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Polystyrene-supported pyridinium chloroaluminate ionic liquid as a new heterogeneous Lewis acid catalyst for selective synthesis of benzimidazoles

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Abstract: Polystyrene-supported pyridinium chloroaluminate ionic liquid was prepared from the reaction of a Merrifield resin with pyridine followed by reaction with aluminium chloride. This catalyst was used as a new chemoselective Lewis acid catalyst for the exclusive synthesis of 2-substituted benzimidazoles from the reaction of aldehydes with *o*-phenylenediamines. The catalyst was stable (as a benchtop catalyst) and could easily be recovered and reused without appreciable change in its efficiency.

Keywords: ionic liquids; chloroaluminate salts; heterogeneous catalysis; polymer-supported ionic liquids; benzimidazoles.

INTRODUCTION

The most common group of ionic liquids (ILs) are chloroaluminate molten salts.[1–3] These compounds, composed of mixtures of aluminium chloride with the corresponding 1,3-dialkylimidazolium or 1-alkylpyridinium chlorides, are liquid at or below ambient temperature over a wide range of compositions. The acidity of the resulting IL 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 Cl^- and $AlCl_4^-$, a Lewis bases. A melt having an $AlCl_3$ mole fraction of exactly 0.5, where $AlCl_4^-$ is the only anion present, is referred to as a neutral melt. Finally, an acidic chloroaluminate melt is one in which the $AlCl_3$ mole fraction is larger than 0.5. In such acidic melts, $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ exist, which act as very strong Lewis acids.[2]

Despite the unique physical and chemical properties of chloroaluminate ILs and their widespread application in organic synthesis, either as solvents or acidic

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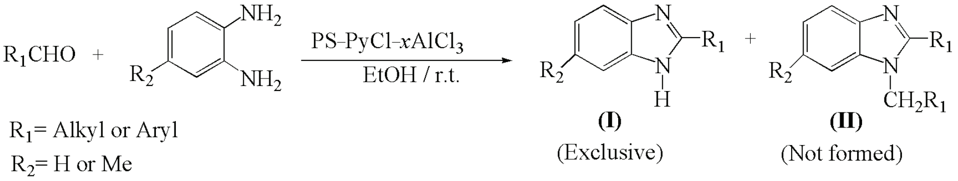
catalysts, most of them suffer from one or more of the following drawbacks such as laborious work-up procedures, difficulty in recovery and recycling, disposal of spent catalyst, difficulty in handling and corrosion problems. Most importantly, they are extremely hygroscopic and labile towards hydrolysis.[2] Thus, these shortcomings make them a prime target for heterogenization. Although there are several reports on the immobilization of ILs on solid supports,[4–13] to the best of our knowledge, few examples are known for immobilized chloroaluminate ILs.[9,12]

The benzimidazole and its derivatives constitute a very important, privileged class of nitrogen-containing heterocyclic compounds that show various biological activities, such as anticonvulsant,[14] antidepressant,[15] antihistamine,[16] anti-ulcer,[17] antihypertensive,[18] anticancer,[19] anti-inflammatory,[20] anthelmintic,[21] antiprotozoal[22] and antitumour properties.[23] In addition, benzimidazoles are very important intermediates in organic reactions.[24] Therefore, their preparations have received increasing attention of synthetic organic chemists and biologists. Usually, two different approaches have been performed for the preparation of benzimidazoles. The first is the coupling of *o*-phenylenediamines and carboxylic acids or their derivatives (nitriles, amides, orthoesters and acid chlorides), which often requires strongly acidic conditions, sometimes combined with high temperatures.[25–28] Another synthetic approach is the condensation of aldehydes with *o*-phenylenediamines, which involves a two-step procedure including the oxidative cyclodehydration of aniline Schiff bases, which are often generated *in situ* from the reaction of an aldehyde and *o*-phenylenediamine. Various oxidative and catalytic reagents, such as $Yb(OTf)_3$,[29] $I_2/KI/K_2CO_3$,[30] $In(OTf)_3$,[31] $BF_3\cdot OEt_2$,[32] H_2O_2/HCl,[33] TsOH–SiO_2,[34] NaY zeolite,[35] porphyrinatoiron(III) complex supported on silica,[36] Dess–Martin-periodinane,[37] scolecite,[38] AIKIT-5,[39] WO_x//ZrO_2,[40] H_2O_2/SiO_2–$FeCl_3$[41] and Amberlite IR-120[42] have been employed for this purpose. However, many of the above methods suffer from drawbacks such as strong oxidizing nature, the formation of bis-anil and dihydrobenzimidazoles as the main side products, involvement of more than one step in the synthesis of these compounds, the generation of environmentally perilous waste material, tedious work-up, long reaction times, complicated operations and the use of moisture-sensitive, expensive, hazardous, difficult to handle or non-reusable catalysts. In view of these, the search for finding a cost effective, mild and simple chemoselective protocol especially using heterogeneous catalysts for the synthesis of benzimidazoles is still relevant.

