



Silica gel supported $-SO_3H$ functionalised benzimidazolium based ionic liquid as a mild and effective catalyst for rapid synthesis of 1-amidoalkyl naphthols

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ABSTRACT

The use of ionic liquid in catalysis is attracting more and more attention in the field of chemistry. In line with the research we have studied Supported Ionic Liquid Catalyst (SILC) which consist of benzimidazolium based ionic liquid immobilized on silica based solid support. The SILC proved to be an efficient heterogeneous catalyst for solvent less synthesis of 1-amidoalkyl naphthols from 2-naphthol, amides and aldehydes. The process represents a simple, ecologically safer, cost effective route to 1-amidoalkyl naphthol with high product quality, as well as easy product recovery and catalyst recycling.

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1. Introduction

Devising reactions that achieve multi-bond formation in one-operation is becoming one of the major challenges in step economic process. Multicomponent reactions (MCRs) have emerged as an important tool for building of diverse and complex organic molecules through carbon-carbon and carbon-heteroatom bond formations taking place in tandem manner [1–4]. *o*-Quinone methides (*o*-QMs) have emerged as interesting molecules due to their toxicological properties against both normal and cancerous cells and also proposed intermediary in the formation of many biologically important polymers [5]. *o*-QMs also act as intermediates for the synthesis of antitumor agents [6]. One of the tandem reactions which involves the *in situ* generation of *o*-QMs and its reaction with acetamide or benzamide gives amidoalkyl naphthols [7]. 1-Amidoalkyl naphthols can be easily hydrolysed to 1-aminoalkyl naphthol, which shows biological activities like depressor and brady-cardiac effect [8,9]. This 1-aminoalkyl alcohol-type ligand has been used for asymmetric synthesis and also as a catalyst [10,11]. Amidoalkyl naphthols can be prepared by the multicomponent condensation of aldehydes, 2-naphthols and amides using different catalysts such as Montmorillonite K10 [12], p-TSA [7], I_2 [13], $K_5CoW_{12}O_{40} \cdot 3H_2O$ [14], $HClO_4-SiO_2$ [15], $Fe(HSO_4)_3$ [16], $FeCl_3-SiO_2$ [17], BAIL [18,19], P_2O_5 [20], cyanuric chloride [21],

thiamine hydrochloride [22], trityl chloride [23], [FemSILP] L-proline [24], silica sulphuric acid [25,26], 1-hexane sulphonic acid sodium salt [27], Zwitterionic-type molten salt [28]. However, some of these reported procedures suffer from one or more drawbacks such as long reaction times, high temperatures, low yields of products, use of toxic organic solvents, use of expensive metal salts as catalysts and tedious work up procedures. Therefore, there is still an increasing interest in catalytic system for the synthesis of 1-amidoalkyl naphthols.

In recent years, ionic liquids (ILs) have become powerful alternatives to conventional molecular organic solvents due to their particular properties, such as undetectable vapour pressure and the ability to dissolve many organic and inorganic substances [29]. In addition, ILs are readily recycled and tuneable to specific chemical tasks. One type is Bronsted acidic ILs (BAILs). The acidic nature of these ILs as catalyst has been exploited for many other important organic reactions, which proceed with excellent yields and selectivities and demonstrate the great potential of these ILs in catalytic technologies for chemical production [30–34].

Recently, immobilization process involving acidic ILs on solid supports has been designed. The heterogenization of catalysts and reagents can offer important advantages in handling, separation and reuse procedures. Based on economic criteria, it is desirable to minimize the amount of IL utilized in a potential process. Immobilized acidic ILs have been used as novel solid catalysts for many acid catalysed reactions such as esterification, nitration reaction and acetal formation [35,36]. On the other hand examples for the synthesis of amidoalkyl naphthol using efficient heterogeneous

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systems with solid acids, polymer supported peracids, zeolites or amberlyst 15 with various groups deposited onto silica are known [37,38].

In continuation of our recent studies to develop mild and environmentally friendly procedures using ILS in organic synthesis, herein, we report our results on the efficient and rapid synthesis of 1-amidoalkyl naphthols using sulfonic acid functionalised benzimidazolium based Supported Ionic Liquid Catalyst (SILC) as a mild and effective catalyst under solvent free conditions.

