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Study on Selective Dimerization of α-Methylstyrenes Promoted by Ionic Liquids

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Abstract The catalytic systems composed of ionic liquids containing BF_4^- anion and HBF_4 showed high catalytic activity to produce 4-methyl-2,4-diphenyl-1-pentene (MDP-1) or 1,1,3-trimethyl-3-phenylindan (TPI) under different temperature conditions. Up to 90.8% selectivity to MDP-1 with a 98.7% conversion of α-methylstyrene was obtained at 60 °C in the presence of $[HexMIm]BF_4–HBF_4$, while exclusive TPI was yielded when the reaction temperature increased to 120 °C. Further studies showed that another ionic liquid, $[BMIm]Cl \cdot 2AlCl_3$, could act as an excellent catalyst and solvent for the dimerization of α-methylstyrene to produce TPI. The dimerization of α-methylstyrene catalyzed by $[HexMIm]BF_4–HBF_4$ and $[BMIm]Cl \cdot 2AlCl_3$ performed the same reaction mechanism and the proton was the active species.

Keywords Dimerization · α-Methylstyrene · Ionic liquid · Tetrafluoroboric acid · $[BMIm]Cl \cdot 2AlCl_3$

1 Introduction

A number of products can be formed in the acid-catalyzed dimerization of α-methylstyrene. The products of the dimerization generally include 4-methyl-2,4-diphenyl-1-pentene (MDP-1), 4-methyl-2,4-diphenyl-2-pentene (MDP-2), 1,1,3-trimethyl-3-phenylindan (TPI) and some oligomers (Scheme 1). Among them, the open chain unsaturated dimer MDP-1 and cyclodimer TPI are industrially important [1–3]. MDP-1 can be used as molecular weight regulator or chain-transfer reagent in the production of polymers, while TPI is widely used as an intermediate in synthesis of luboil.

The dimerization of α-methylstyrene has been previously studied under several different catalytic systems. With sulfuric acid as the catalyst and methanol as the additive, MDP-1 was obtained as the main product in a liquid-liquid process for the dimerization of α-methylstyrene [1]. In the presence of acidic ion exchange resin Amberlyst 15, MDP-1 was selectively obtained with 85% conversion of α-methylstyrene [2]. Over the catalyst of highly dispersed Nafion® in silica, a selectivity of more than 86% to MDP-1 and MDP-2 was obtained in a continuous-flow process of the dimerization of α-methylstyrene [4]. Resin-based solid acids have been reported as effective catalysts in the dimerization of α-methylstyrene, and high selectivity to MDP-1 (>90%) could be obtained [5, 6]. The MCM-41/Nafion® composite was a good catalyst to produce MDP-1 in the dimerization reaction of α-methylstyrene at the reaction temperature of 60 °C, while 91% yield of TPI could be selectively obtained at 100 °C [7]. The dimerization reaction of α-methylstyrene to produce TPI has been developed in the presence of cation-exchanged montmorillonite, a 75% yield of TPI was achieved [8]. Recently, metallic catalysts such as $RuCl_3 \cdot H_2O$, $InBr_3$ and $Pd(OAc)_2/PPh_3/In(OTf)_3$, have been used in the dimerization reaction of α-methylstyrene, and moderate to good product selectivities were obtained [9–11].

In recent years, catalytic reactions performed in ionic liquids have attracted considerable interest because of their unique advantages of high thermal stability, negligible vapor pressure, high loading capacity, tunable polarity, immiscibility with a number of organic solvents,

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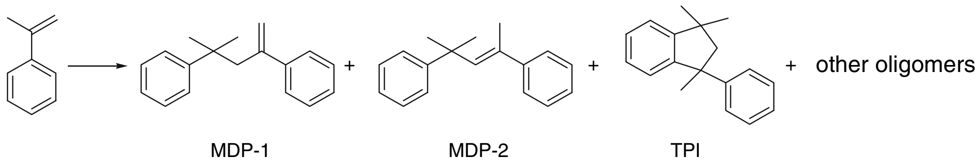
Scheme 1 Dimerization of α-methylstyrene



