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# $SO_3H$-functionalized ionic liquid as efficient, green and reusable acidic catalyst system for oligomerization of olefins ☆

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**Abstract**

$SO_3H$-functionalized ionic liquids have been employed as an alternative reaction medium to conventional acid catalysts for oligomerization of various olefins, to produce branched olefin derivatives in high conversions and excellent selectivity. The ionic liquid plays a dual role as both catalyst and solvent, providing an efficient and reusable acidic catalyst system for the oligomerization of olefins.

*Keywords:* Ionic liquid; Olefins; Oligomerization; Catalysis

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As one of the most important areas in chemical and oil refining industries, catalytic oligomerization of lower alkenes has attracted much attention in the past years. Since the report of silica supported phosphoric acid, which was the first commercial application catalyst [1]. Various solid acids such as H-ZSM-5 zeolite [2], large-pore zeolites with high silica-to-alumina ratio [3] and cation-exchanged clays [4], were widely investigated. But till today, the poor controllability in product distribution and rapid deactivation of the catalysts were still insolvable because the restricted accessibility of uniform acidic sites, high molecular weight/active-site ratios, and water, coking resistant solid acids.

Ionic liquids have received a great deal of attentions in the last few years due to their broad range of potential uses [5]. In oligomerization reactions, chloroaluminate ionic liquid [6] was successfully used as solvents for nickel catalysts to overcome deactivation of catalysts while its sensitivity to air and water severely limited their further application. The designability of the ionic liquids gave us more chance to achieve fitful ionic liquids of special properties according to given reactions. A typical example was the appearance of the air, water stable and strong Brønsted acid ionic

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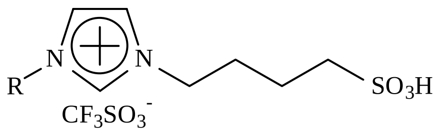
liquids, in which an alkane sulfonic acid group was covalently tethered to the imidazolium cation [7]. This series of functional ionic liquids offered a new possibility for developing environmental friendly acid catalysts because it combined the advantages of liquid acids and solid acids, uniform acid sites, water and air stable, easy separation and reusable.

In this paper, we report the use of these ionic liquids, 1-(4-sulfonic acid) butyl-3-alkylimidazolium triflate (Fig. 1, **I** and **II**), as solvent and catalyst independently for oligomerization of olefins without using other catalyst [9].

Oligomerization of olefins with different structures were conducted in the above ionic liquids **I** and **II**. As it was shown in Table 1, when the oligomerization of *i*-butene was conducted, 68% of conversion and 99% of total selectivity to $C_8 + C_{12}$, which were now regarded as one of the main alternatives for the production of high-octane gasoline, were obtained over ionic liquid **I** (entry 1). When ionic liquid **I** was replaced by **II**, the conversion reached to 94% and almost same selectivity to $C_8 + C_{12}$ was maintained (entry 2). The greatly increase in catalytic activity could be attributed to high solubility of *i*-butene in ionic liquid **II** because the lipophilicity of ionic liquid increases with the increasing of carbon number of substituted alkyl in imidazolium cation. In addition, the products of this oligomerization reaction were insoluble in these two ionic liquids and, therefore, the products could be simply decanted out from the ionic liquid after reaction. The ionic liquid could be reused directly and only slightly deactivation occurred even at the seven times (Fig. 3).

It was worth to note that 36% of $C_{12}$ selectivity in the ionic liquid **II** was three times than that obtained in the ionic liquid **I** and the reason might be attributed to the high dissolvability of $C_8$ in ionic liquid **II**. Further experiments indicated that lower reaction temperature and shorter reaction time were unfavorable for the conversion of *i*-butene (entry 3 and 4). Some $H_2O$ was added to investigate its effect on the catalytic activity of ionic liquid **II** and similar result as ionic liquid **I** was obtained (entry 5). The decrease of the lipophilicity of ionic liquid might be the main reason for this change and it also offered us a possible method to control the distribution of the products. All these results reminded us to examine other oligomerization of olefins to check the catalytic activity of the $SO_3H$-functionalized ionic liquid (see Fig. 2).



