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Brönsted acidic ionic liquid supported on rice husk ash (RHA–[pmim]HSO_4): a highly efficient and reusable catalyst for the formylation of amines and alcohols

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In this work, rice husk ash (RHA), as a natural source of amorphous silica, was used as a support for the immobilization of 1-methyl-3-(trimethoxysilylpropyl)-imidazolium hydrogen sulfate. The immobilized acidic ionic liquid was characterized with a variety of techniques including infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and pH analysis. The catalytic performance of this heterogeneous ionic liquid was probed for the *N*-formylation of a variety of amines using formic acid under solvent free conditions. It is also useful for the formylation of benzylic alcohols. The procedure gave the products in excellent yields in very short reaction times. Also this catalyst can be reused ten times without loss of its catalytic activity.

Introduction

Formamides are among the most important intermediates in organic synthesis. *N*-Formyl compounds have been used as precursors for the synthesis of formamidines[1] and isocyanides,[2] the aminocarbonylation of aryl halides,[3] and as reagents in the classical Vilsmeier formylation reactions.[4] Furthermore, they are valuable intermediates in the construction of various medicinally important compounds such as quinolone antibiotics,[5] and cancer chemotherapeutic agents.[6] Various drugs such as acetiamine, octotiamine, fursultiamine, and formoterol, which are in clinical use, have formamide groups in their skeletons. The formyl group is also an important amino protecting group, especially during peptide synthesis,[7] because the selective deprotection process is possible in the presence of other groups like acetyl or benzoyl. In addition, formamides were found to be effective Lewis bases that catalyze several useful reactions such as allylation and hydrosiylation of carbonyl compounds.[8] Among various procedures that have been developed and documented for the preparation of formamide derivatives,[9,10] the reaction between amines and formic acid is the most simple and important approach. For this purpose, a variety of catalysts and reagents have been used to facilitate this reaction.[11–18] Although these procedures provide an improvement in the synthesis of these compounds, many of them suffer from disadvantages such as long reaction times, harsh reaction conditions, need to excess amounts of the reagent, thermal instability, by-products formation, use of toxic reagents and non-recoverability of the catalyst. Therefore, introducing of simple, efficient and mild procedures with easily separable and reusable solid catalysts to overcome these problems is still in demand.

Over the last years, ionic liquids have been extensively used in almost all application fields of chemistry such as organic and inorganic syntheses, catalysis, electrochemistry and chromatography. It is due to their remarkable properties such as non-flammability, negligible vapor pressure, wide liquid range and high thermal, chemical and electrochemical stability. However, their high cost, large consumption and difficult recovery and the separation of products cause limitations in the large-scale application of them. Furthermore, the ionic liquids (especially Brönsted acidic ionic liquids) have some degree of instability in the presence of air and moisture. Immobilization of the ionic liquid on the surface of a solid support is a useful way to combine the advantageous characteristics of ionic liquids and solid properties. In other words, the immobilized ionic liquids offer the additional features compared to the pure ionic liquids that facilitate the handling, separation and reuse procedures, and minimizing the amount of IL utilized in reactions.[19]

Utilization of waste materials is a very desirable goal for a green environment and green chemistry. Rice husk, the outer covering of rice grains that obtained during the milling process, is one of the main agricultural residues. Societies often dispose of the rice husk waste using open burning that leads to environmental pollution and damages to the land and the surrounding area in which it was dumped. Application of rice husk as an energy source for biomass power plants, rice mills and brick factories is increasing due to its high calorific power.[20] In this combustion, rice husk ash (RHA) is produced. RHA has a

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light weight, therefore, the disposal of bulky RHA could be a problem. RHA contains considerable amount of amorphous silica up to 80% and small proportion of impurities such as K_2O, Na_2O and Fe_2O_3.[21] Therefore, RHA possesses high silica content, so it has been employed to produce zeolites and silica powders.[22,23]

Several papers have been published on the application of the modified amorphous silica obtained from rice husk ash as the catalyst.[24–26] Although useful, the reported method for the preparation of pure silica from rice husk ash needs various stages and a long time.[22] On the basis of these points and our investigations we concluded that, at the same conditions, the use of RHA as a support for the preparation of the catalysts is better than the use of silica which is prepared *via* precipitation method during various stages and long time.[27,28]

Experimental section

Reagents and materials

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All yields refer to the isolated products. Products were characterized by comparison of their physical constants and also their IR and NMR spectra with authentic samples and those reported in the literature. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silicagel polygram SILG/UV 254 plates.