In 2001, Hölderich *et al.* reported the synthesis and application of silica gel supported chloroaluminate IL as a heterogeneous Lewis acidic IL.[12] This supported IL was prepared by adding $AlCl_3$ to imidazolium chloride grafted onto the silica surface. The prepared catalyst was used for Friedel-Crafts alkylations. Unfortunately, this catalyst is moisture sensitive and hence demands moisture-free reactants and also must be handled under a dry atmosphere. Hölderich suggested that the predominant acidic chloroaluminate species in this immobilized IL was $Al_2Cl_7^-$.

In a continuation of research work on the development of synthetic methodologies using solid acid catalysts, herein, the above-mentioned strategy to support pyridinium chloroaluminate IL on a Merrifield resin, and the employment of the obtained polymer catalyst as an effective and highly chemoselective heterogeneous catalyst for the coupling of aldehydes and *o*-phenylenediamines to afford 2-aryl and alkylbenzimidazoles (Scheme 1) are reported.



Scheme 1. The coupling reaction of aldehydes and *o*-phenylenediamines to afford 2-aryl and alkyl benzimidazoles, catalyzed by pyridinium chloroaluminate IL supported on a Merrifield resin.

EXPERIMENTAL

Chemicals were either laboratory prepared or purchased from Merck or Fluka. The IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. The ^{1}H-NMR spectra were recorded on a Bruker DPX-300 spectrometer using DMSO-d_6 as solvent and TMS as the internal standard. Melting points were determined on a Fisher–Jones melting-point apparatus and are uncorrected. The capacity of the catalyst was determined by the atomic absorption technique using a Philips atomic absorption instrument. Monitoring of the reaction progress and purity determination of the products were accomplished by GLC or TLC on silica-gel polygram SILG/UV_{254} plates.

Preparation of poly[styrene-co-1-((4-vinylphenyl)methyl)pyridinium chloroaluminate] (PS–PyCl–xAlCl$_3$)

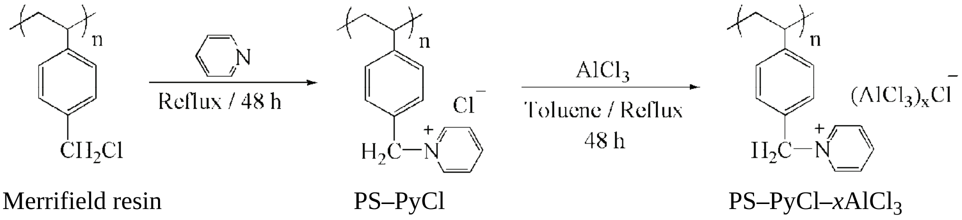
In a round bottomed flask (50 mL) equipped with a reflux condenser, a solution of Merrifield resin (1 g, 2 % divinylbenzene) in pyridine (25 mL) was refluxed for 48 h. Afterwards, the mixture was filtered, washed with distilled water (20 mL) and dried at 80 °C overnight. Then, 1 g of the obtained resin was added to a solution of $AlCl_3$ (0.5 g) in toluene (10 mL) and stirred under reflux condition for 24 h under an N_2 atmosphere. Next, $AlCl_3$ (0.4 g) was added again and the mixture was stirred for 24 h and filtered and then the excess of $AlCl_3$ was removed by extraction with ethanol using a Soxhlet apparatus.

Typical procedure for benzimidazole synthesis

To a solution of aldehyde (1 mmol) and *o*-phenylenediamine (1 mmol) in ethanol (5 mL) was added PS–PyCl–*x*AlCl$_3$ (0.1 mmol), and the resulting mixture was magnetically stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and washed with EtOH (2×5 mL) and the filtrate was concentrated on a rotary evaporator under reduced pressure to afford the crude product. Whenever required, the products were purified by column chromatography on silica gel (*n*-hexane/EtOAc) or recrystallization from ethanol. The spent catalyst from different experiments was washed with EtOH and reused without further drying. The analytical and spectral data of the obtained compounds are given in the Supplementary material to this paper.