recyclability and interesting intrinsic physicochemical characteristics [12–15]. Ionic liquid $Et_3NHCl–FeCl_3$ was reported as the catalyst to produce MDP-1 in the dimerization of α-methylstyrene, but tertiary amyl alcohol must be added as the solvent. Interestingly, TPI was obtained as the major product using ionic liquid $Et_3NHCl–2FeCl_3$ as the catalyst without organic solvents [3]. SO_3H-functionalized ionic liquids have been employed as alternative reaction media to conventional acid catalysts for oligomerization of α-methylstyrene, but the highest selectivity to MDP-1 was only 65% with a 68% conversion of α-methylstyrene, while the selectivity to trimer was as high as 12% [16]. The dimerization of α-methylstyrene in a Bronsted acidic ionic liquid, *N*-methylimidazolium tetrafluoroborate, was also reported [17, 18].

As a part of our interest in performing organic reactions in ionic liquids [19, 20], we report herein that ionic liquids containing BF_4^- anion act as powerful media in the HBF_4-catalyzed dimerization of α-methylstyrene. The experimental results showed that these ionic liquids played important roles not only for accelerating the reaction but for improving the product selectivities. The product distribution was strongly dependent on the reaction temperature. High selectivity to MDP-1 was obtained at 60 °C, while exclusive TPI at 120 °C. In addition, the chloroaluminate ionic liquid composed of $AlCl_3$ and 1-butyl-3-methylimidazolium chloride, a common Lewis acidic ionic liquid, was used as both solvent and catalyst to obtain TPI in the dimerization of α-methylstyrene. Moreover, all effective catalytic systems could be easily recovered and reused for several times without loss of catalytic activity.

2 Experimental

2.1 Materials

α-Methylstyrene (Shanghai Chemical Reagent Company) and 4-chloro-α-methylstyrene (ACROS) were of analytical grade and directly used without further purification. 50% Aqueous HBF_4 solution was purchased from Dongyang Flysun Fluoro Chem Co. China.

Ionic liquids including 1-*n*-butyl-3-methylimidazolium chloride ([BMIm]Cl), 1-*n*-butyl-3-methylimidazolium bromide ([BMIm]Br), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($[BMIm]BF_4$), 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIm]BF_4$), 1-*n*-hexyl-3-methylimidazolium tetrafluoroborate ($[HexMIm]BF_4$), 1-*n*-butyl-3-methylimidazolium bisulfate ($[BMIm]HSO_4$), 1-*n*-butyl-3-methylimidazolium dihydrogen phosphate ($[BMIm]H_2PO_4$), 1-methylimidazolium *p*-toluenesulfonate ([HMIm]Tsa), 1-methylimidazolium trifluoroacetate ([HMIm]Tfa), 1-*n*-butylimidazolium *p*-toluenesulfonic acid ([HBIm]Tsa), 1-*n*-butylimidazolium nitrate ($[HBIm]NO_3$), 1-*n*-butylimidazolium tetrafluoroborate ($[HBIm]BF_4$) and 1-*n*-butyl-3-methylimidazolium chloroaluminate ($[BMIm]Cl \cdot 2AlCl_3$), were synthesized according to the procedures described in the literature [19–24].

2.2 Analysis

The dimerization reaction was monitored by gas chromatography (GC-9790) equipped with an FFAP capillary column (30 m × 0.25 mm). The injector and FID detector temperature were 240 °C and 250 °C, respectively. The temperature program started at 50 °C, holding for 2 min, and ended at 240 °C with a heating rate of 20 °C/min. The products obtained were purified and identified by ^1H NMR spectroscopy (Varian PLUS-400) and GC-MS (Finnigan Trace GC Ultrar-Finnigan Trace DSQ).

2.3 Reaction Procedure

The dimerization reaction was carried out in a 10 mL three-necked flask equipped with a thermometer, a nitrogen inlet and a magnetic stirrer.

In a typical experiment, ionic liquid (1.0 g), 50% aqueous HBF_4 solution (1.5 mmol) and α-methylstyrene (10 mmol) were added into the flask. Then the mixture was heated to 60 °C under a nitrogen atmosphere. The reaction was monitored by GC. Once the reaction was completed, the reaction mixture was allowed to cool to room temperature. The upper organic layer was separated from ionic liquid simply by decanting and analyzed by GC. A small quantity of products remaining in the ionic liquid layer was extracted with hexane and the ionic liquid containing HBF_4 could be reused.

