Catal Lett
DOI 10.1007/s10562-016-1721-x

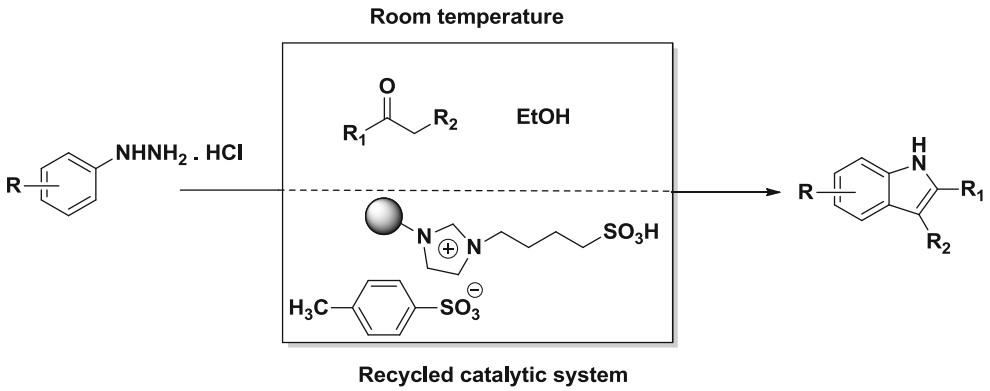
Novel and Efficient Heterogeneous 4-Methylbenzenesulfonic Acid-Based Ionic Liquid Supported on Silica Gel for Greener Fischer Indole Synthesis

Yu-Lin Hu[1,2] · Dong Fang[3] · Dong-Sheng Li[1,2]

Received: 19 February 2016 / Accepted: 23 February 2016

Abstract In this work, a functionalizing active species 4-methylbenzenesulfonic acid-based IL on silica gel (IL-SO_3H-SiO_2) has been prepared, and characterized by FT-IR, XRD, TGA, SEM and EDX spectra. Then, IL-SO_3H-SiO_2 was utilized as an efficient and heterogeneous catalyst for the synthesis of indoles via the one-pot Fischer reaction of phenyl hydrazines with ketones or aldehydes at room temperature. The heterogeneous catalyst could be recovered easily by filtration and reused many times without significant loss of its catalytic activity.

Graphical Abstract



Keywords Supported catalyst · Ionic liquid · Silica gel · Fischer indole synthesis · Heterogeneous catalysis

✉ Yu-Lin Hu
huyulin1982@163.com

✉ Dong-Sheng Li
lidongsheng1@126.com

[1] College of Materials and Chemical Engineering, China Three Gorges University, Yichang 443002, People's Republic of China

[2] Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, People's Republic of China

[3] College of Chemistry and Chemical Engineering, Yancheng Teachers University, Yancheng 224002, People's Republic of China

1 Introduction

Indoles are important classes of heterocyclic compounds used extensively for the synthesis of a variety of fine or special chemicals such as natural products, drugs, materials, etc. [1–3]. Therefore, there has been tremendous interest in developing efficient methods for the synthesis of these molecules [4–8], and a well known method constitutes the Fisher indole synthesis [8]. Traditional methods for performing such a transformation generally involve the use of

Published online: 29 February 2016

stoichiometric amount of the bronsted or lewis acids (i.e., H_2SO_4, HCl, polyphosphoric acid, $ZnCl_2$, $FeCl_3$, $AlCl_3$, etc.) [9], and suffer from considerable drawbacks such as low yield, harsh or delicate reaction condition, and a large amount of waste byproducts. Recently, a range of catalysts have been used to promote the reaction such as tartaric acid/dimethylurea melt [10], $Pb(OAc)_2/ZnCl_2$ [11], 2,4,6-trichloro-1,3,5-triazine [12], Ag/SiO_2–ZnO [13], propylphosphonic anhydride [14], CH_3COOH [15], $TiCl_4$/t-$BuNH_2$ [16], and other reagents [17–21]. However, these protocols, are generally associated with one or more disadvantages, such as high temperatures, prolonged reaction times, tedious work-up, problematic side reactions, the use of expensive, toxic and moisture sensitive reagents, difficulty in separating the catalyst from the reaction mixture as well as recycling of it, and environmental concerns associated with the use of poorly manageable catalysts. Consequently, search for new and environmentally benign synthetic methodologies for the synthesis of indoles that address these drawbacks remains to be of value and interest.

