ORIGINAL PAPER

Novel and highly efficient preparation of pyrroles using supported ionic liquid ILCF$_3$SO$_3$@SiO$_2$ as a heterogeneous catalyst

Yang Liu[1] · Yu Lin Hu[1]

Abstract

A supported ionic liquid ILCF$_3$SO$_3$@SiO$_2$ was synthesized and used as a highly efficient catalyst in the Paal–Knorr reaction for the preparation of pyrroles. The heterogeneous catalyst could be easily recovered and recycled for five times without noticeable loss of catalytic activity. Also a possible reaction mechanism is provided.

Graphical Abstract
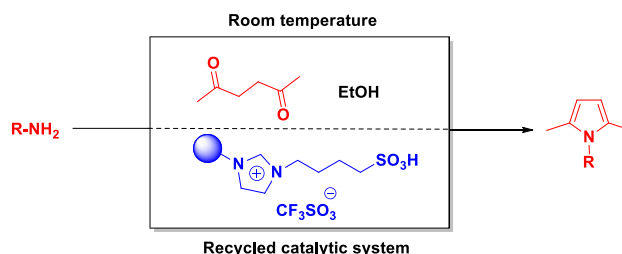
Introduction

Pyrroles are important compounds commonly encountered in biologically relevant synthetic compounds, drugs, etc. [1–3]. Thus, many methods have been developed in the preparation of these compounds, and a renowned method is the Paal–Knorr reaction [3]. Generally, the reaction is typically carried out with stoichiometric amount of the Bronsted or lewis acids catalysts (i.e., H$_2$SO$_4$, p-toluene sulfonic acid and BiCl$_3$) [4–6] and suffers from some drawbacks such as low yield, harsh reaction condition and tedious workup. Recently, many catalytic systems, such as UO$_2$(NO$_3$)·6H$_2$O [7], Sc(OTf)$_3$ [8], Et$_2$Zn [9], HCOONH$_4$ [10], Mg$_3$N$_2$ [11], IRMOF-3 [12], NH$_4$OAc/AcOH [13], MgI$_2$ [14], nano β-PbO [15] and other systems [16–20], have been developed for this conversion. However, these methods are still associated with the use of expensive, toxic and moisture-sensitive reagents, difficulties in separation and catalyst recovery. Hence, there is extremely important in developing efficient and green methods in the preparation pyrroles.

Ionic liquids (ILs) as environmentally benign materials have broad applications in the field of separation, synthetic chemistry, electrochemistry and catalysis [21–24]. Up to now, their application as catalysts in the preparation of pyrroles was reported [25–28]. Although good catalytic activities of these ILs, there exist some disadvantages such as partially ILs wasted and tedious workup. Along this line, a useful method to overcome these limitations is the development of supported IL catalysts [29–31]. The homogeneous catalytic reactions of ILs could be transferred into the

✉ Yu Lin Hu
huyulin1982@163.com

1 College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, People's Republic of China

heterogeneous systems, which have attractive features such as high catalyst efficiency, high system stability, the facilitation of catalyst recovery and reusability [31].

In this study, a supported IL, ILCF$_3$SO$_3$@SiO$_2$, has been synthesized and exhibited good thermal and chemical stability, which was utilized as a novel and efficient catalyst in the preparation of pyrroles by Paal–Knorr reaction of 1,4-diketone or succinaldehyde or ethyl 2-acetyl-4-oxo-4-phenylbutanoate with amines (Scheme 1). As well as this, the reusability of the supported IL was also studied.

Experimental

General

All chemicals were analytical grade. SEM and EDX spectra were recorded on a JSM-7500F apparatus. FT-IR spectra were recorded on a Nicolet Nexus 470 apparatus. XRD spectra were recorded on a Rigaku Ultima IV apparatus. TG spectra were analyzed by a STA 449 apparatus. GC spectra were recorded on a Shimadzu-14B apparatus. ^{1}H and ^{13}C NMR spectra were measured at 500 MHz on a Bruker apparatus with CDCl$_3$ as the solvent. Elemental analysis was performed on a Vario EL III instrument. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Synthesis of supported IL (Scheme 2)

Synthesis 1: Imidazole (13.6 g, 0.2 mol), (3-chloropropyl) triethoxysilane (48.2 g, 0.2 mol) and toluene (350 mL) were refluxed for 22 h, and then triethylamine (20.2 g, 0.2 mol) was added to the mixture and refluxed for another 2 h. Then, the slurry was filtrated and the filter was washed with toluene; the solvent was removed to afford 1.

Synthesis 2: 1 (27.2 g, 0.1 mol), silica (28 g) and toluene (250 mL) were refluxed for 24 h; the solvent was removed to give 2.

