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Short Communication

Synthesis and application of a novel strong and stable supported ionic liquid catalyst with both Lewis and Brønsted acid sites

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Poly(4-vinylpyridine)-supported ionic liquid with both Lewis and Brønsted acid sites was easily prepared from its starting materials and used as a novel and highly efficient heterogeneous catalytic system for the synthesis of biscoumarins by two-component one-pot domino Knoevenagel-type condensation/Michael reaction between various aliphatic and aromatic aldehydes with 4-hydroxycoumarin. The Lewis and Brønsted acidic sites loading in [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) were found to be 2.15 and 0.9 mmol per gram of catalyst, respectively. The effect of the simultaneous presence of Lewis and Brønsted acid sites was evaluated. The catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), elemental analysis, and atomic absorption technique. The catalyst is stable (as a bench top catalyst) and reusable.

1. Introduction

Brønsted acidic ionic liquids are of special important because they possess simultaneously the proton acidity and the characteristic properties of ionic liquid [1]. Among them, SO_3H-functionalized ionic liquids are of particular value, because of their negligible vapor pressure, outstanding acidity, and tunable solubility for some organic species [2–4]. Thus, they are designed to replace traditional mineral liquid acids such as sulfuric acid and hydrochloric acid in chemical procedures.

Chloroaluminate molten salts are another type of ionic liquids which have been extensively used as a catalyst or solvent in various organic transformations [1,5]. These ionic liquids are prepared by simple addition of $AlCl_3$ to the corresponding 1,3-dialkyl-imidazolium or 1-alkyl-pyridinium chlorides. The acidity of the resulting ionic liquid can be controlled by varying the relative amounts of $AlCl_3$ and organic chloride. Chloroaluminate melts are designated as basic when the $AlCl_3$ mole fraction is smaller than 0.5 and the melts contain the anions Cl^- and $AlCl_4^-$, a Lewis base. A neutral melt is referred to at an $AlCl_3$ mole fraction of exactly 0.5, where $AlCl_4^-$ is the only anion present. Finally, an acidic chloroaluminate melt is one in which the $AlCl_3$ mole fraction is larger than 0.5. In such acidic melts, the anions $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ exist, which act as very strong Lewis acids [5,6]. Despite unique physical and chemical properties of chloroaluminate ionic liquids and their widespread application in organic synthesis, they are extremely hygroscopic and labile towards hydrolysis.

Coumarin and its derivatives are known to possess a wide range of biological activities including anti-HIV, anti-biotic, anti-fungal, anti-bacterial, anti-oxidant, anti-cancer, and anti-coagulant [7–10]. Among various derivatives of coumarin, biscoumarins have aroused considerable interest. They are usually prepared from the reaction of aldehydes with two equivalents of 4-hydroxycoumarin in the presence of a catalyst. However, only a few reports were found describing the synthesis of these compounds. Piperidine [11], tetrabutylammonium bromide [12], I_2 [13], sodium dodecyl sulfate [14], ionic liquids [15,16], *p*-dodecylbenzenesulfonic acid/piperidine [17], $NaHSO_4$ [18], and $B(HSO_4)_3$ [19] have been reported as catalysts for the preparation of biscoumarins so far. Although these methods are suitable for certain synthetic conditions, there exist some drawbacks such as low yields, long reaction times, drastic reaction conditions, require tedious work-up leading to the generation of large amount of toxic waste, inefficiency of method when aliphatic aldehydes are used in the reaction, and the use of unrecyclable, hazardous or difficult to handle catalysts.