RESULTS AND DISCUSSION

Poly[styrene-*co*-1-((4-vinylphenyl)methyl)pyridinium chloroaluminate], denoted as PS–PyCl–*x*$AlCl_3$, was prepared by the procedure shown in Scheme 2. In the first stage, commercially available Merrifield resin (2 % divinylbenzene, 2.1 mmol Cl per gram) was reacted with pyridine to give poly[styrene-*co*-1-((4-vinylphenyl)methyl)pyridinium chloride], denoted as PS–PyCl. The obtained material was a cream solid which was analyzed by elemental analysis to quantify the percentage loading of the pyridinium moiety by measuring the nitrogen content, giving 1.89 mmol Py per gram. The PS–PyCl was further treated with excess amounts of $AlCl_3$ in refluxing toluene to form PS–PyCl–*x*$AlCl_3$. The resulting pale brown solid was reasonably stable to air and moisture and could be kept as a bench-top catalyst for more than 1 year without appreciable change in its efficiency. It is believed that the hydrophobic nature of the polystyrene 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 atomic absorption technique gave 3.3 mmol Al per g of the catalyst. Considering the aluminium and pyridine contents of PS–PyCl–*x*$AlCl_3$, it is clear that the $AlCl_3$ mole fraction ($AlCl_3$/$AlCl_3$+Py) in this catalyst was larger than 0.5 and thus it could be imagined that it is the Lewis acid $Al_2Cl_7^-$ (as the predominant aluminium species) that plays an important role in the catalytic activity in PS–PyCl–*x*$AlCl_3$.[2,12]



Scheme 2. Preparation procedure to poly[styrene-*co*-1-((4-vinylphenyl)methyl)pyridinium chloroaluminate] (PS–PyCl–*x*$AlCl_3$).

The successful immobilization of $AlCl_3$ on the polymer was confirmed by FT-IR spectroscopy. The FT-IR spectra of the Merrifield resin, PS–PyCl and PS–PyCl–*x*$AlCl_3$ are shown in Fig. 1. The IR spectra of the PS–PyCl showed absorption peaks due to the pyridine ring at 3020, 2900, 1640, 1500, 1475, 775 cm^{-1}.[43] As can be seen in the spectrum of PS–PyCl–*x*$AlCl_3$, when $AlCl_3$ was complexed with PS–PyCl, new peaks appeared at 575, 500, 430, 385 cm^{-1}, which can be assigned to Al–Cl stretching modes of $Al_2Cl_7^-$.[43,44]

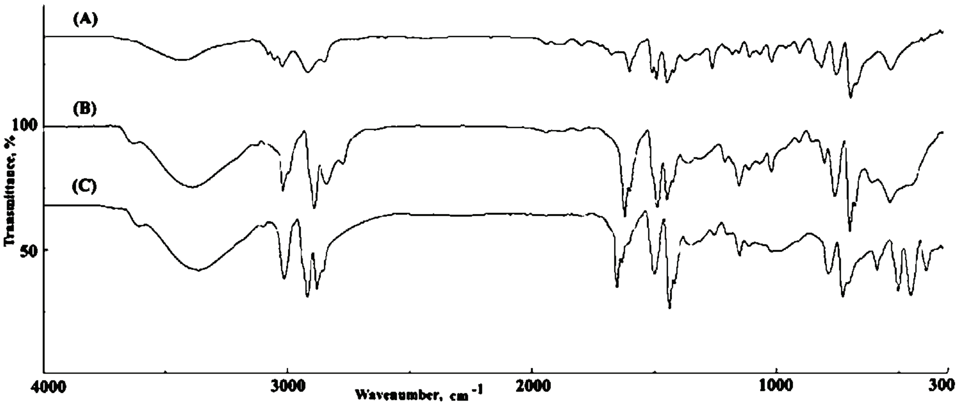
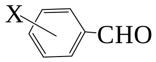
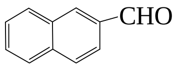
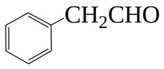
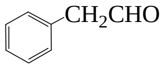
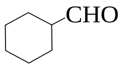
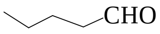
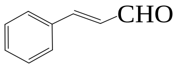
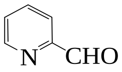
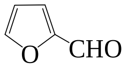
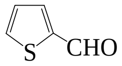


Fig. 1. FT-IR spectra of A) Merrifield resin, B) PS–PyCl and C) PS–PyCl–*x*AlCl$_3$.

