimidazole with moving from traditional catalyst to supported heterogeneous catalyst. Nowadays, lot of researchers

Table 1
Brønsted and Lewis acid catalyst used for synthesis of 2-aryl benzimidazole.

Sr. No.	Catalyst	Reaction condition	% Yield / Time (h)	[Ref.]
1	No catalyst	Reflux in Ethanol	27 / 6	[33]
2	0.3 wt% ZrO(NO ₃) ₂	Reflux in Ethanol	58 / 3	[33]
3	1 wt% ZrO(NO ₃) ₂	Reflux in DCM	70 / 4	[33]
4	0.05 mmol Yb(OTf) ₃	R.T., Solvent free	66 / –	[51]
5	5 wt% FeCl ₃ /PANI	R.T., in Ethanol	50 / 1.5	[52]
6	19 wt% FeCl ₃ /PANI	R.T., in Ethanol	70 / 3	[52]
7	5 wt% H ₃ BO ₃	R.T., in water	60 / 1	[53]
8	BLAIL	R.T., in Ethanol	20 / 12	This work
9	0.1 mmol PS-PyCl-xAlCl ₃	R.T. in Ethanol	83-95 / 6–30 min.	[54]
10	BAIL gel	130 °C, Solvent free	88 / 5	[8]

focused on the solid supported heterogeneous catalyst for efficient synthesis hence we have plan for such benzimidazole synthesis and to the best of our knowledge this is the second report for such synthesis using dual acidic ionic liquid immobilized on silica. The Thai Nguyen et al. have been used only Brønsted acidic ionic liquid [8] but we have employed Brønsted and Lewis dual acidic ionic liquid for such synthesis. Because of both acidic sites in the catalyst the reaction condition such as temperature, time decreases drastically.

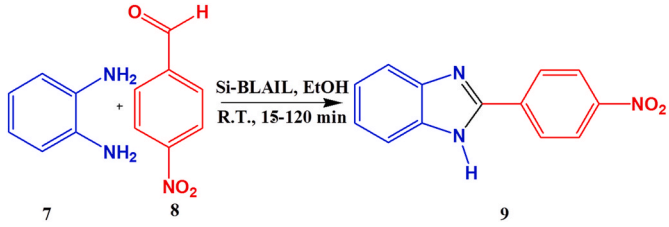
3.2.1. optimization of reaction condition

The condensation and aromatization reaction between OPD and 4-nitrobenzaldehyde to form 2-(4-nitrophenyl)-1-H-benzimidazole has been considered as a model reaction to study the catalytic activity of the Si-BLAIL. The silica gel does not show any product formation after 48h for condensation reaction between OPD and 4-nitrobenzaldehyde. Then we have tested the efficiency of Si-BLAIL towards product formation by changing the quantity of catalyst and it was observed that 4.2 mg (see table- 2) of catalyst is good enough to form benzimidazole in possibly minimum time with good yield. The most effective catalytic activity involves the less energy consumption with respect to mild reaction condition and amount of catalyst [55]. Hence the amount of Si-BLAIL of 4.2 mg is considered as effective for the formation of product. Moreover, the effect of solvents on the reaction condition has been carried out. The solvent mixture Ethanol-Water takes longer time to complete the reaction with minimum yield of the product. Also Table 2 reveals that, the ethanol is good solvent for this reaction as it shows good yield (87.04%) only in 60 min Also the ethanol is referred as good and relatively less volatile solvent in organic synthesis. Hence, the ethanol is selected as best fit solvent for this synthesis. The formation of 2-(4-nitrophenyl)-1H-benzimidazole (9) has been confirmed by FTIR and ¹H-NMR as representative example (cf. Fig. S4).

3.2.1.1. Typical reaction mechanism. The detailed mechanism was not clearly understood hence by considering the Thai Nguyen et al. proposed reaction mechanism; possible route for the formation of benzimidazole has been discussed by considering the concept of cooperative catalysis. During the aromatization, the participation of Si-BLAIL is also expected. The interaction of aldehydes with acidic site of the catalyst leads to protonation of carbonyl oxygen of aldehyde. The protonated aromatic aldehyde reacts with –NH₂ group of OPD gives an intermediate (X). The intermediate (X) on dehydration leads to formation of imine (Y) and another –NH₂ group of (Y) attacks imine to generate intermediate (Z) [8]. It has been mentioned earlier that the Lewis acid sites are responsible for aromatization of isobutane [35] and acidic site of the catalyst in presence of oxidizing agent is liable for the catalytic oxidation of the

Table 2

The optimization of solvents, time and amount of catalyst for the synthesis of benzimidazole by using Si-BLAIL as a catalyst.



