

Polymer Support Immobilized Acidic Ionic Liquid: Preparation and Its Application as Catalyst in the Synthesis of Hantzsch 1,4-Dihydropyridines

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A polymer support immobilized acidic ionic liquid was prepared by copolymerization of 3-vinyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate with styrene in the presence of benzoyl peroxide and its primary application as a solid acidic heterogeneous catalyst to the synthesis of Hantzsch 1,4-dihydropyridines through a one-pot three-component reaction of aromatic aldehydes, ethyl acetoacetate and ammonium acetate was investigated. The results showed that this heterogeneous catalyst has high catalytic activity and the desired products were obtained in good to high yields. Moreover, the catalyst was found to be reusable and a considerable catalytic activity still could be achieved after third run.

Key Words : Immobilized acidic ionic liquid, Polymer support, Hantzsch 1,4-dihydropyridines

Introduction

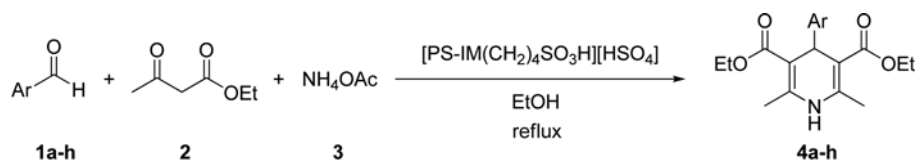
In recent years, heterogeneous catalysts have gained importance due to economic and environmental consideration.¹⁻⁵ The major problem associated with most homogenous catalyst systems is the separation of catalyst from the reaction mixture and the recycling of the catalyst. Heterogeneous catalysts can be easily separated from the reaction products and reused in successive runs. Also, heterogeneous catalyst is more suitable for continuous flow operation that is more appropriated than batchwise processes for large scale industrial synthesis. Therefore, a general trend in the field of catalysis is to replace homogeneous catalysts by non-toxic, non-corrosive, easy to handle and environmentally friendly heterogeneous catalysts. One of the important routes for preparing heterogeneous catalysts is immobilizing the homogenous precursors on a solid support. There are several reports for using of polymer supports for immobilizing the catalysts.⁶⁻⁹ However, despite intensive research efforts over the past few years, the number of polymer-supported catalysts known is still just a small fraction of the catalysts commonly used in traditional solution-phase organic synthesis.

Ionic liquids (ILs) are defined as salts that are in a liquid form at or below 100 °C.¹⁰ They have been used in the fields of synthesis, analysis, catalysis, separation, and energy supply because they possess a number of unique physico-chemical properties such as the negligible vapor pressure, unique solvation properties, good ion conductivity as well as catalytic activity and selectivity.¹¹⁻¹⁴ It has been reported that various kinds of catalytic reactions have smoothly performed in ILs.¹⁵⁻¹⁹ Increasingly, research activities have been focused on the design of ILs to produce task-specific ILs for specific functions e.g., acidic²⁰ or basic²¹ ILs. The introduction of Brønsted-acidic functional groups into cations or anions of the ILs, especially the SO₃H-functional group, obviously enhanced their acidities and water solubilities.²²⁻²⁴ Therefore, these ILs can be used as highly efficient acid catalysts and

have been receiving extensive interest as green substitute for H₂SO₄, HF and AlCl₃ catalysts in chemical processes.²⁵ Recently, several reports have become available describing the use of the immobilized ILs in various acid-catalyzed reactions.²⁶⁻²⁹ Compared to pure acidic ILs, e.g. SO₃H-functionalized ILs, such heterogeneous catalysts show additional advantages, which include the facilitation of catalyst separation from reaction system, decreased consumption of IL and lower contamination of product.

1,4-Dihydropyridines that are of importance from view point of biological activities,³⁰⁻³² are generally synthesized by Hantzsch reaction which involves the condensation of aldehydes, β-ketoester and ammonia or ammonium acetate. A number of improved methods have been reported in the literature for this condensation which involve the use of microwave,³³ trifluoroethanol,³⁴ cyanuric chloride,³⁵ PPh₃,³⁶ Sc(OTf)₃,³⁷ and CeCl₃·7H₂O.³⁸ Many of these procedures suffer from lack of selectivity, unsatisfactory yields, being costly, toxicity of the reagents, or required special conditions. These limitations prompted us towards further investigation in search for a new reusable heterogeneous catalyst, which will carry out the synthesis of Hantzsch 1,4-dihydropyridines under simpler experimental set up and eco-friendly conditions.