2. Experimental

2.1. Materials and instrumentation

Silica gel 230–440 mesh (0.037–0.063 mm) was purchased from Spectrochem, India and was used for the preparation of the support. (3-Chloropropyl)triethoxysilane, benzimidazole, 1,3-propanesultone, were purchased from Sigma–Aldrich, India and were used without further purification. FT-IR spectra were recorded on ABB FTIR, Canada, using KBr pellets. Thermal gravimetric analysis (TGA) data was obtained with a heating rate of 5 °C/min on a TGA/DTA (TA instruments model 5000/2960 thermogravimetric analyser, USA). C, H, N elemental analysis was carried out on Perkin Elmer, USA (2400, Series II). The synthesized amidoalkyl naphthols were identified by ¹H and ¹³C NMR, (400 MHz Bruker Scientific, Switzerland).

2.2. Synthesis of 3-chloropropyl silica (1)

3-Chloropropyl silica (1) was prepared by modifying the method used by Adam et al. [39]. A mixture of silica (5.0 g) and (3-chloropropyl)triethoxysilane (5.0 mL, 42.5 mmol) were taken in 10 mL of toluene was allowed to stir at room temperature for 15 min and then refluxed for 24 h. After completion of reaction, reaction mixture was cooled, and the product was filtered and repeatedly washed with toluene (3 × 5 mL) and dried under reduced pressure at 100 °C for 8 h to produce 3-chloropropyl silica (1) (4.9 g).

IR: 473, 805, 959, 1091, 1631, 3422 cm⁻¹.

TGA: Data shows that the prepared silica is stable up to 245 °C. Complete loss of all the covalently attached organic structure is seen at about 618 °C and the amount of organic moiety was about 15% against solid catalyst silica.

2.3. Synthesis of 3-(1-benzimidazole)propyl silica (2)

A solution of benzimidazole (1.17 g, 10 mmol) was prepared in dry benzene to which 50% sodium hydride in mineral oil (0.479 g, 10 mmol) was added and stirred at room temperature for 3 h under nitrogen atmosphere to give sodium benzimidazole. Then 3-chloropropyl silica (1) (5.00 g) was added and the mixture was refluxed under a nitrogen atmosphere for 24 h. The resulting product was filtered and washed with ethanol and dried under vacuum at 100 °C for 24 h to give 4.89 g of 3-(1-benzimidazole)propyl silica (2).

IR: 479, 743, 803, 1088, 1463, 1629, 3424 cm⁻¹.

TGA: Data shows that complete loss of the covalently attached organic moiety occurs at 536 °C and the amount of organic moiety was about 23% against the solid support and the loading of benzimidazole group was found to be 0.743 mmol/g.

2.4. Synthesis of sulfonic acid functionalised solid support (3)

3-(1-Benzimidazole)propyl silica (2) (4.00 g, 3 mmol of benzimidazole group) was suspended in 10 ml of toluene and 1,3-propane sultone (0.378 g, 3.1 mmol) was added to it. The reaction mixture was allowed to stir at 100 °C for 6 h. The resultant is cooled to

Table 1

The effect of different amounts of SILC on the reaction of 2-naphthol, acetamide and 3-nitrobenzaldehyde.

| Entry | Immobilized IL (mg) | Time (min) | Yield % |
|-------|---------------------|------------|-------------|
| 1 | 0 | 60 | No reaction |
| 2 | 10 | 60 | 32 |
| 3 | 30 | 20 | 52 |
| 4 | 50 | 15 | 78 |
| 5 | 80 | 7 | 95 |
| 6 | 100 | 7 | 95 |
| 7 | 120 | 6 | 92 |

room temperature, filtered and washed several times with toluene. This was further treated with 36% w/w concentrated hydrochloride (3 mmol) and allowed to stand at room temperature for 24 h. The obtained material was then washed with ether, dried under vacuum at 100 °C for 24 h to give sulfonic acid functionalised Supported Ionic Liquid Catalyst (SILC) (3).

IR: 463, 795, 1088, 1158, 1566, 1643, 1859, 2962, 3472 cm⁻¹.

TGA: Data shows complete loss of covalently attached organic moiety occurs at 542 °C and the amount of organic moiety was about 24% against solid support.