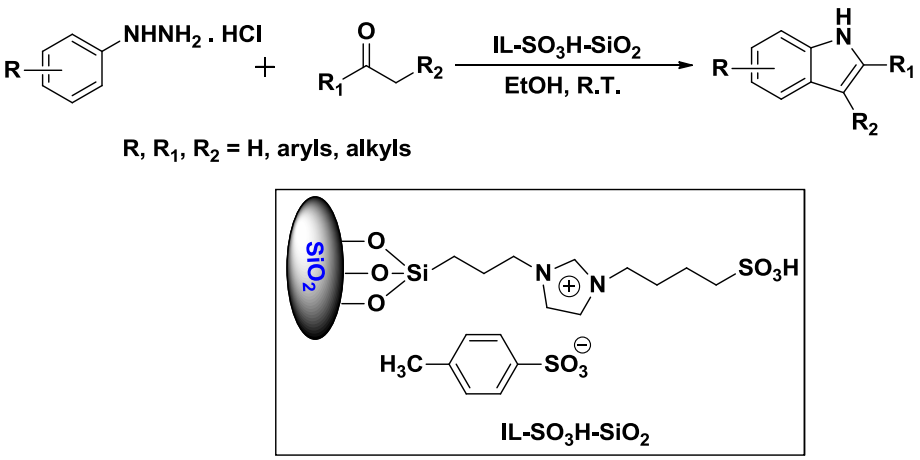
Recently, ionic liquids (ILs) have become an active area of research, ILs possess favourable properties such as very low vapor pressure, wide liquid temperature range, good ionic conductivity, excellent electrochemical properties, and strong ability to dissolve many chemicals [22]. Therefore, they have been widely employed in the field of separation, chemical synthesis, electrochemistry, and catalysis [23–25]. Up to now, examples of their application as catalysts in the synthesis of indoles were also reported [26–28]. In spite of high catalytic activity of these ILs presented, they suffered from serious drawbacks in terms of separation and recycling of costly ILs, equipment corrosion as well as ILs toxicity. A useful approach to overcome these limitations is the development of supported functional ionic liquid catalytic system [29–31]. The supported IL system dispersed onto a high surface area support. The homogeneous catalytic reactions of ILs could transfer into the heterogeneous systems which provide attractive features such as gaining high catalyst efficiency by using only smaller amounts of ILs, high system stability, facilitating the catalyst recovery and high reusability [31].

In continuation of our interest on the preparation and application of supported functional ionic liquids in organic synthesis, we attempt to design a catalyst functionalizing active species 4-methylbenzenesulfonic acid-based IL on silica gel (IL-SO_3H-SiO_2). Here, the prepared material, IL-SO_3H-SiO_2, exhibited advanced chemical behaviors and has the advantage of being a solid, which is used in heterogeneous catalysis and can reach high reaction efficiency for the preparation of indoles via Fischer indolization (Scheme 1). Furthermore, it shows that the IL-SO_3H-SiO_2 catalyst can be easily recovered and reused for the reaction without any significant loss of catalytic activity.