Scheme 1 Synthesis of pyrroles catalyzed by ILCF$_3$SO$_3$@SiO$_2$
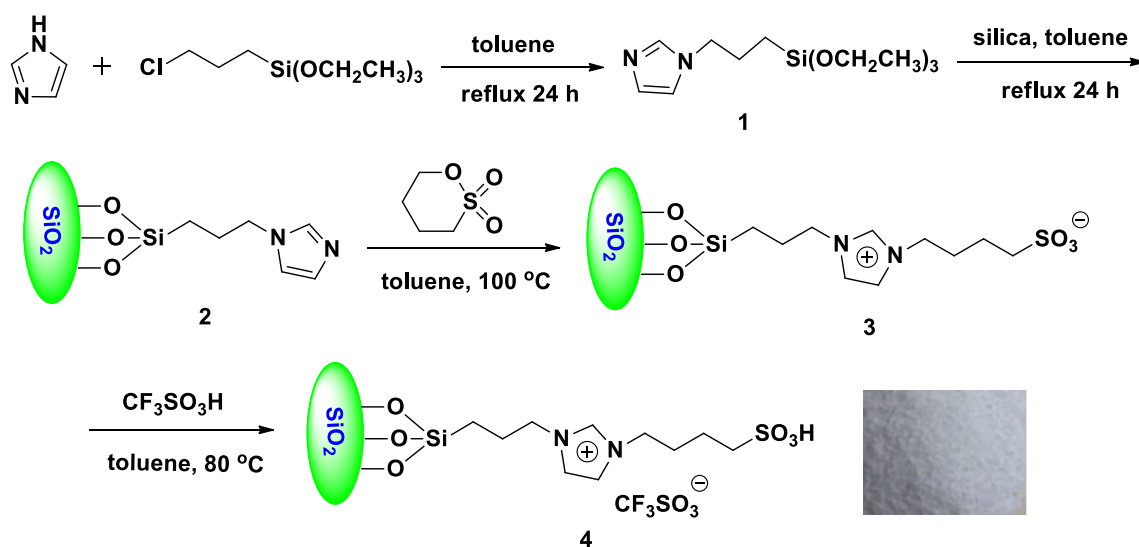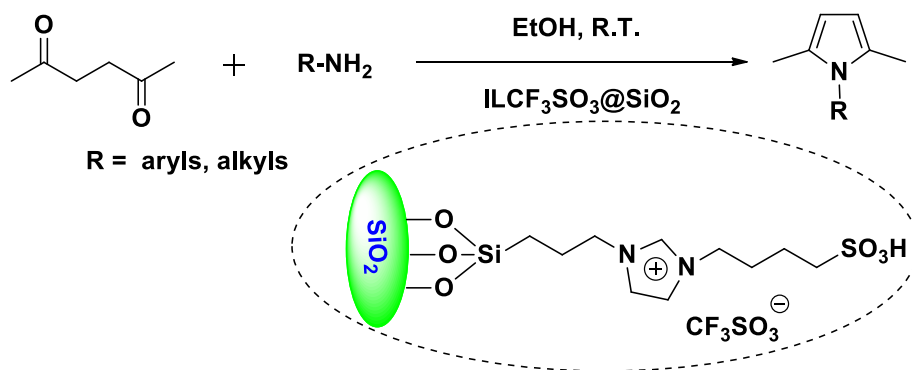
Scheme 2 Synthesis of ILCF$_3$SO$_3$@SiO$_2$

Synthesis 3: 2, toluene (200 mL) and 1,4-butane sultone (13.6 g, 0.1 mol) were stirred at 100 °C for 8 h. The resulting material was isolated by filtration and dried under vacuum at 80 °C to give white solid **3**.

Synthesis 4: CF_3SO_3H (15 g, 0.1 mol) was added into **3** in toluene (200 mL) and stirred at 80 °C for 6 h. Then, the material was filtrated and dried under vacuum at 80 °C to afford **4** $ILCF_3SO_3@SiO_2$.

Typical procedure in the preparation of pyrroles

A mixture of amine (0.1 mol), 1,4-diketone (0.1 mol) and ethanol (20 mL) $ILCF_3SO_3@SiO_2$ (0.8 g) were stirred for a specific time (Table 3) at room temperature. On completion (monitored by GC), the catalyst was recovered by filtration, dried and reused for the next run. The solvent was removed under reduced pressure to yield the desired product. The products were identified by ^1H NMR, ^{13}C NMR and elemental analysis, and the characterization spectra are provided in the supporting information.

2,5-Dimethyl-1-phenyl-1H-pyrrole (Table 3, entry 1) White solid; m.p. 51–53 °C (Ref. [9] 51–52 °C). ^1H NMR: $\delta = 2.14$ (s, 6H, 2CH$_3$), 6.06 (s, 2H, pyrrole), 7.24–7.33 (m, 2H, Ar–H), 7.47–7.58 (m, 3H, Ar–H) ppm; ^{13}C NMR: $\delta = 12.9$, 105.7, 127.8, 128.6, 129.1, 139.8 ppm; Anal. Calcd for $C_{12}H_{13}N$: C, 84.13; H, 7.61; N, 8.14. Found: C, 84.17; H, 7.65; N, 8.18.

2,5-Dimethyl-1-(p-tolyl)-1H-pyrrole (Table 3, entry 2) White solid; m.p. 59–61 °C (Ref. [11] 58–60 °C). ^1H NMR: $\delta = 2.13$ (s, 6H, 2CH$_3$), 2.57 (s, 3H, ArCH$_3$), 6.02 (s, 2H, pyrrole), 7.21–7.23 (m, 2H, Ar–H), 7.32–7.37 (m, 2H, Ar–H) ppm; ^{13}C NMR: $\delta = 13.1$, 21.4, 105.5, 128.0, 128.9, 136.2, 137.6 ppm; Anal. Calcd for $C_{13}H_{15}N$: C, 84.25; H, 8.13; N, 7.52. Found: C, 84.28; H, 8.16; N, 7.56.

1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole (Table 3, entry 3) White solid; m.p. 56–58 °C (Ref. [12] 55–57 °C). ^1H NMR: $\delta = 2.07$ (s, 6H, 2CH$_3$), 3.87 (s, 3H, OCH$_3$), 5.93 (s, 2H, pyrrole), 6.96–6.99 (m, 2H, Ar–H), 7.12–7.16 (m, 2H, Ar–H) ppm; ^{13}C NMR: $\delta = 13.2$, 55.3, 105.4, 114.6, 128.7, 129.5, 132.1, 158.7 ppm; Anal. Calcd for $C_{13}H_{15}NO$: C, 77.56; H, 7.48; N, 6.94; O, 7.93. Found: C, 77.58; H, 7.51; N, 6.96; O, 7.95.