CHN: Found C, 8.02; H, 2.133; N, 1.79%.

Calc. for SiO₂·0.0458(C₁₃H₂₀N₂–SO₃Cl)·0.5H₂O: C, 8.54; H, 2.29; N, 1.86%.

Determination of acidic sites: In a typical experiment 0.05 g of immobilized IL (vacuum dried sample to remove moisture presence) was added to 10 g aqueous solution of NaCl (2 M). The resulting suspension was allowed to equilibrate for 48 h and then titrated potentiometrically with 0.01 M NaOH (aq) using phenolphthalein as an indicator [40].

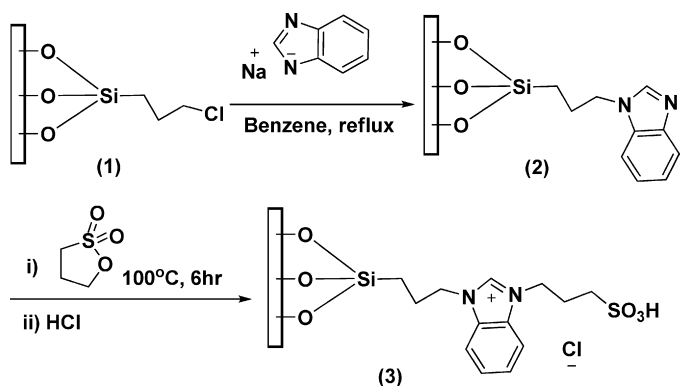
2.5. General synthesis for the preparation of amidoalkyl naphthols

A mixture of aldehyde (20 mmol), 2-naphthol (20 mmol), amide (24 mmol) and SILC (80 mg) were taken in round bottom flask and stirred for the desired time (as indicated by TLC) at 100 °C in a pre-heated oil bath. The resultant solid was then washed with hot water to remove excess amide. Then acetone was added to it stirred well and filtered off. The solid catalyst (residue) was washed with acetone and dried. The filtrate was evaporated to remove solvent and the crystalline material left was taken up in ethanol for recrystallisation. The synthesized amidoalkyl naphthols were characterized by ¹H NMR and ¹³C NMR and comparison of their physical data with the literature.

Spectral data of N-[(2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl]acetamide (Table 3, entry 7): pale yellow solid; M.P. 248–249 °C. ¹H NMR (400 MHz, DMSO-*d*₆): 2.032 (s, 3H), 7.18–7.42 (m, 6H), 7.80–8.15 (m, 5H), 8.56 (d, 1H), 10.11 (s, H); ¹³C NMR (400 MHz, DMSO-*d*₆): 23.0, 48.3, 118.3, 118.8, 123.0, 123.4, 123.7, 127.1, 127.6, 128.4, 128.9, 129.1, 129.3, 132.6, 142.1, 146.4, 151.7, 153.8, 170.1.

2.6. Reuse of the sulfonic acid functionalised solid support

The reusability of SILC was tested for the reaction of 3-nitrobenzaldehyde, acetamide and 2-naphthol. After completion of reaction acetone was added to the reaction mixture for dissolution of product. The catalyst was filtered, washed with acetone and dried under vacuum at 80 °C for 24 h. This recycled catalyst was used for the synthesis of amidoalkyl naphthols using procedure Section 2.5. The SILC was then recycled for five runs and the catalytic activity displayed very good reusability.



Scheme 1. Synthesis of sulfonic acid functionalised benzimidazolium based Supported Ionic Liquid Catalyst (SILC).

3. Results and discussion

3.1. Preparation and characterization of the catalyst

Supported Ionic Liquid Catalysts are prepared either by simple physical adsorption or by covalent attachment of ILs onto the surface of a solid support. We choose the later method to immobilize the IL since this provides better stability in the catalytic reaction and less leaching during the work up. Sulfonic acid functionalised benzimidazolium based Supported Ionic Liquid Catalyst (SILC) was synthesized in two steps. In the initial step (3-chloropropyl) triethoxysilane was first treated with silica gel, where the binding between the groups occurs through covalent bonds giving 3-chloropropyl silica (1). After this, nucleophilic addition of the chlorine with benzimidazole gave 3-(1-benzimidazole)propyl silica (2). Condensation of 3-(1-benzimidazole)propyl silica with 1,3-propane sultone produced the benzimidazole salt, which was treated with one equivalent of hydrochloric acid to give SILC (3) (Scheme 1). This is a simple two step synthesis of acidic IL grafted silica when compared with the earlier approach for the preparation of a similar catalyst [39].