In another typical experiment, $[BMIm]Cl \cdot 2AlCl_3$ (1.0 g) and α-methylstyrene (10 mmol) were added into the flask. The temperature of the reaction mixture significantly increased due to the exotherm of the fast dimeriztion reaction. The reaction mixture was stirred for 5 min under a nitrogen atmosphere. Then the upper organic layer was separated from $[BMIm]Cl \cdot 2AlCl_3$ by decanting and analyzed by GC. A small quantity of products remaining in $[BMIm]Cl \cdot 2AlCl_3$ was extracted with diethyl ether and the residual $[BMIm]Cl \cdot 2AlCl_3$ could be reused.

3 Results and Discussion

3.1 Effect of Catalytic Systems

The acid-catalyzed dimerization of α-methylstyrene was carried out at 60 °C for 2 h in the presence of different ionic liquids. The results were listed in Table 1. Without an ionic liquid, the dimerization of α-methylstyrene could be slightly catalyzed by HBF_4. The conversion of α-methylstyrene was only 6.5%, and the selectivities to MDP-1, MDP-2 and TPI were 74.9%, 19.2% and 5.9%, respectively (Entry 1). In the presence of $[HexMIm]BF_4$, the conversion of α-methylstyrene (98.7%) and the selectivity to MDP-1 (90.8%) were remarkably improved in the HBF_4-catalyzed dimerization of α-methylstyrene (Entry 3), although neat $[HexMIm]BF_4$ showed no catalytic activity in this reaction (Entry 2).

Then catalytic systems composed of $[HexMIm]BF_4$ and different acids were investigated (Entries 4–8). The conversions of α-methylstyrene were observed to be more than 95% when $[HexMIm]BF_4$-H_2SO_4 and $[HexMIm]BF_4$-HBr were used as the catalytic systems. But the product selectivities (MDP-1, MDP-2 and TPI) were poor (Entries 4,5). $[HexMIm]BF_4$-CF_3COOH and $[HexMIm]BF_4$-HCl showed low catalytic activity by comparing with other catalytic systems (Entries 6,7). Not only was the conversion of α-methylstyrene rather low, but no MDP-1 was obtained. In the presence of $[HexMIm]BF_4$-CF_3SO_3H, α-methylstyrene was almost completely converted and a relatively high selectivity to MDP-1 (70.3%) was obtained (Entry 8). The high catalytic activities of $[HexMIm]BF_4$–HBF_4 and $[HexMIm]BF_4$–CF_3SO_3H in this acid-catalyzed dimerization reaction might be ascribed to the superacidic property of HBF_4 and CF_3SO_3H.

The effect of other ionic liquids in the HBF_4-catalyzed dimerization of α-methylstyrene were also examined (Entries 9–16). All of these neat ionic liquids showed no catalytic activity for dimerization without HBF_4 in the blank tests. When $[BMIm]Cl$–HBF_4, $[BMIm]Br$–HBF_4 and $[HMIm]Tfa$–HBF_4 were used as the catalytic systems, no

Table 1 Acid-catalyzed dimerization of α-methylstyrene in the presence of different ionic liquids[a]