Recently, Qiao and co-workers³⁹ have reported a new method to immobilize a Brønsted acidic IL on solid support by copolymerization of 3-vinyl-1-(4-sulfonic acid)butylimidazolium trifluoromethanesulfonate with styrene in the presence of AIBN and used as catalyst for acetalization of various aldehydes. According to this method and due to our interest in the applications of reusable catalysts in organic reactions⁴⁰⁻⁴⁷ in this paper firstly a similar polystyrene immobilized SO₃H-functionalized IL with different anion are prepared by copolymerization of 3-vinyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate with styrene in the presence of benzoyl peroxide (denoted as [PS-IM(CH₂)₄SO₃H][HSO₄]) and then its catalytic activity to the synthesis of Hantzsch 1,4-dihydropyridines *via* a one-pot three-component reaction of



Scheme 1. Synthesis of Hantzsch 1,4-dihydropyridines catalyzed by [PS-IM(CH₂)₄SO₃H][HSO₄].

aromatic aldehydes, ethyl acetoacetate and ammonium acetate are investigated (Scheme 1).

Experimental

All chemicals were available commercially and used without additional purification. Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The ¹H NMR (500 MHz) spectra were recorded with a Bruker DRX500 spectrometer. GPC analysis was performed on a Agilent 1100 GPC instrument with concentration 1 g/L in THF at 25 °C.

Preparation of the Catalyst [PS-IM(CH₂)₄SO₃H][HSO₄]. To a magnetically stirred of 1-vinylimidazole (10 mmol), 1,4-butane sultone (10 mmol) was slowly added at 0 °C. Then the mixture was heated in the oil bath at 80 °C for 2 h until it turned into solid. The obtained solid was washed repeatedly with diethyl ether and dried in vacuo at room temperature to give the white solid zwitterion.³⁹ Then, a stoichiometric amount of concentrated sulfuric acid (98%) was added dropwise to the zwitterion at 0 °C, and the mixture was heated in the oil bath at 60 °C for 12 h. The produced liquid was washed with diethyl ether and dried in vacuo at 50 °C for 2 h to get the viscous clear 3-vinyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate [VIM(CH₂)₄SO₃H][HSO₄]. A mixture of this IL (3 mmol, 10 mol % based on styrene), purified styrene (30 mmol), and benzoyl peroxide (5% of vinyl groups of both IL and styrene) in ethanol (50 mL) was heated under reflux for 24 h. After this time, the reaction mixture was cooled to room temperature, the obtained solid was separated by filtration, repeatedly washed with ethanol, and dried under vacuum for 0.5 h. The precipitate was grind in mortar to afford polystyrene immobilized SO₃H-functionalized IL in the form of white powder ([PS-IM(CH₂)₄SO₃H][HSO₄]).

General Procedure for the Synthesis of 1,4-Dihydropyridines Catalyzed by [PS-IM(CH₂)₄SO₃H][HSO₄]. A mixture of an aromatic aldehyde **1a-h** (1 mmol), ethyl acetoacetate **2** (2 mmol), ammonium acetate **3** (1 mmol), and [PS-IM(CH₂)₄SO₃H][HSO₄] (0.03 g) as catalyst in ethanol (5 mL) was heated under reflux for the appropriate time. The progress of the reaction was monitored by TLC. Upon completion, the catalyst was filtered under hot condition. Ethanol was evaporated under vacuo and *n*-hexane was then added. The precipitate was collected and recrystallized from ethanol to give 1,4-dihydropyridines **4a-h** in good to high yields.

Recycling and Reusing of [PS-IM(CH₂)₄SO₃H][HSO₄].

The catalyst was insoluble in hot ethanol and it could therefore be recycled by a simple filtration. The separated catalyst was washed with cold ethanol, dried at 50 °C under vacuum for 1 h and reused in another reaction. The catalyst could be used at least three times with only slight reduction in the catalytic activity.