1-(4-Bromophenyl)-2,5-dimethyl-1H-pyrrole (Table 3, entry 4) Yellow solid; m.p. 75–76 °C (Ref. [8] 75–77 °C). ^1H NMR: $\delta = 2.03$ (s, 6H, 2CH$_3$), 5.92 (s, 2H, pyrrole), 7.08–7.12 (m, 2H, Ar–H), 7.57–7.61 (m, 2H, Ar–H) ppm; ^{13}C NMR: $\delta = 12.9$, 106.2, 128.1, 128.6, 129.2, 133.2, 138.1 ppm; Anal. Calcd for $C_{12}H_{12}BrN$: C, 57.58; H, 4.81; Br, 31.92; N, 5.57. Found: C, 57.62; H, 4.84; Br, 31.94; N, 5.60.

4-(2,5-Dimethyl-1H-pyrrol-1-yl)benzoic acid (Table 3, entry 5) White solid; m.p. 182–183 °C (Ref. [13] 181–184 °C). ^1H NMR: $\delta = 2.06$ (s, 6H, 2CH$_3$), 5.96 (s, 2H, pyrrole), 6.62 (br, 1H, COOH), 7.29–7.34 (m, 2H, Ar–H), 8.23–8.27 (m, 2H, Ar–H) ppm; ^{13}C NMR: $\delta = 13.1$, 106.3, 127.6, 127.9, 128.3, 130.9, 143.7, 171.2 ppm; Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.51; H, 6.07; N, 6.48; O, 14.84. Found: C, 72.54; H, 6.09; N, 6.51; O, 14.87.

2,5-Dimethyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrrole (Table 3, entry 6) Yellow solid; m.p. 55–56 °C (Ref. [15] 55–57 °C). ^1H NMR: $\delta = 2.11$ (s, 6H, 2CH$_3$), 6.01 (s, 2H, pyrrole), 7.35–7.38 (m, 2H, Ar–H), 7.74–7.78 (m, 2H, Ar–H) ppm; ^{13}C NMR: $\delta = 12.9$, 106.8, 122.1, 125.4, 126.3, 127.5, 128.8, 142.4 ppm; Anal. Calcd for $C_{13}H_{12}F_3N$: C, 65.24; H, 5.03; F, 23.80; N, 5.82. Found: C, 65.27; H, 5.06; F, 23.82; N, 5.85.

1-Benzyl-2,5-dimethyl-1H-pyrrole (Table 3, entry 7) White solid; m.p. 43–44 °C (Ref. [10] 43–45 °C). ^1H NMR: $\delta = 2.36$ (s, 6H, 2CH$_3$), 5.14 (s, 2H, CH$_2$), 6.12 (s, 2H, pyrrole), 7.11–7.23 (m, 2H, Ar–H), 7.47–7.56 (m, 3H, Ar–H) ppm; ^{13}C NMR: $\delta = 12.5$, 46.8, 105.7, 125.8, 127.1, 128.2, 128.7, 138.6 ppm; Anal. Calcd for $C_{13}H_{15}N$: C, 84.25; H, 8.14; N, 7.53. Found: C, 84.28; H, 8.16; N, 7.56.

2,5-Dimethyl-1-(4-methylbenzyl)-1H-pyrrole (Table 3, entry 8) Yellow solid; m.p. 61–62 °C; ^1H NMR: $\delta = 2.32$ (s, 6H, 2CH$_3$), 2.54 (s, 3H, CH$_3$), 5.06 (s, 2H, CH$_2$), 6.03 (s, 2H, pyrrole), 6.91–6.94 (m, 2H, Ar–H), 7.18–7.23 (m, 2H, Ar–H) ppm; ^{13}C NMR: $\delta = 12.4$, 21.8, 46.7, 105.9, 126.0, 127.2, 128.3, 126.4, 137.6 ppm; Anal. Calcd for $C_{14}H_{17}N$: C, 84.34; H, 8.58; N, 7.01. Found: C, 84.37; H, 8.60; N, 7.03.

1-(4-Methoxybenzyl)-2,5-dimethyl-1H-pyrrole (Table 3, entry 9) Yellow solid; m.p. 65–67 °C; ^1H NMR: $\delta = 2.21$ (s, 6H, 2CH$_3$), 3.91 (s, 3H, OCH$_3$), 5.03 (s, 2H, CH$_2$), 5.96 (s, 2H, pyrrole), 6.88–6.91 (m, 2H, Ar–H), 7.21–7.23 (m, 2H, Ar–H) ppm; ^{13}C NMR: $\delta = 12.2$, 46.3, 55.4, 105.3, 114.3, 126.8, 128.0, 130.6, 158.7 ppm; Anal. Calcd for $C_{14}H_{17}NO$: C, 78.05; H, 7.92; N, 6.47; O, 7.40. Found: C, 78.10; H, 7.96; N, 6.51; O, 7.43.

1-(4-Chlorobenzyl)-2,5-dimethyl-1H-pyrrole (Table 3, entry 10) Yellow solid; m.p. 90–92 °C; ^1H NMR: $\delta = 2.27$
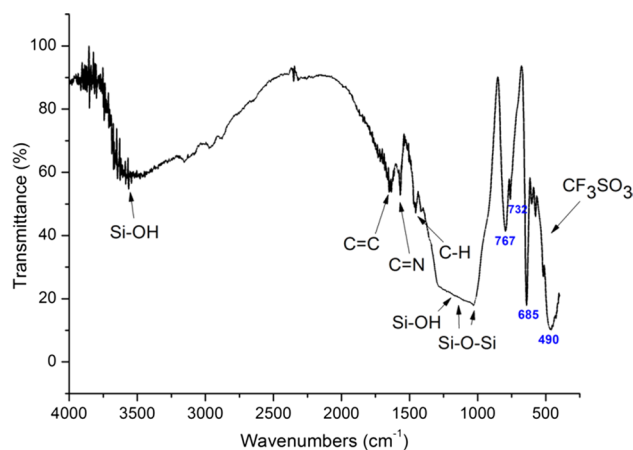
Fig. 1 FT-IR spectra of $ILCF_3SO_3@SiO_2$