Entry	Ionic liquid	Acid	Conversion of α-methylstyrene (%)	Selectivity (%)			
				MDP−1	MDP−2	TPI	Others
1	–	50%HBF_4	6.5	74.9	19.2	5.9	0
2	$[HexMIm]BF_4$	–	0	0	0	0	0
3	$[HexMIm]BF_4$	50%HBF_4	98.7	90.8(87.6[b])	9.1	0.1	0
4	$[HexMIm]BF_4$	50%H_2SO_4	97.6	18.8	2.0	79.2	0
5	$[HexMIm]BF_4$	40%HBr	95.6	59.1	40.9	0	0
6	$[HexMIm]BF_4$	CF_3COOH[c]	3.6	0	50.0	0	50.0
7	$[HexMIm]BF_4$	35%HCl	13.7	0	0	0	100
8	$[HexMIm]BF_4$	CF_3SO_3H[c]	99.8	70.3	29.7	0	0
9	[BMIm]Cl	50%HBF_4	0	0	0	0	0
10	[BMIm]Br	50%HBF_4	0	0	0	0	0
11	[HMIm]Tfa	50%HBF_4	0	0	0	0	0
12	$[BMIm]HSO_4$	50%HBF_4	5.2	97.4	0	0	2.6
13	$[BMIm]H_2PO_4$	50%HBF_4	6.6	96.8	0	0	3.2
14	[HMIm]Tsa	50%HBF_4	37.9	89.6	8.7	1.7	0
15	[HBIm]Tsa	50%HBF_4	4.4	49.5	0	0	50.5
16	$[HBIm]NO_3$	50%HBF_4	28.1	0	0	0	100
17	$[BMIm]HSO_4$	50%H_2SO_4	99.7	44.6	53.9	1.5	0
18	[HMIm]Tfa	CF_3COOH	99.8	24.5	60.7	14.8	0
19	[BMIm]Cl	35%HCl	0	0	0	0	0
20	[BMIm]Br	40%HBr	0	0	0	0	0
21	[HBIm]Tsa	TsOH[d]	0	0	0	0	0
22	$[BMIm]BF_4$	50%HBF_4	98.2	89.8	10.0	0.2	0
23	$[EMIm]BF_4$	50%HBF_4	98.9	88.5	11.4	0.1	0
24	$[HBIm]BF_4$	50%HBF_4	99.3	88.3	11.3	0.4	0

[a] Reaction conditions: ionic liquid (1.0 g), acid (1.5 mmol), α-methylstyrene (10 mmol), 60 °C, 2 h

[b] Isolated yield

[c] 50% Solution in water

[d] TsOH = *p*-toluenesulfonic acid

dimerization reaction occurred (Entries 9–11). Although high selectivity to MDP-1 (>89%) was observed with [BMIm]HSO_4–HBF_4, [BMIm]H_2PO_4–HBF_4, or [HMIm]Tsa–HBF_4 as catalytic systems, the conversion of α-methylstyrene was rather low (Entries 12–14). [HBIm]Tsa–HBF_4 showed very low catalytic activity, the conversion of α-methylstyrene and selectivity to MDP-1 were 4.4% and 49.5%, respectively (Entry 15). When [HBIm]NO_3–HBF_4 was used, no desired products were obtained (Entry 16). These results showed that [BMIm]Cl, [BMIm]Br, [BMIm]HSO_4, [BMIm]H_2PO_4, [HMIm]Tsa, [HBIm]Tsa and [HMIm]Tfa would restrain the catalytic activity of HBF_4. Probably there existed anion exchange between ionic liquid and HBF_4, and relatively weak acids were released which had low catalytic activity for dimerization.

Considering that [HexMIm]BF_4 and HBF_4 had a common anion and [HexMIm]BF_4–HBF_4 provided high catalytic ability and good selectivity to MDP-1, we were strongly interested in testing other catalytic systems, in which ionic liquid and acid possessed the same anion, for the dimerization of α-methylstyrene (Entries 17–21). To our surprise, [BMIm]Cl–HCl, [BMIm]Br–HBr and [HBIm]Tsa–TsOH showed no catalytic activity in this reaction (Entries 19–21). It might be due to that acidity of the three acids was unsufficiently strong and the three ionic liquids were unsuitable for dimerization. The dimerization of α-methylstyrene could be catalyzed by [BMIm]HSO_4–H_2SO_4 and [HMIm]Tfa–CF_3COOH, and the conversion of α-methylstyrene was higher than 99%. But the product selectivities were not good, and MDP-2 was found as the main product (Entries 17,18).

Based on the above results, our later investigation of the dimerization of α-methylstyrene focused on the following catalysis systems, [BMIm]BF_4–HBF_4, [HMIm]BF_4–HBF_4 and [EMIm]BF_4–HBF_4. The results were very promising, although neat ionic liquids showed no catalytic activity in our repeated experiments. α-Methylstyrene was almost completely converted, and MDP-1 was observed as the major product with selectivity higher than 88% in all three tested catalytic systems (Entries 22–24).