Characterization

The FT-IR spectra were run on a VERTEX 70 Brucker company (Germany). Thermogravimetric analyses (TGA) were performed on Polymer Laboratories PL-TGA thermal analysis instrument (England). Samples were heated from 25 to 600 °C at ramp 10 °C min^{-1} under N_2 atmosphere. Scanning election microphotographs (SEM) were obtained on a SEM-Philips XL30. X-ray diffraction (XRD) measurements were performed at room temperature on diffractometer Model XRD 6000, PHILIPS Xpert pro using Co-Kα radiation ($K = 1.7890$ Å) with the beam voltage and a beam current of 40 kV and 30 mA, respectively.

Preparation of 1-methyl-3-(trimethoxysilylpropyl)-imidazolium chloride ([pmim]Cl)

A mixture of 10 mmol 1-methylimidazole and 10 mmol (3-chloropropyl)trimethoxysilane was refluxed at 90 °C for 30 h. Then, the reaction mixture was cooled down. The crude product was washed with Et_2O (2 × 5 mL) and dried under vacuum. The product (slightly yellow viscous oil) was obtained.

Preparation of 1-methyl-3-(trimethoxysilylpropyl)-imidazolium chloride supported on RHA (RHA–[pmim]Cl)

0.6 g (2 mmol) of [pmim]Cl was dissolved in 25 mL of CH_2Cl_2 and treated with 2 g of RHA (used in our previous report[27]). The reaction mixture was refluxed with stirring for 3 days. Then, the reaction mixture was cooled to room temperature, the solid was isolated by filtration and washed with 20 mL of boiling dichloromethane to remove the unreacted ionic liquid. In the next step, the material was dried to give 2.5 g RHA–[pmim]Cl as a gray powder.

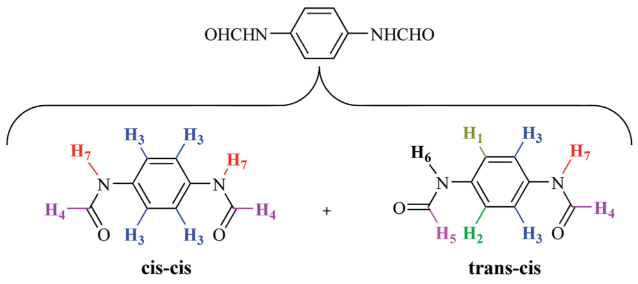
Preparation of 1-methyl-3-(trimethoxysilylpropyl)-imidazolium hydrogen sulfate supported on RHA (RHA–[pmim]HSO_4)

3 g of RHA–[pmim]Cl was suspended in 20 mL of dry CH_2Cl_2. Under vigorous stirring 2.9 mmol of concentrated H_2SO_4 (97%) was added dropwise in an ice bath (0 °C). The mixture was then warmed to room temperature and heated under reflux for 30 h. When the formed HCl was completely distilled off the solution was cooled and CH_2Cl_2 was removed under vacuum to afford RHA–[pmim]HSO_4 (3.16 g) as the product (Scheme 1).

General procedure for *N*-formylation of amines

Amine (1 mmol) was added to a mixture of RHA–[pmim]HSO_4 (10 mg, 0.8 mol%) and formic acid (2 mmol) and the resulting mixture was stirred at 60 °C for the appropriate time. After completion of the reaction (monitored by TLC), ethylacetate (10 mL) was added and the catalyst was separated by filtration. The organic phase was washed with water (2 × 10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford the desired product. The spectral data of new compounds are as follow:

N,*N*′-(1,4-phenylene)-diformamide:



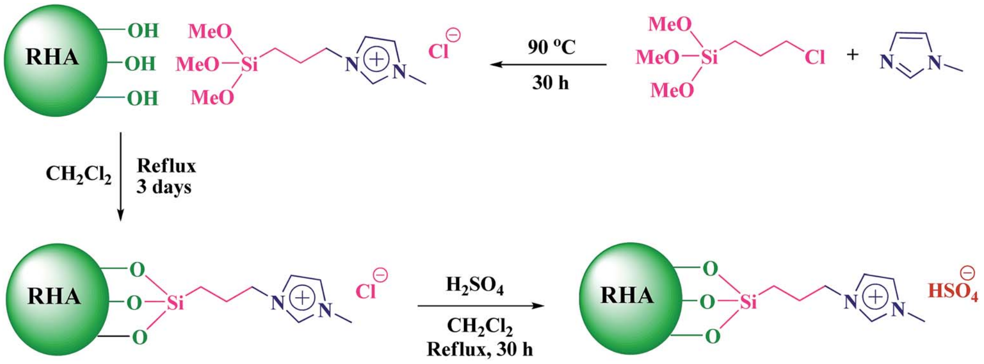
^1H NMR (DMSO-d_6, 400 MHz): 7.13 (s, 1H, H_1), 7.15 (d, $J = 2.4$ Hz, 1H, H_2), 7.52–7.54 (m, 6H, H_3), 8.23 (s, $J = 2$ Hz, 3H, H_4), 8.6 (dd, $J_1 = 11.2$ Hz, $J_2 = 2.4$ Hz, 1H, H_5), 10.07 (d, $J = 11.2$ Hz, 1H, H_6), 10.14 (s, 3H, H_6); ^{13}C NMR (DMSO-d_6, 100 MHz): 118.7, 119.3, 120.1, 120.6, 134.4, 134.4, 134.8, 159.7, 159.7, 162.9.

Results and discussion

Catalyst characterization

The infrared spectra of RHA and RHA–[pmim]HSO_4 are shown in Fig. 1. In the case of RHA, the peaks at 3460 cm^{-1} is attributed to the asymmetric stretching mode of –OH group and the peaks at 1640 cm^{-1} is attributed to the bending mode of the adsorbed water. The strong peak at 1100 cm^{-1} is assigned to the asymmetric stretching mode of Si–O–Si and the peaks at 801 and 468 cm^{-1} are assigned to the symmetric stretching and bending modes of Si–O, respectively.[17]

The RHA–[pmim]Cl and RHA–[pmim]HSO_4 are also characterized on the basis of their FT-IR (Fig. 1). The peaks at 1575 and



Scheme 1 Preparation of the acidic ionic liquid supported on RHA (RHA–[pmim]HSO_4).

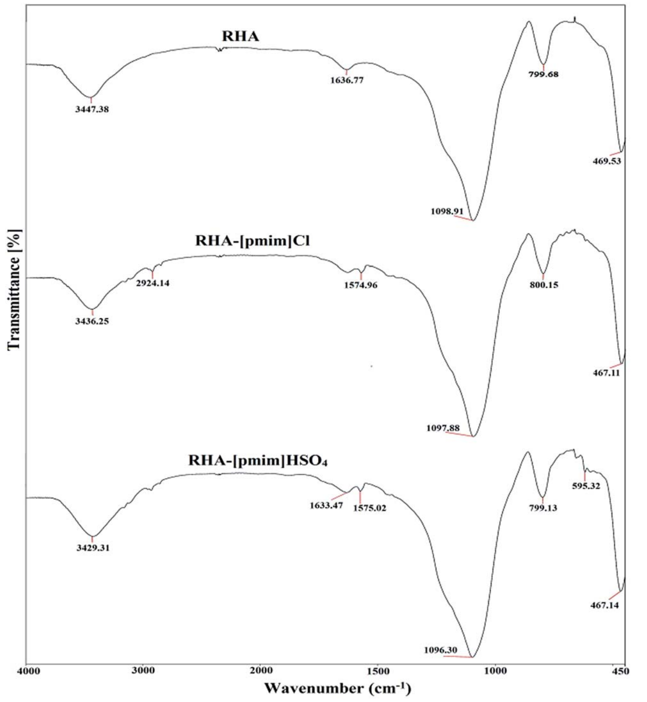


Fig. 1 FT-IR spectra of RHA, RHA–[pmim]Cl and RHA–[pmim]HSO_4.

