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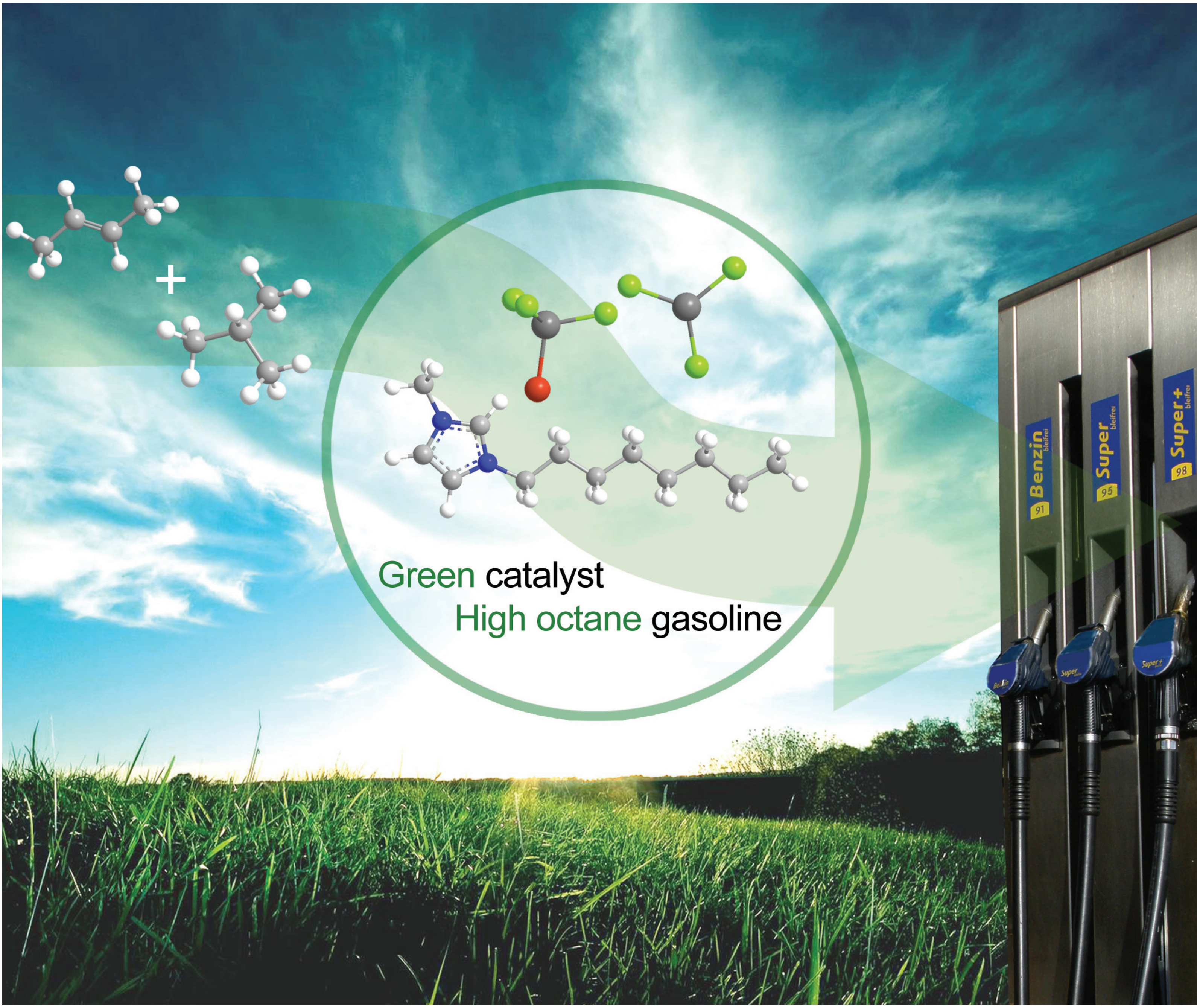

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Alkylation of isobutane with 2-butene using ionic liquids as catalyst

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Alkylation of isobutane with 2-butene was performed in a batch reactor using the ionic liquid 1-n-octyl-3-methylimidazolium bromide aluminium chloride ([OMIM]Br-$AlCl_3$) pure, and in a mixture with compounds containing SO_3H-groups. The acidity of the ionic liquid (IL) was modified by the addition of acid cation exchange resins (dry or with a small amount of water), or by the addition of a second IL ([(HO_3SBu)MIM]HSO_4). A high content of the desired trimethylpentanes (up to 64%) and thus a high research octane number (RON up to 96) of the alkylate was obtained. The reusability of the IL systems was studied and compared with a catalyst commercially used at present (H_2SO_4).