Among the tested catalytic systems, the combinations of HBF_4 with the following four ionic liquids, [HexMIm]BF_4, [BMIm]BF_4, [HMIm]BF_4 and [EMIm]BF_4, showed good catalytic activity with high selectivity to MDP-1. The experimental results suggested that ionic liquids containing BF_4^- anion could act as powerful media in the HBF_4-catalyzed dimerization of α-methylstyrene to produce MDP-1, while cations of ionic liquids had no significant influence.

3.2 Effect of the Molar Ratio of HBF_4/α-Methylstyrene

Effect of the molar ratio of HBF_4/α-methylstyrene on the substrate conversion and product selectivity was examined in detail using [HexMIm]BF_4 as medium at 60 °C, and the results were listed in Table 2. With a molar ratio of 0.05 between HBF_4 and α-methylstyrene, 95.2% conversion of α-methylstyrene was obtained, and the selectivities to MDP-1, MDP-2 and TPI were 87.4%, 12.3% and 0.3%, respectively. Increasing the molar ratio of HBF_4/α-methylstyrene from 0.05 to 0.15, both the conversion of α-methylstyrene and the selectivity to MDP-1 slightly increased. Up to 90.8% selectivity to MDP-1 was obtained when the molar ratio of HBF_4/α-methylstyrene was 0.15. Although further increasing the molar ratio of HBF_4/α-methylstyrene to 0.20 did increase the substrate conversion to 99.4%, the selectivity to MDP-1 was slightly decreased (88.7%). In addition, the higher loading of HBF_4 resulted in generating undesired impurities. Therefore, an optimal molar ratio of HBF_4/α-methylstyrene should be no more than 0.15 in this reaction.

3.3 Effect of [Hexmim]Bf_4 Dosage

As mentioned above, ionic liquids containing BF_4^- anion could accelerate the HBF_4-catalyzed dimerization of α-methylstyrene and improve the selectivity to MDP-1. So effect of ionic liquid [HexMIm]BF_4 dosage on the dimerization of α-methylstyrene was studied. The reaction (10 mmol of α-methylstyrene, 1.5 mmol of HBF_4) was carried out at 60 °C for 2 h, and the results were listed in Table 3. When [HexMIm]BF_4 dosage increased from 0.5 to 2.0 g, the conversion of α-methylstyrene increased from 97.3% to 99.3%. While the highest selectivity to MDP-1 was obtained with 1.0 g of [HexMIm]BF_4. It might be related to the concentration of HBF_4 in [HexMIm]BF_4.

Table 2 Effect of HBF_4/α-methylstyrene molar ratio on the dimerization of α-methylstyrene[a]

Entry	HBF_4/α-methylstyrene (mol/mol)	Conversion of α-methylstyrene (%)	Selectivity (%)			
			MDP-1	MDP-2	TPI	Others
1	0.05	95.2	87.4	12.3	0.3	0
2	0.10	97.1	89.3	10.2	0.5	0
3	0.15	98.7	90.8	9.1	0.1	0
4	0.20	99.4	88.7	7.6	0.2	3.5

[a] Reaction conditions: [HexMIm]BF_4 (1.0 g), α-methylstyrene (10 mmol), 60 °C, 2 h

Table 3 Effect of [HexMIm]BF_4 dosage on the dimerization of α-methylstyrene[a]

Entry	[HexMIm]BF4 dosage (g)	Conversion of α-methylstyrene (%)	Selectivity (%)			
			MDP-1	MDP-2	TPI	Others
1	0.5	97.3	84.6	14.6	0.8	0
2	1.0	98.7	90.8	9.1	0.1	0
3	1.5	99.1	86.3	13.6	0.1	0
4	2.0	99.3	77.5	22.2	0.3	0

[a] Reaction conditions: α-methylstyrene (10 mmol), HBF_4 (1.5 mmol), 60 °C, 2 h

Table 4 Effect of reaction temperature on the dimerization of α-methylstyrene[a]

Entry	T (°C)	Conversion of α-methylstyrene (%)	Selectivity (%)			
			MDP-1	MDP-2	TPI	Others
1	40	48.5	92.1	7.8	0.1	0
2	60	98.7	90.8	9.1	0.1	0
3	80	99.5	71.1	27.3	1.5	0.1
4	100	100	25.8	21.4	52.8	0.1
5	120	100	0	0	100	0

