Immobilization of acidic ionic liquids by copolymerization with styrene and their catalytic use for acetal formation

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Abstract

A novel method to immobilize Brønsted acidic ionic liquid on solid support was described; involving the copolymerization of 1-vinylimidazolium based acidic ionic liquids with styrene and their use as effective and reusable catalysts for acetal formation under mild reaction condition.

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1. Introduction

Acetalization is one of the most useful methods for protecting carbonyl compounds. Conventionally, this reaction is carried out in a homogeneous system in the presence of corrosive acids such as p-toluenesulfonic acid (PTSA), triflic acid or dry HCl, which inevitably leads to a tedious work-up procedure [1]. Moreover, neutralization of the strong acid media will produce undesired wastes. Therefore, there have been great deals of efforts to overcome these drawbacks by employing solid acid catalysts. Some of the heterogeneous catalysts include SO₃H-functionalized silica, 1-butyl-3-methylimidazolium tetrachlorogallate, iron trichloride and indium trichloride [2].

Over the past few years, there have been increasing recognitions that polymer supported reagents and catalysts are important tools for organic synthesis. For example, a collective of works focused on polymer supported reagents and catalysts was recently published as a special issue in Tetrahedron [3]. Immobilization of homogeneous catalysts on polymeric supports could offer some practical benefits including easy separation of the catalyst from reagents and reaction products, and simplification of the methods of recycling the catalysts.

Brønsted acidic ionic liquids are of special important because they possess simultaneously the proton acidity and the characteristic properties of ionic liquid [4]. Our previous works have demonstrated that they were effective catalysts for alkylation, nitration and Koch reaction [5]. They were also immobilized on silica gel by radical transfer reaction in the presence of AIBN, and were used as effective catalysts for esterification and nitration [6].

In this letter, we describe another method to immobilize Brønsted acidic ionic liquid on solid support as well as a new application of it for acid-catalyzed organic synthesis. It was found that 1-vinylimidazolium based Brønsted acidic ionic liquid could be copolymerized with styrene in the presence of AIBN in ethanol to generate polymer support immobilized acidic ionic liquid, which was demonstrated to be effective catalyst for acetalization of various aldehydes under mild reaction condition.

2. Experimental and discussions

Preparations of the ionic liquid supported polystyrene are shown in Fig. 1. Firstly, 1-vinylimidazolium contained Brønsted acidic ionic liquid, i.e. 3-vinyl-1-(4-sulfobutyl)imidazolium trifluoromethanesulfonate, was synthesized using...
the method described in previous paper [6]. To copolymerize the above acidic ionic liquid with styrene, purified styrene (30 mmol), ionic liquid (3.5–10% eq.) and AIBN (5% of vinyl group) were added to the solution of ethanol (50 mL), and then the mixture was stirred at reflux temperature for 24 h. After cooling down, the precipitate was separated by filtration and washed with ethanol for three times. Followed by drying in vacuo at room temperature to remove ethanol, the precipitate was grind in mortar to afford ionic liquid immobilized polystyrene in the form of

\[ \text{CH}_2\text{N}+\text{CH}_2\text{N}^- \text{SO}_3\text{H. CF}_3\text{SO}_3^- \text{PS-IL} \]

of vinyl group) were added to the solution of ethanol (50 mL), and then the mixture was stirred at reflux temperature for 24 h. After cooling down, the precipitate was separated by filtration and washed with ethanol for three times. Followed by drying in vacuo at room temperature to remove ethanol, the precipitate was grind in mortar to afford ionic liquid immobilized polystyrene in the form of

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**Table 1**

<table>
<thead>
<tr>
<th>Run</th>
<th>PS-IL</th>
<th>Initial ratio (%)</th>
<th>IL amount (wt%)</th>
<th>( M_w )</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3.5</td>
<td>0.45</td>
<td>3809</td>
<td>95 (97) b</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>5</td>
<td>0.81</td>
<td>4024</td>
<td>94 (75) b</td>
</tr>
</tbody>
</table>

- \(^a\) Ethanol, 3 g; hexanal, 1.5 mmol; PS-IL, 10%; Temp., 50 °C; and time, 0.5 h.
- \(^b\) Results of second cycle are in parentheses.

\[ \text{CH}_2\text{N}+\text{CH}_2\text{N}^- \text{SO}_3\text{H. CF}_3\text{SO}_3^- \text{PS-IL} \]

**Table 2**

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td></td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>89 (^b)</td>
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<td>3</td>
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<td>90</td>
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</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>79</td>
</tr>
</tbody>
</table>

- \(^a\) Ethanol, 3 g; Sub., 1.5 mmol; PS-IL, 10%; Temp., 50 °C; and time, 0.5 h.
- \(^b\) Yield after four recycles.
white powder (denoted as PS-IL), which was further washed with ethanol to remove any remained un-bound acidic ionic liquid, and was finally dried in vacuo at room temperature.