It is well known that, both Lewis and Brønsted acid sites were important for acid-catalyzed reactions and the solid supports or ionic liquids functionalized with both Lewis and Brønsted acid sites would become more efficient, which combined the advantages of Lewis and Brønsted acid sites [1,20,21]. More importantly, the acidity of these compounds can be controlled by varying relative amounts of the Lewis and Brønsted acidic component. In this pursuit, and in a continuation of our work on the development of efficient and environmentally benign procedures using poly(vinylpyridine)-supported reagents and catalysts [22], herein, we now report the synthesis of poly(4-vinylpyridine-*co*-1-sulfonic acid butyl-4-vinylpyridinium) chloroaluminate ([P_4VPy-BuSO_3H]Cl-X($AlCl_3$)) as a supported ionic

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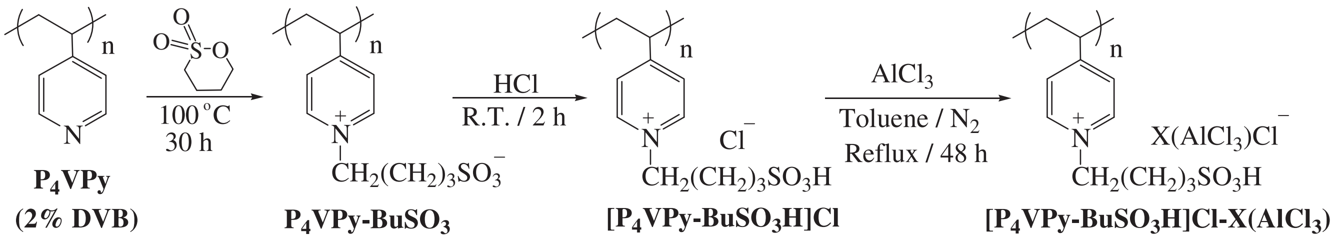


Scheme 1. Synthesis of [P_4VPy-BuSO_3H]Cl-X($AlCl_3$).

liquid containing both Lewis and Brønsted acid sites. [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) was used as a catalyst for the synthesis of biscoumarins.

2. Experimental

2.1. Synthesis of [P_4VPy-BuSO_3H]Cl-X($AlCl_3$)

In a round bottomed flask (50 mL) equipped with a reflux condenser, 1 g of the P_4VPy was added to 1,4-butane sultone (1.5 mL) and the mixture was stirred at 100 °C for 30 h, filtered, washed with distilled water (20 mL), and dried at 80 °C overnight to give [P_4VPy-BuSO_3]. Then, HCl (3 M, 5 mL) was added to the obtained resin and the mixture was stirred at room temperature for 2 h, filtered, washed with distilled water (20 mL), and dried at 80 °C overnight to give [P_4VPy-BuSO_3H]Cl. Afterwards, 1 g of the obtained resin was added to a solution of $AlCl_3$ (0.5 g) in toluene (10 mL) and stirred under reflux condition for 24 h under N_2 atmosphere. Then, $AlCl_3$ (0.4 g) was added again and the mixture was stirred under reflux condition for 24 h and filtered and then the excess of $AlCl_3$ was removed by extraction with ethanol (95%) in an Soxhlet apparatus for 72 h.

2.2. Typical procedure for synthesis of biscoumarins

To a solution of benzaldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), and toluene (3 mL), was added [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) (0.07 mmol) and the resulting mixture was magnetically stirred at 90 °C. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was filtered off and washed with toluene (2 × 5 mL) and the filtrate was concentrated on a rotary evaporator under reduced pressure. The crude product was recrystallized from ethanol to give 3,3′-benzylidene-bis-(4-hydroxycoumarin).