1. Introduction

Alkylation of C_4-isoparaffins with C_4-olefins forms an alkylate consisting of branched paraffins which are useful as a high octane and environmentally friendly blending component for gasoline.[1,2] The two industrial catalysts employed at present are sulfuric acid and anhydrous hydrofluoric acid. However, the application of the alkylation process is restricted as both acids are highly or extremely toxic (HF), corrosive, and harmful to the environment.[3,4] Of the two, H_2SO_4 is safer because it stays in the liquid form at ambient conditions, but the consumption of H_2SO_4, which is the result of the formation of tars and SO_2, is high (up to 100 kg per t-alkylate). Furthermore, legislation (*e.g.* of the US) is directed to restriction or even elimination of HF in alkylation units. Thus, research is now focused on the need for less hazardous and more effective catalysts.

The success of zeolites in fluid catalytic cracking, which can be viewed as the reverse of alkylation, has triggered the research on solid acid catalysts as potential substitutes to overcome the problems associated with conventional alkylation catalysts. Although the alkylation performance of solid acid catalysts is (initially) remarkable the rapid deactivation by formation of carbonaceous deposits is still an important drawback.[1,5–7] The regeneration costs are high and the activity cannot be completely recovered. In the past ten years, researchers have investigated the use of supercritical fluids (SCF) like SC isobutane as media for solid acid catalysed alkylation in order to extract the carbon deposits from the porous network.[8–10] By this means, the lifetime of the solid acid catalyst (*e.g.* of the promising zeolite H-Beta) is enhanced by cleaning of the external surface of the small zeolite crystallites.[10] Nevertheless, deactivation still takes place to a certain extent, and the efficiency of SCFs to remove carbon deposits within the micropores remains questionable.[10]

Ionic liquids (ILs), especially acidic ILs, are recognised as very promising candidates to manage the handicaps of industrially employed homogeneous catalysts (HF, H_2SO_4) as well as solid catalysts (zeolites) investigated up to now as alternatives. This is attributed to the fact that physical and chemical properties of ILs depend on the constitution and configuration of the cation and anion, and can be tuned resulting in a broad variety of applications: liquid/liquid extraction,[11,12] membrane separating processes,[13] catalysis,[14] electrochemistry,[15] biocatalysis[16] and polymerisation.[17] Ionic liquids are stable with a wide range of organic and inorganic materials, have very low vapour pressures, and potential for recycling. Some ILs are immiscible in organic compounds, thus separation (after mixing and reaction) is straightforward. Particularly important for alkylation is that the Brønsted as well as the Lewis acidity of ILs can be tuned from neutral to superacidic,[18] which makes them promising alkylation catalysts since highly acidic catalysts are required. According to the accepted mechanism, highly Brønsted acidic protons are the catalytic active species.[19] Such species can be generated from the interaction between a strong Lewis acid and a Brønsted acid which has been demonstrated for Lewis acidic chloroaluminate ILs with HCl.[20]

The acidity is a crucial parameter in alkylation and is controlled by the molar fraction of the Lewis acid and the addition of electron donating substances *i.e.* CuCl, benzene, nitrogen bases *etc*. Hence, most research is done with ILs based on strong Lewis acids like $AlCl_3$, $ZrCl_4$, or BF_3.[21–25] Depending on the acidity, ILs show catalytic performances from poor to very good; too highly acidic ILs enhance oligomerisation and cracking, which leads to a decrease of the yield and quality (octane number) of the alkylate.