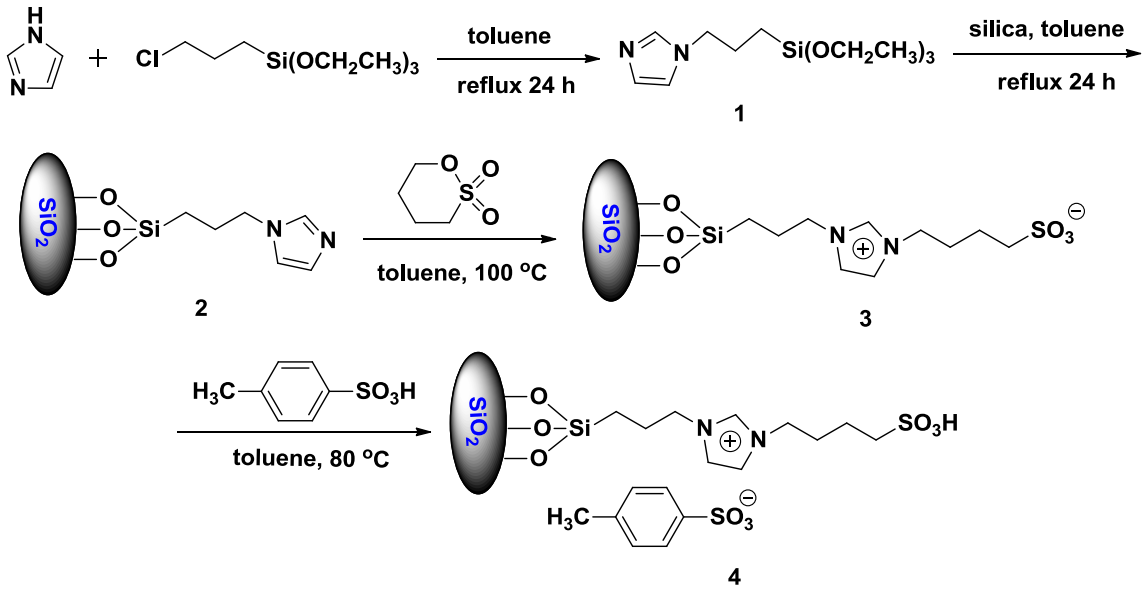
2 Experimental

2.1 Apparatus and Reagents

All the chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The silica functionalized sulfonic acids were synthesized according to the literature procedures [32, 33]. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a Nicolet Nexus 470 Fourier transform infrared spectrometer, using KBr pellets at room temperature. The powder X-ray diffraction (XRD) analysis was carried out on a Rigaku Ultima IV diffractometer with high-intensity Cu Ka radiation. Energy dispersive X-ray analysis (EDX) was used to conduct the elemental analysis of the IL. Scanning electron microscopy studies were conducted on a JSM-7500F Scanning Electron Microscope



Scheme 1 Fischer indole synthesis catalyzed by IL-SO_3H-SiO_2



Scheme 2 The synthetic process of IL-SO_3H-SiO_2

(SEM). Thermogravimetric analysis (TGA) were analyzed by a Netzsch Thermoanalyzer STA 449 with a heating rate of 10 °C/min under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Bruker 500-MHz spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. GC analyses were performed on a Shimadzu-14B gas chromatography equipped with HP-1 capillary column (30 m, 0.25 mm, 0.25 mm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Elemental analysis were performed on a Vario EL III instrument (Elmentar Anlalysensy Teme GmbH, Germany).

2.2 Synthesis of the Supported Ionic Liquid

The preparation process were according to known process [34, 35] and shown in Scheme 2. (i) Silica pretreatment and activation: silica gel (50 g) was activated by standing in hydrochloric acid solution (10 %, 500 mL) for 12 h at room temperature and then washed thoroughly with distilled water. The sample was then dried at 60 °C for 24 h. (ii) Preparation of **1**: A mixture of imidazole (6.8 g, 0.1 mol), (3-chloropropyl) triethoxysilane (24.1 g, 0.1 mol) and toluene (180 mL) were added into a 500 mL round flask connected to a reflux condenser, and the mixture was refluxed for 22 h under a nitrogen atmosphere. Then, triethylamine (10.1 g, 0.1 mol) was added dropwise to the resulted mixture at 50 °C in 3 min, and stirred for another 2 h under reflux conditions. After the reaction, the slurry was filtrated and the filter cake was washed with toluene (3 × 10 mL). The combined toluene solution was removed under reduced pressure to afford 1-(3-(triethoxysilyl)propyl)-1H-imidazole **1** as a viscous liquid. (iii) Preparation of **2**: a mixture of **1** (27.2 g, 0.1 mol), activated silica (28 g), and toluene (250 mL) was stirred vigorously in a 500 mL round flask under a nitrogen atmosphere. After 24 h stirring under reflux conditions, the white solid **2** was obtained by filtration and washed with toluene (3 × 20 mL). (iv) Preparation of **3**: In this step, 1,4-butane sultone (13.6 g, 0.1 mol), the obtained solid **2**, and toluene (200 mL) were stirred at 100 °C for 8 h under nitrogen flow, the white solid **3** was obtained by filtration and washed with toluene (3 × 20 mL). (v) Preparation of **4**: Then, 4-methylbenzenesulfonic acid (17.2 g, 0.1 mol) was added into the above silica supported IL **3** in toluene (200 mL) in 10 min. The final mixture was stirred at 80 °C for 6 h and by filtration, washed with dichloromethane (3 × 20 mL) and dried under vacuum at 60 °C to afford the supported ionic liquid **4** as a white powder.

2.3 General Procedure for the Synthesis of Indoles

To a solution of phenylhydrazine (10 mmol) and ketone or aldehyde (10 mmol) in ethanol (15 mL) was added catalyst IL-SO_3H-SiO_2 (1.2 g). The mixture was allowed to stirring at room temperature for a period time specified in Table 2. The reaction was monitored by TLC and GC. After completion of the reaction, the catalyst was recovered by filtration. Evaporation of the solvent under reduced pressure gave the crude product. Further purification was achieved by flash column chromatography on a silica gel to give the desired product. The recovered catalyst was dried and reused for the next run. Spectroscopic data for selected products is as follows.

2.4 Spectral Data of Selected Products

2.4.1 3-Isobutyl-2-methyl-1H-indole (Table 2, Entry 4)

Colourless oil; ^{1}H NMR: $\delta = 0.98$ (d, 6H, CH_3), 1.92–2.01 (m, 1H, CH), 2.41 (s, 3H, CH_3), 2.55 (d, 2H, CH_2), 7.08–7.25 (m, 3H, Ar–H), 7.54 (m, 1H, Ar–H), 7.72 (s, 1H, NH) ppm; Anal. Calcd for $C_{13}H_{17}N$: C, 83.34; H, 9.13; N, 7.45. Found: C, 83.37; H, 9.15; N, 7.48.

