A silica gel supported dual acidic ionic liquid: an efficient and recyclable heterogeneous catalyst for the one-pot synthesis of amidoalkyl naphthols

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A supported dual acidic ionic liquid catalyst was prepared *via* anchoring 3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium hydrogen sulfate onto silica gel by covalent bonds. The novel immobilized acidic ionic liquid effectively catalyzed the one-pot synthesis of amidoalkyl naphthols by the multicomponent condensation of aldehydes with 2-naphthol and amides under solvent-free conditions. Moreover, the catalyst could be recycled six-times without a significant loss of catalytic activity.

1. Introduction

Multicomponent reactions (MCRs) are very elegant and efficient methods to access complex structures in a single synthetic operation from simple building blocks, and can show simple procedures, high atom-economy and high selectivity due to the formation of carbon–carbon and carbon–heteroatom bonds in one-pot.[1] Compounds bearing 1,3-amino-oxygenated functional groups are usually found in various biologically important natural products and potent drugs, including nucleoside antibiotics and HIV protease inhibitors.[2] Among them, 1-amidoalkyl-2-naphthol derivatives are of particular value because of their promising biological and pharmacological activities.[3] Amidoalkyl naphthols can be prepared by the multicomponent condensation of aldehydes, 2-naphthols and amides using different catalysts, such as montmorillonite K10,[4] *p*-TSA,[5] iodine,[6] $Fe(HSO_4)_3$,[7] $K_5CoW_{12}O_{40}\cdot 3H_2O$,[8] $HClO_4$–SiO_2,[9] cation-exchange resins,[10] silica sulfuric acid,[11] thiamine hydrochloride,[12] zwitterionic salts,[13] acidic ionic liquids[14] and [FemSILP]L-prolinate.[15] However, these procedures each have some drawbacks, such as high reaction temperature, prolonged reaction time, the use of toxic solvents or low yields. The recovery and reusability of the catalyst is also a problem. Therefore, it is still desirable to seek a green and eco-friendly protocol that uses a highly efficient and reusable catalyst for the preparation of amidoalkyl naphthols.

Ionic liquids (ILs), as eco-friendly reaction media or catalysts, have attracted increasing attention due to their particular properties, such as undetectable vapor pressure, high thermal stability, excellent solubility, and ease of recovery and reuse.[16] Among them, Brønsted acidic ILs used in some acid-catalyzed processes have aroused considerable interest because they have the combined advantages of solid acids and mineral acids.[17] Moreover, SO_3H-functionalized ILs with a hydrogen sulfate counteranion have been intensively studied as a class of dual acidic functionalized ILs during the last five years, because the existence of both SO_3H functional groups and hydrogen sulfate counteranions can obviously enhance their acidities.[18] These strongly acidic ILs have been exploited as efficient catalysts for many organic reactions, and generally can afford higher yields and selectivities against traditional acid catalysts.[19] Despite their widespread use in acid-catalyzed reactions, a series of drawbacks, such as product isolation, catalyst recovery and the use of large amounts of ILs in biphasic systems, which is costly and may cause toxicological concerns, still exist.[20] Immobilized ILs combine the benefits of ILs and heterogeneous catalysts, such as high designability, high "solubility" of the catalytic site, ease of handling, separation and recycling. Thus, some immobilization processes for acidic ILs on solid supports have been designed.[21] These immobilized acidic ILs have been widely applied as novel solid catalysts, *e.g.*, in esterification, nitration,[22] Baeyer–Villiger reactions,[23] acetal formation[24] and the hydrolysis of cellulose.[25]

In our continuous work on the development of efficient and environmental benign procedures using dual acidic ILs,[26] herein, we report a simple and efficient procedure for the one-pot, three-component synthesis of amidoalkyl naphthols using a silica gel supported dual acidic IL as an effective and reusable catalyst under solvent-free conditions (Scheme 1). To the best of our knowledge, no attempt to use immobilized acidic ILs as catalysts for this three-component reaction has been made so far.

2. Results and discussion

2.1 Preparation and characterization of the catalyst

Supported ionic liquid catalysts (SILC) are prepared either by simple physical adsorption or covalent attachment of ILs onto the surface of a solid support. We chose the latter method to immobilize the IL since this provides better stability in the catalytic reaction and less leaching during the work-up. The supported dual acidic IL catalyst was prepared *via* anchoring 3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium hydrogen sulfate onto common silica gel by covalent bonds. During the preparation of the silica gel supported dual acidic IL catalyst, (3-chloropropyl)triethoxysilane was first treated with imidazole to give *N*-(3-propyltriethoxysilane) imidazole (**1**)