Entry	Solvent	Cat. / (mg)	Time / min.	% Yield
1	EtOH	SiO ₂ -only	–	–
2	EtOH	4.200	60	87.00
3	EtOH	8.400	60	81.04
4	EtOH	16.800	70	97.84
5	EtOH	40.000	115	93.33
6	EtOH:H ₂ O (9:1)	4.200	120	72.98

reaction site [56,57]. Hence, it is considered that the intermediate (Z) either in presence of Si-BLAIL and air oxygen (O_2) undergoes partial oxidation to form the benzimidazole or in presence of Lewis acid site of the Si-BLAIL in the reaction mixture undergoes aromatization and leads to formation of benzimidazole by dehydrogenation. The enhancement in the yield with reduction in the amount of catalyst and changing the reaction medium suggest the special kind of reaction mechanism. Hence, the formation of benzimidazole was considered by the fact that cooperative catalysis effect of Brønsted and Lewis acidic sites of the Si-BLAIL (see the Scheme 2) and such Cooperative catalysis was reported by for Mannich reaction [26], Biginelli reaction [27].

3.2.2. Entry

To estimate the substrate scope of the Si-BLAIL, the Si-BLAIL has been tested for the synthesis of other substituted benzimidazole and the product formation was confirmed by comparing the melting point (MP), characterization of synthesized compound with that reported in the literature. The result is presented in Table 3, it is evident from Table 3 that the yield and time required to complete the reaction depends on the position and electronic character of the substituent on the benzaldehyde. The catalyst shows medium to good product formation capability in 15–240 min. Hence, it can be interpreted that the Si-BLAIL has good catalytic activity as a heterogeneous catalyst over the selected range of substituent on benzaldehydes.

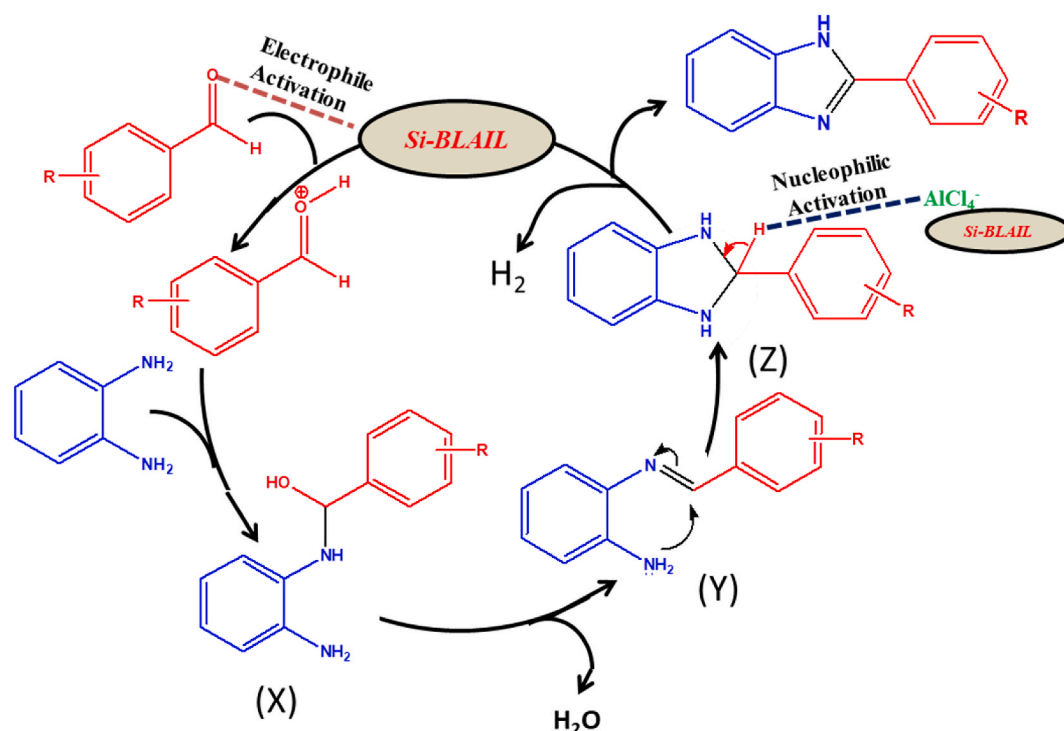
3.3. Reusability study

The efficiency of catalyst is largely determined by their ability to show the catalytic activity after number of runs. Hence, the reusability of the Si-BLAIL was monitored for the model reaction OPD, 4-nitrobenzaldehyde in ethanol at room temperature. After completion of a reaction monitored by TLC, the product was isolated by the dilution of reaction mixture with ethanol and catalyst was recovered by centrifugation followed by washing with hexane and dried in oven at 100 °C for 2h. And the white free flow powder is used for next run. The recoverability of the catalyst was recorded and presented in Fig. 5. Fig. 5 reveals that Si-BLAIL can be used at least four successive runs without

considerable loss in its catalytic activity. The present results clearly indicate the sustainability and reusability of the Si-BLAIL under the given reaction condition. The catalyst leaching has been investigated by hot filtration type test [36,60]. In the hot filtration test, continuous monitoring of the TLC for reaction between OPD and 4-chlorobenzaldehyde has been carried out. The TLC of a reaction mixture at after 70 min (50% completion of reaction) shows the unreacted aldehyde in the reaction mass. The same reaction mixture was then centrifuged and filtered to separate the Si-BLAIL and filtrate continue to stirring for next 240 min After 150 min The TLC shows again unreacted starting aldehyde. Further, after 240 min monitoring of TLC shows unreacted starting material. In presence of catalyst the starting was completely consumed in 150 min but on removing the catalyst after 70 min The reaction was not complete after 310 min suggest that, the possibility of leaching of Si-BLAIL is minimum.