[a] Reaction conditions: α-methylstyrene (10 mmol), HBF_4 (1.5 mmol), [HexMIm]BF_4 (1.0 g), 2 h

3.4 Effect of Reaction Temperature

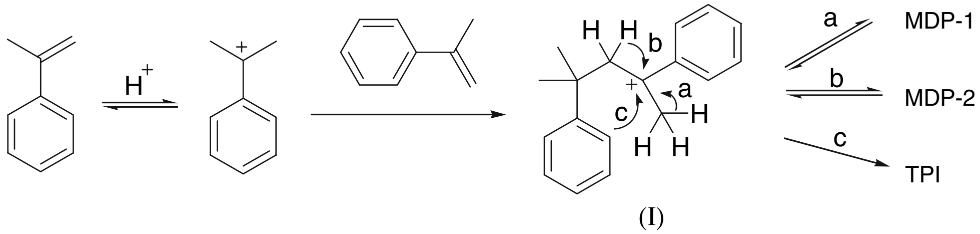
Effect of reaction temperature on α-methylstyrene conversion and product distribution in the dimerization of α-methylstyrene at the molar ratio of HBF_4/α-methylstyrene of 0.15 for a period of 2 h was depicted in Table 4. At 40 °C, the conversion of α-methylstyrene and the selectivity to MDP-1 were 48.5% and 92.1%, respectively. As the reaction temperature increased from 40 to 120 °C, the selectivity to MDP-1 decreased, while the selectivity to TPI increased. At 120 °C, 100% conversion of α-methylstyrene with 100% selectivity to TPI was obtained.

According to Chaudhuri's suggestion, a plausible mechanism of acid-catalyzed dimerization of α-methylstyrene is that one molecule of α-methylstyrene accepted one donating proton from the acid and then quickly reacted with the other free molecule of α-methylstyrene to generate a carbocation intermediate Ph–C$(CH_3)_2$–CH–$C^+(CH_3)$–Ph (**I**), which could convert to MDP-1, MDP-2 or TPI (Scheme 2) [1]. The conversion processes of **I** to MDP-1 and MDP-2 might be reversible, while **I** to TPI might be irreversible. It was confirmed by the following investigation. When MDP-1 or MDP-2 (4 mmol), together with [HexMIm]BF_4 (1 g) and HBF_4 (1.5 mmol), was stirred at 100 °C for 2 h, a mixture of MDP-1, MDP-2 and TPI could be observed via the GC analysis. On the contrary, using TPI instead of MDP-1 or MDP-2 under the same conditions, no MDP-1 and MDP-2 were detected. The next experimental result was a more powerful evidence to demonstrate this transformation between MDP-1, MDP-2, intermediate carbocation **I** and TPI. When MDP-1 was stirred at 120 °C in [HexMIm]BF_4/HBF_4 system for 24 h, it was completely converted into TPI. In addition, Peppe and co-workers have presumed that chemoselectivity towards MDP-1 was determined by kinetically controlled conditions, while thermodynamic control produced TPI [10]. Our experimental results were consistent with observations of Chaudhuri and Peppe. That is, MDP-1 was the main product at the reaction temperature of 60 °C, while TPI was the exclusive product at a high reaction temperature of 120 °C.

3.5 Reusing of [HexMIm]BF_4–HBF_4

In view of "green chemistry", reuse of the catalytic system is necessary. In the dimerization of α-methylstyrene, [HexMIm]BF_4–HBF_4 could be recovered after decanting the upper organic layer and being washed with hexane. The dimerization of α-methylstyrene was repeatedly carried out