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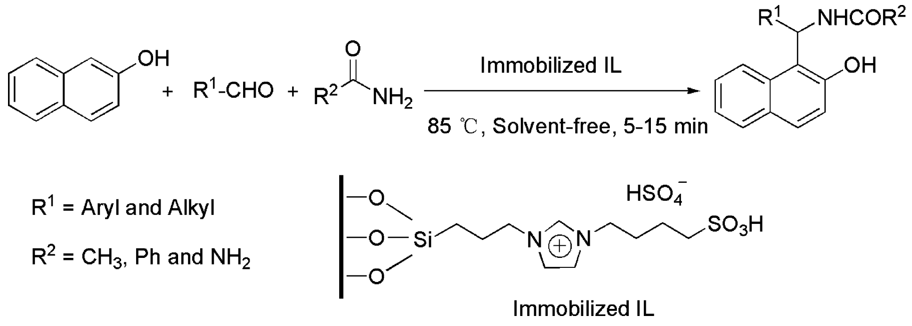
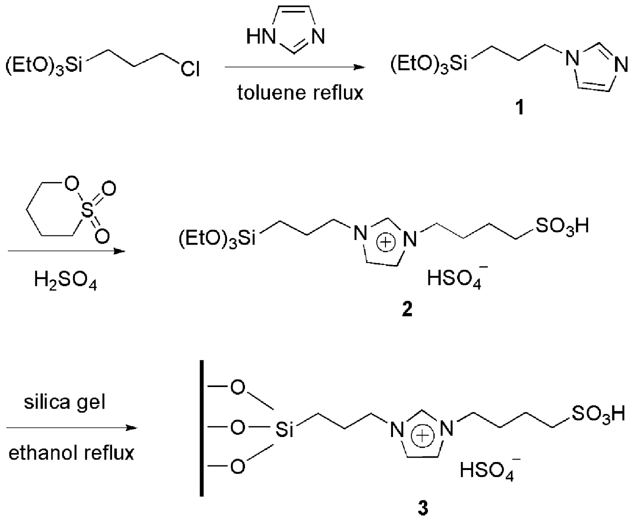


Scheme 1 Synthesis of amidoalkyl naphthols.

(Scheme 2), which was reacted with 1,4-butane sultone and further treated with sulfuric acid to form precursor IL **2**. In the last immobilization step, the common silica gel with an ethanol solution of complex **2** was refluxed for 24 h to undergo a condensation reaction, which afforded immobilized IL **3**.



Scheme 2 Synthesis of the silica gel supported IL catalyst.

Supported IL **3** was characterized by FT-IR spectroscopy, ^{13}C NMR cross-polarization magic-angle spinning (CP/MAS), scanning electron microscope (SEM), thermogravimetric-derivative thermogravimetric analysis (TG-DTG) and elemental analysis. As can be seen from Fig. 1, the FT-IR spectra of immobilized IL **3** exhibits two characteristic peaks at 1563 and 1635 cm^{-1}, which are due to C═N and C═C vibrations of the imidazole ring.[27] Additional bands at 3154, 2971 and 1452 cm^{-1} are due to C–H stretching and deformation vibrations of the imidazole moiety and alkyl chain. Moreover, two important peaks at 1165 and 1046 cm^{-1}, assigned to the S═O stretching vibration, are observed.[28] All of these characteristic peaks of the functionalized IL cannot be observed in the IR spectrum of silica gel. The Si–O–Si stretching modes of the silica gel can be observed as a strong peak at 1101 cm^{-1} and a broad feature is seen at 3421 cm^{-1} belonging to the Si–OH groups and adsorbed water in silica.