It should be noted that although PS-IL could be readily prepared with the initial ionic liquid/styrene ratio (in mol) below 10%, it will become a little viscous when the initial ionic liquid/styrene ratio was too high. Typically, initial ratio below 5% could offer PS-IL in very well physical form as white powder. PS-IL involved in the following experiments was prepared mainly using two different initial ratios, i.e. 3.5% and 5% respectively.

Immobilization of acidic ionic liquid on PS-IL was confirmed by both FTIR and 1H NMR measurements. Loading amount of acidic ionic liquid was determined by element analysis of N, and weight-average molecular weight ($M_w$) was achieved by GPC analysis.

Characterization results of PS-IL 1 and 2 and their use as catalyst for the probe reaction of acetalization of $n$-hexanal with ethanol are summarized in Table 1 [7]. Element analysis revealed that loading amount of acidic ionic liquids on PS-IL was obviously dependent on the initial ionic liquid/styrene ratio. Initial ratios at 3.5% and 5% resulted different loading amount in final product, as 0.45 and 0.81 wt% correspondingly. In contrast, however, no such initial ratio-dependent manner was observed regarding to their molecular weight $M_w$. GPC analysis showed that PS-IL 1 and 2 shared a very close molecular weight.

Both PS-IL 1 and 2 were very effective catalysts for $n$-hexanal acetalization with ethanol. High yields of acetals were attained after 0.5 h reaction at 50 °C. The acetal could be separated by a simple filtration and washing of the catalyst with ethanol, followed by evaporation of the solvent. GC and 1H NMR analyses showed no measurable by-products, indicating the acetalization reaction was carried out in high selectivity.

The major difference of PS-IL 1 and 2 was laid in their reusability. As can be seen from the results of second cycle, PS-IL 1, with a 3.5% initial ratio, exhibited nearly no any loss in activity, while PS-IL 2, which held a 5% initial ratio, suffered a remarkable decreasing in activity. In addition, an obvious color change from white to yellow was observed in the case of PS-IL 2, which was, however, absent from PS-IL 1. Taking into consideration their different ionic liquid loading amount, we were inclined to think that the relative higher loading amount of PS-IL 2 was probably the major reason that caused decreasing activity and color change, for it was very possible that some side reactions occurred over a higher-acid-loading catalyst to form undesired by-products that finally degraded the catalytic performance of PS-IL 2.

As demonstrated in above experiment as effective catalyst for acetalization reaction with ethanal, PS-IL 1 was then applied to a wider range of substrates, and the results are listed in Table 2. In the beginning, reusability of PS-IL 1 was further investigated by repeating using in more recyclings for acetalization of $n$-hexanal with ethanol. As can be seen, yield of $n$-hexanal acetal could still keep as 89% at the fourth cycle (Run 2), which indicated a good reusability of PS-IL. Aliphatic aldehydes, $n$-heptanal and $n$-octanal, were converted to corresponding acetals in high yields (Runs 3 and 4). Likewise, acetalization reaction with ethanol was equally successful for a variety of aromatic aldehydes including benzaldehyde, o-methylbenzaldehyde and p-chlorobenzaldehyde, producing the corresponding acetals in 90–98% yields (Runs 5–7). Interestingly, however, when p-hydroxybenzaldehyde was examined, 4,4’-oxydibenzaldehyde as the only product was formed instead of the corresponding acetal (Run 8). Moreover, 1H NMR analysis also showed that no further acetalization reaction between 4,4’-oxydibenzaldehyde and ethanol had occurred, suggesting an electron-donating group at para position may disturb the acetalization of aromatic aldehydes in this catalytic system.

3. Conclusions

In conclusion, we demonstrated herein a novel way to immobilize Brønsted acidic ionic liquid on solid support by copolymerization of 1-vinylimidazolium based ionic liquid with styrene in the presence of AIBN. The polymeric support immobilized acidic ionic liquid could be used as effective and reusable catalyst for acetalization reaction under mild reaction condition.

References

[7] In a typical procedure, ethanol (3 g) and substrate aldehyde (1 mmol) were placed in a 10 ml test tube, and PS-IL was added. The reaction mixture was stirred at 50 °C for 30 min. The product was separated by filtration and washing of the catalyst with ethanol, followed by evaporation of the solvent in vacuo and analyses with GC and 1H NMR.