Highly acidic protons are inherently present in halogenoaluminate ILs due to the reaction of $AlCl_3$ with the cation, or traces of water if the preparation is not done in a very dry atmosphere. Therefore, the Brønsted acidity of such halogenoaluminate ILs depends directly on the Lewis acidity and on the molar ratio of $AlCl_3$, respectively, since anions of Lewis acidic melts like $[Al_2Cl_7]^-$ or $[Al_3Cl_{10}]^-$ represent the dissolved aluminium chloride available to form the active species.

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The high potential of ILs as an alkylation catalyst is best expressed by the fact that an industrial alkylation plant in China is now running with an IL as the catalyst[26] although further details (*e.g.* structure of the IL) have been up to now not reported. The use of ILs was also studied by industrial companies, *e.g.* by the IFP in a pilot plant,[18] but to the best of our knowledge, a technical realisation was up to now not reported.

In the present paper, the catalytic performance of 1-n-octyl-3-methylimidazolium bromide aluminium chloride ([OMIM]Br-$AlCl_3$) based ILs was investigated for the alkylation of isobutane and 2-butene. The acidity of the IL was modified by addition of water, acid cation exchange resins or 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate [(HO_3SBu)MIM]HSO_4. The activity, selectivity and deactivation behaviour with and without additives were studied in order to find the best catalytic composition.

2. Experimental

2.1 Preparation of ionic liquids

1-Methylimidazole supplied by BASF was purified before use. 1-Bromooctane was purchased from Fluka and used without further purification. Aluminium chloride was purchased from Merck and used without further purification.

1-Methyl-3-octylimidazolium bromide ([OMIM]Br). Equimolar amounts of 1-methylimidazole and 1-bromooctane were added in a flask containing a magnetic stir bar. The flask was connected to a reflux condenser and immersed in an oil bath. The reaction mixture was stirred for about 100 h at 70 °C. Unreacted material was removed under vacuum at 110 °C. The residual ionic liquid was washed three times with ethyl acetate and then dried under vacuum at 110 °C.

1-Methyl-3-octylimidazolium bromide aluminium chloride ([OMIM]Br-$AlCl_3$). The reaction was performed in a Schlenk flask containing a magnetic stir bar under an inert atmosphere. Aluminium chloride was slowly added under stirring to [OMIM]Br and cooled with an ice bath to avoid a temperature increase due to the exothermic reaction. After complete addition of $AlCl_3$, the cooling bath was removed and the reaction mixture was allowed to warm up to ambient temperature.

1-(4-Sulfobutyl)-3-methylimidazolium betaine [(^-O_3SBu)-MIM]$^+$. During 30 minutes, 27.2 g (0.2 mmol) of 1,4-butanesultone was added dropwise into a stirred solution of 16.4 g (0.2 mmol) of 1-methylimidazole and 10 ml of toluene. The mixture was stirred at room temperature for 4 days. The precipitate was washed three times with toluene and dried under vacuum.

1-(4-Sulfobutyl)-3-methylimidazolium hydrogensulfate [(HO_3-SBu)MIM] HSO_4. [(^-O_3SBu)MIM]$^+$ was added to a round bottomed flask. Then an equimolar amount of sulfuric acid was added dropwise. The mixture was stirred for 6 h at 80 °C, washed twice with 30 ml of toluene and ether to remove non-ionic residues, and finally dried under vacuum at 120 °C.

2.2 Pre-treatment of resin

Two sulfonic resins (Amberlyst 15 (H), Dowex Marathon (H)) were purchased from Sigma Aldrich. The particles with a diameter in the range of 0.35 to 0.85 mm (Dowex) and 0.35 to 1.2 mm (Amberlyst) were used as received. Before use, the resins were pre-treated by washing with methanol, water and 4% NaOH solution, and rinsing with deionised water. Then the resin was put into the protonated form with a 15% solution of H_2SO_4 and finally rinsed with deionised water until the washing water was free of acid. The resin was stored in deionised water.