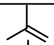
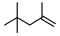
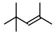
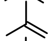
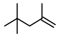
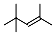
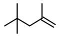
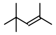
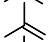
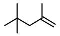
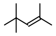
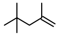
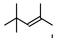
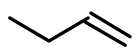
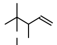
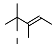
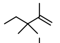
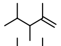
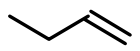
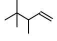
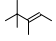
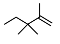
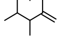
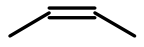
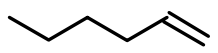
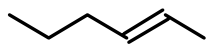
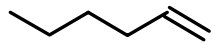
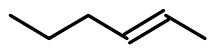
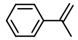
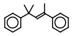
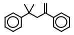
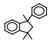
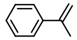
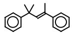
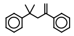
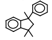
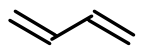
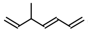
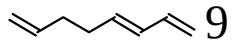
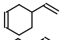
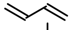
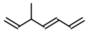
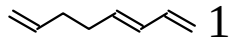
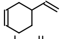
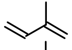
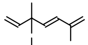
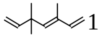
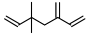
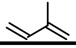
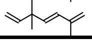
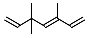
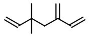
**I**: $R = CH_3$
**II**: $R = CH_2CH_2CH_2CH_2CH_2CH_3$

Fig. 1. The structure of $SO_3H$-functionalized ionic liquids.

In the oligomerization of 1-butene over the $SO_3H$-functionalized ionic liquid **I**, large amounts of 2-butene (including 2-(*E*)-butene and 2-(*Z*)-butene), which was the isomerization products of 1-butene, was detected (entry 6) while the desired $C_8$ and $C_{12}$ products were only 16% and 10%, respectively. The use of ionic liquid **II** could improve the reactivity in some extent and the selectivity to $C_{12}$ reached to 15% (entry 7). If longer terminal olefin, such as 1-hexene, was used as reactant, it was found that only isomerization reaction occurred (entry 8 and 9).

Oligomerization of α-methylstyrene was successfully conducted, especially in ionic liquid **II**. Nearly 100% of conversion was achieved and the selectivity to dimer products exceeded 90% (entries 10 and 11). Small amounts of 2,3-dihydro-1,1,3-trimethyl-3-phenyl-1-H-indene was also detected in the dimer beside 2,4-diphenyl-4-methyl-2-pentene (*E* and *Z*) and 2,4-diphenyl-4-methyl-1-pentene which indicated that alkylation between aromatic ring and olefinic bond occurred. The controllability of the $SO_3H$-functionalized ionic liquid for oligomerization of olefins was further studied by the reaction of 1,3-butadiene. In the ionic liquid **I**, 84% of $C_8$ as well as 14% of $C_{12}$ were detected in the products, it indicated that the main reaction was dimerization (entry 12). While ionic liquid **II**, the more lipophilic ionic liquid, was used as catalytic system, the selectivity to $C_{12}$ exceeded 80% (entry 13). A similar result was achieved when isoprene was used as reactant (entry 14 and 15). All these results exhibited the strong controllability of the catalytic activity by modulating the

Table 1
Oligomerization of olefins in ionic liquid with $SO_3H$[a]

| Entry | Olefins | ILs | Con. (%)[b] | Sel.(%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | dimer | trimer | isomer | tetramer |
| 1 |  | I | 68 |  65  22 | 12 | 0 | 1 |
| 2 |  | II | 94 |  46  15 | 36 | 0 | 3 |
| 3[c] |  | II | 50 |  32  11 | 56 | 0 | 1 |
| 4[d] |  | II | 67 |  41  13 | 44 | 0 | 2 |
| 5[e] |  | II | 82 |  63  21 | 15 | 0 | 1 |
| 6 |  | I | 59 |  16    | 10 |  +  74 | 0 |
| 7 |  | II | 68 |  14    | 15 |  +  71 | 0 |
| 8 |  | I | 9 | 0 | 0 |  76  24 | 0 |
| 9 |  | II | 13 | 0 | 0 |  75  25 | 0 |
| 10 |  | I | 95 |  64  21  10 | 5 | 0 | 0 |
| 11 |  | II | 99 |  60  20  11 | 9 | 0 | 0 |
| 12 |  | I | 100 |  54  9  8 Others 13 | 15 | 0 | 1 |
| 13 |  | II | 100 |  8  1  1 Others 1 | 80 | 0 | 9 |
| 14 |  | I | 100 |  21  15  23 Others 22 | 11 | 0 | 8 |
| 15 |  | II | 100 |  4  2  3 Others 1 | 79 | 0 | 11 |

[a] Reaction conditions: 10 mmol ionic liquid (3.75–4.48 g), 41.7 mmol olefin, temperature 120 °C, time 6 h.

