Preparation and characterization of acidic ionic liquids for alkylation of isobutene with 2-butene

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Introduction

Alkylation of isobutane with 2-butene is an industrially significant process, since the ensuing products, alkylates, have high octane numbers and clean burning characteristics [1]. However, the capacity of the alkylation process is relatively small due to constraints imposed by the use of highly corrosive and environmentally detrimental sulphuric and hydrofluoric acid as commercial catalysts. Even though solid acid catalysts have been investigated, they have yet to achieve commercial use as alkylation catalysts because of rapid catalyst decay [2]. Consequently, there is ongoing interest in replacing conventional liquid acids with newer clean catalysts.

Room temperature ionic liquids (RTILs) have received wide spread attention as an alternative to conventional volatile solvents with potential applications [3]. Most of these ionic salts are good and stable solvents for a wide range of organic and inorganic materials. They are polar but consist of poorly coordinating ions and provide a polar alternative for biphasic systems. Other important attributes of these ionic liquids include negligible vapor pressure, potential for recycling, compatibility with various organic compounds.

In the alkylation of isobutane with 2-butene, the salient features of a good homogeneous catalyst and reaction media are the acid strength and the solubility of isobutane in the catalyst [1]. The protonation of the olefins in the feed is dependent on the acidity of the catalyst, whereas the amount of the carbenium ions formed strongly depends on the solubility of isobutane. From this point of view, various 1-alkyl-3-methylimidazolium halides-aluminum halides [CnMIM]X-AlX_3 (where n = 4, 6, and 8) have been examined as a potential relatively benign catalyst for this reaction and our results on activity and selectivity of the catalysts are summarized.

Experimental

A number of 1-alkyl-3-methylimidazolium halides-aluminum halides ([CnMIM]X-AlX_3

where X= Cl, Br, I) are prepared and characterized using protocols described earlier [4]. The aluminum halide melts are prepared by careful mixing of anhydrous aluminum halides with 1-alkyl-3-methylimidazolium halides under inert atmosphere. The activity of the ionic liquids prepared for the alkylation is then evaluated using a continuous–flow reactor. The experiments are carried out in a double walled glass reactor with constant supply of gaseous mixture of isobutane and 2-butene (molar ratios = 20) at atmospheric pressure. In all experiments, 15 g of ionic liquid is used and the reactor effluents are taken periodically and then analyzed using a gas chromatograph.

Results and Discussion

Catalytic activities determined for the alkylation of isobutane with 2-butene over various ionic liquids are depicted in Fig. 1. The ionic liquids bearing a larger alkyl group on their cation ([C_8MIM]) exhibit higher a activity than a smaller one ([C_6 or C_4 MIM]) with a same anion composition, either Cl-$AlCl_3$ or Br-$AlCl_3$ for entire reaction time. This is attributable to the high solubility of ionic liquid for the feed, especially isobutane. This useful property of ionic liquid can be adjusted by variation of the alkyl group on the cation. This study corroborates the earlier report that with increasing length of alkyl group, the solubility of hydrocarbons increases significantly [5] and is in good agreement with our alkylation results (see Fig. 1).

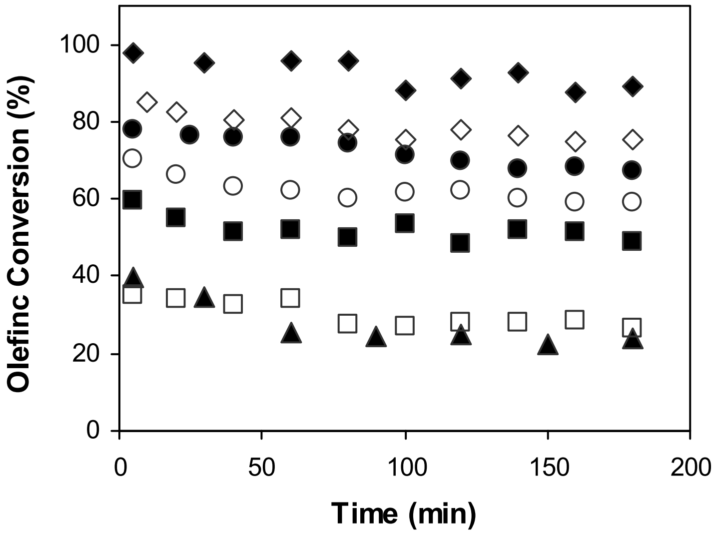

Figure 1. Catalytic conversion of 2-butene versus reaction time over various ionic liquids: [C_8mim]Br-$AlCl_3$ (♦), [C_8mim]Cl-$AlCl_3$ (●), [C_8mim]I-$AlCl_3$ (■), [C_6mim]Br-$AlCl_3$ (◊), [C_6mim]Cl-$AlCl_3$ (○), [C_4mim]Br-$AlCl_3$ (□), and [C_4mim]Cl-$AlCl_3$ (▲). Reactions were performed at LHSV = 24 h^{-1} and 80 °C.