Scheme 2 Plausible mechanism of α-methylstyrene dimerization reaction



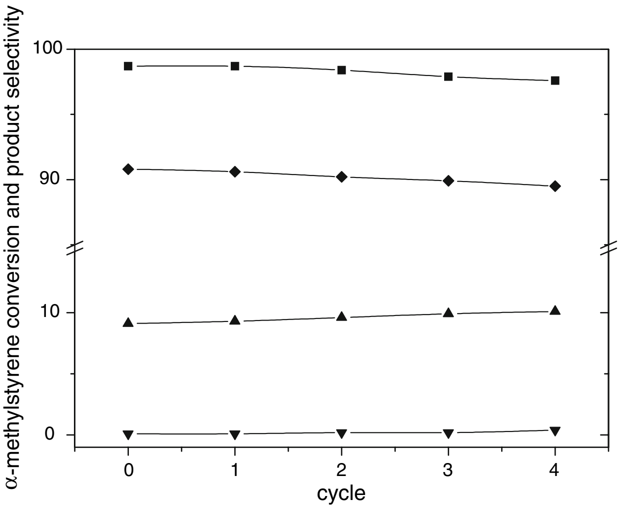


Fig. 1 Reusing of [HexMIm]BF_4–HBF_4 in the dimerization of α-methylstyrene. Reaction conditions: α-methylstyrene (10 mmol), HBF_4 (1.5 mmol), [HexMIm]BF_4 (1.0 g), 60 °C, 2 h. (■) Conversion of α-methylstyrene; selectivity to MDP-1 (◆), MDP-2 (▲), TPI (▼)

in the recovered [HexMIm]BF_4–HBF_4. As shown in Fig. 1, high conversion of α-methylstyrene (97.6%) and high selectivity to MDP-1 (89.5%) were maintained when [HexMIm]BF_4–HBF_4 was reused four times. The slight decrease of conversion and selectivity might be due to the slight loss of [HexMIm]BF_4–HBF_4 in the recycling process.

3.6 Using [BMIm]Cl · $2AlCl_3$ in the Dimerization of α-Methylstyrene

The chloroaluminate ionic liquid composed of $AlCl_3$ and [BMIm]Cl, a common Lewis acidic ionic liquid, could play the dual role of a catalyst and solvent in many reactions [15, 20, 25, 26]. It also attracts our interest to its potential application in the dimerization of α-methylstyrene. The Lewis acidity of the chloroaluminate ionic liquid varies with the molar ratio of $AlCl_3$ to [BMIm]Cl. If excess $AlCl_3$ is used, the resulting ionic liquid is acidic and the formation of the Lewis acid $Al_2Cl_7^-$ is strongly favored. When [BMIm]Cl is in excess, the ionic liquid is basic. The effect of $AlCl_3$/[BMIm]Cl molar ratio on the dimerization reaction was investigated and the results were listed in Table 5.

When the molar ratio of $AlCl_3$/[BMIm]Cl was 1, the conversion of α-methylstyrene was very low (4.9%) and the selectivity to TPI was only 11.7%. Most of the substrate was converted into undesired by-products. When the molar ratio of $AlCl_3$/[BMIm]Cl increased from 1 to 2, the satisfied result was obtained. A 100% conversion of α-methylstyrene with 100% selectivity to TPI was achieved. At the $AlCl_3$/[BMIm]Cl molar ratio of 3, the selectivity to TPI decreased to 94.2%. Therefore, the ionic liquid [BMIm]Cl · $2AlCl_3$ was the appropriate catalyst and solvent to produce TPI in the dimerization of α-methylstyrene.

In general, chloroaluminate ionic liquid [BMIm]Cl · $2AlCl_3$ possessed strong Lewis acidity. On the other hand, superacidic protons (Bronsted acid) also existed in [BMIm]Cl · $2AlCl_3$ due to the hydrolysis of a few $AlCl_3$ molecules [3, 27]. Oligomerizing of olefins to dimmers, trimers and tetramers could be catalyzed by Lewis acidic chloroaluminate ionic liquid when the formation of superacidic protons was restrained [28]. That the superacidic proton in Lewis acidic ionic liquid was considered as the active species in the dimerization reaction has also been reported [3]. Therefore, investigation aimed at identifying which acid played crucial role in this dimerization reaction was carried out with the weak base 2,6-di-*tert*-butylpyridine (DBP), which only bound to proton and was unable to coordinate to aluminum due to the bulky *tert*-butyl groups. α-Methylstyrene (10 mmol) was added to a mixture of [BMIm]Cl · $2AlCl_3$ (3 mmol) and DBP (0.6 mmol) and stirred for 2 h at room temperature. The experimental result showed that no α-methylstyrene was converted. In other word, ionic liquid [BMIm]Cl · $2AlCl_3$ was unable to induce the dimerization of α-methylstyrene in the presence of the weak base DBP. This result strongly suggested that proton was crucial for the dimerization reaction. To further elucidate the potential reaction pathway in ionic liquid [BMIm]Cl · $2AlCl_3$, an experiment to explain the transconversion was carried out. MDP-1 (5 mmol) was slowly