SILC was characterized by FT-IR spectroscopy, thermogravimetric–derivative thermogravimetric analysis (TG–DTA) and elemental analysis. As can be seen from Fig. 1, the FT-IR spectra of SILC exhibits two characteristic peaks at 1566 cm^{-1} and 1643 cm^{-1} which are due to C=N and C=C vibra-

Table 2

The effect of temperature on the reaction of 2-naphthol, acetamide and 3-nitrobenzaldehyde.

| Entry | Temperature ($^{\circ}\text{C}$) | Time (min) | Yield % |
|-------|------------------------------------|------------|---------|
| 1 | 40 | 240 | 72 |
| 2 | 60 | 150 | 77 |
| 3 | 80 | 45 | 83 |
| 4 | 100 | 7 | 95 |
| 5 | 110 | 7 | 94 |
| 6 | 120 | 6 | 92 |

tions of the benzimidazole ring. Moreover, two important peaks at 1088 cm^{-1} and 1165 cm^{-1} assigned to S=O stretching vibration [41,42]. The broad peak at 3472 cm^{-1} belongs to Si–OH groups and adsorbed water in silica. Additional bands at 2962, 1859 cm^{-1} are due to C–H stretching deformation vibrations of the benzimidazole moiety and alkyl chain.

The stability of the SILC was determined by thermogravimetric analysis (Fig. 2). The TG curve indicates initial weight loss of 3.6% up to 66°C due to surface silanol groups and the adsorbed water in silica. Complete loss of all the covalently attached organic structure is seen in the temperature range of $230\text{--}660^{\circ}\text{C}$. The shouldering observed from 357°C onwards may be due to the decomposition of alkyl-sulfonic acid groups. The amount of organic moiety was found to be about 24% against total solid catalyst. From the thermogravimetric analysis data, the empirical formula of the catalyst can be calculated as $\text{SiO}_2 \cdot 0.0458(\text{C}_{13}\text{H}_{20}\text{N}_2\text{--SO}_3\text{Cl}) \cdot 0.5\text{H}_2\text{O}$ and was also in consideration with the elemental analysis results.

The amounts of sulfonic acid groups after synthesis of SILC were measured by means of acid–base titration. Ion-exchange capacities of the sulfonic acid group were determined using aqueous solution of sodium chloride as exchange agents. The acidic site loading in SILC was found to be 0.588 mmol/g and the nitrogen analysis of SILC indicates 0.64 mmol/g of acidic IL was grafted on to the surface of the silica support. The agreement between the ion exchange capacities measured using sodium as exchange ions as well as with the organic group loading determined by TGA (0.546 mmol/g), is in clear evidence that the sulfonic groups are principally located on the porous surfaces of the silica, where they are accessible for adsorption and catalytic reaction processes.

3.2. Synthesis of 1-amidoalkyl naphthols using SILC

To optimize the reaction conditions, reaction of 2-naphthol, 3-nitrobenzaldehyde and acetamide in presence of SILC was selected as a model reaction. To check the activity, initially the reaction was stirred at 100°C for 10 min, and the corresponding product was obtained in 95% yield. With this result in hand, we gradually increased the amount of SILC from 0 to 120 mg (Table 1). The result shows that in absence of SILC no reaction was observed over a period of 1 h. As the amount of SILC increased, there is gradual increase in yield and on further increase up to 120 mg a little decrease in the yield was observed. Thus we used 80 mg of SILC for the synthesis of 1-amidoalkyl naphthol. Then to optimize the temperature of the reaction, we carried out the reaction using 80 mg of SILC at various temperatures under solvent free conditions (Table 2). The results clearly show that 100°C is an effective temperature in terms of reaction time and yield obtained. Therefore we used 80 mg of SILC for the synthesis of amidoalkyl naphthols from various aldehydes, amides or urea and 2-naphthols under solvent free conditions at 100°C . To check the reproducibility of the catalyst, the same reaction was carried out five times; it gave the same yield of the product ($\pm 2\%$). Possible mechanism of the reaction is shown in Scheme 2. The sulfonic acid functionalised part participate in the reaction which activate the aldehyde followed by nucleophilic addition of 2-naphthol forming the

