



Imidazolium ionic liquid-supported sulfonic acids: Efficient and recyclable catalysts for esterification of benzoic acid

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Abstract

Several imidazolium ionic liquid (IL)-supported sulfonic acids with different anions, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{BF}_4$, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{PF}_6$, and $[\text{C}_3\text{SO}_3\text{Hmim}]\text{CF}_3\text{SO}_3$, were synthesized and applied as catalysts for esterification reaction of benzoic acid. The experimental results indicate that imidazolium IL-supported sulfonic acid containing anion of HSO_4^- shows the best catalytic activity. Only when less $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ (0.3 equiv.) applied, was the product obtained with high yield of 97%. Furthermore, the produced esters could be separated by decantation, and the catalyst could be reused after the removal of water.

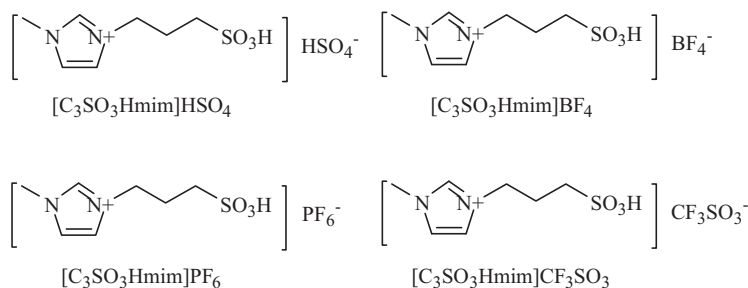
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Arylic esters are important products or intermediates in the chemical and pharmaceutical industries. Popular catalysts for esterification reactions from undergraduate laboratories to chemical manufacturing plants are mineral acids (sulfuric acid, hydrochloric acid, and orthophoric acid) as well as Lewis acids (boric acid and AlCl_3) [1]. In recent years, from the viewpoint of environmental consciousness, solid acids are being more widely used since they are deemed less noxious than traditional liquid acids [2]. However, these solid acids suffer from drawbacks like restricted accessibility of the matrix-bound acidic sites, high molecular weight/active-site ratios, and rapid deactivation from coking [3]. On the other hand, ionic liquids (ILs) have attracted more and more interests in various chemical processes due to their many fascinating and intriguing properties such as nonvolatile, thermally stable properties, and ease of recyclability [4]. Recently, esterification reaction in the presence of ILs with or without an additional catalyst has been investigated and showed good performance [5]. For example, Zhao *et al.* reported the esterification of aliphatic acid only with 0.5–1.0 mol% SO_3H -functionalized ionic liquids [5i]. Nevertheless, in most cases aliphatic esters synthesis in ILs were discussed, and few reports on acrylic esters synthesis in ILs were found. Xing *et al.* [1] synthesized task-specific ionic liquids (TSILs) that bear an alkane sulfonic acid group in pyridinium cation, and also investigated their catalytic activities for esterification reaction of benzoic acid. However, the reaction was accomplished by combining 1:1 molar quantity of substrate and catalyst, which hindered their industrial applications. A following work by Gui and

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Scheme 1.

co-workers [5g] showed that esterification of aromatic acids was more difficult compared with that of aliphatic acids and longer reaction time (16 h) was utilized [5g] using SO₃H-functionalized ionic liquid as a catalyst. Therefore, we focused our attention on the application of a highly active catalyst, which was expected to utilize only as a catalyst with less amount for esterification in less reaction time. For this purpose, we now wish to report on a novel and appealing strategy for the application of several TSILs bearing an alkane sulfonic acid group in imidazolium cation with different anions, [C₃SO₃Hmim]HSO₄, [C₃SO₃Hmim]BF₄, [C₃SO₃Hmim]PF₆, and [C₃SO₃Hmim]CF₃SO₃. By which the esterification reactions of benzoic acid with alcohols have been studied from aspects of activity, recyclability, separation work-up, and substrate availability.

The imidazolium IL-supported sulfonic acids, [C₃SO₃Hmim]HSO₄, [C₃SO₃Hmim]BF₄, [C₃SO₃Hmim]PF₆, and [C₃SO₃Hmim]CF₃SO₃ could easily be prepared according to Ref. [6] (Scheme 1).

For the initial studies on the catalytic activity of the imidazolium IL-supported sulfonic acids, the esterification of benzoic acid with ethanol was chosen as a model reaction, which was carried out in the presence of [C₃SO₃Hmim]HSO₄ without other additional solvents. The reaction conditions were optimized in terms of temperature, catalyst concentration, reaction time, and ratio of benzoic to ethanol. As we expected, the results in Table 1 indicated that the reaction proceeded smoothly with excellent yields (97–98%) for esterification with less amount of [C₃SO₃Hmim]HSO₄, compared to [PSPy]HSO₄ reported by Xing *et al.* (Table 1, entry 8), which could be decreased by about three folds from 1 molar to 0.3 molar quantities of benzoic acid without the activity loss (Table 1, entries 1, 3

Table 1
The esterification reaction of benzoic acid with ethanol catalyzed by TSILs.^a