3. Results and discussion

[P_4VPy-BuSO_3H]Cl-X($AlCl_3$) was prepared by the procedure shown in Scheme 1. At the first stage, commercially available poly(4-vinylpyridine) (P_4VPy, 2% divinylbenzene) reacted with 1,4-butane sultone to give the poly(4-vinylpyridine-*co*-1-sulfonate butyl-4-vinylpyridinium) ([P_4VPy-BuSO_3]) as a cream solid. In a second step, the [P_4VPy-BuSO_3] was treated with HCl to form poly(4-vinylpyridine-*co*-1-sulfonic acid butyl-4-vinylpyridinium)chloride ([P_4VPy-BuSO_3H]Cl) as a white cream solid. Afterward, the [P_4VPy-BuSO_3H]Cl was further treated with excess amounts of $AlCl_3$ in refluxing toluene to form [P_4VPy-BuSO_3H]Cl-X($AlCl_3$). The resulting pale brown solid was analyzed by elemental analysis to quantify the percentage loading of the sulfonate moiety by measuring the sulfur content, giving 0.9 mmol sulfonate moiety per gram. Also, the Brønsted acidic sites ($-SO_3H$) loading in [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) obtained by means of acid–base titration were found to be 0.83 mmol/g [23]. The atomic absorption technique gave 2.15 mmol Al per gram of [P_4VPy-BuSO_3H]Cl-X($AlCl_3$). Considering the aluminum and sulfur contents of [P_4VPy-BuSO_3H]Cl-X($AlCl_3$), it is clear that the $AlCl_3$ mole fraction ($AlCl_3$/[$AlCl_3$ + P_4VPy-BuSO_3H]) in this catalyst is larger than 0.5. On the other hand, it is well known that in highly Lewis acidic chloroaluminate ionic liquids (containing $Al_2Cl_7^-$ as a strong Lewis acid) the $AlCl_3$ mole fraction is larger than 0.5 [5]. Thus, it could be imagined that it is the Lewis acid $Al_2Cl_7^-$ (as the predominant aluminum species) that plays an important role in the catalytic activity in [P_4VPy-BuSO_3H]Cl-X($AlCl_3$). [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) was reasonably stable to air and moisture and could be kept as a bench top catalyst for more than 1 year without appreciable

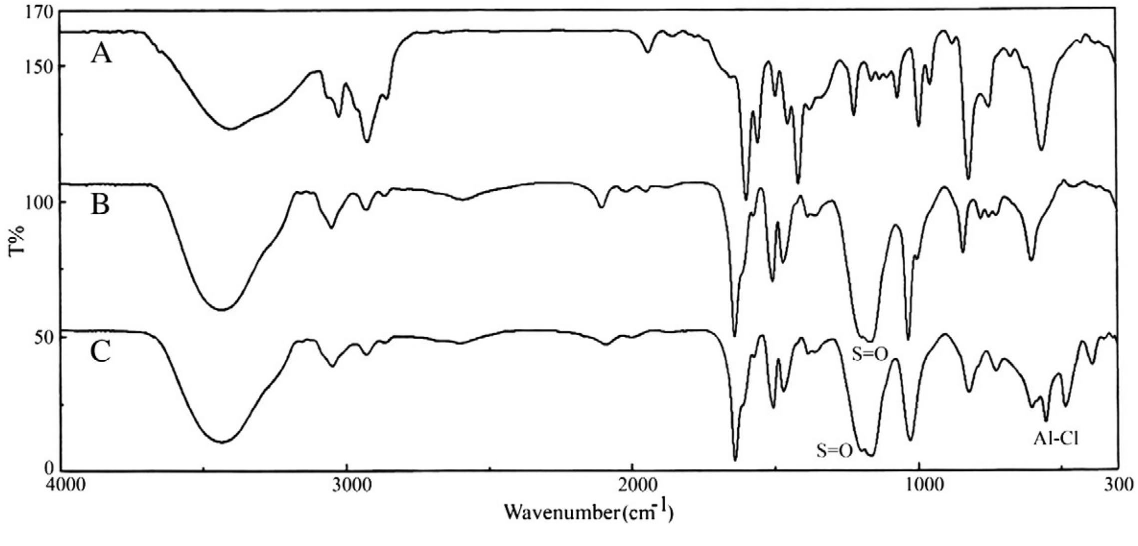


Fig. 1. FT-IR spectra of P_4VPy (A), [P_4VPy-BuSO_3H]Cl (B), and [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) (C).