2.4.2 6-Methoxy-2,3,4,9-tetrahydro-1H-carbazole (Table 2, Entry 8)

White soild; ^{1}H NMR: $\delta = 1.71$–1.89 (m, 4H, CH_2CH_2), 2.61–2.72 (m, 4H, CH_2), 3.75 (s, 3H, OCH_3), 6.64 (m, 1H,

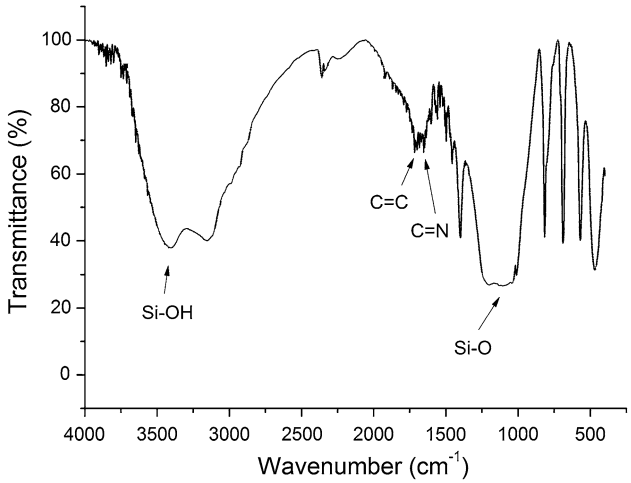


Fig. 1 FTIR spectra of IL-SO_3H-SiO_2

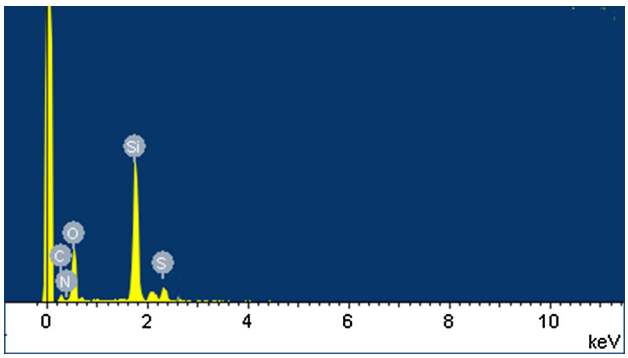


Fig. 3 EDX image of IL-SO_3H-SiO_2

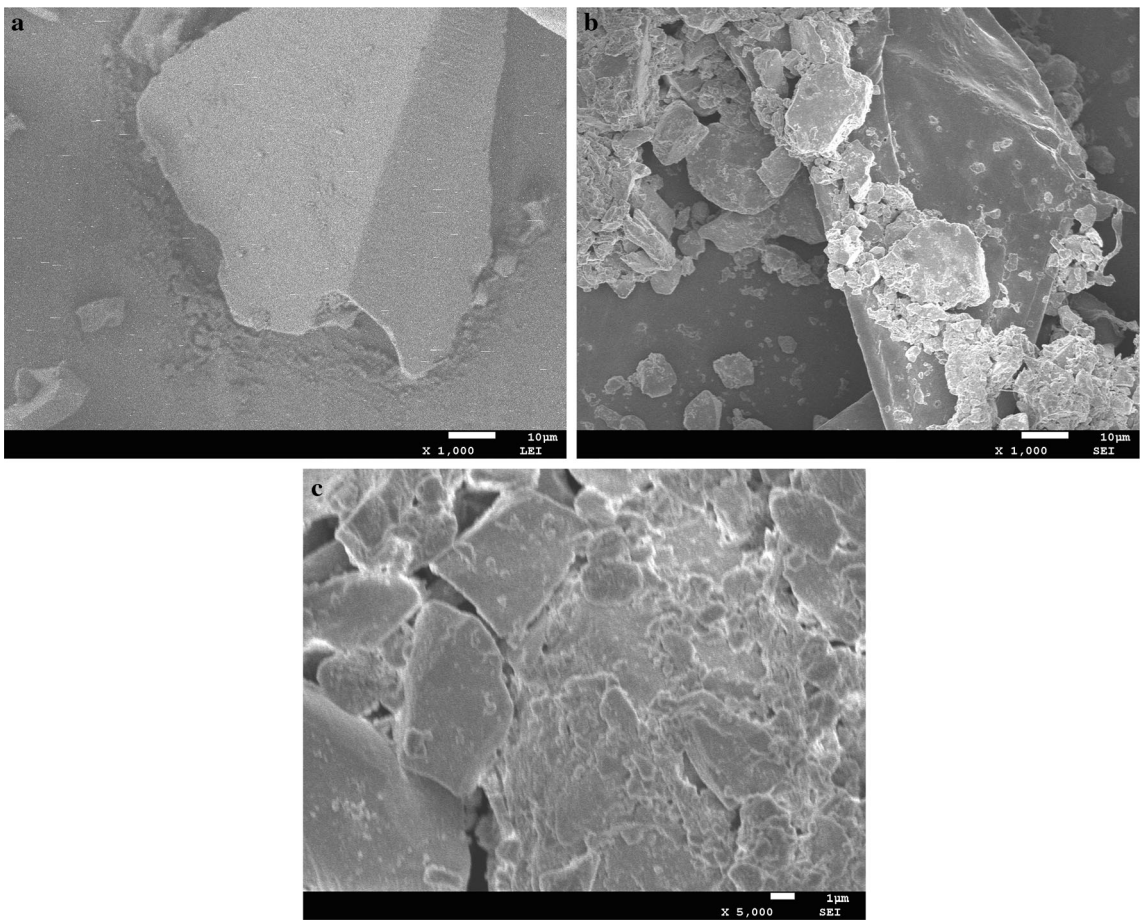


Fig. 2 SEM images of silica gel (**a**), IL-SO_3H-SiO_2 (**b**), the recycled catalyst (**c**)

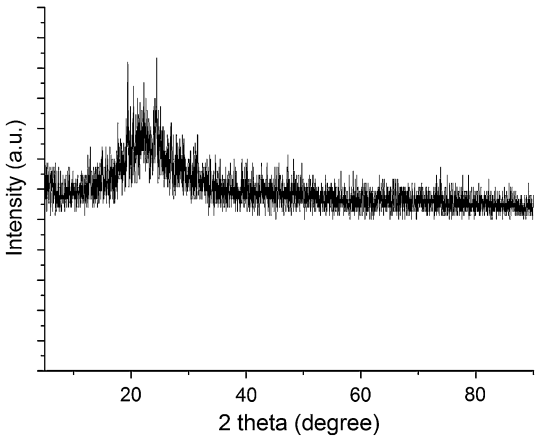


Fig. 4 XRD pattern of IL-SO_3H-SiO_2

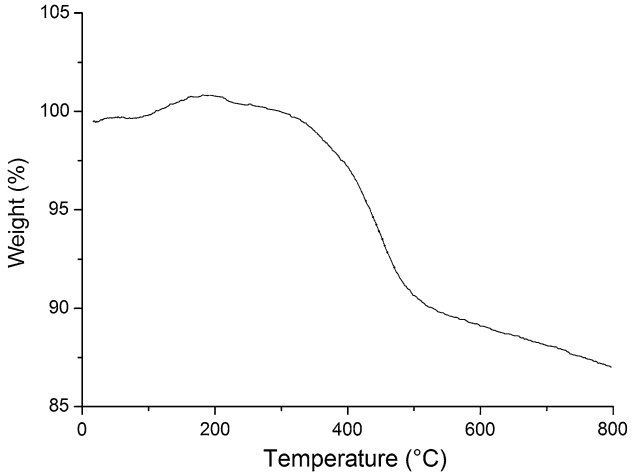


Fig. 5 TG curve for the supported IL catalyst

Ar–H), 6.83 (s, 1H, Ar–H), 7.08 (m, 1H, Ar–H), 10.52 (s, 1H, NH) ppm; Anal. Calcd for $C_{13}H_{15}NO$: C, 77.53; H, 7.49; N, 6.92; O, 7.94. Found: C, 77.58; H, 7.51; N, 6.96; O, 7.95.