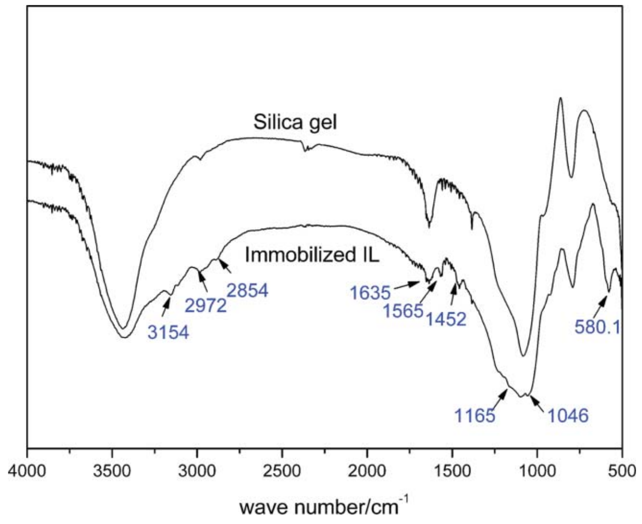
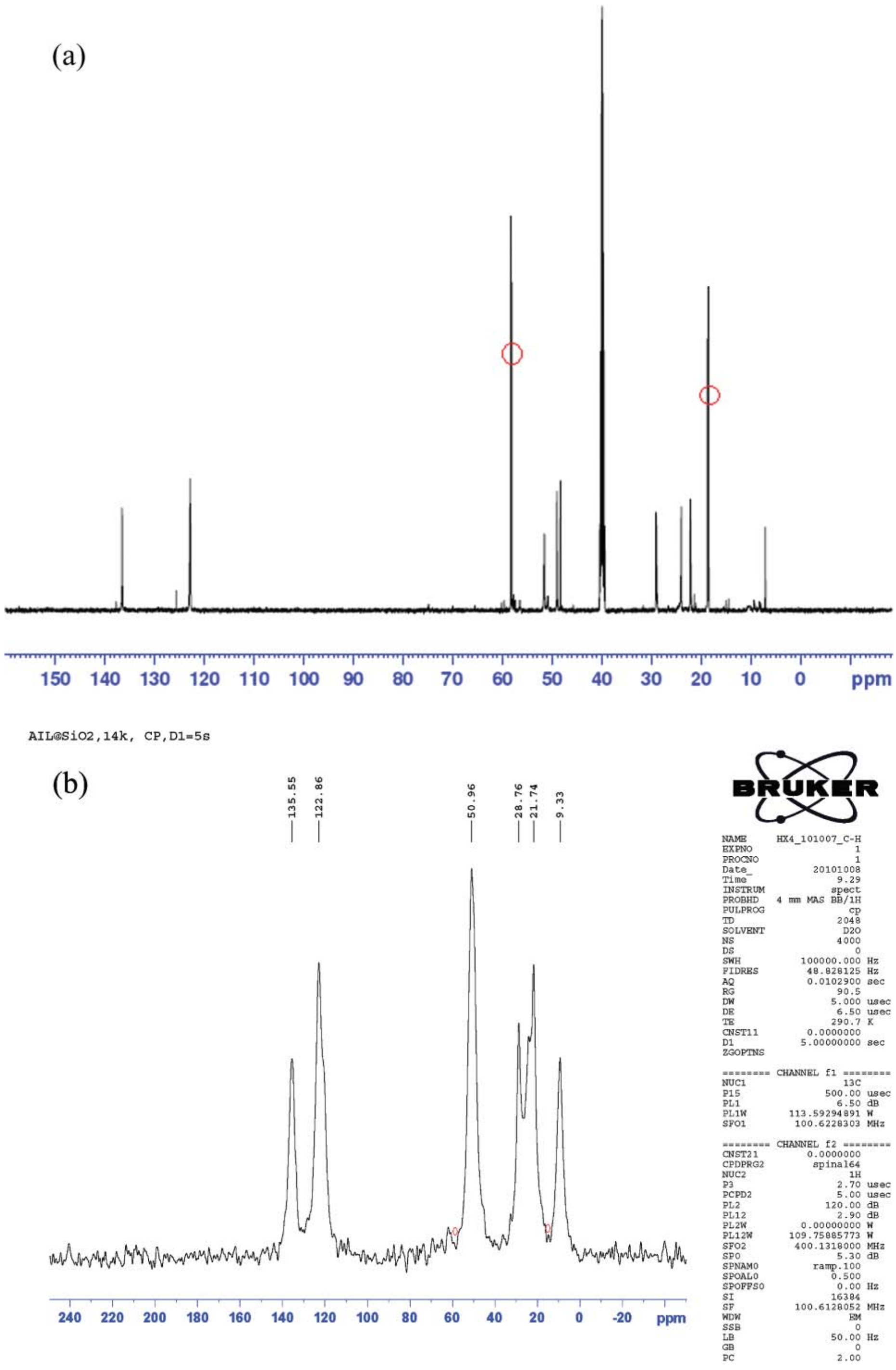


Fig. 1 FT-IR spectra comparison of silica gel and immobilized IL **3**.

Fig. 2 compares the ^{13}C NMR spectrum of pure IL **2** (liquid state NMR, Fig. 2a) with immobilized IL **3** (solid state NMR, Fig. 2b). Some important carbon signals attributed to the imidazole ring and alkyl chain are all observed in the two spectra. Moreover, the absence of the strong characteristic peaks of the triethoxysilyl group [–Si(OEt)$_3$] at 18.6 and 58.3 ppm in immobilized IL **3** excludes the possibility of IL **2** adsorbing a homologous material. Hence, the above results convinced us that the IL was successfully grafted onto the silica gel by covalent bonds.

The shape and surface morphology of the samples were investigated by SEM. As shown in Fig. 3, the particle size of the silica gel supported IL **3** is similar to that of silica gel, which demonstrates that the particles of silica gel had a good mechanical stability during the immobilization step. However, the surface morphology of these two samples is different. Fig. 3a shows that the surface of the SiO_2 was very slick, and a small aggregate was obvious on the surface of silica gel supported IL **3** (Fig. 3b).

The stability of supported IL **3** was determined by thermogravimetric analysis (Fig. 4). The TG curve indicates an initial weight loss of 5.1% up to 110 °C due to the adsorbed water in silica. Complete loss of the IL covalently grafted onto the silica is seen in the temperature range 230 to 480 °C, and the amount of organic moiety was about 23.8% against the total solid catalyst. Meanwhile, the DTG curve shows that decomposition of the



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PROCNO                   1
Date_             20101008
Time                  9.29
INSTRUM              spect
PROBHD    4 mm MAS BB/1H
PULPROG                 cp
TD                    2048
SOLVENT                D2O
NS                    4000
DS                       0
SWH             100000.000 Hz
FIDRES           48.828125 Hz
AQ               0.0102900 sec
RG                    90.5
DW                   5.000 usec
DE                    6.50 usec
TE                   290.7 K
CNST11           0.0000000
D1              5.00000000 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                   13C
P15                 500.00 usec
PL1                   6.50 dB
PL1W          113.59294891 W
SFO1           100.6228303 MHz

======== CHANNEL f2 ========
CNST21           0.0000000
CPDPRG2           spinal64
NUC2                    1H
P3                    2.70 usec
PCPD2                 5.00 usec
PL2                 120.00 dB
PL12                  2.90 dB
PL2W            0.00000000 W
PL12W         109.75885773 W
SFO2           400.1318000 MHz
SP0                   5.30 dB
SPNAM0            ramp.100
SPOAL0               0.500
SPOFFS0               0.00 Hz
SI                   16384
SF             100.6128052 MHz
WDW                     EM
SSB                      0
LB                   50.00 Hz
GB                       0
PC                    2.00
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Fig. 2 ^{13}C NMR spectra of IL **2** in the liquid state (a) and immobilized IL **3** in the solid state (b).

organic structure mainly occurred in one step from 280 to 420 °C, which is related to the main weight loss of 18.5%. The peak in the DTG curve shows that the fastest loss of the IL occurred at 360 °C. Therefore, the supported IL catalyst is stable below about 230 °C.