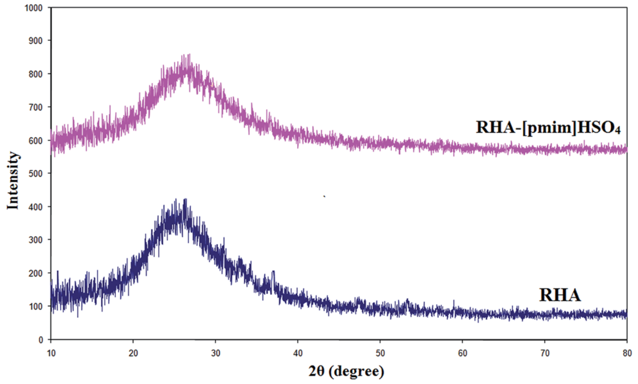


Fig. 2 XRD patterns of RHA in comparison of RHA–[pmim]HSO_4.

1633 cm^{-1} can be assigned to C=N and C=C bands of the imidazolium ring attached to a silica surface. Additional bands at 3160, 2924 and 1454 cm^{-1} were due to C–H stretching and deformation vibrations, confirming the functionalization of the material with the ionic liquid.[29] In FT-IR spectra of RHA–[pmim]HSO_4, absorption of the S=O stretching modes lie in 1170 and 1060 cm^{-1}, so the broad band around 1100 cm^{-1} can be assigned to stretching modes of Si–O and S=O bands which are overlapped together. The S–O stretching mode of sulfuric acid functional group lies around 595 cm^{-1} proving the successful preparation of the catalyst.[30]

Fig. 2, represents the X-ray diffraction (XRD) patterns of the RHA and RHA–[pmim]HSO_4. As it can be seen in the RHA pattern, a broad peak appeared around 2θ equal to 22° clearly indicated that the silica of rice husk ash was mainly in the amorphous form.[31] The peak intensities of RHA–[pmim]HSO_4 are remained almost unchanged compared to RHA pattern that indicate an ordered mesoporosity of the support even after modification.

The samples of RHA and RHA–[pmim]HSO_4 were analyzed by scanning electron microscopy (SEM) for determining the size distribution, particle shape and surface morphology, as represented in Fig. 3. The pictures show that RHA has a porous and irregular shape.[31] These images also show that the primary morphology of RHA is changed after modification with ionic liquid. Indeed, the comparison of RHA and RHA–[pmim]HSO_4 clearly indicated that the particles are aggregated after modification.

The thermal stability of the samples was investigated by thermogravimetric analysis (TGA) in which the observed weight loss was associated with the loss of the organic components attached to the RHA (Fig. 4). The results indicate that RHA showed a weight change below100 °C due to the loss of the physically adsorbed water and then had a steady weight loss at the temperature lower than 600 °C, which could be ascribed to the loss of terminal groups such as –OH terminal groups.[27] After immobilization of the ionic liquid, the weight loss increased which was due to the further increase of the organic components on the RHA. The TGA analysis of RHA–[pmim]HSO_4 shows completely different decomposition from RHA. The first step appeared at <150 °C because of the loss of water and the second weight loss started at 230 °C can be attributed to the