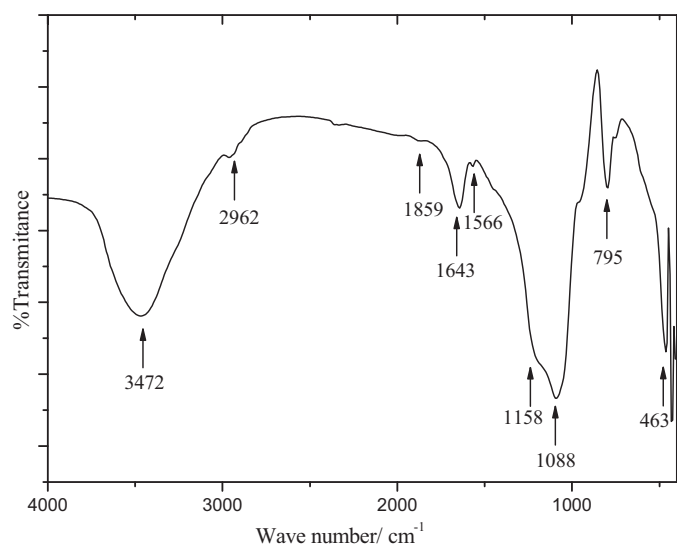


Fig. 1. FT-IR spectrum of SILC.

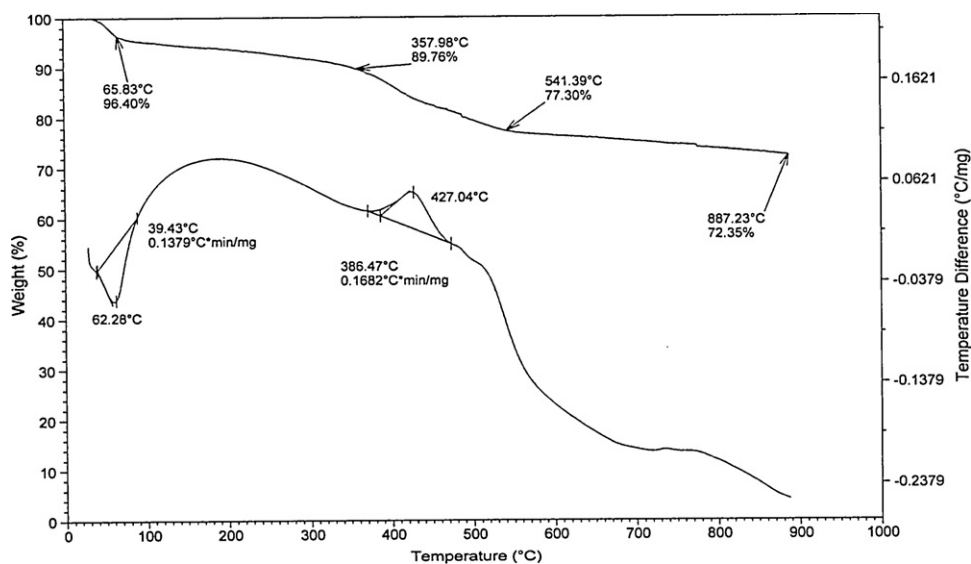


Fig. 2. TGA-DTA of SILC.

intermediate *ortho*-quinone methides (*o*-QMs). The *o*-QMs then react with amides or urea *via* a Michael addition to afford the expected amidoalkyl naphthols.