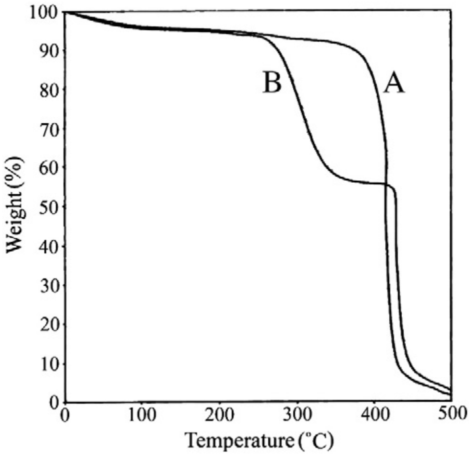


Fig. 2. TGA curves of P_4VPy (A) and $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl)_3$ (B).

change in its efficiency. We believe that hydrophobic nature of poly(4-vinylpyridine) protects the water-sensitive Lewis acid from hydrolysis by atmospheric moisture until it is suspended in an appropriate solvent where it can be used in a chemical reaction.

The characterization of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ was also confirmed by FT-IR spectroscopy (Fig. 1). As can be seen in the spectra of $[P_4VPy\text{-}BuSO_3H]Cl$ and $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ new peaks appeared at 1160 and 1210 cm^{-1}, which can be assigned to S═O stretching vibration [24]. As can be seen in the spectrum of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$, when $AlCl_3$ was complexed with $[P_4VPy\text{-}BuSO_3H]Cl$ new peaks appeared at 393, 486, 545, and 595 cm^{-1}, which can be assigned to Al – Cl stretching modes of the $Al_2Cl_7^-$ anion [25].

Fig. 2 shows the TGA curves of P_4VPy and $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$. A weight loss was observed in each case around 100 °C due to the loss of moisture. In the case of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$, the second weight loss that started at about 200 °C is mainly assigned to the decomposition of alky-sulfonic acid groups and chloroaluminate counteranions. In TGA curves of P_4VPy and $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ the last weight losses were observed at about 355 °C and 425 °C, respectively, which are attributed to the degradation of polymer backbone.

An attempt was made to investigate the morphology of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ catalyst using scanning electron microscopy (SEM) (Fig. 3). From the image of P_4VPy, the surface of P_4VPy is somewhat coarse and irregular with many pores on the surface, whereas the SEM photographs of $[P_4VPy\text{-}BuSO_3H]Cl$ and $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ showed that with chemical modification the primary structure of P_4VPy was changed and the polymer support has survived the sequence of functionalization steps.

The catalytic activity of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ was studied in the synthesis of biscoumarins by the condensation reaction of aldehydes with 4-hydroxycoumarin (Table 1). The best results in terms of yield as well as reaction time were obtained at 90 °C in toluene which proved to be the solvent of choice among other organic solvents. The optimum molar ratio of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ to aldehyde was found to be 0.07:1. Various types of substituted benzaldehydes (entry 1a–i), heteroaromatic aldehydes such as 2-furyl, 2-thienyl, and 2-pyridyl carbaldehyde (entries 2–4), and aliphatic aldehydes (entries 5–7) reacted with 4-hydroxycoumarin to give the corresponding biscoumarin products. To access the feasibility of applying this method on a preparative scale, we carried out the condensation of benzaldehyde (30 mmol) with 4-hydroxycoumarin (60 mmol) in toluene at 90 °C in the presence of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$. The reaction proceeded smoothly and the corresponding product was obtained in 93% yield after 1 h.