The loading amount of the acidic IL on silica gel was determined by elemental analysis. The nitrogen analysis of supported IL **3** (N, 1.39 mmol g^{-1}) indicates that 0.696 mmol g^{-1} of acidic IL **2** was grafted onto the surface of the silica gel (theoretical loading 0.725 mmol g^{-1}).

2.2 Synthesis of 1-amidoalkyl-2-naphthols catalyzed by the immobilized IL 3

To investigate the feasibility of the synthetic methodology for amidoalkyl naphthols, the reaction was initially carried out by simply mixing 3-nitrobenzaldehyde (2 mmol), 2-naphthol (2 mmol) and acetamide (2.4 mmol) in the presence of 40 mg of immobilized IL **3** under solvent-free conditions. The mixture was stirred at 85 °C for 10 min, and the corresponding product was obtained in 81% yield. Encouraged by this result, we gradually

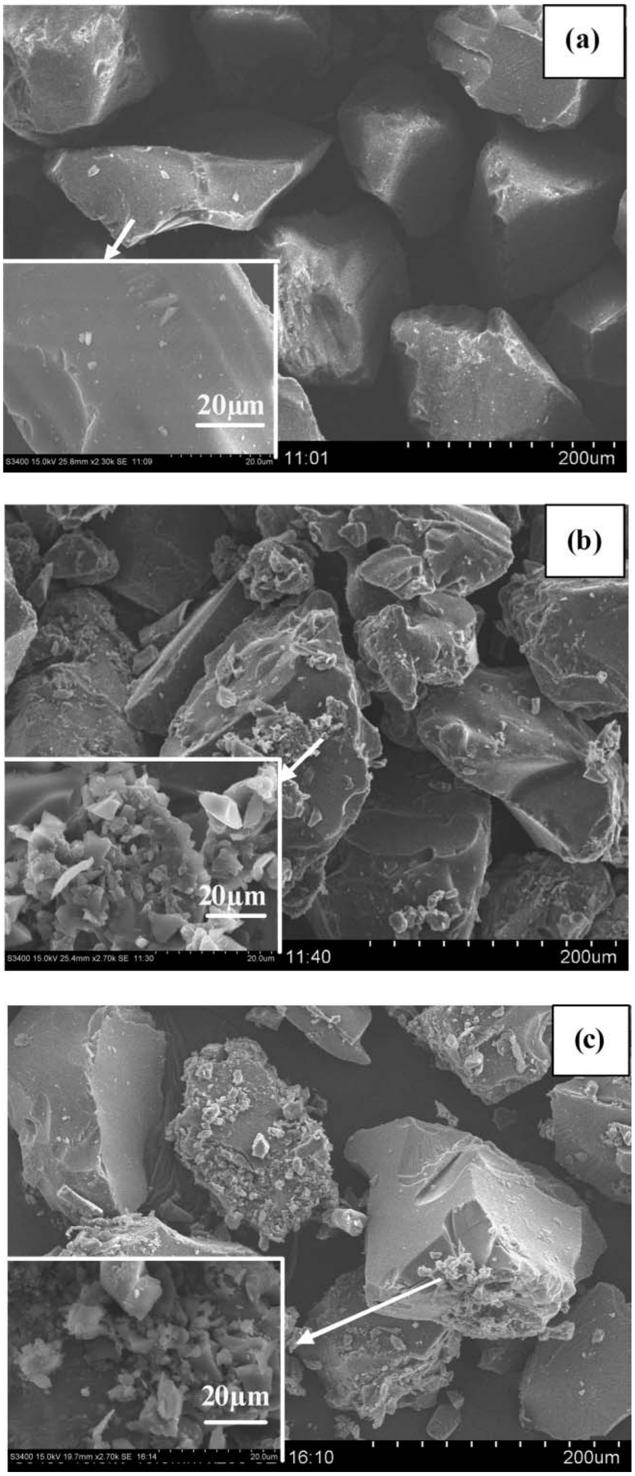


Fig. 3 Scanning electron micrographs (SEM) images of silica gel (a), immobilized IL **3** (b) and six-times reused catalyst (c).

Table 1 Effect of different amounts of immobilized IL on the reaction of 3-nitrobenzaldehyde, 2-naphthol and acetamide

Entry	Immobilized IL/mg	Time/min	Yield (%)[a]
1	0	30	< 5[b]
2	20	15	45
3	40	10	81
4	80	5	92
5	120	5	93
6	160	5	91
7	200	5	90

[a] Isolated yield. [b] Determined by HPLC.