2.3 Alkylation

The reaction was carried out in a batch autoclave under argon atmosphere. Isobutane was charged into the reactor, which contained the IL catalyst. The resulting mixture was stirred for 30 min for good contact between the IL and isobutane. Then 2-butene was charged into the reactor. The molar ratio of isobutane to 2-butene was adjusted to a value of 13 to 1. The mixture was stirred for 60 min at 5 °C and 600 kPa, which leads to almost complete conversion of 2-butene (> 98%). The product was analysed by gas chromatography. To characterise the result of each alkylation experiment, the product composition (without unconverted isobutane) was calculated. The alkylate selectivity was defined as the ratio between the total weight of products (C_{5+}) and the weight of converted butene. For pure (true) isobutane–butene alkylation one should have a selectivity of 204 wt% whereas for butene dimerisation one should have 102 wt%. For multiple alkylation (C_8 + 2-butene → C_{12}) one should expect a value of 152%. In all experiments (including those conducted with H_2SO_4 as the catalyst), the conversion of isobutane was almost complete (> 98%). Hydrocarbons with less than 5 carbon atoms were only formed in a negligible extent (< 1%). The RON was calculated based on the alkylate composition—without unconverted isobutane—and the RON of all individual compounds.

3. Strategy of catalyst selection

It is the target of the alkylation to produce high octane gasoline. In order to maximise the yield of the desired trimethylpentanes (TMPs), a certain acidic regime is needed. Leaving this regime leads to an enhancement of side reactions. In order to generate suitable systems we followed different routes.

Firstly, the acidity was adjusted by variation of the molar fraction of the Lewis acid $AlCl_3$. Hereby, we gained our standard acidic ionic liquid catalyst in the [OMIM]Br-$AlCl_3$ system. The molar fraction x of $AlCl_3$ is simply calculated by:

$$x = \text{mol of } AlCl_3/(\text{mol of } AlCl_3 + \text{mol of [OMIM]Br})$$

Lewis acidic ILs usually have a molar fraction of $AlCl_3$ in the range of 0.5 to 0.67 since higher fractions lead to solids at low or ambient temperatures. Hence, the influence of the fraction of $AlCl_3$ on the product distribution was studied in this range to determine the optimal $AlCl_3$ fraction and to establish a reference halogenoaluminate IL. Thereafter, the effect of protic additives on the alkylation was studied based on this reference.

The structures of the model IL [OMIM]Br-$AlCl_3$ and of the sulfonic acid containing additives are depicted in Fig. 1.

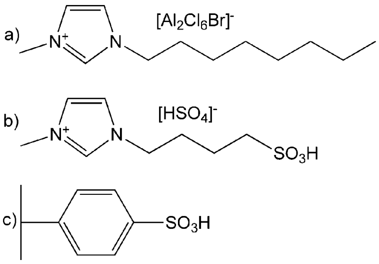
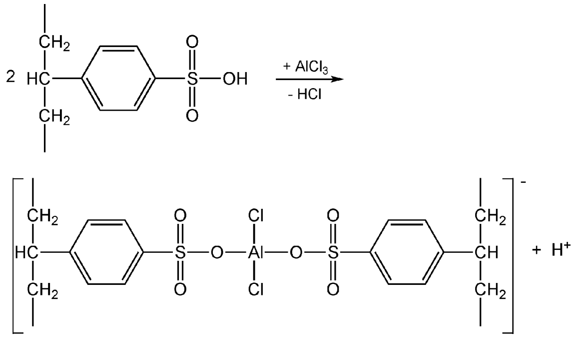


Fig. 1 Structure of IL catalysts and resins studied; (a): 1-n-octyl-3-methylimidazolium bromide aluminium chloride ([OMIM]Br-$AlCl_3$); (b): 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate ($[(HO_3SBu)MIM]HSO_4$); (c): sulfonic acid resins.

Since highly or superacidic protons are needed, we followed two routes to generate such species. One route to obtain such Brønsted acidic ILs is the mixing of a Brønsted acid and an IL with Lewis acidic sites. Here, we investigated water and a Brønsted acidic IL (1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate). Both compounds react with the Lewis acid ($[Al_2Cl_7]^-$) resulting in a conjugate Brønsted–Lewis superacid. Therefore, the source of superacidic protons is the formation of binary superacids.