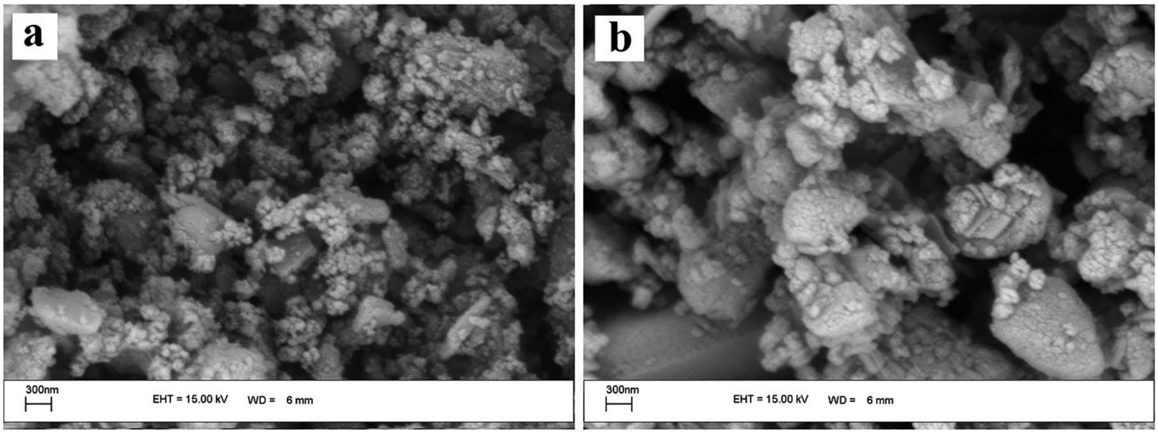


Fig. 3 SEM images of RHA (a) and RHA–[pmim]HSO_4 (b).

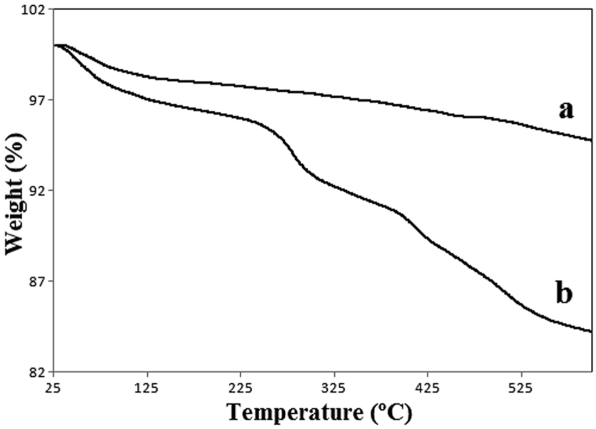
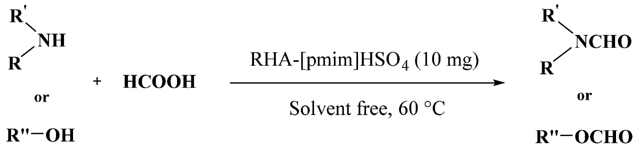


Fig. 4 TGA curves of RHA (a) and RHA–[pmim]HSO_4 (b).

decomposition of the immobilized ionic liquid moieties. Complete loss of all the covalently attached organic structure is seen in the temperature range of 230–570 °C.[29] These results indicate that the immobilized acid catalyst is apparently stable up to about 230 °C. Furthermore, the tendency of the absorption of water on the surface of the catalyst is increased after immobilization of the Brönsted acidic ionic liquid.

For pH analysis of the catalyst, to 25 mL of an aqueous solution of NaCl (1 M) with a primary pH 5.2, RHA–[pmim]HSO_4



Scheme 2 Formylation of amines and alcohols catalyzed by RHA–[pmim]HSO_4.

Table 2 Effect of different catalysts (10 mg) in the *N*-formylation of aniline at 60 °C under solvent-free conditions

Entry	Catalyst	Time (min)	Conversion (%)
1	$AlCl_3$	20	85
2 (ref. 32)	Al_2O_3 (DMSO)	4 h	70
3	$CaCl_2 \cdot 2H_2O$	40	90
4	$FeCl_3$	15	85
5	SiO_2	30	90
6	RHA	15	95
7	RHA–[pmim]Cl	9	100
8	RHA–[pmim]HSO_4	5	100

Table 1 Optimization of the reaction conditions catalyzed by RHA–[pmim]HSO_4

Entry	Catalyst (mg)	HCOOH (mmol)	Temperature (°C)	Time (min)	Conversion (%)
1	30	3	35	20	90
2	30	3	50	10	95
3	30	3	60	5	100
4	30	3	70	5	100
5	30	2	60	5	100
6	30	1.5	60	30	90
7	20	2	60	5	100
8	10	2	60	5	100
9	5	2	60	10	90
10	0	2	60	60	<20