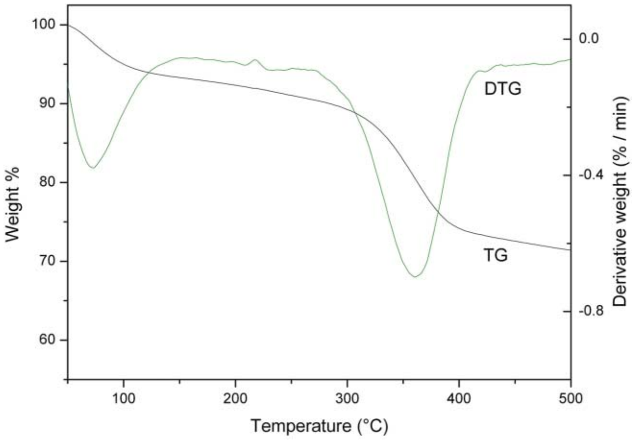


Fig. 4 TG-DTG analysis for the supported IL catalyst.

increased the amount of immobilized IL **3** from 0 to 200 mg (Table 1).

As shown in Table 1, only trace product was detected in the absence of immobilized IL **3** (Table 1, entry 1). The yield improved as the amount of immobilized IL increased from 0 to 80 mg and became almost steady when the amount of immobilized IL **3** was further increased beyond this. Therefore, we used 80 mg of immobilized IL **3** for the one-pot synthesis of amidoalkyl naphthols from various aldehydes, amides or urea and 2-naphthol under solvent-free conditions at 85 °C. The results are summarized in Table 2.

As seen from Table 2, the procedure was highly effective for the preparation of amidoalkyl naphthols. A variety of aromatic aldehydes with electron-donating and electron-withdrawing groups were converted to amidoalkyl naphthols in excellent yields (80–94%) with a high TOF in the range 1.91–6.73 min^{-1} and in short reaction time (5–15 min). Acetamide, benzamide and urea all underwent smooth transformations under the reaction conditions. In particular, *n*-butyraldehyde, as a typical aliphatic aldehyde, was tested under the reaction conditions and the corresponding desired products were isolated in good yields (Table 2, entries 10 and 18). In all cases, amidoalkyl naphthols were the sole products and no by-product was observed.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 3. We suppose that the reaction proceeds *via ortho*-quinone methides (*o*-QMs),[29] which form by the nucleophilic addition of 2-naphthol to the aldehyde, assisted by immobilized IL **3**. The *o*-QMs then react with amides or urea *via* a Michael addition to afford the expected amidoalkyl naphthols. The immobilized IL **3** could provide dual acidic sites for activating aldehydes efficiently, so facilitating the reaction.

In comparison with other catalysts employed for the synthesis of *N*-[(3-nitro-phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl] acetamide from 3-nitrobenzaldehyde, 2-naphthol and acetamide, immobilized IL **3** showed a much higher catalytic activity in terms of very short reaction time and mild conditions (Table 3).

Table 2 Immobilized IL **3** catalyzed one-pot synthesis of amidoalkyl naphthols

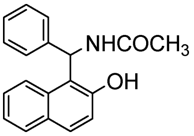
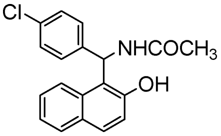
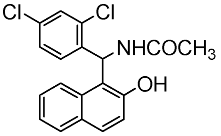
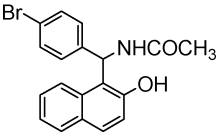
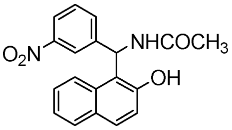
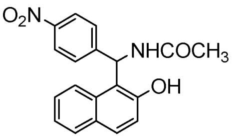
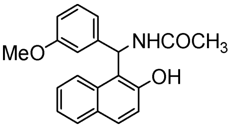
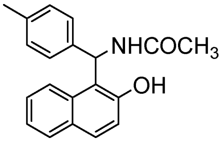
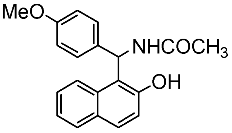
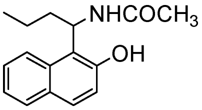
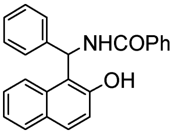
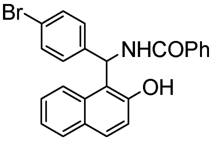
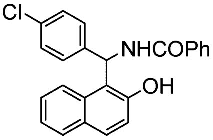
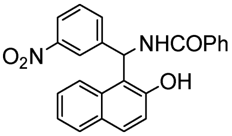
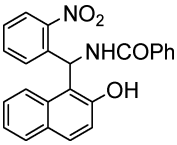
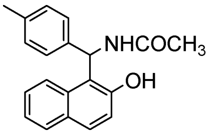
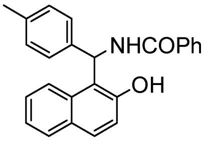
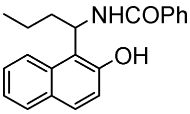
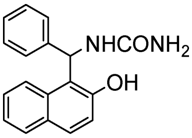
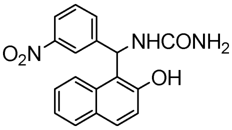
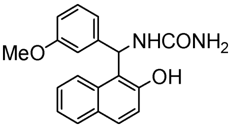
Entry	Aldehyde R^1	Amide R^2	Time/min	Product	Yield (%)[a]	TOF/min^{-1}	mp/°C
1	Ph	CH_3	5		90	6.43	242–244
2	4-Cl–C_6H_4	CH_3	10		89	3.18	226–228
3	2,4-Cl_2–C_6H_3	CH_3	8		86	3.84	202–204
4	4-Br–C_6H_4	CH_3	10		88	3.15	228–230
5	3-NO_2–C_6H_4	CH_3	5		92	6.59	241–242
6	4-NO_2–C_6H_4	CH_3	5		93	6.65	243–245
7	3-MeO–C_6H_4	CH_3	10		86	3.07	203–205
8	4-Me–C_6H_4	CH_3	10		87	3.11	221–223
9	4-MeO–C_6H_4	CH_3	15		80	1.91	181–183
10	*n*-C_3H_7	CH_3	10		85	3.04	222–223
11	Ph	Ph	5		92	6.59	232–234