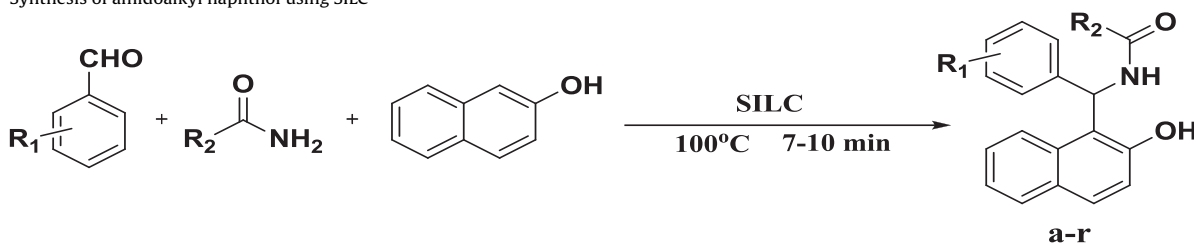
After optimizing the reaction conditions, and understanding the mechanism, we extended the scope of present method using SILC as a catalyst for a variety of aromatic aldehydes. Various aromatic aldehydes with substituent's carrying either e^- donating or e^- withdrawing groups reacted successfully and gave the products in high yields (Table 3). The aromatic aldehydes with e^- withdrawing groups reacted faster as compared with those having e^- donating groups. As per earlier report [17], the lower energy of LUMO of the alkene containing e^- withdrawing groups (a carbonyl group as in

o-QM intermediate) as compared to that of alkene containing e^- donating groups may be responsible for making the present reaction faster. These are in accordance with the proposed mechanism.

In comparison with other catalyst employed for the synthesis of amidoalkyl naphthol from 3-nitrobenzaldehyde, acetamide and 2-naphthol, SILC showed a much higher activity in terms of short reaction time and mild conditions (Table 4).

In addition, the recyclability of SILC was investigated for the reaction of 3-nitrobenzaldehyde, acetamide and 2-naphthol. After completion of reaction the separated catalyst can be reused after washing with acetone and drying at 80 °C. The catalyst was recovered in excellent yield and was used in the mentioned reaction for

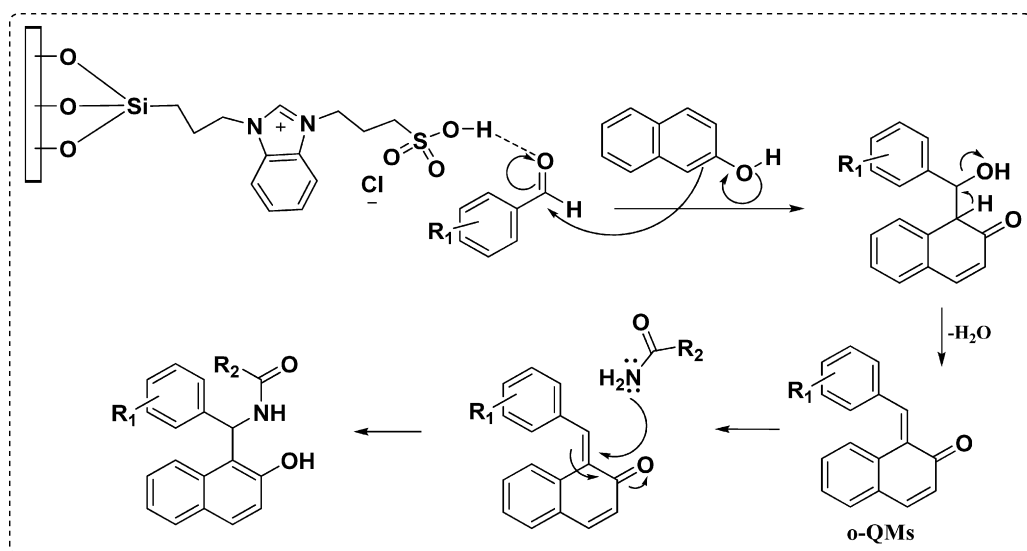
Table 3
Synthesis of amidoalkyl naphthol using SILC