Fig. 2 SEM images of silica (**a**), ILCF$_3$SO$_3$@SiO$_2$ (**b**) and recycled catalyst (**c**); EDX image of ILCF$_3$SO$_3$@SiO$_2$ (**d**)
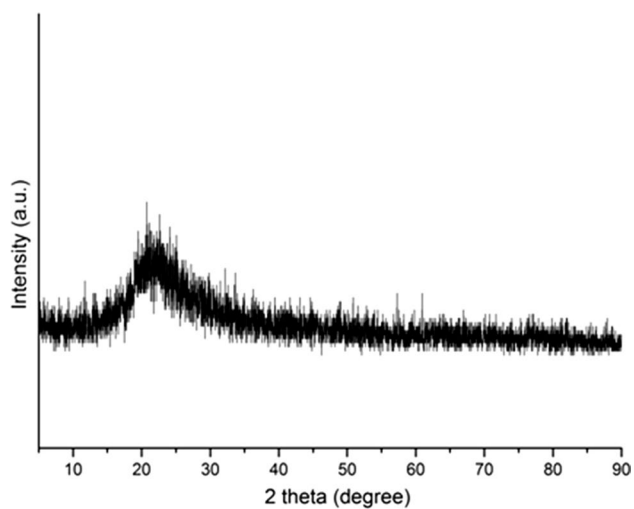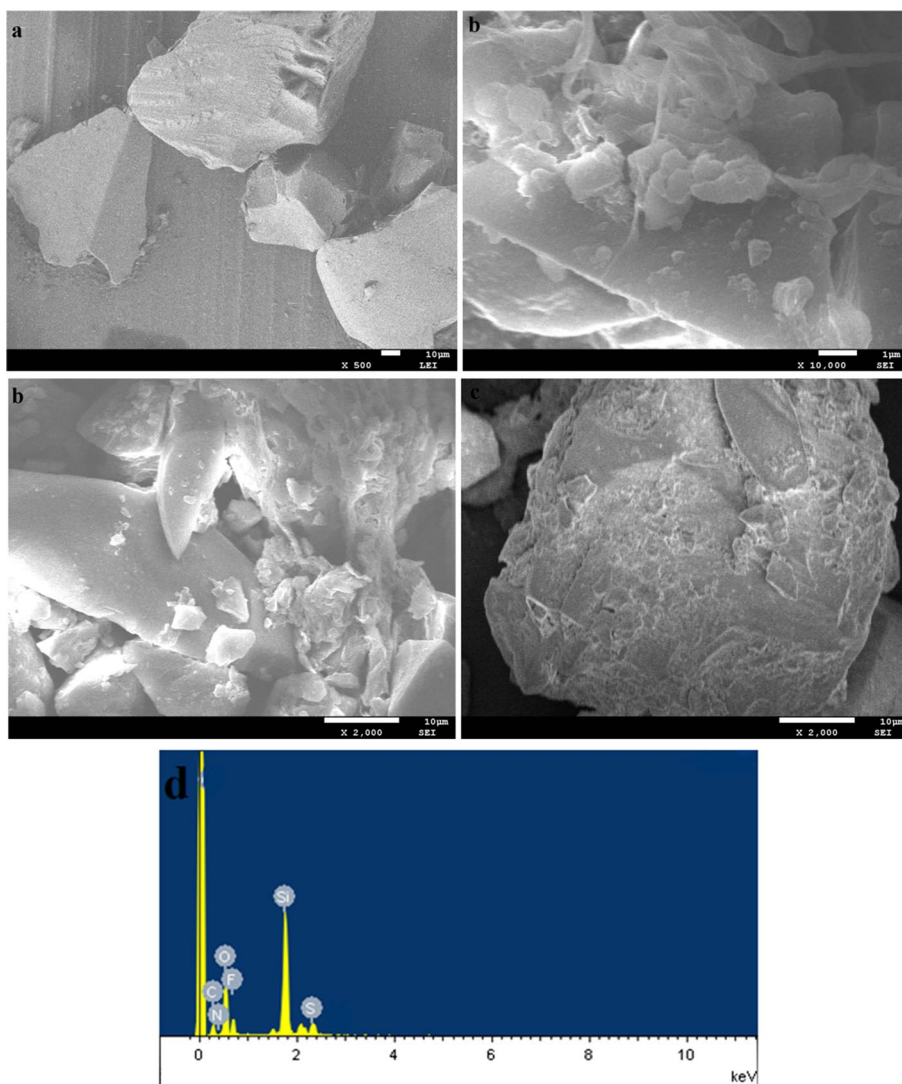
Fig. 3 XRD pattern of ILCF$_3$SO$_3$@SiO$_2$
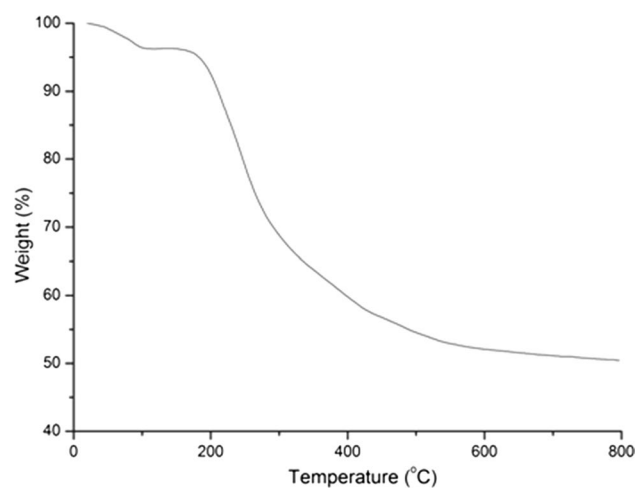
Fig. 4 TG curve of ILCF$_3$SO$_3$@SiO$_2$