Among the ionic liquids with same alkyl group on their cation, [C_8MIM]Br-$AlCl_3$ is shown to outperform others under identical experimental conditions. The higher activity is believed to be a result of adequate acidic nature of the catalyst determined by anion group. According to the accepted mechanism [1], the primary alkylation reaction is completed by a hydride transfer reaction, which requires strong acidic sites. Hence, strong acid strength is crucial to maintain stable activity. It is reported that the bromide containing aluminates are more acidic than the corresponding chloride ones [3]. Present study also shows that the reactivity of the bromide based aluminates are higher than the corresponding tetrachloroaluminates.

The change in olefin conversion with time on stream for H_2SO_4 and the ideal ionic liquid ([C_8mim]Br-$AlCl_3$), which showed most desirable performance, is illustrated in Fig. 2. It can be seen that both catalysts showed different catalytic behaviour under identical reaction conditions (LHSV = 240 h^{-1} and temperature = 80 ^{o}C). For sulfuric acid system, even though it showed very high activity initially, the olefin conversion quickly decreases with time on stream. It is mainly attributed to the formation of acid soluble oil (ASO) also referred to as conjunct polymers or red oil. According to the open literature, these materials have empirical compositions of about $(C_{1.0}H_{1.75})_n$, where n averages from about 10 to 30 [6]. These highly unsaturated cyclic hydrocarbons relatively rapidly deactivate the acid catalyst [7].

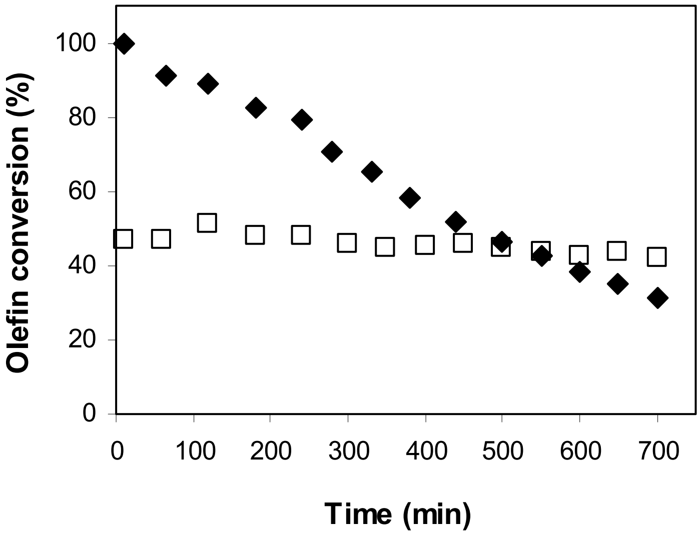

Figure 2. Catalytic conversion of 2-butene versus reaction time over [C_8mim]Br-$AlCl_3$ (□) and H_2SO_4 (♦).Reactions were performed at LHSV = 24 h^{-1} and 80 ^{o}C.

In the case of bromide bearing ionic liquid, the olefin conversion barely changed during the entire reaction time. This catalytic stability can be explained by the tunable coordinating ability of the anions. Highly electrophilic metal center involved as the active sites can be stabilized in the solvent without loss of their activity [8]. Moreover, the ionic liquid employed in this study can be considered as a biphasic system. In the case of biphasic catalysis it is assumed that the active catalytic species is soluble in the solvent but reaction products, especially heavier hydrocarbons, are however not [9]. The hydrocarbon materials dissolved in ionic liquid were identified to support the above discussion. Most of the extracted carbonaceous species from spent ionic liquid are smaller than C8 hydrocarbon e.g. 2,3-dimethylbutane, 3-methylpentane, 2-methyl-2-petene, n-hexane, 3-methylhexane and isoheptane. This means that larger hydrocarbons causing deactivation of acidic sites, such as ASO, were barely formed in ionic liquid and hence, ionic liquid can be used as a stable catalyst for this reaction.