¹H NMR and IR Data for Compounds **4a-h**.

Compound 4a (Ar = Ph): ¹H NMR (CDCl₃, δ): 1.25 (t, 6H, *J* = 7.1 Hz, 2CH₃ at C-3 and C-5), 2.37 (s, 6H, 2CH₃ at C-2 and C-6), 4.05-4.20 (m, 4H, 2CH₂, diastereotopic protons), 5.02 (s, 1H, CH), 5.58 (s br., 1H, NH), 7.10-7.35 (m, 5H, arom-H); IR (KBr): ν 3342 (NH), 1688 (C=O) cm⁻¹.

Compound 4b (Ar = 4-BrC₆H₄): ¹H NMR (CDCl₃, δ): 1.25 (t, 6H, *J* = 7.1 Hz, 2CH₃ at C-3 and C-5), 2.36 (s, 6H, 2CH₃ at C-2 and C-6), 4.05-4.20 (m, 4H, 2CH₂, diastereotopic protons), 4.98 (s, 1H, CH), 5.61 (s br., 1H, NH), 7.19 (d, 2H, *J* = 8.4 Hz, arom-H), 7.35 (d, 2H, *J* = 8.4 Hz, arom-H); IR (KBr): ν 3361 (NH), 1694 (C=O) cm⁻¹.

Compound 4c (Ar = 4-ClC₆H₄): ¹H NMR (CDCl₃, δ): 1.25 (t, 6H, *J* = 7.1 Hz, 2CH₃ at C-3 and C-5), 2.36 (s, 6H, 2CH₃ at C-2 and C-6), 4.00-4.20 (m, 4H, 2CH₂, diastereotopic protons), 4.99 (s, 1H, CH), 5.66 (s br., 1H, NH), 7.20 (d, 2H, *J* = 8.3 Hz, arom-H), 7.24 (d, 2H, *J* = 8.3 Hz, arom-H); IR (KBr): ν 3358 (NH), 1697 (C=O) cm⁻¹.

Compound 4d (Ar = 4-FC₆H₄): ¹H NMR (CDCl₃, δ): 1.24 (t, 6H, *J* = 7.2 Hz, 2CH₃ at C-3 and C-5), 2.36 (s, 6H, 2CH₃ at C-2 and C-6), 4.05-4.20 (m, 4H, 2CH₂, diastereotopic protons), 4.99 (s, 1H, CH), 5.68 (s br., 1H, NH), 6.91 (t, 2H, *J* = 8.4 Hz, arom-H), 7.26 (dd, 2H, *J* = 8.2, 6.0 Hz, arom-H); IR (KBr): ν 3343 (NH), 1723 (C=O) cm⁻¹.

Compound 4e (Ar = 4-MeOC₆H₄): ¹H NMR (CDCl₃, δ): 1.26 (t, 6H, *J* = 7.1 Hz, 2CH₃ at C-3 and C-5), 2.36 (s, 6H, 2CH₃ at C-2 and C-6), 3.79 (s, 3H, OCH₃), 4.05-4.20 (m, 4H, 2CH₂, diastereotopic protons), 4.96 (s, 1H, CH), 5.58 (s br., 1H, NH), 6.78 (d, 2H, *J* = 8.6 Hz, arom-H), 7.23 (d, 2H, *J* = 8.6 Hz, arom-H); IR (KBr): ν 3342 (NH), 1689 (C=O) cm⁻¹.

Compound 4f (Ar = 4-MeC₆H₄): ¹H NMR (CDCl₃, δ): 1.26 (t, 6H, *J* = 7.1 Hz, 2CH₃ at C-3 and C-5), 2.31 (s, 3H, CH₃ at aromatic ring), 2.36 (s, 6H, 2CH₃ at C-2 and C-6), 4.05-4.20 (m, 4H, 2CH₂, diastereotopic protons), 4.99 (s, 1H, CH), 5.60 (s br., 1H, NH), 7.04 (d, 2H, *J* = 7.8 Hz, arom-H), 7.20 (d, 2H, *J* = 7.8 Hz, arom-H); IR (KBr): ν 3360 (NH), 1696 (C=O) cm⁻¹.