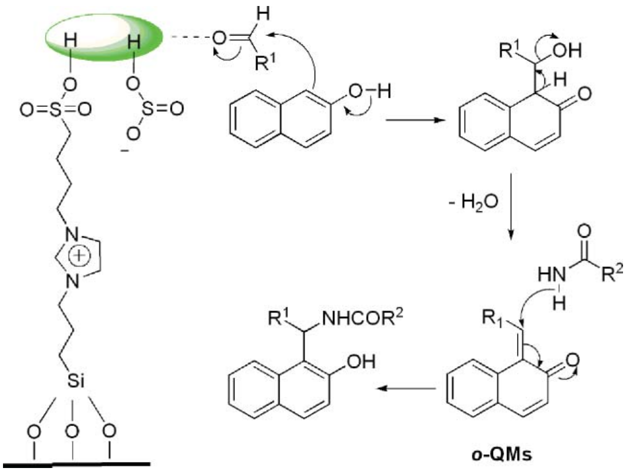
Table 2 *(Contd.)*

Entry	Aldehyde R^1	Amide R^2	Time/min	Product	Yield (%)[a]	TOF/min^{-1}	mp/°C
12	4-Br–C_6H_4	Ph	10		89	3.19	181–183
13	4-Cl–C_6H_4	Ph	10		91	3.26	179–181
14	3-NO_2–C_6H_4	Ph	5		94	6.73	240–242
15	2-NO_2–C_6H_4	Ph	7		90	4.60	263–265
16	4-Me–C_6H_4	Ph	10		88	3.15	213–215
17	4-MeO–C_6H_4	Ph	15		83	1.98	196–198
18	*n*-C_3H_7	Ph	10		83	2.97	220–222
19	Ph	NH_2	5		81	5.80	175–177
20	3-NO_2–C_6H_4	NH_2	5		84	6.01	191–193
21	3-MeO–C_6H_4	NH_2	10		80	2.86	167–169

[a] Isolated yield.

Table 3 Comparison of different catalysts for the one-pot three-component reaction of 3-nitrobenzaldehyde, 2-naphthol and acetamide

Entry	Catalyst	Conditions/°C	Time/min	Yield (%)	Reference
1	Zwitterionic salt	80	90	88	13
2	[TEBSA][HSO_4]	120	10	89	14
3	$Fe(HSO_4)_3$	85	25	97	7
4	Montmorillonite K10	125	30	96	4
5	*p*-TSA	125	240	90	5
6	Iodine	125	300	81	6
7	$K_5CoW_{12}O_{40}\cdot 3H_2O$	125	180	78	8
8	$HClO_4–SiO_2$	110	30	95	9
9	[FemSILP]L-prolinate	100	300	87	15
10	Immobilized IL **3**	85	5	92	This work



Scheme 3 A plausible mechanism for the synthesis of amidoalkyl naphthols using immobilized IL **3**.

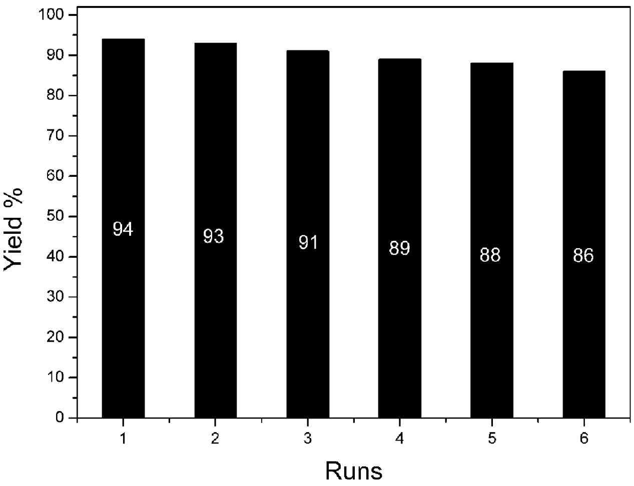


Fig. 5 Recycling experiment of immobilized IL **3**.