The change of C8 product distribution with respect to reaction time is showed in Fig. 3A and 3B. At the initial stages of the reaction, generally, sulfuric acid maintains a high hydrogen transfer and cracking activity, which suppresses the formation of bulky carbonaceous materials. The 2-butene molecules react with butyl carbenium ions to form C8 intermediates, which then transform into the main products, such as trimethylpentanes (TMPs) or dimethylhexanes (DMHs) [1]. Thus, the primary alkylation activities are dominant at the initial stage of the reaction. After a certain time on stream, the stronger acidic sites, which form alkylated products (mainly TMPs) deactivate faster than weak and medium acidic sites. This results in a rapid decrease in TMP, while weaker acidic sites still remain active for olefin oligomerization, which produces olefins and heavier products (ASO). In ionic liquid system, however, C8 product distribution hardly changed with time on stream.

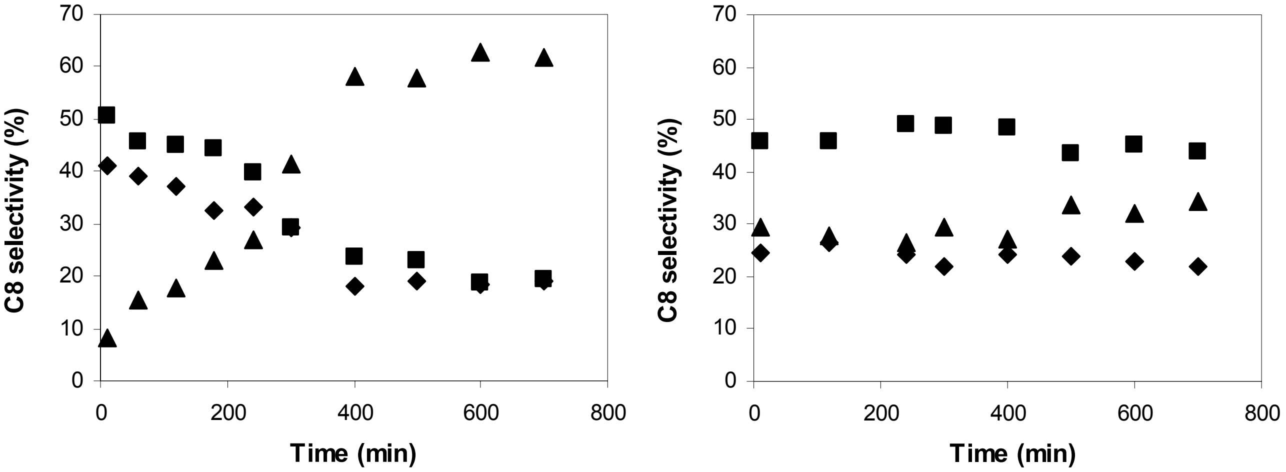

Figure 3. Selectivity of C8 products versus time on stream for TMPs (◆), DMHs (■) and Olefins (▲) over (A: left) H_2SO_4 and (B: right) [C_8mim]Br-$AlCl_3$. Reactions were performed at LHSV = 24 h^{-1} and 80 °C.

The influence of liquid hourly space velocity (LHSV) on olefin conversions with respect to the time on stream is illustrated in Fig 4. For sulfuric acid system, a rapid decrease of the olefin conversion was observed with increasing LHSV of reactants (see Fig. 4A). This deactivation behavior is typical in the hydrocarbon reaction; large amount of olefin introduced into system can lead to the formation of coking materials by oligomerization. The olefin concentration in the acid phase is presumably increased with LHSV and then subsequent oligomerization accelerates the deactivation of catalyst.