Table 1 Optimization of the reaction conditions

Entry	Solvent	Catalyst (g)	Time (min)	Isolated yield (%)
1	Solvent-free	0.5	60	75
2	Water	0.5	100	48
3	Ethanol	0.5	20	87
4	Methanol	0.5	20	83
5	Acetonitrile	0.5	40	75
6	Trichloromethane	0.5	40	69
7	Ethyl acetate	0.5	40	81
8	Ethanol	0	120	27
9	Ethanol	0.2	40	70
10	Ethanol	0.6	10	92
11	Ethanol	0.8	10	95
12	Ethanol	1.0	10	95
13	Ethanol	1.2	10	95
14	Ethanol	0.8	80	61[a]

Reaction conditions: hexane-2,5-dione (0.1 mol), aniline (0.1 mol), catalyst (ILCF$_3$SO$_3$@SiO$_2$), solvent (20 mL), R.T
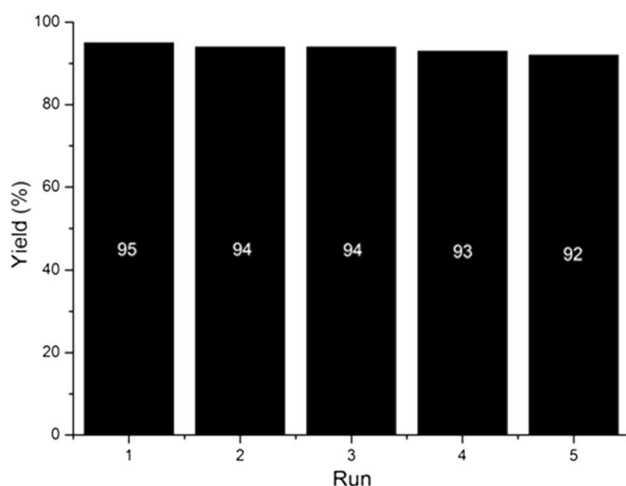
[a]The reaction was carried out using SiO$_2$ as catalyst at R.T

Fig. 5 The reused reactions of hexane-2,5-dione (0.1 mol) with aniline (0.1 mol) and ethanol (20 mL) catalyzed by the recycled ILCF$_3$SO$_3$@SiO$_2$

(s, 6H, 2CH$_3$), 5.08 (s, 2H, CH$_2$), 6.03 (s, 2H, pyrrole), 6.87–6.94 (m, 2H, Ar–H), 7.38–7.42 (m, 2H, Ar–H) ppm; ^{13}C NMR: δ = 12.3, 46.2, 105.7, 127.1, 127.9, 128.6, 133.9, 136.7 ppm; Anal. Calcd for C$_{13}$H$_{14}$ClN: C, 71.03; H, 6.40; Cl, 16.11; N, 6.36. Found: C, 71.07; H, 6.42; Cl, 16.14; N, 6.38.

1-Butyl-2,5-dimethyl-1H-pyrrole (Table 3, entry 11) Yellow oil; ^{1}H NMR: δ = 1.04 (t, 3H, CH$_3$), 1.46–1.53 (m, 2H, CH$_2$), 1.67–1.76 (m, 2H, CH$_2$), 2.39 (s, 6H, 2CH$_3$), 3.83 (m, 2H, CH$_2$), 5.94 (s, 2H, pyrrole) ppm; ^{13}C NMR: δ = 12.4,

13.9, 20.3, 33.3, 43.5, 104.9, 127.4 ppm; Anal. Calcd for C$_{10}$H$_{17}$N: C, 79.36; H, 11.31; N, 9.24. Found: C, 79.41; H, 11.33; N, 9.26.

1-Cyclopentyl-2,5-dimethyl-1H-pyrrole (Table 3, entry 12) Yellow oil; ^{1}H NMR: δ = 1.63–1.74 (m, 4H, CH$_2$CH$_2$), 1.81–2.17 (m, 4H, 2CH$_2$), 2.35 (s, 6H, 2CH$_3$), 3.77 (m, 1H, CH), 5.86 (m, 2H, pyrrole) ppm; ^{13}C NMR: δ = 13.1, 24.7, 31.6, 58.4, 105.5, 127.6 ppm; Anal. Calcd for C$_{11}$H$_{17}$N: C, 80.90; H, 10.48; N, 8.54. Found: C, 80.93; H, 10.50; N, 8.58.

1-Phenyl-1H-pyrrole (Table 3, entry 13) White solid; m.p. 58–59 °C (Ref. [9] 60–61 °C). ^{1}H NMR: δ = 6.51 (t, 2H, pyrrole), 7.24 (t, 2H, pyrrole), 7.38–7.59 (m, 5H, Ar–H) ppm; ^{13}C NMR: δ = 110.2, 119.3, 120.4, 125.2, 129.3, 140.5 ppm; Anal. Calcd for C$_{10}$H$_9$N: C, 83.83; H, 6.31; N, 9.75. Found: C, 83.88; H, 6.34; N, 9.78.