The catalytic activity of PS–PyCl–*x*AlCl$_3$ was studied in the synthesis of benzimidazoles by the condensation reaction of different aldehydes (aromatic and aliphatic) with *o*-phenylenediamines (Scheme 1). Initially, to optimize the reaction conditions, the conversion of benzaldehyde (1 mmol) to 2-phenyl-1*H*--benzimidazole with *o*-phenylenediamine (1 mmol) and PS–PyCl–*x*AlCl$_3$ in the presence of a variety of solvents at room temperature was attempted. It was observed that this reaction goes well in ethanol among the commonly used organic solvents, such as acetonitrile, methanol, 1,2-dichloroethane, dichloromethane and tetrahydrofuran. Afterwards, to optimize the quantity of PS–PyCl–*x*AlCl$_3$, 0.05––0.15 mmol of the catalyst was used in the above reaction. It was found that a 0.1:1 mmol ratio of catalyst:benzaldehyde was sufficient to obtain 2-phenyl-1*H*--benzimidazole in 94 % yield within 6 min. Then, under the optimal conditions, a wide variety of aromatic aldehydes (containing both electron withdrawing and donating groups) were treated with *o*-phenylenediamines, and the corresponding 2-substituted benzimidazoles (Scheme 1, I) were obtained exclusively in excellent yields (Table I, entry 1). 2-Naphthaldehyde was also converted to the corresponding benzimidazole in 93 % yield (entry 2). Aliphatic aldehydes required slightly longer times to produce the corresponding benzimidazoles in moderate yields (entries 3–6). It was pleasing to observe that even acid-sensitive aldehydes such as cinnamaldehyde, 2-pyridyl, 2-furyl and 2-thienyl carbaldehyde gave the corresponding benzimidazoles without the formation of any side products, which are normally encountered under acidic conditions (entries 7–10). It is noteworthy that only small activities were observed when PS–PyCl or basic or neutral PS––PyCl–*x*AlCl$_3$ were used as the catalyst.[45,46] To assess the feasibility of applying this method on the preparative scale, the condensation of benzaldehyde with *o*-phenylenediamine in a 30-mmol scale in ethanol at room temperature in the presence of PS–PyCl–*x*AlCl$_3$ was performed. The reaction proceeded smoothly and 2-phenyl-1*H*-benzimidazole was obtained in 90 % yield after 15 min.

TABLE I. PS–PyCl–*x*$AlCl_3$ catalyzed synthesis of 2-substituted benzimidazoles in the reactions of aldehydes with *o*-phenylenediamines; ratio of aldehyde:*o*-phenylenediamine was 1:1. Unless otherwise noted, all reactions were performed in the presence of 0.1 mmol of PS–PyCl–*x*$AlCl_3$

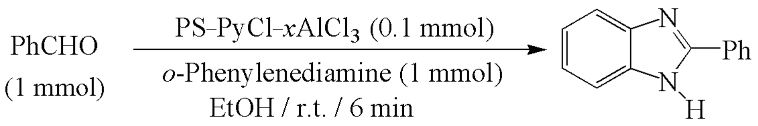
Entry	Aldehyde	R_2	Time, min	Yield[a], %
1		–	–	–
1a	X = H	H	6(7)[b]	94(93)[b]
1b	X = H	Me	10	90
1c	X = 4-CH_3	H	7	93
1d	X = 4-CH_3	Me	11	91
1e	X = 4-OCH_3	H	6(6)[b]	94(92)[b]
1f	X = 4-Cl	H	9	95
1g	X = 4-Cl	Me	15	90
1h	X = 2-Cl	H	10	93
1i	X = 4-Br	H	10	94
1j	X = 3-NO_2	H	11	92
1k	X = 4-NO_2	H	13	91
1l	X = 2-OH	H	14	91
1m	X = 4-OH	H	16	93
1n	X = 3-OH	H	16	91
1o	X = 4-CN	H	14	92
2		H	16	93
3		H	21(20)[b]	89(88)[b]
4		Me	30	83
5		H	21	89
6		H	30	82
7		H	11(10)[b]	93(90)[b]
8		H	11	94
9		H	11	92
10		H	11	92

[a]Isolated yields. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples;[32,35,36,39,40] [b]value in parenthesis when the reaction was performed in the presence of 1-butylpyridinium chloroaluminate ionic liquid (1-BuPyCl–*x*$AlCl_3$; *x* is the mole fraction of $AlCl_3$ which is equal to 0.7)[46] at 40 °C. Molar ratio of aldehyde:*o*-phenylenediamine:1-BuPyCl–*x*$AlCl_3$ was 1:1:0.15

In order to confirm the true heterogeneity of the catalytic system (*i.e.*, the absence of leaching of the $AlCl_3$ into the reaction mixture), PS–PyCl–*x*$AlCl_3$ was added to ethanol and the mixture was stirred at room temperature for 2 h. Then, the catalyst was filtered off and the filtrate was analyzed for its aluminium content, which showed a negligible release of $AlCl_3$. The filtrate was found to be inactive for the condensation reaction of *o*-phenylenediamines with aldehydes. These observations indicate that PS–PyCl–*x*$AlCl_3$ is stable under the reaction conditions, and there was no leaching of acid moieties during the reactions.