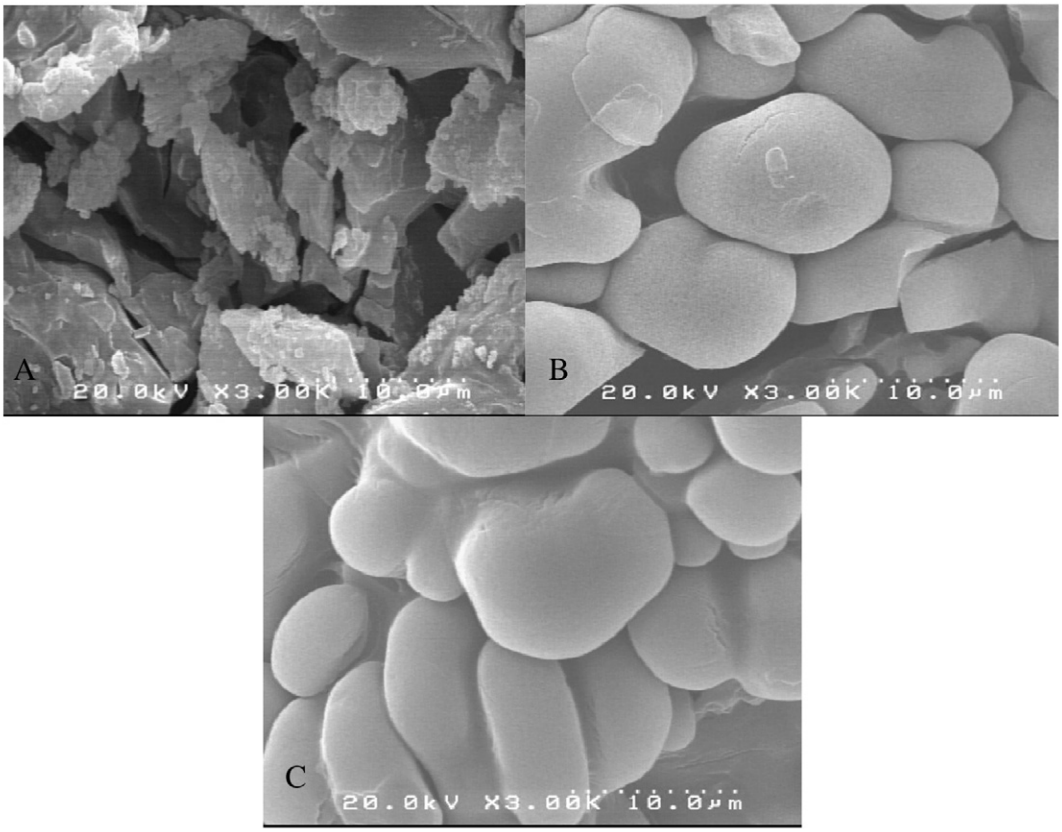
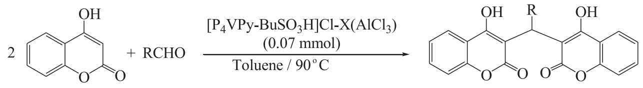
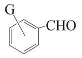
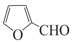
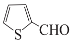
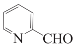
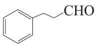
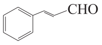


Fig. 3. SEM photographs of P_4VPy (A), $[P_4VPy\text{-}BuSO_3H]Cl$ (B), and $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl)_3$.

Table 1
Synthesis of biscoumarin derivatives.



Entry	RCHO	Time (h)	Yield (%)[a]
1			
	a: G = H	0.6	95
	b: G = 4-CH_3	0.7	94
	c: G = 4-OCH_3	0.8	92
	d: G = 4-Cl	0.6	93
	e: G = 3-Cl	0.7	96
	f: G = 4-OH	0.8	90
	g: G = 3-NO_2	0.5	96
	h: G = 4-NO_2	0.5	96
	i: G = 2-OH	0.9	90
2		0.7	91
3		0.7	91
4		0.6	91
5		0.7	92
6		0.8	92
7		0.8	93

[a] Isolated yield; all products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples.

Table 2
The reaction of benzaldehyde (1 mmol) with 4-hydroxycoumarin (2 mmol) in toluene at 90 °C in the presence of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ (0.023 g) with different $AlCl_3$ contents.