Ethyl 2-methyl-1,5-diphenyl-1H-pyrrole-3-carboxylate (Table 3, entry 14) White solid; m.p. 94–96 °C. ^{1}H NMR: δ = 1.33–1.39 (t, 3H, CH$_3$), 2.43 (s, 2H, CH$_2$), 4.37 (m, 2H, CH$_2$), 6.87 (s, 1H, pyrrole), 7.03–7.46 (m, 10H, Ar–H) ppm; ^{13}C NMR: δ = 12.5, 14.3, 59.1, 108.9, 112.6, 126.4, 127.5, 127.8, 128.7, 129.2, 129.5, 133.4, 134.9, 138.6, 151.7, 165.9 ppm; Anal. Calcd for C$_{20}$H$_{19}$NO$_2$: C, 78.62; H, 6.23; N, 4.56; O, 10.45. Found: C, 78.66; H, 6.27; N, 4.59; O, 10.48.

Results and discussion

Characterization of the supported IL was studied using FT-IR, SEM, EDX, XRD and TG analysis. The FT-IR spectra of the supported IL are presented in Fig. 1. The ILs exhibit absorptions at about 1078 and 972 cm^{-1}, which correspond to the stretching vibration of Si–O–Si. Characteristic peaks at the positions of about 1470, 1520 and 1610 cm^{-1} correspond to C–H bending vibrations, C=C and C=N stretching vibrations of the imidazolium ring [32, 33]. The peaks at about 490, 685, 732, 767 cm^{-1} related to vibrational modes of CF$_3$SO$_3^-$, and the peaks at about 1145 and 3500 cm^{-1} assigned to the Si–OH group were also observed.

The surface morphology and chemical composition of the supported IL were studied by SEM and EDX. Figure 2a shows the SEM image of silica and Fig. 2b shows the SEM image of the supported IL; it clearly shows IL particles were well defined. The chemical composition of the IL was investigated by EDX (Fig. 2d), which showed the presence of the elements in its structure. The loading amount of the IL on silica was confirmed by both nitrogen analysis and weight gain, providing the supported IL ILCF$_3$SO$_3$@SiO$_2$ with loading ratio of 0.723 mmol/g. XRD pattern is shown in Fig. 3 and the IL had peak at $2\theta \approx 21.5°$, which was the presence of the amorphous nature of SiO$_2$ support [33, 34].

The stability of supported IL was determined by TG (Fig. 4). In the curve, the small weight loss of 3.6% up to

Table 2 Comparison of different catalysts for the condensation of hexane-2,5-dione with aniline

Entry	Catalyst	Temperature (°C)	Time (min)	Isolated yield (%)	References
1	$UO_2(NO_3)_2 \cdot 6H_2O$/ultrasonic irradiation	Reflux	30	94	[7]
2	IRMOF-3	R.T.	60	92	[12]
3	MgI_2	70	120	93	[14]
4	Nano β-PbO	R.T.	60	92	[15]
5	Silica sulfuric acid	R.T.	15	90	[17]
6	[Bmim]I	R.T.	180	94	[25]
7	[Bmim]HSO$_4$	90–95	180	90	[26]
8	ILCF$_3$SO$_3$@SiO$_2$	R.T.	10	95	This work
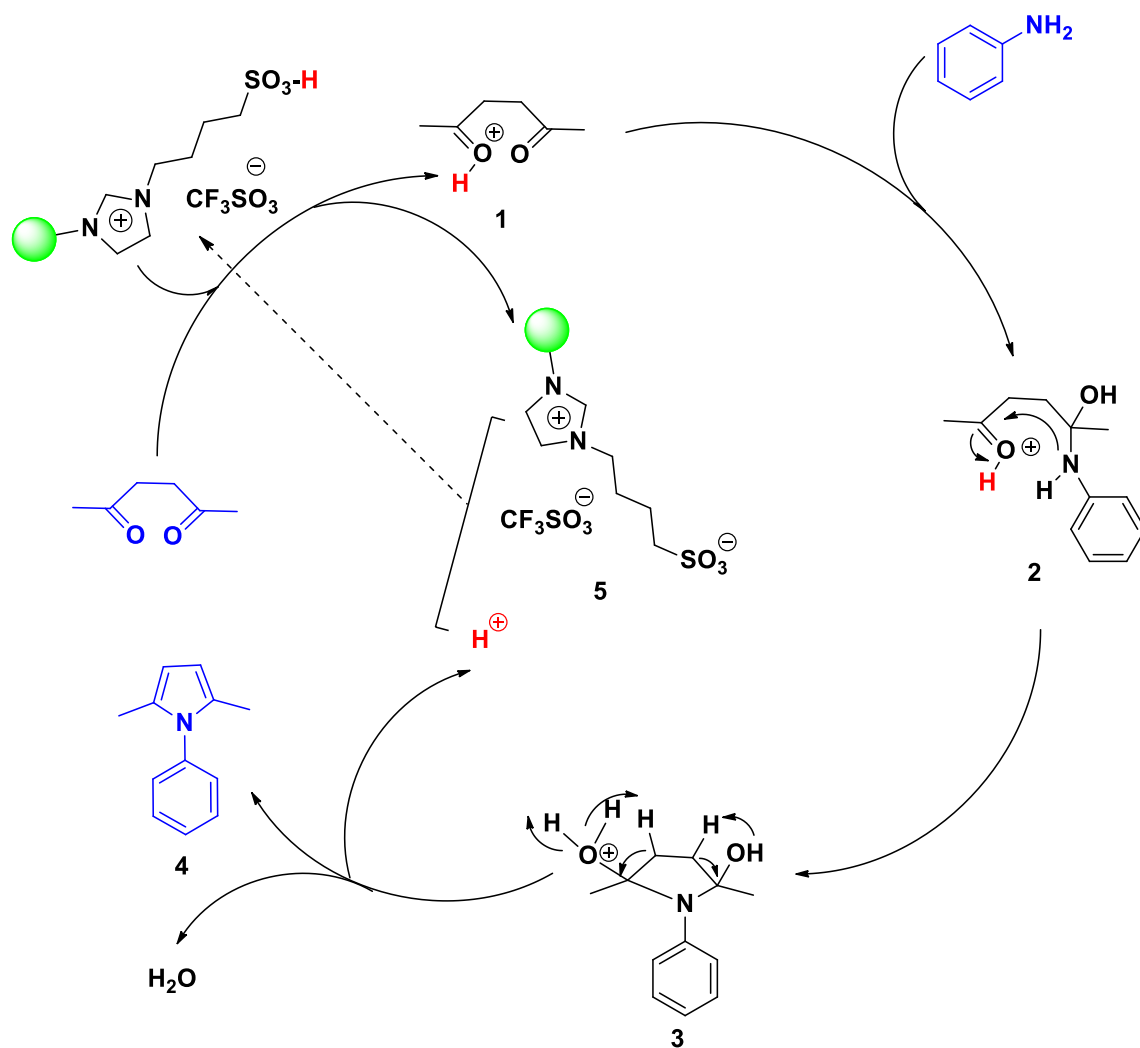
Scheme 3 Possible reaction mechanism