Table 5 Effect of $AlCl_3$/[BMIm]Cl molar ratio on the dimerization of α-methylstyrene[a]

Entry	$AlCl_3$/[BMIm]Cl (mol/mol)	Conversion of α-methylstyrene (%)	Selectivity (%)			
			MDP-1	MDP-2	TPI	Others
1	1	4.9	0	0	11.7	88.3
2	2	100 (97.5[b])	0	0	100	0
3	3	100	3.4	0	94.2	2.4

[a] Reaction conditions:
α-methylstyrene 10 mmol, ionic liquid 1.0 g, reaction time 5 min

[b] Isolated yield

added to 1 g of [BMIm]Cl · $2AlCl_3$ under stirring at −20 °C for 0.5 h. A mixture of MDP-1 (26.3%), MDP-2 (60.7%) and TPI (13.9%) was obtained. However, when the above mixture of MDP-1, MDP-2 and TPI was added to [BMIm]Cl · $2AlCl_3$ and stirred at room temperature for 2 h, MDP-1 and MDP-2 were completely converted to TPI. These results indicated that the reaction mechanism of dimerization of α-methylstyrene in [BMIm]Cl · $2AlCl_3$ was the same as the plausible mechanism depicted in Scheme 2. The environment of chloroaluminate ionic liquid was beneficial to formation of TPI.

Ionic liquid [BMIm]Cl · $2AlCl_3$ could also be recovered after decanting the upper organic layer and being washed with diethyl ether. Complete conversion of α-methylstyrene with 100% selectivity to TPI was still obtained when [BMIm]Cl · $2AlCl_3$ was reused three times.

3.7 Dimerization of 4-Chrolo-α-Methylstyrene in Ionic Liquids

Under the optimal reaction condition, 1.0 g of [HexMIm]BF_4, 1.5 mmol of 50% aqueous HBF_4 solution, the dimerization of 4-chrolo-α-methylstyrene (10 mmol) was performed at 80 °C for 2 h. Up to 95.1% conversion of 4-chrolo-α-methylstyrene was observed, the selectivities to 4-methyl-2,4-bis(4-chlorophenyl)-1-pentene, 4-methyl-2,4-bis(4-chlorophenyl)-2-pentene, 4-chloro-3-(4-chlorophenyl)-1,1,3-trimethylindan were 93.1%, 6.8% and 0.1%, respectively. While under the similar condition as the dimerization of α-methylstyrene in [BMIm]Cl · $2AlCl_3$, no reaction was observed after mixing [BMIm]Cl · $2AlCl_3$ and 4-chrolo-α-methylstyrene. Probably the electron-withdrawing substituent group resulted in the low activity of 4-chrolo-α-methylstyrene in this reaction system.

4 Conclusion

The dimerization of α-methylstyrene was studied in the presence of various catalytic systems. The catalytic systems composed of ionic liquids containing BF_4^- anion and HBF_4 showed high catalytic activity. Under the optimal reaction condition, 1.0 g of [HexMIm]BF_4, 1.5 mmol of 50% aqueous HBF_4 solution, 10 mmol of α-methylstyrene, at 60 °C for 2 h, the conversion of α-methylstyrene and the selectivity to MDP-1 were 98.7% and 90.8%, respectively. When the reaction temperature was increased to 120 °C, TPI was obtained as the exclusive product. In addition, the ionic liquid [BMIm]Cl · $2AlCl_3$ was found to work well as the catalyst and solvent in the dimerization of α-methylstyrene to form TPI. In the two different ionic liquids [HexMIm]BF_4–HBF_4 and [BMIm]Cl · $2AlCl_3$, the dimerization of α-methylstyrene performed the same reaction mechanism and the proton was the active species. Moreover, [HexMIm]BF_4–HBF_4 and [BMIm]Cl · $2AlCl_3$ could be easily reused for several times without significant loss of catalytic activity.

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