Compound 4g (Ar = 3-O₂NC₆H₄): ¹H NMR (CDCl₃, δ): 1.25 (t, 6H, *J* = 7.1 Hz, 2CH₃ at C-3 and C-5), 2.40 (s, 6H, 2CH₃ at C-2 and C-6), 4.05-4.20 (m, 4H, 2CH₂, diastereotopic protons), 5.13 (s, 1H, CH), 5.75 (s br., 1H, NH), 7.40

(t, 1H, $J = 7.9$ Hz, arom-H), 7.67 (dt, 1H, $J = 7.7, 1.3$ Hz, arom-H), 8.03 (ddd, 1H, $J = 8.2, 2.3, 1.0$ Hz, arom-H), 8.16 (t, 1H, $J = 1.9$ Hz, arom-H); IR (KBr): ν 3345 (NH), 1706 (C=O), 1525 & 1348 (NO_2) cm^{-1} .

Compound 4h (Ar = 4-O₂NC₆H₄): ¹H NMR (CDCl₃, δ): 1.25 (t, 6H, $J = 7.1$ Hz, 2CH₃ at C-3 and C-5), 2.39 (s, 6H, 2CH₃ at C-2 and C-6), 4.05-4.20 (m, 4H, 2CH₂, diastereotopic protons), 5.13 (s, 1H, CH), 5.72 (s br., 1H, NH), 7.48 (d, 2H, $J = 8.7$ Hz, arom-H), 8.11 (d, 2H, $J = 8.7$ Hz, arom-H); IR (KBr): ν 3321 (NH), 1702 (C=O), 1518 & 1348 (NO_2) cm^{-1} .

Results and Discussion

The catalyst, [PS-IM(CH₂)₄SO₃H][HSO₄] (Figure 1) was prepared according to the method reported by Qiao and co-

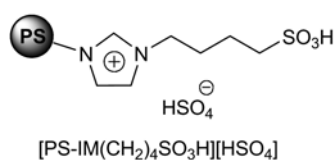


Figure 1. Polystyrene immobilized acidic IL structure.

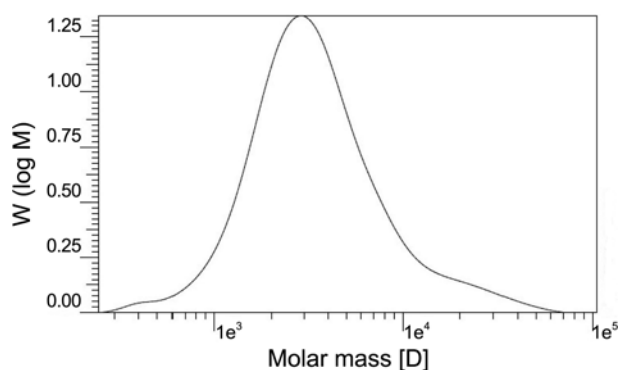


Figure 2. GPC curve for [PS-IM(CH₂)₄SO₃H][HSO₄].

Table 1. Synthesis of compound **4c** in the presence of [PS-IM(CH₂)₄SO₃H][HSO₄] as catalyst in different reaction conditions^a

Entry	Catalyst (g)	Solvent	T (°C)	Time (h:min)	Yield (%) ^b
1	None	EtOH	Reflux	100	Trace
2	0.01	EtOH	Reflux	3:00	83
3	0.02	EtOH	Reflux	3:00	86
4	0.03	EtOH	Reflux	2:20	90
5	0.05	EtOH	Reflux	2:20	87
6	0.10	EtOH	Reflux	2:20	85
7	0.03	CHCl ₃	Reflux	3:30	44
8	0.03	H ₂ O	Reflux	5:00	45
9	0.03	CH ₃ CN	Reflux	2:20	50
10	0.03	CH ₂ Cl ₂	Reflux	4:00	41
11	0.03	Solvent-free	105	2:00	57
12	0.03	Solvent-free	140	2:00	60

^a1 mmol 4-chlorobenzaldehyde, 2 mmol ethyl acetoacetate, and 1 mmol ammonium acetate. ^bThe yields were calculated based on 4-chlorobenzaldehyde and refer to the pure isolated product.