2.4.3 6-Fluoro-2,3,4,9-tetrahydro-1H-carbazole (Table 2, Entry 9)

White soild; ^{1}H NMR: $\delta = 1.78$–1.85 (m, 4H, CH_2CH_2), 2.59–2.74 (m, 4H, CH_2), 6.85 (m, 1H, Ar–H), 7.09 (m, 1H, Ar–H), 7.22 (m, 1H, Ar–H), 10.79 (s, 1H, NH) ppm; Anal. Calcd for $C_{12}H_{12}FN$: C, 76.17; H, 6.39; F, 10.04; N, 7.40. Found: C, 76.17; H, 6.39; F, 10.04; N, 7.40.

2.4.4 3-Butyl-5-methyl-2-phenyl-1H-indole (Table 2, Entry 11)

Colourless oil; ^{1}H NMR: $\delta = 0.86$ (t, 3H, CH_3), 1.35 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 2.51 (s, 3H, CH_3), 2.83 (t, 2H, CH_2), 6.89–6.95 (m, 2H, Ar–H), 7.31–7.37 (m, 2H, Ar–H), 7.51-7.56 (m, 2H, Ar–H), 7.59-7.66 (m, 2H, Ar–H), 10.78 (s, 1H, NH) ppm; Anal. Calcd for $C_{19}H_{21}N$: C, 86.62; H, 8.01; N, 5.29. Found: C, 86.65; H, 8.04; N, 5.32.