Entry	Catalyst	Acid/ethanol/IL ratio	Time (h)	Temperature (°C)	Yield ^b (%)
1	[C ₃ SO ₃ Hmim]HSO ₄	1:3:1	3.0	100	98
2	[C ₃ SO ₃ Hmim]HSO ₄	1:4:0.5	3.0	100	96
3	[C ₃ SO ₃ Hmim]HSO ₄	1:3:0.5	3.0	100	97
4	[C ₃ SO ₃ Hmim]HSO ₄	1:2:0.5	3.0	100	84
5	[C ₃ SO ₃ Hmim]HSO ₄	1:3:0.3	2.5	100	97
6	[C ₃ SO ₃ Hmim]HSO ₄	1:3:0.3	2.5	95	97
7	[C ₃ SO ₃ Hmim]HSO ₄	1:3:0.25	2.5	95	84
8 ^c	[PSPy]HSO ₄	1:2:1	3	85	92
9	[C ₃ SO ₃ Hmim]HSO ₄	1:3:0.3	2.5	85	86
10	[C ₃ SO ₃ Hmim]HSO ₄	1:3:0.3	2.0	95	80
11	[C ₃ SO ₃ Hmim]BF ₄	1:3:0.3	2.5	95	83
12	[C ₃ SO ₃ Hmim]PF ₆	1:3:0.3	2.5	95	81
13	[C ₃ SO ₃ Hmim]CF ₃ SO ₃	1:3:0.3	2.5	95	85
14 ^d	[C ₃ SO ₃ Hmim]HSO ₄ (2nd run)	1:3:0.3	2.5	95	96
15 ^d	[C ₃ SO ₃ Hmim]HSO ₄ (3rd run)	1:3:0.3	2.5	95	96
16 ^d	[C ₃ SO ₃ Hmim]HSO ₄ (4nd run)	1:3:0.3	2.5	95	95
17 ^d	[C ₃ SO ₃ Hmim]HSO ₄ (5nd run)	1:3:0.3	2.5	95	95

^a Benzoic acid (5 mmol).

^b Isolated yield based on benzoic acid.

^c Report by Xing *et al.* [1].

^d Reuse of the catalyst.

Table 2

The esterification reaction of benzoic acid with alcohols catalyzed by $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$.^a

Entry	Alcohols	Time (h)	Yield (%) ^b
1	Methanol	2.0	98
2	Butanol	2.5	95
3	Cyclohexanol	3.5	83
4	Benzenemethanol	4.0	85
5	Lauryl alcohol	4.0	86

^a The molar ratios of benzoic acid/alcohol/ $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ /are 1:3:0.3, the temperature 95 °C.^b Isolated yield based on benzoic acid.

and 5). Additionally, the optimal yield to the desired product was obtained when benzoic acid reacted with 3 equiv. of ethanol at 95 °C for 2.5 h (Table 1, entry 6). Further inspection revealed that the anion influenced the esterification dramatically, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ exhibited relatively better activity over $[\text{C}_3\text{SO}_3\text{Hmim}]\text{BF}_4$, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{PF}_6$, and $[\text{C}_3\text{SO}_3\text{Hmim}]\text{CF}_3\text{SO}_3$ under the same catalytic conditions (Table 1, entries 6, 11–13). The optimal condition was achieved in the presence of $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ (Table 1, entry 6), whereas lower yields of the products were observed when $[\text{C}_3\text{SO}_3\text{Hmim}]\text{BF}_4$, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{PF}_6$, and $[\text{C}_3\text{SO}_3\text{Hmim}]\text{CF}_3\text{SO}_3$ were used. The higher yields of esters in $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ are probably owing to higher Brønsted acidity of $[\text{HSO}_4]^-$ as well as best immiscibility of $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ with the produced ester, which facilitates the shifting of the esterification reaction equilibrium to the product side [1].

The recovery and reuse of catalysts are important from economic consideration and environmental concerns. Along this issue, the stability and recyclability of $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ were examined in the reaction of benzoic acid with ethanol under the optimized reaction conditions. It was found that the activity and stability of $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ maintained very well (yields: 95–98%) even after five recycles (Table 1, entries 6, 14–17).

To explore the generality of the esterification reaction catalyzed by $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$, a variety of alcohols were selected to react with benzoic acid. As summarized in Table 2, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ showed good catalytic activities in esterification of other alcohols like methanol, butanol, cyclohexanol, benzenemethanol, and lauryl alcohol with good to excellent yields (83–98%). The results also showed that the steric bulk of alcohols affected the reactions. Esterification of methanol and butanol (Table 2, entries 1 and 2) was easier compared with that of cyclohexanol, benzenemethanol, as well as lauryl alcohol (Table 2, entries 3, 4, and 5) and higher yields were obtained.

In summary, we have developed an efficient, simple and recyclable method for esterification of benzoic acid with alcohols catalyzed by imidazolium IL-supported sulfonic acids. Among the catalysis system with different anions, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{BF}_4$, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{PF}_6$, and $[\text{C}_3\text{SO}_3\text{Hmim}]\text{CF}_3\text{SO}_3$, $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ showed the highest activity and stability to catalyze the esterification reactions of benzoic acid. Compared to the reported pyridinium IL-supported sulfonic acids, high yields of the esters were afforded with 0.3 equiv. of IL-supported sulfonic acids. Moreover, the stability of $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ facilitated high yields of the product without the activity loss even after five recycling uses.

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