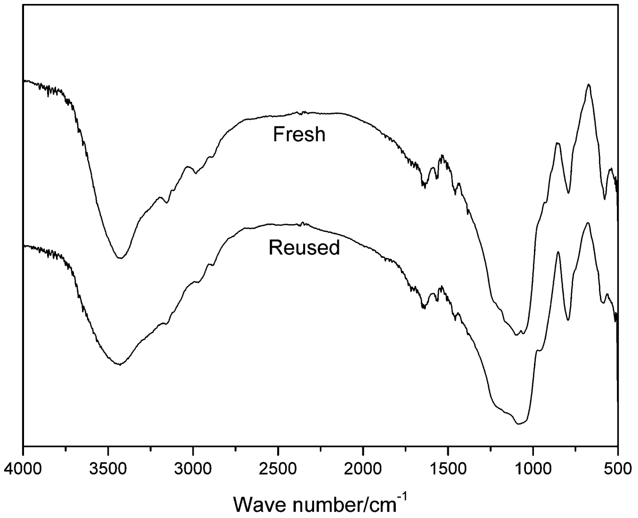


Fig. 6 FT-IR spectrum comparison of the fresh catalyst and the six times used catalyst.

2.3 Reusability of immobilized IL 3

The recovery and reuse of catalysts is highly preferable for a greener process. Thus, the reusability of the catalyst was investigated by using 3-nitrobenzaldehyde, 2-naphthol and benzamide as model substrates. The catalyst was easily recovered by filtration after the reaction and washed with acetone. After being dried, it was subjected to another reaction with identical substrates. The procedure was repeated and the results indicated that the catalyst could be cycled six times with only a slight loss of catalytic activity (Fig. 5).

The recovered catalyst after six runs had no obvious change in structure, referring to the FT-IR spectrum in comparison with fresh catalyst (Fig. 6). An SEM observation of the recovered catalyst after six runs was also made, and there was no obvious change in the morphology and size in comparison with fresh catalyst (Fig. 3c). Furthermore, the loading amount of the six times used catalyst was determined by elemental analysis, and it was found that 0.637 mmol g^{-1} of acidic IL **2** was grafted onto the surface of the silica gel against 0.696 mmol g^{-1} for the fresh catalyst. These results indicate that the catalyst was very stable and could endure this reaction's conditions.

2.4 Hot filtration test for immobilized IL 3

To figure out whether the catalytic process involved in the participation of homogenous species in equilibrium with the heterogeneous catalyst, the reaction of 4-methylbenzaldehyde (2 mmol), 2-naphthol (2 mmol) and acetamide (2.4 mmol) catalyzed by immobilized IL **3** (80 mg) was investigated. When the neat mixture was stirred at 85 °C for 4 min, hot acetone (20 mL) was added and the solid catalyst quickly removed by hot filtration. The solution was averagely divided into two sections (**S1** and **S2**). The corresponding product of **S1** was obtained in 39% yield. Meanwhile, the neat **S2** was stirred at 85 °C for an additional 30 min to afford the product in 43% yield, which was similar to **S1** and much less than normal (87%; Table 2, entry 8). Therefore, the above results convinced us that the catalytic process did not involve the participation of any homogeneous species in equilibrium with the heterogeneous catalyst.

3. Conclusion

In summary, we have developed a facile, efficient and eco-friendly procedure for the one-pot synthesis of amidoalkyl naphthols *via* a three-component condensation reaction of aldehydes with 2-naphthol and amides using a silica gel supported dual acidic IL as a powerful and recyclable catalyst under solvent-free conditions. The notable advantages of this method are high catalytic activity, short reaction time, excellent yields, simple work-up, reusable catalyst and mild reaction conditions. Thus, this procedure is a better and more practical alternative to existing methods.

4. Experimental

4.1 Materials and equipment

Melting points were determined on a Perkin-Elmer differential scanning calorimeter and uncorrected. The IR spectra were run on a Nicolete spectrometer (KBr). ^{1}H NMR spectra were recorded on a Bruker DRX500 (500 MHz) and ^{13}C NMR spectra on Bruker DRX500 (125 MHz) spectrometer. Solid-state Bloch decay and cross-polarization magic-angle spinning (CP/MAS) ^{13}C NMR spectra were recorded on a Bruker Avance III (400 MHz) spectrometer. Elemental analysis was performed on an Elementar Vario MICRO spectrometer. Thermogravimetric analysis was carried out in nitrogen using a Shimadzu TGA-50 spectrometer. Mass spectra were obtained with an automated Fininigan TSQ Advantage mass spectrometer. The shape and surface morphology of the samples were examined on a scanning electron microscope (SEM) (Hitachi S-3400N, Japan). Silica gel (60–100 mesh) was dried at 300 °C for 6 h before use. All solvents used were strictly dried according to standard operations and stored over 4A molecular sieves. All other chemicals (AR grade) were commercially available and used without further purification.

4.2 Preparation of the silica gel supported dual acidic IL catalyst

4.2.1 Synthesis of N-(3-propyltriethoxysilane) imidazole (1). Compound **1** was prepared according to known process.[30] To a solution of imidazole (3.4 g, 53 mmol) in dry toluene (50 mL), 3-chloropropyltriethoxysilane (9.2 mL, 50 mmol) was added and the mixture was refluxed overnight under a nitrogen atmosphere. The solvent was removed by rotatory evaporation under reduced pressure, and the product *N*-(3-propyltrimethoxysilane) imidazole was obtained as a transparent liquid by neutral Al_2O_3 column chromatography.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.07 (s, 1H), 6.93 (s, 1H), 3.96 (t, J = 7.5 Hz, 2H), 3.82 (q, J = 7.0 Hz, 6H), 1.90 (m, 2H), 1.23 (t, J = 7.0 Hz, 9H), 0.57 (t, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 7.2, 18.1, 24.8, 48.9, 58.2, 118.6, 129.0, 137.0.