3 Results and Discussion

The structure of the supported ionic liquid was characterized by FT-IR, XRD, TG, EDX, and SEM analysis. The FTIR spectra of the supported ionic liquid catalyst IL-SO_3H-SiO_2 is presented in Fig. 1. Two characteristic peaks at the positions of 1530 and 1625 cm^{-1}, which were attributed to the imidazole ring, indicating that imidazole was successfully grafted on the surface of silica gel.

Table 1 Optimization of the reaction conditions

Entry	Solvent	Catalyst	Amount (g)	Time (h)	Yield (%)[a]
1	Solvent-free	IL-SO_3H-SiO_2	0.6	6	68
2	Water	IL-SO_3H-SiO_2	0.6	6	70
3	Ethanol	IL-SO_3H-SiO_2	0.6	6	75
4	Methanol	IL-SO_3H-SiO_2	0.6	6	72
5	Ethyl acetate	IL-SO_3H-SiO_2	0.6	6	65
6	Acetonitrile	IL-SO_3H-SiO_2	0.6	8	50
7	Ethanol	IL-SO_3H-SiO_2	0.8	4	82
8	Ethanol	IL-SO_3H-SiO_2	1.0	4	91
9	Ethanol	IL-SO_3H-SiO_2	1.2	4	94
10	Ethanol	IL-SO_3H-SiO_2	1.4	4	94
11	Ethanol	SiO_2-Pr-SO_3H	1.2	8	85
12	Ethanol	SiO_2-SO_3H	1.2	8	72

The reactions were carried out with phenyl hydrazine hydrochloride (10 mmol), cyclohexanone (10 mmol), catalyst, and solvent (15 mL) at room temperature

[a] Isolated yield

Additional bands at 3100, 2970 and 1520 cm^{-1} are due to C–H stretching and deformation vibrations of the imidazole moiety and alkyl chain. Also, the peaks observed at 490–870 cm^{-1} related to vibrational modes of 4-CH_3 $PhSO_3$. Moreover, the stretching vibration peaks of Si–O–Si (1087 cm^{-1}), O–H (1685 cm^{-1}) and the stretching vibration Si–OH (3478 cm^{-1}) were clearly observed.

The shape and surface morphology of the IL-SO_3H-SiO_2 were studied by SEM (Fig. 2). Figure 2a is the SEM image of silica gel, which is made up of block structures with a size of several micrometers. Figure 2b is the SEM image of the supported IL **4**, it clearly shows the supported IL particles were well-defined and had distinct size owing to the immobilization of the IL. The particle size of the supported IL is smaller to that of silica gel, which demonstrates that the particles of silica gel had a good mechanical stability during the immobilization step. The change of the parent structure of the silica to well defined particles in supported IL indicated that IL-SO_3H had been immobilized on the surface of the silica particles. EDX of the supported IL showed the presence of the expected elements in its structure (Fig. 3). Figure 4 displayed the wide-angle XRD pattern of the supported IL. As can be seen in Fig. 4, the catalyst had obvious characteristic peak at $2\theta \approx 22°$, which was attributed to the amorphous nature of the SiO_2 support.