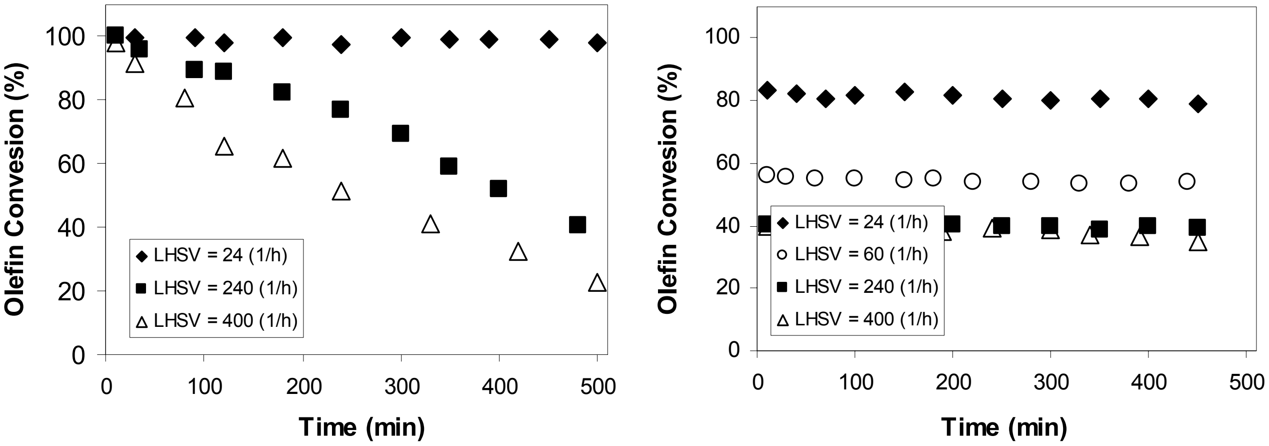

Figure 4. Catalytic conversion of 2-butene versus reaction time with various LHSV over (A: left) H_2SO_4 and (B: right) $[C_8mim]Br-AlCl_3$ at 80 °C

In contrast, ionic liquid exhibited a different trend as shown in Fig 4B. In lower LHSV conditions (24 h^{-1}), the catalytic activity was very high without further deactivation. With increasing LHSV, the catalytic activity decreased gradually. This reduction of catalytic activity is mainly attributed to the fact that resident time of reactants decreased with LHSV. At higher LHSV condition, some of reactant passed over acid site without being involved in the reaction. Interestingly, higher than 240 h^{-1} of LHSV, the activity remained at the same level. Thus, the ionic liquid can always yield higher than 40% of olefin conversion at this reaction temperature (80 °C).

The olefin conversion obtained with time on stream over both catalysts is shown with different reaction temperature in Fig. 5. For sulfuric acid, it can be observed that the olefin conversion decreased rapidly with increasing reaction temperature. This is attributed to oxidation reactions, leading to the formation of ASO, are sensitive to temperature. At temperatures above (25 °C), oligomerization of olefin becomes significant and the activity decreased with temperature.

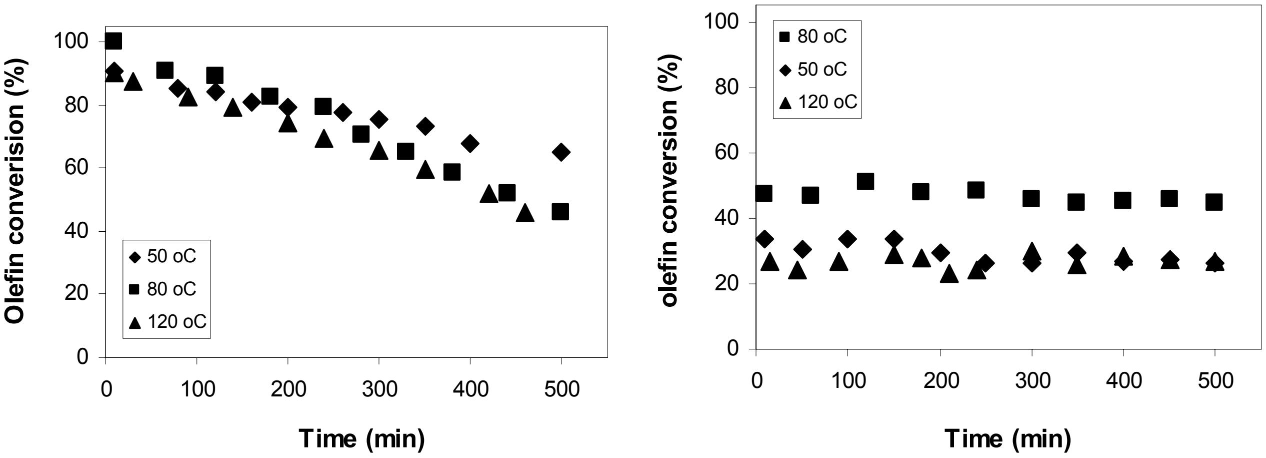

Figure 5. Catalytic conversion of 2-butene versus reaction time with various reaction temperature over (A: left) H_2SO_4 and (B: right) [C_8mim]Br-$AlCl_3$ at LHSV = 240 h^{-1}.