160 °C is related to the desorption of adsorbed water in silica. The drastic weight loss between 210 and 400 °C is attributed to the breakdown of the organic moieties. From the curve depicted, it can be seen that the IL is thermally stable below 210 °C.

Initially, the condensation of hexane-2,5-dione with aniline for the synthesis of 2,5-dimethyl-1-phenyl-1H-pyrrole was selected as a reaction model (Table 1) to test the catalytic activity of supported IL. The reaction does not progress effectively in water (Table 1, entry 2). The reaction

Table 3 Catalytic synthesis of pyrroles

Entry	Amine	Product	Time (min)	Isolated yield (%)	M.p. (ºC)
1	(aniline, NH2)	(1-phenyl-2,5-dimethylpyrrole)	10	95	51–53
2	(4-methylaniline, NH2)		10	97	59–61
3	(4-methoxyaniline, O–, NH2)		10	98	56–58
4	(Br–, NH2)	(Br–)	30	92	75–76
5	(HOOC–, NH2)	(HOOC–)	30	93	182–183
6	(F3C–, NH2)	(F3C–)	30	89	55–57
7	(benzylamine, NH2)		10	94	43–44
8	(4-methylbenzylamine, NH2)		10	96	61–62
9	(4-methoxybenzylamine, NH2)		10	98	65–67
10	(Cl–, NH2)	(Cl–)	20	93	90–92
11	(butylamine, NH2)		5	98	Oil
12	(cyclopentylamine, NH2)		5	99	Oil
13	(aniline, NH2)		10	98[a]	58–59
14	(aniline, NH2)		10	91[b]	94–96

Reaction conditions: hexane-2,5-dione (0.1 mol), amine (0.1 mol), ILCF$_3$SO$_3$@SiO$_2$ (0.8 g), ethanol (20 mL), R.T

[a] The reaction was carried out with aniline (0.1 mol), succinaldehyde (0.1 mol), ILCF$_3$SO$_3$@SiO$_2$ (0.8 g), ethanol (20 mL) at R.T

[b] The reaction was carried out with aniline (0.1 mol), ethyl 2-acetyl-4-oxo-4-phenylbutanoate (0.1 mol), ILCF$_3$SO$_3$@SiO$_2$ (0.8 g), ethanol (20 mL) at R.T

in ethanol, methanol, acetonitrile, trichloromethane, ethyl acetate as well as solvent-free conditions resulted in 68–83% yield of product (Table 1, entries 1, 3–7). The results show that ethanol is a better solvent (Table 1, entry 3). The effect of the catalyst amount is also studied and the product yield raised up as the amount of catalyst increased to 0.8 g. However, further increasing in the amount of catalyst does not improve the reaction result (Table 1, entries 12 and 13), while decreased the amount of catalyst resulted in lowering the product yield and reaction rate (Table 1, entries 8–10). It is noteworthy that the reaction in SiO$_2$ catalyst led only very low yield of the product even at prolonged reaction time (Table 1, entry 14), and apparently bulk SiO$_2$ is not the highly efficient catalyst for the reaction. Therefore, a catalyst loading of 0.8 g ILCF$_3$SO$_3$@SiO$_2$ was considered to be suitable for the reaction (Table 1, entry 11).

The ILCF$_3$SO$_3$@SiO$_2$ catalyst can be easily separated and recovered by filtration after the reaction (Fig. 5). Results indicate that the isolated yield in each run is above 92% with no notable decline in catalytic efficiency during the consecutive runs. The recovered catalyst after five runs had no obvious change in the morphology and size (Fig. 2c). To show the merit of ILCF$_3$SO$_3$@SiO$_2$ in comparison with other reported catalysts, we compared the results of the condensation of hexane-2,5-dione with aniline with other reported in the literature (Table 2) and our catalyst showed milder reaction conditions and good yield compared to the other catalysts.

According to the literatures [4, 5] and the observations in our reactions, we propose a possible mechanism (Scheme 3). Firstly, hexane-2,5-dione is activated by ILCF$_3$SO$_3$@SiO$_2$ to produce **1**. Then, aniline attacks to hexane-2,5-dione to afford **2** and subsequently, an intramolecular cyclization to form **3** and **3** then rapidly undergoes dehydration to yield **4**. The **5** is form into the catalyst to complete the cycle.

To demonstrate generality and efficiency of ILCF$_3$SO$_3$@SiO$_2$, condensation of other substrates was tested (Table 3). Various types of amines were reacted with hexane-2,5-dione to give the corresponding pyrroles in good to excellent yield and aromatic amines with electron-withdrawing substituents were less reactive and longer reaction time were needed. To

our delight, the reaction of aliphatic amines (Table 3, entries 11 and 12) is faster than that of aromatic amines (Table 3, entries 1–10). To obtain more insight into the catalytic possibilities of $ILCF_3SO_3@SiO_2$, other substrates such as succinaldehyde or ethyl 2-acetyl-4-oxo-4-phenylbutanoate were also studied in the reaction and good yields of the desired products were afforded (Table 3, entries 13 and 14).