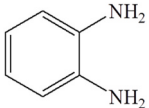
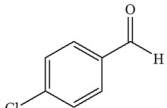
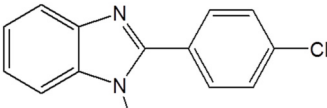
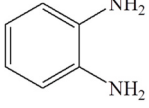
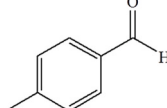
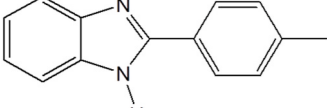
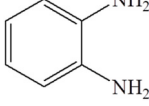
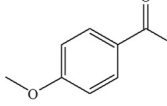
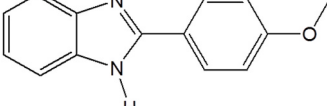
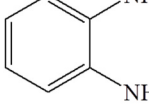
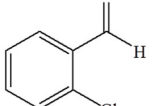
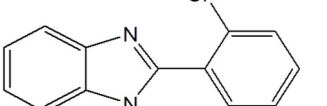
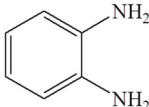
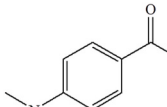
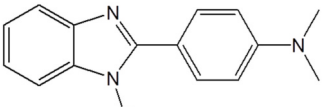
4. Conclusion

In conclusion, The Si-BLAIL contains both the hydrogen bond donor and acceptor moiety that activates both electrophilic and nucleophilic sites of the reaction system. Further, the reduction in the amount of catalyst and the large decreases in the reaction time with optimal reaction condition recommend the participation of both the cations as well as anions of Si-BLAIL. The presence of hydrogen bonding ability and both cations and anions increases the efficiency of Si-BLAIL as a heterogeneous catalyst. Hence, we have prepared heterogeneous, green, and efficient silica immobilized 1-methyl-3-(4-sulphobutyl)-1H-imidazolium tetrachloroaluminate (Si-BLAIL) as a cooperative catalyst for synthesis of 2(4-nitrophenyl)-1H-benzimidazole. The Si-BLAIL catalyzes the condensation-aromatization reaction compliantly. Moreover, the optimum reaction condition with respect to reaction time, temperature and solvent system were achieved using only 4.2 mg of Si-BLAIL. The ideal reaction condition, simplicity of catalyst preparation and characterization method and reusability makes the Si-BLAIL as an effective cooperative catalyst.



Scheme 2. Proposed reaction mechanism of the synthesis of benzimidazole.

Table 3
Substrate scope of Si-BLAIL toward synthesis of more benzimidazoles derivatives.

Substrate	Aldehyde	Time / min.	Product	% Yield	M.P. / °C [Ref.]
		150		86.02	292–295 °C [54]
		60		87.00	236–239 °C [58]
		240		71.14	217–220 °C [58]
		60		79.00	230–232 °C [54]
		15		93.00	236–240 °C [59]

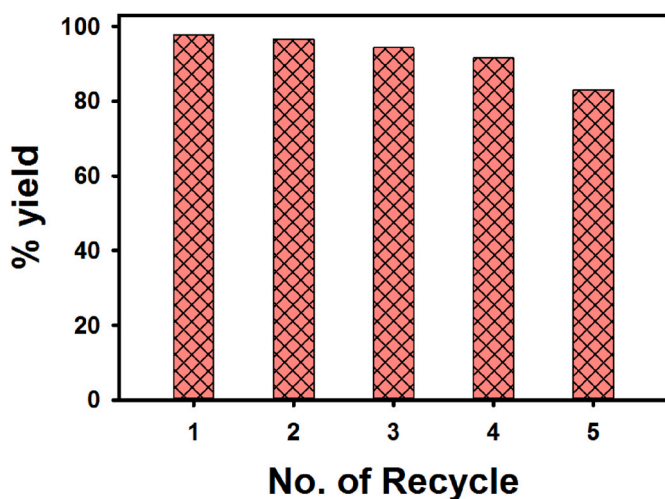


Fig. 5. Reusability study of Si-BLAIL for a model reaction of Ortho-phenylenediamine (OPD) (**7**), (0.200g, 1.85 mmol) and 4-nitrobenzaldehyde (**8**) (0.279g, 1.85 mmol) in 10 ml absolute ethanol and Si-BLAIL (0.0042g) was added with constant stirring at room temperature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

No any financial interest / personal relationship are considered as potential competing interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jics.2022.100550>.

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