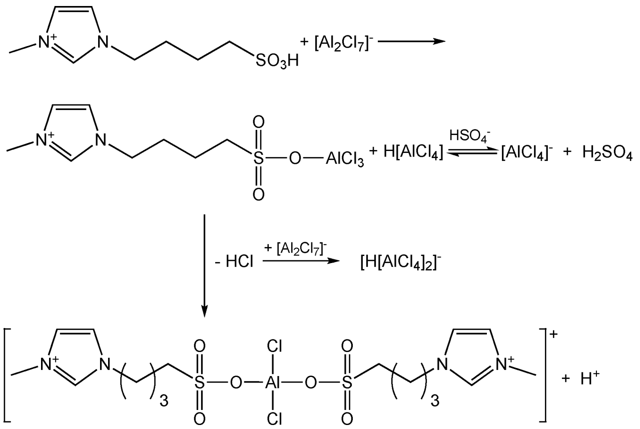
A further concept forming superacidic protons in ILs is the reaction of a sulfonic acid containing polymeric resin with a Lewis acidic IL resulting in a Lewis acid-complexed sulfonic acid resin (Scheme 1).



Scheme 1 Formation of superacidic protons by reaction of an acidic resin with $AlCl_3$.[31]

Resins like Dowex 50 are comparable in acid strength to HCl.[27] Gates and co-workers showed that the acidity of these resins increases significantly by treating them with a strong Lewis acid like $AlCl_3$.[28–30] Such resin catalysts successfully isomerise and crack n-hexane.[28] We concluded that ILs treated with such resins or with Brønsted acidic ILs containing sulfonic acid groups, may lead to species suitable for catalysing the alkylation of isobutane and 2-butene. Furthermore, we assumed that the addition of small amounts of water to resin-IL systems should have a supporting effect on the product distribution. The reaction of the Lewis acidic halogenoaluminate with the resins leads to a complex depicted in Scheme 1.[31] Here, the superacids are formed by the reaction of two sulfonic acid groups of the resin with the Lewis acid (Scheme 1). Thereby, HCl is formed and reacts with the $[Al_2Cl_7]^-$ anions. If the acid generated from the resin and $AlCl_3$ is stronger when compared to $H[AlCl_4]$, the latter is formed and is capable of moving through the IL since it is dissolved in there. Hence, more catalytically active species are available for the hydrocarbons in the IL layer, where the alkylation takes place which reduces or prevents polymer formation.

If 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate ($[HO_3SBuMIM]HSO_4$) is used, $AlCl_3$ is able to react either with the cation or anion. In both cases, highly acidic protons are formed (Scheme 2). Analogously to the mechanism shown in Scheme 1, the reaction of the sulfonic acid group with $AlCl_3$ leads to a dimeric structure generating superacidic protons which can react either with the hydrogensulfate or the $[Al_2Cl_7]^-$ anion species. Again, highly acidic protons are formed. On the other hand, the Lewis acid is able to react with hydrogensulfate which leads to HCl and another highly acidic proton. In return, the HCl interacts with the $[Al_2Cl_7]^-$ anion leading to $H[AlCl_4]$ which is regarded as a superacid.



Scheme 2 Formation of superacidic species by the reaction of Brønsted and Lewis acidic ionic liquids.

With regard to the optimal reaction conditions for alkylation, the temperature, efficient stirring, the paraffin/olefin ratio, and the residence time are important parameters. Here, we present only the results of the influence of the catalyst. The influence of the reaction conditions were determined in separate experiments (details in ref. 32). For the conditions of the experiments in this work, the conversion of 2-butene was always almost complete (> 98%). It was also proven that the product distribution does not change by consecutive reactions when complete conversion of 2-butene is reached.

4 Results and discussion

4.1 [OMIM]Br-$AlCl_3$ without additives as alkylation catalyst

Mixtures of a dialkylimidazolium bromide and a strong Lewis acid were chosen because the anionic species formed, $[AlCl_3Br]^-$ or $[Al_2Cl_6Br]^-$, show higher Lewis acidity compared to complexes containing only chloride as the halogenide. These species were already successfully tested for the alkylation of isobutane with 2-butene.[22] The experiments were carried out with different fractions of $AlCl_3$ in order to find the best composition of the [OMIM]Br-$AlCl_3$ system. The molar fraction was chosen in the range from 0.56 to 0.66 (Fig. 2).