Conclusions

In conclusion, a supported catalyst $ILCF_3SO_3@SiO_2$ was prepared and tested as an efficient heterogeneous catalyst in the preparation of pyrroles. Various amines were condensed with hexane-2,5-dione or succinaldehyde or ethyl 2-acetyl-4-oxo-4-phenylbutanoate to give the corresponding products in good to excellent yields. The advantages of the method are highly efficient, easy workup, green and steady reuse.

References

1. B. Pacorel, S.C. Leung, A.V. Stachulski, J. Davies, L. Vivas, H. Lander, S.A. Ward, M. Kaiser, R. Brun, P.M. O'Neill, J. Med. Chem. **53**, 633 (2010)
2. V. Estévez, M. Villacampa, J.C. Menéndez, Chem. Soc. Rev. **39**, 4402 (2010)
3. N. Yoshikai, Y. Wei, Asian J. Org. Chem. **2**, 466 (2013)
4. S.E. Drewes, C.J. Hogan, Synth. Commun. **19**, 2101 (1989)
5. S. Raghavan, K. Anuradha, Synlett **2003**, 711 (2003)
6. K. Aghapoor, L. Ebadi-Nia, F. Mohsenzadeh, M.M. Morad, Y. Balavar, H.R. Darabi, J. Organomet. Chem. **708–709**, 25 (2012)
7. V.S.V. Satyanarayana, A. Sivakumar, Ultrason. Sonochem. **18**, 917 (2011)
8. J. Chen, H. Wu, Z. Zheng, C. Jin, X. Zhang, W. Su, Tetrahedron Lett. **47**, 5383 (2006)
9. I. Bianchi, R. Forlani, G. Minetto, I. Peretto, N. Regalia, M. Taddei, L.F. Raveglia, J. Comb. Chem. **8**, 491 (2006)
10. G. Yin, Z. Wang, A. Chen, M. Gao, A. Wu, Y. Pan, J. Org. Chem. **73**, 3377 (2008)
11. G.E. Veitch, K.L. Bridgwood, K. Rands-Trevor, S.V. Ley, Synlett **2008**, 2597 (2008)
12. N.T.S. Phan, T.T. Nguyen, Q.H. Luu, L.T.L. Nguyen, J. Mol. Catal. A Chem. **363–364**, 178 (2012)
13. P. Cheng, W. Shao, D.L.J. Clive, J. Org. Chem. **78**, 11860 (2013)
14. X. Zhang, G. Weng, Y. Zhang, P. Li, Tetrahedron **71**, 2595 (2015)
15. S.K. Pasha, V.S.V. Satyanarayana, A. Sivakumar, K. Chidambaram, L.J. Kennedy, Chin. Chem. Lett. **22**, 891 (2011)
16. P.B. Cranwell, M. O'Brien, D.L. Browne, P. Koos, A. Polyzos, M. Peña-López, S.V. Ley, Org. Biomol. Chem. **10**, 5774 (2012)
17. H. Veisi, Tetrahedron Lett. **51**, 2109 (2010)
18. B.H. Kim, S. Bae, A. Go, H. Lee, C. Gong, B.M. Lee, Org. Biomol. Chem. **14**, 265 (2016)
19. H. Cho, R. Madden, B. Nisanci, B. Török, Green Chem. **17**, 1088 (2015)
20. D. Bandyopadhyay, E. Rhodes, B.K. Banik, RSC Adv. **3**, 16756 (2013)
21. O. Goli-Jolodar, F. Shirini, J. Iran. Chem. Soc. **13**, 1077 (2016)
22. B.V.D. Vijaykumar, B. Premkumar, K. Jang, B.I. Choi, J.R. Falck, G.N. Sheldrake, D.S. Shin, Green Chem. **16**, 2406 (2014)
23. L. Sheikhian, M. Shirafkan, J. Iran. Chem. Soc. **13**, 903 (2016)
24. N. Farzadbeh, M.T. Vardini, H. Sheikhloie, J. Iran. Chem. Soc. **13**, 715 (2016)
25. B. Wang, Y. Gu, C. Luo, T. Yang, L. Yang, J. Suo, Tetrahedron Lett. **45**, 3417 (2004)
26. N. Gupta, K.N. Singh, J. Singh, J. Mol. Liq. **199**, 470 (2014)
27. H.C. Hu, Y.H. Liu, B.L. Li, Z.S. Cui, Z.H. Zhang, RSC Adv. **5**, 7720 (2015)
28. D. Li, H. Zang, C. Wu, N. Yu, Ultrason. Sonochem. **20**, 1144 (2013)
29. R. Hajian, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, J. Iran. Chem. Soc. **13**, 1061 (2016)
30. C. Fehér, E. Kriván, J. Hancsók, R. Skoda-Földes, Green Chem. **14**, 403 (2012)
31. N. Candu, C. Rizescu, I. Podolean, M. Tudorache, V.I. Parvulescu, S.M. Coman, Catal. Sci. Technol. **5**, 729 (2015)
32. A.M. Lazarin, Y. Gushikem, S.C. de Castro, J. Mater. Chem. **10**, 2526 (2000)
33. M. Vafaeezadeh, M.M. Hashemi, Chem. Eng. J. **250**, 35 (2014)
34. W. Ding, W. Zhu, J. Xiong, L. Yang, A. Wei, M. Zhang, H. Li, Chem. Eng. J. **266**, 213 (2015)