| Entry | Aldehyde R ₁ | Amide R ₂ | Product | Time | Yield % ^a | M.P. (°C) (±1 °C) ^b |
|-------|--|-------------------------------|---------|------|----------------------|--------------------------------|
| 1 | H | CH ₃ | a | 7 | 90 | 242 |
| 2 | 3-NO ₂ | CH ₃ | b | 7 | 95 | 183 |
| 3 | 4-OH | CH ₃ | c | 10 | 87 | 207 |
| 4 | 4-OCH ₃ | CH ₃ | d | 10 | 89 | 186 |
| 5 | 2-Cl | CH ₃ | e | 7 | 92 | 194 |
| 6 | 4-Cl | CH ₃ | f | 7 | 93 | 226 |
| 7 | 4-NO ₂ | CH ₃ | g | 7 | 89 | 249 |
| 8 | 4-(CH ₃)N | CH ₃ | h | 7 | 80 | 124 |
| 9 | 3,4,5-(OCH ₃) ₃ | CH ₃ | i | 12 | 82 | 193 |
| 10 | H | C ₆ H ₅ | j | 7 | 82 | 236 |
| 11 | 3-NO ₂ | C ₆ H ₅ | k | 7 | 94 | 217 |
| 12 | 4-NO ₂ | C ₆ H ₅ | l | 7 | 90 | 228 |
| 13 | 4-OCH ₃ | C ₆ H ₅ | m | 10 | 89 | 209 |
| 14 | 4-Cl | C ₆ H ₅ | n | 7 | 91 | 178 |
| 15 | 2-Cl | C ₆ H ₅ | o | 7 | 88 | 283 |
| 16 | H | NH ₂ | p | 7 | 86 | 174 |
| 17 | 3-NO ₂ | NH ₂ | q | 7 | 90 | 193 |
| 18 | 4-Cl | NH ₂ | r | 10 | 92 | 168 |

^a Isolated yields of the product.

^b M.P. are in accordance with the reported data [15–17].



Scheme 2. Possible mechanism for the synthesis of amidoalkyl naphthol using SILC.

Table 4
Comparison of different catalyst for the reaction of 3-nitrobenzaldehyde, acetamide and 2-naphthol.

| S. no. | Catalyst (catalyst amount) | Temp./°C | Time | Yield % | TOF (min ⁻¹) | Ref. |
|--------|--|----------|--------|---------|--------------------------|----------|
| 1 | SILC (80 mg) | 100 | 7 min | 95 | 2.84 | Our work |
| 2 | I ₂ (5 mol%) | 125 | 15 h | 89 | 0.026 | 13 |
| 3 | Montmorillonite K10 (0.1 g) | 125 | 0.5 h | 96 | – | 12 |
| 4 | <i>p</i> -TSA | 125 | 4 h | 90 | – | 7 |
| 5 | K ₅ CoW ₁₂ O ₄₀ ·3H ₂ O (1 mol%) | 125 | 3 h | 78 | 0.433 | 14 |
| 6 | Fe(HSO ₄) ₃ (5 mol%) | 85 | 65 min | 83 | 1.7 | 16 |
| 7 | HClO ₄ –SiO ₂ (0.6 mol%) | 110 | 30 min | 95 | 3.87 | 15 |
| 8 | FeCl ₃ –SiO ₂ (25 mg) | 120 | 8 min | 94 | – | 17 |
| 9 | Cyanuric chloride (10 mol%) | 100 | 8 min | 94 | 0.9 | 21 |
| 10 | Thiamine HCl (0.5 mmol) | 80 | 4 h | 88 | – | 22 |
| 11 | P ₂ O ₅ (10 mol%) | 60 | 5 min | 97 | 1.92 | 20 |
| 12 | Zwitterionic salt (10 mol%) | 80 | 1.5 h | 88 | 0.097 | 28 |
| 13 | Immobilized IL (80 mg) | 85 | 5 min | 92 | 6.59 | 26 |
| 14 | Fe–SILP (50 mg) | 100 | – | 86 | 4.29 | 24 |
| 15 | SO ₃ H functionalised IL (10 mol%) | 120 | 3 min | 96 | 4.8 | 18 |

five times giving good to excellent yields of the products. The effect of catalyst was unchanged which was determined by measuring the acidic site loading of the reused SILC and hence conforming the purity of SILC.

4. Conclusions

In summary, we have developed an efficient procedure for the synthesis of amidoalkyl naphthols. This involves the use of the benzimidazolium based IL covalently attached to the surface of the support called as SILC as an inexpensive, stable and easily available Bronsted acidic catalyst. The use of a powerful, easily accessible and recyclable solid catalyst makes this method quite simple and convenient. The high yield of amidoalkyl naphthols, the use of relatively inexpensive catalyst and the straightforward isolation of the products are the advantages of this method over the other procedures reported.

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