Entry	$AlCl_3$ mole fraction[a]	Time (h)	Yield (%)[b]
1	0.4	1	67
2	0.5	1	76
3	0.6	1	89
4	0.7	0.6	95
5	–[c]	2	5
6	–[d]	2	55

[a] $AlCl_3$ mole fraction (X) was measured as follows: $X = n(AlCl_3) / [n(AlCl_3) + n(P_4VPy\text{-}BuSO_3H)]$.

[b] Isolated yield.

[c] Reaction was carried out in the presence of $[P_4VPy\text{-}BuSO_3]Cl$ (0.1 mmol).

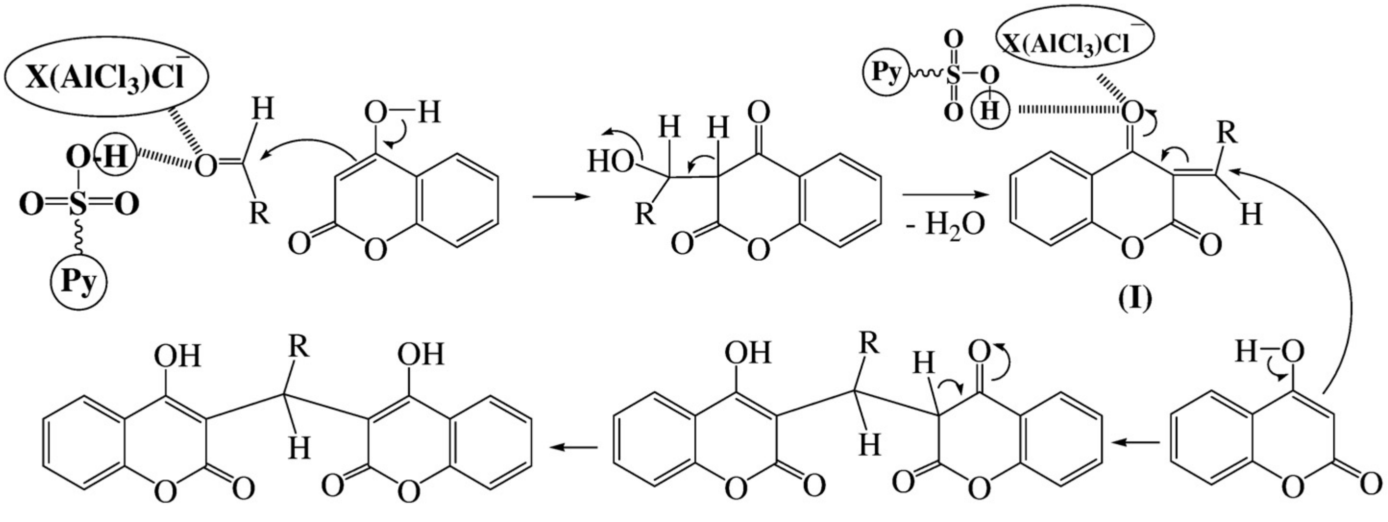
[d] Reaction was carried out in the presence of $[P_4VPy\text{-}BuSO_3H]Cl$ (0.1 mmol).

As shown in Table 1 (entry 1), the aromatic aldehydes with electron withdrawing groups reacted faster than the aromatic aldehydes with electron releasing groups. This observation can be rationalized on the basis of the mechanistic details of the reaction (Scheme 2). An aldehyde was first activated by $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$. Nucleophilic addition of 4-hydroxycoumarin to activated aldehyde was followed by loss of H_2O generated intermediate I, which is further activated by $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$. Then, the 1,4-nucleophilic addition of a second molecule of 4-hydroxycoumarin on activated intermediate I, in the Michael addition fashion, affords the synthesis of biscoumarin product. The electron withdrawing groups substituted on aromatic aldehyde in intermediate I increase the rate of 1,4-nucleophilic addition reaction because the alkene LUMO is at lower energy in their presence compared with electron donating groups [26].