For ionic liquid, one can observe maximum activity at 80 ^{o}C (see Fig. 5B). This result can be explained by the fact that the acidity of ionic liquid as a coordination catalyst is affected by the reaction temperature. Coordination catalysts (consisting of a metal atom or ion, surrounded by a number of electron-pair donors called ligands) can be adjusted by ligand variation. The catalyst complex is generally stable in more than one coordination number and through alteration of chemical bond strength, capable of holding a substrate molecule selectively [10]. These catalysts, therefore, show diversified range of activities [11]. Based on well known mechanism [3], the anionic chemistry of the addition of bromide to aluminium chloride can be described simply by reaction (1)-(3).

$$[Al_2Cl_6] + Br^- \rightarrow [Al_2Cl_6Br]^- \quad (1)$$

$$2[AlCl_3Br]^- \leftrightarrow [Al_2Cl_6Br]^- + Br^- \quad (2)$$

$$2[Al_2Cl_6Br]^- \leftrightarrow [Al_3Cl_9Br]^- + [AlCl_3Br]^- \quad (3)$$

In acidic condition, various anions, such as $[AlCl_3Br]^-$, $[Al_2Cl_6Br]^-$ and $[Al_3Cl_9Br]^-$, can exist. The acidity of an ionic liquid is essentially determined by composition of these anions. Furthermore, strong Lewis acid, $[Al_2Cl_6Br]^-$, can react with hydrogen atom at the 2-position of an imidazolium ion to form Brønsted acid [12, 13] as described in reaction (4).

$$[Al_2Cl_6Br]^- + H^+ \leftrightarrow [AlCl_3Br]^- + [AlHCl_3]^+ \quad (4)$$

Thus, the acidity of ionic liquid can be transformed by the formation of anions determined by the reaction conditions. From the product distribution, it was observed that the nature of acidity could be altered with reaction temperature as shown in Fig. 6. Predominant yield of olefins (85 %) were observed when the reaction was performed at 50 and 120 ^{o}C possibly due to oligomerization activity over dominant Lewis acid at these conditions. In contrast, a large amount of primary product (TMPs) was obtained in alkylation activity at 80 ^{o}C. Based on well-known alkylation mechanism [1], both alkylation and oligomerization are strongly dependant on the nature of acidity. The alkylation and oligomerization usually occur over Brønsted and Lewis acid, receptivity. Hence, the existence of $[AlHCl_3]^+$ as a Brønsted acid could maintain the optimum acidity of ionic liquid determining catalytic performance at this temperature.

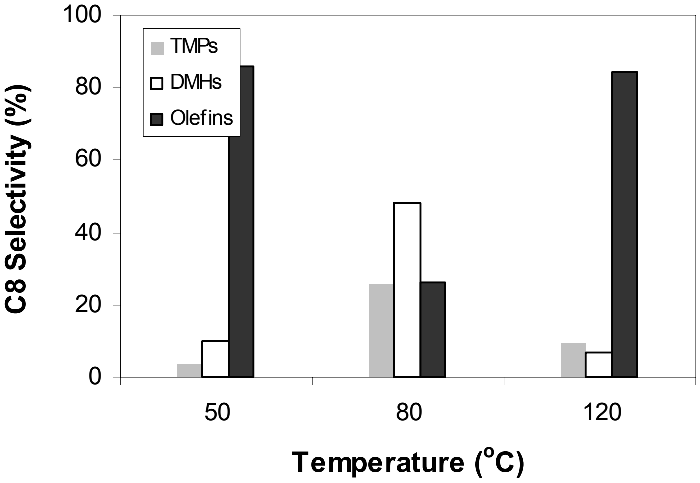

Figure 6. Selectivity of C8 products versus reaction temperature for $[C_8mim]Br\text{-}AlCl_3$ at time on stream 200 min and LHSV = 240 h^{-1}.

Conclusion

Alkylation of isobutane with 2-butene with various 1-alkyl-3-methylimidazolium halides-aluminium chloride catalysts has been successfully demonstrated. Among theses ionic liquids, $[C_8mim]Br\text{-}AlCl_3$ displayed the best performance in terms of activity and selectivity for this reaction. Unlike sulfuric acid, this ionic liquid hardly lost catalytic activity under a variety of reaction conditions in view of the reduced formation of heavy carbonaceous material which mainly causes the deactivation of catalyst. Moreover, the selectivity of C8 product over the ionic liquid was barely changed during the entire reaction time. The catalytic performance of the ionic liquid used in the study is significantly affected by resident time of the reactants and the temperature. Especially, a maximum activity observed at 80 °C is believed to be a result of an optimal level of acidity.

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