Table 2. Synthesis of Hantzsch 1,4-dihydropyridines **4a-h** using [PS-IM(CH₂)₄SO₃H][HSO₄] as catalyst under optimized conditions^a

Entry	Ar	Products ^b	Time (h:min)	Yield (%) ^c	mp (°C)	
					Found	Reported
1			3:30	80	156-158	156-158 ³⁶
2			2:30	90	161-163	162-164 ³⁶
3			2:20	90	146-148	144-146 ³⁴
4			2:00	89	147-149	155-157 ³³
5			2:00	87	160-162	158-160 ³⁶
6			2:30	90	134-137	135-137 ³⁴
7			3:15	85	161-163	163-165 ³⁶
8			2:10	95	129-132	130-132 ³⁶

^a1 mmol aryl aldehyde, 2 mmol ethyl acetoacetate, 1 mmol ammonium acetate, and 0.03 g [PS-IM(CH₂)₄SO₃H][HSO₄] in ethanol at reflux temperature. ^bAll the products were characterized by ¹H NMR & IR spectral data and comparison of their melting points with those of authentic samples. ^cThe yields were calculated based on aryl aldehyde and refer to the pure isolated product.

Table 3. The comparison of efficiency of [PS-IM(CH₂)₄SO₃H][HSO₄] in the synthesis of compound **4h** after five times

Entry	Ar	Yield/% ^a /run				
		First	Second	Third	Fourth	Fifth
4h	4-O ₂ NC ₆ H ₄	95	93	91	90	89

^aIsolated yields

workers.³⁹ In the synthesis of this catalyst we changed the IL anion from trifluoromethanesulfonate to hydrogen sulfate. Using 10 mol % of IL gave the [PS-IM(CH₂)₄SO₃H][HSO₄] in very well physical form as white powder. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined by GPC analysis (Figure 2). The polymer exhibits M_w and M_n of 4.99 × 10³ and 2.52 × 10³ g/mol, respectively and polydispersity index (D_m), 1.98. In order to evaluate the catalytic efficiency of [PS-IM(CH₂)₄SO₃H][HSO₄] in the synthesis of 1,4-dihydropyridines and to determine the most appropriate reaction conditions; initially a model study was carried out on the synthesis of compound **4c** by cyclocondensation of 4-chlorobenzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), and ammonium acetate (1 mmol) in different sets of reaction conditions (Table 1). Among the tested solvents such as EtOH, CHCl₃, H₂O, CH₃CN, CH₂Cl₂ and also solvent-free conditions and various amounts of the catalyst, the reaction was more facile and proceeded to give the highest yield, using 0.03 g of [PS-IM(CH₂)₄SO₃H][HSO₄] in EtOH at reflux temperature (entry 4). Greater amounts of the catalyst were found to have an inhibitory effect on the formation of the product (entries 5, 6).

To show the generality of this method the optimized system was used for the synthesis of other 1,4-dihydropyridine derivatives with various aromatic aldehydes, ethyl acetoacetate and ammonium acetate. As shown in Table 2, different aromatic aldehydes reacted successfully and gave the expected products **4a-h** in good to high yields.

Reusability of the catalyst was also investigated. For this purpose, the synthesis of compound **4h** was studied under optimized conditions. After the completion of the reaction, the catalyst was recovered according to the procedure mentioned in experimental section and reused for a similar reaction. The obtained results are summarized in Table 3. As shown in this table, the catalyst could be used at least five times with only slight reduction in the catalytic activity.

Conclusion

In conclusion, in this paper a polystyrene immobilized acidic IL ([PS-IM(CH₂)₄SO₃H][HSO₄]) prepared by copolymerization of 3-vinyl-1-(4-sulfonic acid)butylimidazolium hydrogen sulfate with styrene in the presence of benzoyl peroxide was used as catalyst in the synthesis of Hantzsch 1,4-dihydropyridines *via* one-pot three-component reaction of aromatic aldehydes, ethyl acetoacetate and ammonium acetate. The catalyst showed high catalytic activity and the

desired products were obtained in good to high yields. The catalyst can be recycled after a simple work-up, and used at least five times in the reactions without substantial reduction in its catalytic activity.

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