[b] Conversion of olefins.

[c] Reaction temperature: 90 °C.

[d] Reaction time: 3 h.

[e] Added 0.75 g (41.7 mmol) water to the ionic liquid.

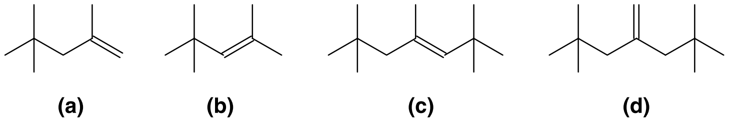


Fig. 2. The structure of $C_8$ and $C_{12}$ in oligomerization of *i*-butene.

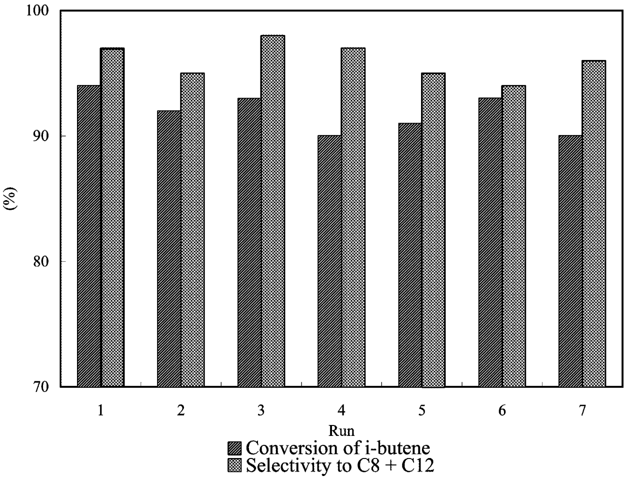


Fig. 3. Reuse of ionic liquid **II** in the oligomerization of *i*-butene.

structure of the $SO_3H$-functionalized ionic liquids. In addition, our acidic ionic liquid system should represent a potential advantage in selectivity to $C_8$ + $C_{12}$ in comparison with conventional solid catalysts which are very difficult to restrict the further oligomerization of *i*-butene [8].

In summary, the ionic liquids attached by $SO_3H$ could be effective, green and reusable catalysts and solvents for oligomerization of olefins. Particular in the reaction of isobutene, high selectivity to $C_8$ + $C_{12}$ was an important feature in comparison with conventional solid acidic materials. The reactivity of olefins can be controlled by the structure of ionic liquid and it could be reused for several times even without deactivation.

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[9] General procedure: the preparation of ionic liquids **I** and **II** were according to [7]. Spectroscopic data for ionic liquid **I**: $^1$H NMR (400 MHz, $D_2O$, neat 25 °C; $\delta$9.161 (s,1H), 7.782 (s,1H), 7.748 (s,1H), 4.210 (t,$J = 7.2$,2H), 3.891 (s,3H), 2.685 (t,$J = 7.2$,2H), 1.903 (q,$J = 7.6$,2H), 1.605 (q,$J = 4.6$, 2H), $C_9H_{15}F_3O_6N_2S_2$ (368.36): calcd. C 29.34, H 4.10, N 7.61, S 17.41; found C 29.39, H 4.28, N 7.54, S 17.27. All reactions were conducted in a 90 ml autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, 0.01 mol ionic liquid (7.2–8.6 g), 0.04 mol olefin were successively introduced and reacted at 120 °C for 6 h. After the reaction, cooled the autoclave to room temperature (the autoclave was cooled to −40 °C when gaseous olefin is used), then the upper organic phase containing the oligomeric products was simply separated from the ionic liquid by decantation. The dissolved organic product in ionic liquid can be removed by distillation under vacuum, and the distillate was combined with upper organic phase followed by GC analysis. The ionic liquid could be reused in next run without any additional treatment. Qualitative and quantitative analyses of organic products were conducted with a HP 6890/5973 GC/MS and a HP 1790 GC equipped with a FID detector. The concentration of reactant and product was directly given by the system of GC chemstation according to the area of each chromatograph peak.