Table 3 Formylation of amines and alcohols in the presence of RHA–[pmim]HSO_4 under solvent-free conditions

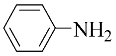
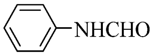
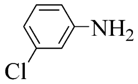
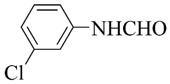
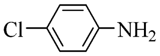
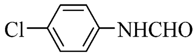
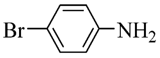
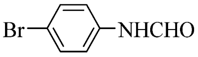
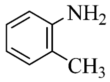
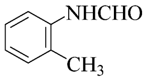
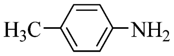
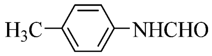
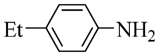
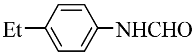
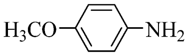
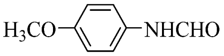
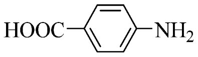
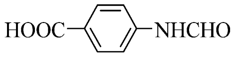
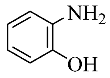
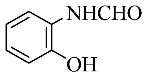
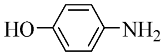
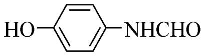
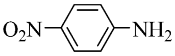
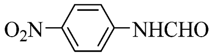
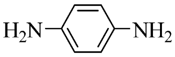
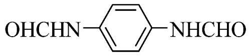
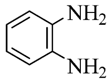
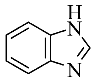
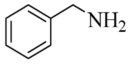
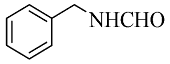
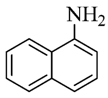
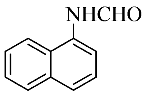
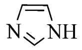
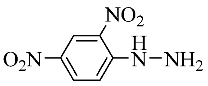
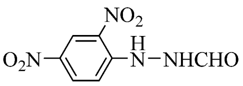
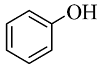
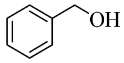
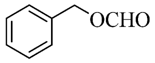
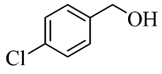
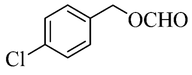
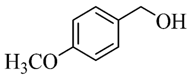
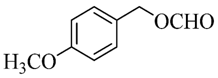
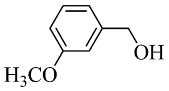
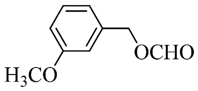
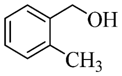
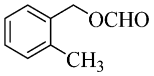
Entry	Substrate	Product	Time (min)	Yield[a] (%)	m.p. (°C)
1			5	94	44–45 (ref. 11)
2			12	95	43–45 (ref. 34)
3			10	94	98–100 (ref. 33)
4			10	94	112–114 (ref. 33)
5			5	95	Oil (ref. 34)
6			8	94	48–50 (ref. 11)
7			5	92	50–52 (ref. 18)
8			2	96	76–78 (ref. 11)
9			4	93	256–258 (ref. 12)
10[b]			10	85	126–128 (ref. 11)
11[b]			5	88	130–132 (ref. 35)
12[b]			10	90	196–198 (ref. 11)
13[b]			10	93	210–212
14			10	92	167–169 (ref. 12)
15			15	93	Oil (ref. 35)
16[b]			14	90	136–138 (ref. 33)
17			4	92	Oil (ref. 11)
18[b]			3	96	181–183 (ref. 12)
19		—	2 h	—	—
20			25	93	Oil (ref. 36)
21			30	92	Oil (ref. 36)

Table 3 (*Contd.*)

Entry	Substrate	Product	Time (min)	Yield[a] (%)	m.p. (°C)
22			10	94	Oil (ref. 36)
23			30	89	Oil (ref. 36)
24			40	92	Oil (ref. 36)

[a] Isolated yields. [b] 4 mmol formic acid was used.