The acid strength of the ILs affects the alkylate quality and is similar to the influence found for sulfuric acid.[33] According to Corma and Martinez,[19] the acid concentration in H_2SO_4 alkylation plants must be maintained at about 90% by adding

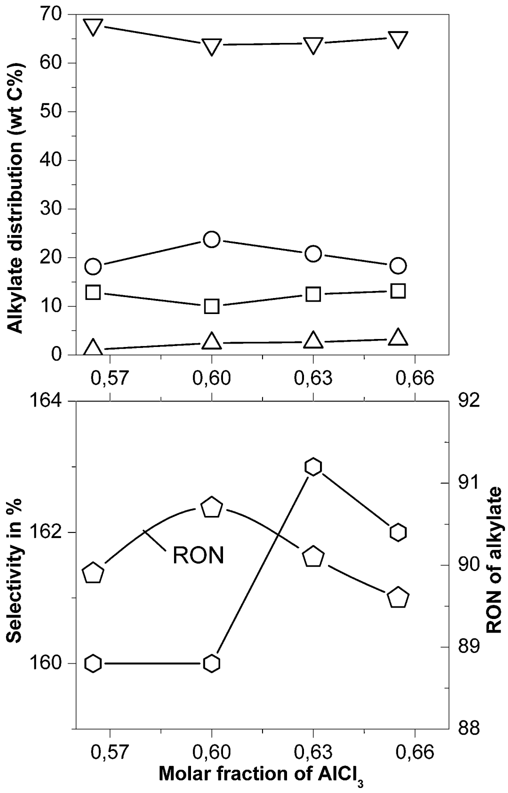


Fig. 2 Effect of [OMIM]Br-AlCl$_3$ acidity (molar fraction of AlCl$_3$) on the alkylate quality (5 °C; 600 kPa; stirring time = 60 min; IL/olefin mol ratio = 0.4, □ C$_5$–C$_7$, ○ TMPS, △ other C$_8$, ▽ C$_{9+}$).

fresh acid of about 99% purity. At concentrations higher than 99%, reaction of SO$_3$ with isobutane occurs, and below 85% concentration the activity of the catalyst is substantially decreased. Maximum quality and alkylate yield are usually obtained with 96 wt% H$_2$SO$_4$.

The acidity of the [OMIM]Br-AlCl$_3$ systems was not determined in this work, but obviously the range of the molar fraction of AlCl$_3$ studied in this work span a Brønsted acidic range comparable to that of concentrated pure sulfuric acid.

Fig. 2 (top) shows that the fraction of AlCl$_3$ affects the product distribution. The highest content of the desired TMPs (about 22 wt%) was obtained with x = 0.6, which also leads to the highest octane number (91, Fig. 2, bottom). Within the TMP isomers, 2,2,4-TMP is the main isomer (about 55%), followed by 2,3,4-TMP (about 25%) and 2,3,3-TMP (about 20%). 2,2,3-TMP was not detected. (This composition of the TMP-fraction was almost the same for all experiments except of the experiment with H$_2$SO$_4$, where 30% 2,2,3-TMP, 21% 2,3,4-TMP, and 49% 2,2,4-TMP were found.)

The alkylate selectivity was about 160% which indicates that not only does true isobutane–butene alkylation take place (selectivity of 204 wt%) but also butene dimerisation (selectivity of 102 wt%) and multiple alkylation (*e.g.* C$_8$ + 2-butene → C$_{12}$) with a selectivity of 152%. A lower or higher content of AlCl$_3$ than 0.6 leads to more by-products by oligomerisation and by cracking.

For all experiments, the IL-catalysts were synthesised under a dry inert atmosphere. Thus, the contamination by water and therefore the formation of Brønsted acidic sites (which speeds up the alkylation) can be assumed to be negligible. Although the TMPs content (max. 22 wt%) and RON (max. 91) are then still only moderate (Fig. 2), this ensures an accurate investigation of the influence of additives on the selectivity of the alkylation.