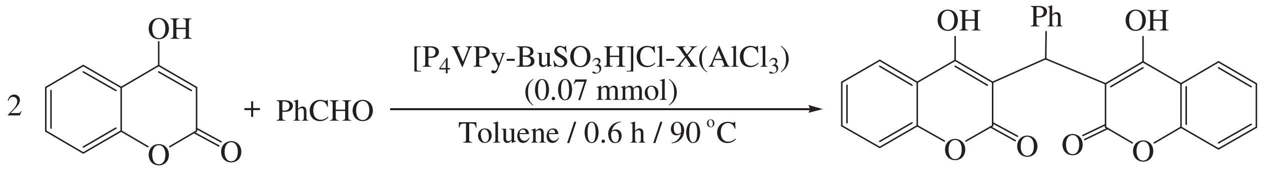
In order to elucidate the effect of $AlCl_3$ on the catalytic activities, different types of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ with different $AlCl_3$ contents were prepared and utilized as the catalysts for the reaction of benzaldehyde with 4-hydroxycoumarin [27]. It could be seen from Table 2 that the catalytic activity of $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ increases with increasing amount of $AlCl_3$ (entries 1–4) and the presence of $AlCl_3$ is necessary to drive the reaction to completion. Low catalytic activity was obtained when $[P_4VPy\text{-}BuSO_3]$ or $[P_4VPy\text{-}BuSO_3H]Cl$ was used (entries 5,6). These observations indicated that both $AlCl_3$ and $-SO_3H$ were important for the reaction.

In order to confirm the true heterogeneity of the catalytic systems, $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ was added to toluene and the mixture was stirred at 90 °C for 2 h. Then, the catalyst was filtered off and the filtrate was analyzed for its acid content, which showed a negligible release of the acidic sites. The filtrate was found to be inactive for the condensation of 4-hydroxycoumarin with aldehydes. These observations indicate that the catalyst is stable under the reaction conditions, and there is no leaching of acid moieties during reactions.

$[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ recovered after a reaction can be washed with toluene and used again at least five times without any noticeable loss of catalytic activity (Scheme 3). The aluminum content of the catalyst after five uses was 2.10 mmol per gram. We also stored the catalyst on the laboratory benchtop for more than 1 year and then it was used for condensation of benzaldehyde with 4-hydroxycoumarin. The product was produced in 93% yield in 0.6 h.



Scheme 2. The proposed mechanism for the synthesis of biscoumarins using $[P_4VPy\text{-}BuSO_3H]Cl\text{-}X(AlCl_3)$ as a catalyst.



Run No.	1	2	3	4	5
Isolated Yield (%)	95	93	92	90	90

Scheme 3. Preparation of biscoumarins using recovered [P_4VPy-BuSO_3H]Cl-X($AlCl_3$).

The aluminum content of the catalyst after 1 year was 2.14 mmol per gram.

4. Conclusion

In conclusion, we have synthesized [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) as a heterogeneous acid catalyst for the synthesis of biscoumarins that favorably combines the properties of ionic liquids and advantages of solid supports. The significant advantages of this methodology are high yields, short reaction times, simple work-up procedure, and easy preparation and handling of the catalyst. In addition, this solid catalyst can be recovered unchanged and used again.

Acknowledgments

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[23] 1 g of dry [P_4VPy-BuSO_3H]Cl was added to 10 mL aqueous solution of NaCl (2 M) and the resulting mixture was stirred for 24 h and then titrated potentiometrically with aqueous solution of NaOH (0.01 mol/L) as titrant and phenolphthalein as an indicator.
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[27] [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) with different $AlCl_3$ contents was prepared by slowly mixing weighted amounts of [P_4VPy-BuSO_3H]Cl and $AlC1_3$. For this purpose, [P_4VPy-BuSO_3H]Cl was first prepared. Then, small amounts of $AlCl_3$ were slowly added to [P_4VPy-BuSO_3H]Cl and the Al content of the obtained [P_4VPy-BuSO_3H]Cl-X($AlCl_3$) was monitored by atomic absorption technique.