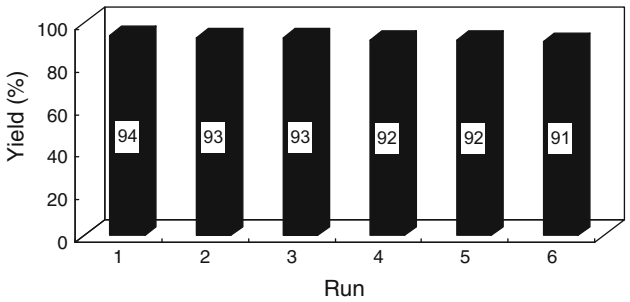
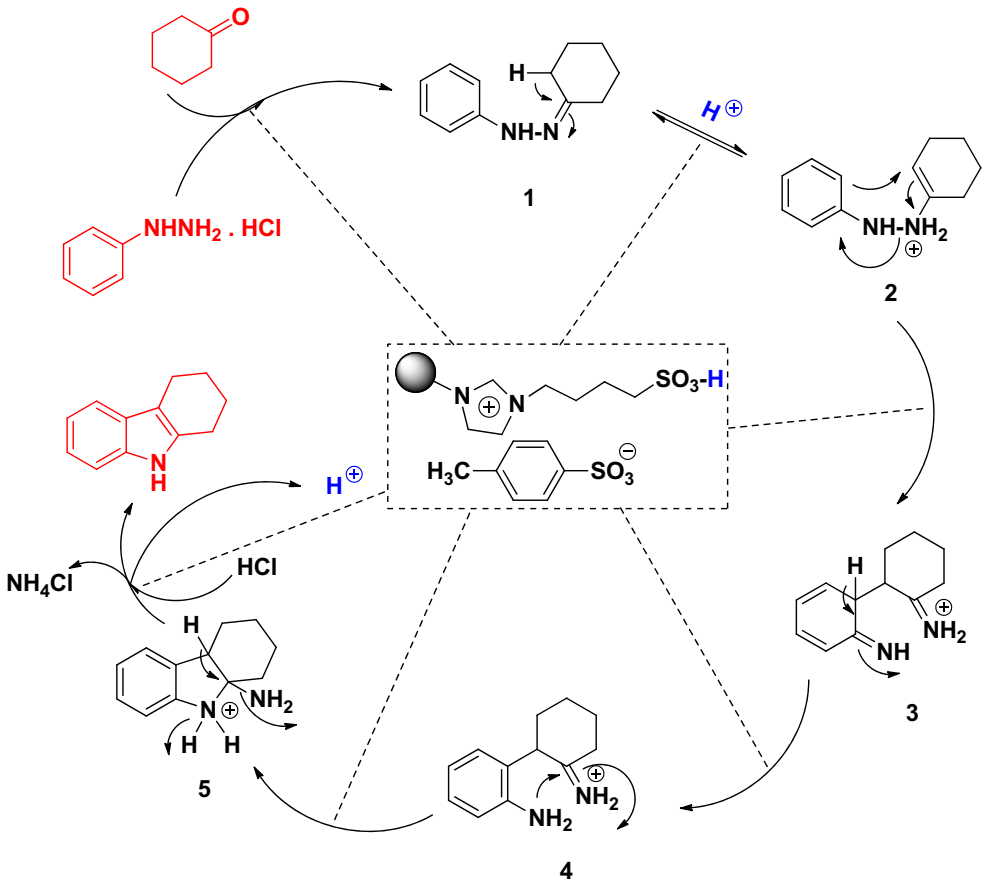


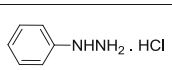
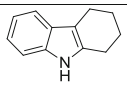
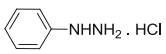
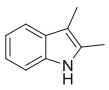
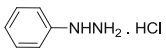
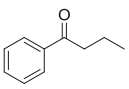
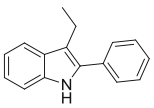
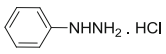
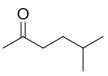
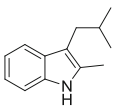
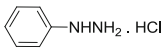
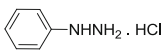
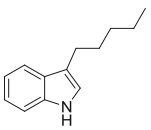
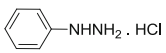
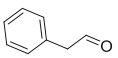
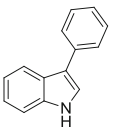
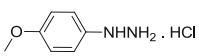
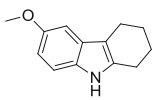
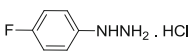
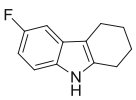
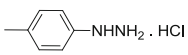
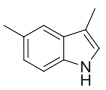
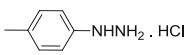
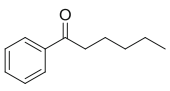
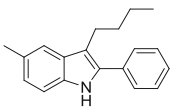
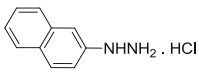
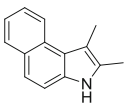
Fig. 6 The repeating reactions of phenyl hydrazine hydrochloride (10 mmol), cyclohexanone (10 mmol) and ethanol (15 mL) in the presence of the recycled IL-SO_3H-SiO_2

The stability of supported IL was determined by thermogravimetric analysis (Fig. 5), the observed weight loss was associated with the loss of the organic components attached to the surface. The TG curve indicates no weight loss occurred before 300 °C, 2.8 % initial weight loss occurred from 300 to 400 °C, complete loss of the IL



Scheme 3 Possible mechanism for the Fischer indole synthesis

Table 2 Catalytic synthesis of indoles in the presence of IL-SO_3H-SiO_2

Entry	Phenyl hydrazine	Ketone/Aldehyde	Product	Time (h)	Yield (%)[a]
1				4	94
2				4	95
3				6	89
4				4	91
5				4	96
6				4	90
7				6	90
8				4	95
9				7	84
10				4	96
11				6	87
12				5	86

Unless otherwise noted, the reactions were carried out with phenylhydrazine (10 mmol), ketone or aldehyde (10 mmol), IL-SO_3H-SiO_2 (1.2 g), and ethanol (15 mL) at room temperature

[a] Isolated yield

covalently grafted onto the silica is seen in the temperature range 400–500 °C, and the amount of organic moiety was about 10 % against the total solid catalyst. From the curve depicted, one can see that IL-SO_3H-SiO_2 is thermally stable below about 300 °C. The good thermal stability of the silica gel supported IL may be beneficial to the catalytic experiments.