4.2.2 Synthesis of 3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium hydrogen sulfate (2). IL **2** was synthesized according to our previous method.[26] 1,4-Butane sultone (1,4-PS, 1.42 g, 10.5 mmol) was added dropwise into a solution of **1** (2.72 g, 10 mmol) in toluene (30 mL) over 30 min, and the mixture was then stirred for 8 h and evaporated under reduced pressure. Then, conc. H_2SO_4 (0.54 mL, 10 mmol) was added dropwise into the solution of the above residual in ethanol (30 mL) over 30 min. The final mixture was stirred at 50 °C for another 8 h and evaporated under reduced pressure to give intermediate **2** as a viscous yellow liquid in 97% yield.

^{1}H NMR (500 MHz, DMSO-d_6): δ 9.19 (s, 1H), 7.80 (s, 2H), 4.18 (t, J = 7.5 Hz, 2H), 4.13 (t, J = 7.5 Hz, 2H), 3.75 (q, J = 7.0 Hz, 6H), 2.44 (t, J = 7.5 Hz, 2H), 1.89–1.83 (m, 4H), 1.54 (m, 2H), 1.15 (t, J = 7.0 Hz, 9H), 0.51 (t, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 7.3, 18.6, 22.1, 24.5, 29.0, 49.0, 50.9, 51.6, 58.3, 122.8, 123.0, 136.6; FT-IR (KBr, cm^{-1}): 3432.5, 3148.7, 2954.2, 2878.2, 1637.9, 1563.3, 1456.5, 1216.7, 1191.8, 1047.0, 889.1, 757.4, 599.4; ESI-MS: m/z 409 (M^+–HSO_4); Anal. calc. for $C_{16}H_{34}N_2O_{10}S_2Si$: C, 37.93; H, 6.76; N, 5.53. Found: C, 37.14; H, 6.94; N, 5.50.

4.2.3 Grafting of 3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium hydrogen sulfate on silica gel (3). The IL **2** (1.0 g) was dissolved in absolute ethanol (30 mL) and treated with silica gel (2.0 g). After heating the slurry under reflux conditions for 24 h, the solid was isolated by filtration and washed with ether (3 × 30 mL). The resulting material was dried under vacuum to give supported dual acidic IL **3** as a slightly yellow powder in 96% yield (theoretical loading: 0.725 mmol g^{-1}).

FT-IR (KBr, cm^{-1}): 3421.4, 3154.5, 2971.8, 2854.2, 1635.5, 1563.3, 1452.1, 1165.5, 1046.3, 1101.2, 792.7, 578.6; ^{13}C NMR (CP/MAS, 400 MHz); δ 9.3, 21.7, 24.1, 28.7, 50.9, 122.8, 135.5; Anal. found: C, 8.85; H, 1.91; N, 1.95; S, 4.50.

4.3 General method for the synthesis of amidoalkyl naphthols

A mixture of aldehyde (2 mmol), 2-naphthol (2 mmol), amide (2.4 mmol) and immobilized IL **3** (80 mg) was stirred at 85 °C in an oil bath for 5–15 min, using TLC to indicate a complete reaction. Then, acetone (15 mL) was added and the reaction mixture filtered. The solid catalyst was washed with acetone (2 × 15 mL) and dried under vacuum. Pure amidoalkyl naphthols were afforded by evaporation of the solvent followed by recrystallization from ethanol. All were characterized by spectral data and comparison of their physical data with the literature. Spectral data for *N*-[(3-nitro-phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl] benzamide (Table 2, entry 14).

^{1}H NMR (500 MHz, DMSO-d_6): δ 10.43 (s, 1H), 9.14 (d, J = 8.0 Hz, 1H), 8.12–8.08 (m, 3H), 7.90–7.84 (m, 4H), 7.72 (d, J = 7.5 Hz, 1H), 7.61–7.49 (m, 5H), 7.40 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.7, 153.9, 148.3, 145.0, 134.5, 133.8, 132.7, 132.0, 130.5, 130.2, 129.2, 128.9, 128.8, 127.8, 127.5, 123.3, 122.9, 122.1, 121.4, 119.1, 117.4, 49.4; FT-IR (KBr, cm^{-1}): 3375, 3260, 3055, 2972, 1632, 1530, 1506, 1477, 1439, 1346, 1252, 1146, 733; Anal. calc. for $C_{24}H_{18}N_2O_4$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.28; H, 4.61; N, 6.97.

4.4 Recycling of immobilized IL 3

The three-component reaction of 3-nitrobenzaldehyde, 2-naphthol and benzamide as a model reaction was studied. When the reaction was completed, acetone was added to dissolve the product. The solid catalyst was filtered off, washed with acetone and dried under vacuum after each cycle, and then reused for the next reaction.

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