4.2 Effect of water addition on the activity of [OMIM]Br-AlCl$_3$ for alkylation

The addition of a Brønsted acid to [OMIM]Br-AlCl$_3$ leads to the formation of a Brønsted superacid. As reported by Smith and coworkers, the acidic strength of HCl in chloroaluminate ILs is comparable to 100% sulfuric acid.[34,35] With AlCl$_3$ based ILs, the Brønsted acidity is simply increased by enhancing the concentration of protons.[36] Adding water as a proton source to halogenoaluminate ILs leads to more complex but very similar acidic compounds compared to HCl,[37] see Scheme 3. The favourable effect of water was also demonstrated for the alkylation of benzene with dodecene.[36]

$$[Al_2Cl_7]^- + H_2O \longrightarrow H[Al_2Cl_7OH]^- \rightleftharpoons [Al_2Cl_6OH]^- + HCl$$

$$HCl + [Al_2Cl_7]^- \longrightarrow H^+ + 2\,[AlCl_4]^-$$

Scheme 3 Reaction pathway generating superacidic acids in Lewis acidic ionic liquids.

Hence, water seems to be a promising additive to tune the acidity of the IL and the selectivity of the alkylation. Water was added to the hydrocarbon phase in a range of 30 ppm to 120 ppm (by weight). The results are shown in Fig. 3.

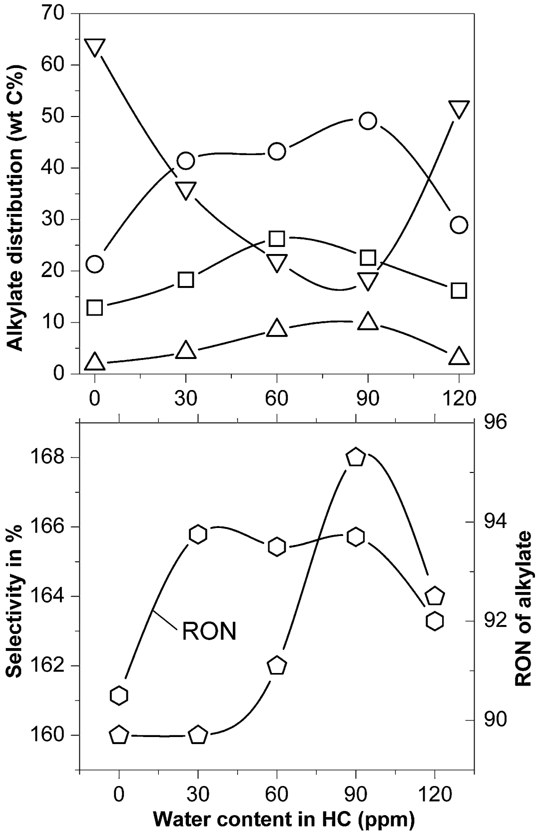


Fig. 3 Influence of water content in HC on the C$_4$-alkylation (−5 °C; 600 kPa; stirring time = 60 min; IL/olefin mol ratio = 0.4; molar fraction of AlCl$_3$ = 0.6, □ C$_5$–C$_7$, ○ TMPS, △ other C$_8$, ▽ C$_{9+}$).

As long as the acidity does not exceed an upper acidity limit the desired reactions to the TMPs are favoured. The best results are obtained for a water content of 90 ppm, *e.g.* the TMP yield rises from 20 wt% (no water) up to 50 wt% (90 ppm water), which corresponds to an increase of the RON from 90.5 to about 94 (Fig. 3). The addition of water also has a positive effect on the content of dimethylhexanes (DMHs) (other C_8) and of the C_5 to C_7 fraction as the yield of both doubles from 5 to 10 wt% and from about 12 to 25 wt%, respectively. In return, the content of the C_{9+}-fraction drops from about 65 wt% (no water) to 15 wt% (90 ppm water). If the water content is increased further (120 ppm), the acidity gets obviously too high, and more higher hydrocarbons (C_{9+}) are formed and the RON drops again.