The initial study was carried out a model reaction between phenyl hydrazine hydrochloride and cyclohexanone for the synthesis of tetrahydrocarbazole to optimize the reaction conditions, and the results are summarized in Table 1. The effect of various solvents on the yield of product is given in Table 1, entries 1–6. The reaction does not progress effectively in acetonitrile (Table 1, entry 6). The reaction in water, ethanol, methanol, ethyl acetate as well as solvent-free conditions resulted in 65–75 % yield of product (Table 1, entries 1–5). The results show that ethanol is a better solvent than the other solvents tested (Table 1, entry 3). To investigate the effect of catalyst concentration, systematic studies were carried out in the presence of various amounts of the catalyst in ethanol, affording tetrahydrocarbazole in 75–94 % isolated yields, respectively (Table 1, entries 3, 7–9). Thus, the best yield is obtained in the presence of just 1.2 g of IL-SO_3H-SiO_2 (Table 1, entry 9). The use of a greater amount of catalyst does not improve the result to an appreciable extent (Table 1, entry 10). Besides IL-SO_3H-SiO_2, silica functionalized sulfonic acids, such as SiO_2-Pr-SO_3H and SiO_2-SO_3H, were tested as heterogeneous catalysts in this model reaction (Table 1, entries 11 and 12), and the results showed that the supported IL IL-SO_3H-SiO_2 demonstrated the best performance in terms of yield and reaction rate. Therefore, IL-SO_3H-SiO_2 is a very efficient catalyst for Fischer indole synthesis.

The reusability of the IL-SO_3H-SiO_2 catalyst was also studied, and the results are summarized in Fig. 6. It was found that the catalyst could be conveniently recovered at the end of reaction, and could be readily reused for the next cycle. The catalyst could be typically recovered and reused for subsequent reactions with no appreciable decrease in yields and reaction rates. An SEM observation of the recovered catalyst after five runs was made, and there was no obvious change in the morphology and size in comparison with fresh catalyst (Fig. 2c). The recycling process involved the removal of the product from the catalyst by a simple filtration. Fresh substrates were then recharged to the recovered catalyst and the mixture was heated to react once again.

The excellent results of IL-SO_3H-SiO_2 suggest the reaction has a particular reaction mechanism. On the basis of previous reports [9–12] and the experiment result, taking the reaction of phenyl hydrazine hydrochloride and cyclohexanone as an example, a possible mechanism is proposed (Scheme 3). At first, the substrates phenyl hydrazine hydrochloride and cyclohexanone are activated by acidic group of IL-SO_3H-SiO_2 to forms a phenylhydrazone **1** which isomerizes to the respective enamine **2**. After protonation, a cyclic [3,3]-sigmatropic rearrangement occurs producing an imine **3**. The resulting imine forms a cyclicaminoacetal **4**. **4** is then very rapidly form into **5**, which under acid catalysis eliminates NH_3, resulting in the energetically favorable product.

Having established optimum conditions, a series of indoles was synthesized by reacting various phenyl hydrazines with ketones/aldehydes in order to showcase the broad scope and generality of this method. It is clear that various types of phenyl hydrazines with ketones or aldehydes in the presence of a catalytic amount of IL-SO_3H-SiO_2 at room temperature, can be efficiently converted to the corresponding indoles in good to high yields (Table 2). In general, electron-rich aromatic amines afforded a higher yield than the electron-deficient aromatic amines, and it was observed that electron-donating groups on the phenyl ring of aromatic amines favoured the formation of the corresponding products in excellent yields (Table 2, entries 8, 10 and 11). In contrast, electron-withdrawing groups associated with aromatic amines slightly decreased the reactivity of the substrate (Table 2, entries 9 and 12). Surprisingly, the Fischer reaction of aliphatic ketones or aldehydes (Table 2, entries 1, 2, 4–6, 8–10 and 12) to the corresponding indoles is faster than aromatic ketones or aldehydes (Table 2, entries 3, 7 and 11).

4 Conclusion

In conclusion, we have shown that 4-methylbenzenesulfonic acid-based IL on silica gel can act as a novel, effective and heterogeneous catalyst for the one-pot synthesis of indoles from commercially available starting materials. Various phenyl hydrazines were reacted with ketones or aldehydes to give the corresponding products in good to excellent yields. Mild reaction conditions, simplicity of operation, high yields, easy isolation of products, and excellent recyclability of the catalyst are the attractive features of this methodology. The scope and synthetic application of this reaction are currently under study in our laboratory.

Acknowledgments The authors would like to acknowledge financial support provided by the National Natural Science Foundation of China (No. 21506115) and the Natural Science Foundation of Jiangsu Province (No. BK20140460) for carrying out this research.

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