(0.5 g) was added and the resulting mixture was stirred for 2 h at room temperature after which the pH of solution decreased to 1.8. This is equal to a loading of 0.8 mmol H^+ per g.[30]

Catalytic activity

On the basis of the information obtained from the studies on RHA–[pmim]HSO_4, we anticipated that this reagent can be used as an efficient solid acid catalyst for the promotion of the reactions which need the use of an acidic catalyst to speed up. So we were interested to investigate the applicability of this reagent in the promotion of the synthesis of formamides.

At first and for optimization of the reaction conditions, the reaction between aniline and formic acid to its corresponding *N*-phenyl formamide was selected as a model reaction and the various conditions including amount of the catalyst (0, 5, 10, 20 and 30 mg), amount of formic acid (1.5, 2 and 3 mmol) and temperature (35, 50, 60 and 70 °C) were examined (Table 1). Finally the best result was obtained using 10 mg of RHA–[pmim]HSO_4 and 2 mmol formic acid at 60 °C under solvent-free conditions (Scheme 2). Any further increase of the catalyst or temperature did not improve the reaction time and yield. To illustrate the efficiency of RHA–[pmim]HSO_4 in these reactions, the model reaction was also carried out in the absence of catalyst and the reaction was not proceeded (Table 1, entry 10). These results indicated that the catalyst is necessary to produce the products.

Furthermore, the X-ray fluorescence (XRF) analysis showed that RHA contains a high value of silica content (up to 80%) and other composition such as Al_2O_3, Fe_2O_3, K_2O, Na_2O and CaO.[27] For this purpose and for the proven the role of the covalently bounded groups, we used various catalysts in the reaction of aniline with formic acid under optimal condition. As it can be seen in Table 2, $CaCl_2 \cdot 2H_2O$, SiO_2, $AlCl_3$ and $FeCl_3$ can also catalyze this type of reactions. So, the available amounts of Ca, Fe and P in RHA can be promoted the reaction, therefore the reaction time in the presence of RHA is shorter than SiO_2.

However, the long time observed for the same reaction using RHA, RHA–[pmim]Cl and RHA–[pmim]HSO_4 confirms the important role of the covalently bounded ionic liquid and also HSO_4^- group in the catalyst to obtain the best performance.

After optimization of the reaction conditions and in order to establish the effectiveness and the acceptability of the method, we explored the protocol with a variety of simple readily available substrates under the optimal conditions. For this purpose, a broad range of aromatic, aliphatic and heterocyclic amines was treated with formic acid, as shown in Table 3. It was observed that under similar conditions, a wide range of aromatic amines containing electron-withdrawing as well as electron-donating groups such as Cl, Br, CH_3, OCH_3, Et, NO_2, COOH and OH in the *ortho*, *meta*, and *para* positions of the benzene ring easily converted to the corresponding formamides in short reaction times with high isolated yields (Table 3, entries 1–12). This method was also found to be useful for the usage of phenylenediamine (Table 3, entry 13, 14). In this reaction, 1,4-phenylenediamine was led to *N*,*N*′-(1,4-phenylene)-diformamide, but in the case of 1,2-phenylenediamine cyclization occurred instead of *N*-formylation and benzimidazole was obtained as the product. Aliphatic (benzyl amine), heterocyclic (imidazole) and polycyclic (1-naphthyl amine) amines were also converted to the corresponding products in high yields (Table 3, entries 15–18).

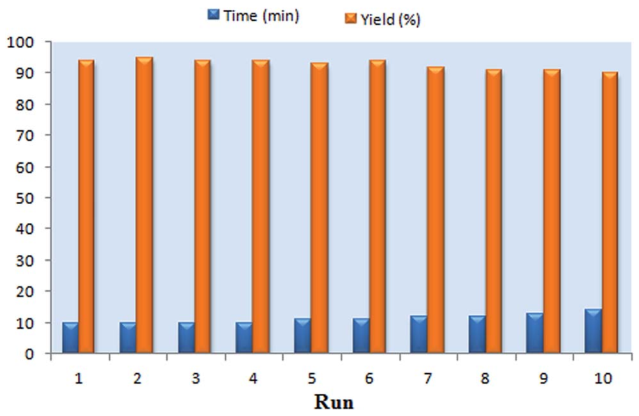
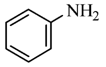
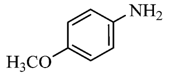
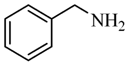


Fig. 5 Reusability of the catalyst.