PS–PyCl–*x*$AlCl_3$ recovered after a reaction can be washed with ethanol and used again at least five times without any noticeable loss of catalytic activity (Table II).

TABLE II. Recovery of PS–PyCl–*x*$AlCl_3$



Use	1	2	3	4	5
Isolated yield, %	94	93	91	91	90

A comparison of the present procedure using PS–PyCl–*x*$AlCl_3$ with selected previously known protocols is collected in Table III. As can be seen, in addition to having the general advantages attributed to solid supported catalysts, PS–PyCl–*x*$AlCl_3$ has a good efficiency compared to other recently reported catalysts in the synthesis of benzimidazoles by the condensation of aldehydes with *o*-phenylenediamines.

TABLE III. Comparison of the efficiencies of a number of different reported catalysts with that of PS–PyCl–*x*$AlCl_3$ for the synthesis of 2-phenyl-1*H*-benzimidazole from the condensation of benzaldehyde with *o*-phenylenediamine

Entry	Reaction conditions	Time, min	Yield[a], %
1	$Yb(OTf)_3$, solvent free, r.t.	30	93[29]
2	($I_2/KI/K_2CO_3$), H_2O, 90 °C	30	90[30]
3	$In(OTf)_3$, solvent free, r.t.	30	95[31]
4	$BF_3\cdot OEt_2$, solvent free, r.t.	30	90[32]
5	(H_2O_2/HCl), CH_3CN, r.t.	35	97[33]
6	TsOH–SiO_2, solvent free, 70 °C	15	32[34]
7	NaY zeolite, EtOH, r.t.	48	50[35]
8	T(*o*-Cl)PPFe^{III}Cl[b], EtOH, r.t.	90	95[36]
9	DMP[c], dioxane, r.t.	10	89[37]
10	Scolecite, EtOH, 70 °C	55	89[38]

TABLE III. Continued

Entry	Reaction conditions	Time, min	Yield[a], %
11	AIKIT-5, CH_3CN, reflux	240	95[39]
12	(WOx/ZrO_2), dioxane, 100 °C	300	92[40]
13	$FeCl_3$–SiO_2, H_2O_2, 150 °C	30	95[41]
14	Amberlite IR-120, solvent free, MW	4	92[42]
15	PS-PyCl-X$AlCl_3$, EtOH, r.t.	6	94

[a]Isolated yields; [b]porphyrinatoiron(III) complex supported on silica gel; [c]Dess-Martin-periodinane

CONCLUSIONS

In conclusion, polymer-supported pyridinium chloroaluminate IL was synthesized as a new heterogeneous Lewis acid catalyst that favourably combines the properties of ILs and advantages of solid supports. This polymer catalyst has an activity in the synthesis of 2-substituted benzimidazoles comparable to that of 1-butylpyridinium chloroaluminate IL as far as was tested but offers its own advantages originating from being supported on a polymeric matrix, enhanced stability (as a bench-top catalyst), easier handling, high chemoselectivity, simple product workup, separation and isolation, as well as reuse of the catalyst at least five times without significant change in its catalytic activity.

SUPPLEMENTARY MATERIAL

Physical and spectral data of the obtained compounds are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

Acknowledgement. We gratefully acknowledge the partial support of this study by the Shahrekord University Research Council.

ИЗВОД

ЈОНСКА ТЕЧНОСТ ПИРИДИНИЈУМ-ХЛОРОАЛУМИНАТ НА ПОЛИСТИРЕНУ КАО ЛУИСОВА КИСЕЛИНА И НОВ ХЕТЕРОГЕНИ КАТАЛИЗАТОР ЗА СЕЛЕКТИВНУ СИНТЕЗУ БЕНЗИМИДАЗОЛА

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Јонска течност пиридинијум-хлороалуминат на полистирену добијена је од Мерифилдове смоле и пиридина, након чега следи реакција са алуминијум-хлоридом. Овај катализатор је коришћен за хемоселективну катализу као Луисова киселина за добијање 2-супституисаних бензимидазола као јединих производа из реакције алдехида са *о*-фенилдиаминима. Катализатор је стабилан и може се лако изоловати и поново користити без уочљивог губитка ефикасности.

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