Table 4 Comparison of the result obtained from the *N*-formylation of aniline, 4-methoxy aniline and benzyl amine in the presence of RHA–[pmim]HSO_4 with those obtained using some of the other catalysts

							
Entry	Catalyst (mol%)$^{Ref.}$	Time (yield)	TOF^a (h^{-1})	Time (yield)	TOF^a (h^{-1})	Time (yield)	TOF^a (h^{-1})
1	γ-Fe_2O_3@HAp-SO_3H (0.9 mol%)[11]	20 (97)	323	20 (97)	323	40 (92)	153
2	HCOONa (20 mol%)[12]	60 (95)	5	180 (99)	1.6	150 (85)	1.7
3	TiO_2–SO_4^{2-} (7.5 mol%)[13]	30 (99.2)	26	240 (99)	3.3	—	—
4	$HClO_4$–SiO_2 (2.5 mol%)[14]	15 (96)	154	25 (93)	89	40 (92)	55
5	Sulfated tungstate (10 mol%)[15]	10 (99)	59	10 (98)	59	10 (99)	59
6	Melamine trisulfonic acid (3 mol%)[16]	60 (98)	33	60 (97)	32	90 (91)	20
7	Protic ionic liquid (5 mol%)[17]	10 (95)	114	10 (92)	110	10 (98)	117
8	Silica sulfuric acid (12.5 mol%)[18]	7 (99)	68	—	—	5 (85)	82
9	RHA–[pmim]HSO_4 (0.8 mol%)$^{This\ work}$	5 (94)	1428	1 (97)	7275	15 (93)	465

[a] Turn over frequency (TOF) represents the average number of substrate molecules converted into the product per molecule of catalyst per hour.

This method was also a very useful method for the formylation of benzyl alcohols with formic acid under mild reaction conditions and the corresponding *O*-formylated products were obtained in high yields (Table 3, entries 20–24). It is known that these reactions give the products in longer reaction times than formylation of amines. Phenolic –OH group formylation was not take place (Table 3, entry 19), thus with aromatic amines containing both an amino and a phenolic group, *N*-formylated product was selectively obtained that indicates the chemoselectivity of the protocol (Table 3, entries 10–11).

To check the reusability of the catalyst, the reaction of 4-chloroaniline and formic acid under the optimized reaction conditions was studied again. When the reaction completed, ethyl acetate was added and the catalyst was separated by filtration. The recovered catalyst was washed with ethyl acetate, dried and reused for the same reaction. This process was carried out over ten runs and all reactions led to the desired products without significant changes in terms of the reaction time and yield which clearly demonstrates practical recyclability of this catalyst (Fig. 5).

In order to show the efficiency of the present method, we have compared our result obtained from the reactions of aniline, 4-methoxy aniline and benzyl amine with formic acid catalyzed by RHA–[pmim]HSO_4 with other results reported in the literature (Table 4). It is clear that the present method is superior in terms of the reaction time and catalyst amount. Furthermore, to compare the applicability and efficiency of RHA–[pmim]HSO_4 with the other catalysts, we have calculated the TOF of these catalysts in these reactions. As it is clear, the TOF values showed that RHA–[pmim]HSO_4 is more effective than the compared catalysts.

Conclusions

In conclusion, in this study we have introduced RHA–[pmim]HSO_4 as a highly powerful supported acidic ionic liquid for the simple, efficient and chemoselective formylation of various amines and alcohols in short reaction times with high TOF. The reaction rate was faster for the amines than for the primary alcohols. The catalyst shows high thermal stability and was recovered and reused without any noticeable loss of activity. Furthermore, no side reactions, ease of preparation and handling of the catalyst, simple experimental procedure, use of inexpensive and reusable catalyst with lower loading and solvent free conditions are other advantages of this method. Further studies on some more practical applications of the RHA–[pmim]HSO_4 catalyst in other organic reactions are currently underway in our laboratory.

Acknowledgements

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