4.3 Influence of additives containing a sulfonic acid group

Since water as a protic compound shows a remarkable effect on the alkylation, other additives containing acidic protons like SO_3H-groups seem to be promising as the $AlCl_3$ may react with sulfonic acid, and superacidic protons are generated.[31] Here, two cation exchange resins (Dowex, Amberlyst) as well as the IL [(HO$_3$SBu)MIM]HSO$_4$ were chosen as additives as they represent a homogeneous (IL) and a solid catalyst/promotor (resin), respectively. For the resin, the influence of water addition was also studied.

The results are depicted in Fig. 4. The TMPs content increases from 21 wt% (without additive) to 41 wt% (Dowex as additive), and further to 47 wt%, if Dowex and water (30 ppm in the organic phase) are used as additive. Further investigations on the effect of the resin and on the effect of both resin and water are discussed below.

The highest yield in these series of experiments is 53 wt%, which is reached with [(HO$_3$SBu)MIM]HSO$_4$ as the additive. The corresponding RON value increases from 90.5 to 95, respectively (Fig. 4). An increase of the hydrocarbon chain length of the cation containing the sulfonic acid group leads to a very similar result ([(HO$_3$SBu)HIM]HSO$_4$, 53 wt% of TMPs and RON 95).

The positive effect both of the resin (Dowex) and of the IL [(HO$_3$SBu)MIM]HSO$_4$ has to be referred to the reaction between [OMIM]Br-AlCl$_3$ and the sulfonic acid groups of the resin or of [(HO$_3$SBu)MIM]HSO$_4$, respectively, which leads to superacidic species (Scheme 2). This is confirmed by the result that the alkylation does not take place when either [(HO$_3$SBu)MIM]HSO$_4$) or the resin are used alone as the catalyst.

An increase of the hydrocarbon chain length of the cation containing the sulfonic acid group leads to a very similar result ([(HO$_3$SBu)HIM]HSO$_4$) (about 53 wt% of TMPs and RON 95). To the contrary, the variation of the anion shows a significant influence on the stirring and mixing ability under the chosen conditions. The anions *p*-toluenesulfonate (PTSA), trifluoromethanesulfonate ($CF_3SO_3^-$), and methylsulfonate ($CH_3SO_3^-$) formed highly viscous mixtures producing enormous difficulties in stirring and mixing during the alkylation. The high viscosity is probably the result of the reaction of sulfonate anions with the Lewis acid.

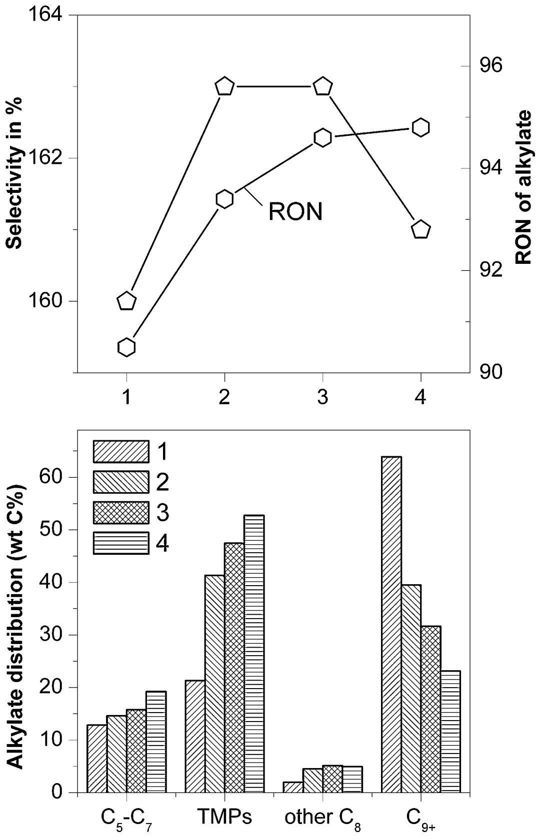


Fig. 4 Influence of additives containing SO_3H-group on alkylation of isobutane with 2-butene (conditions see Fig. 2). (1): [OMIM]Br-AlCl$_3$ (without additive); (2): [OMIM]Br-AlCl$_3$ + Dowex (0.16 g/g of [OMIM]Br-AlCl$_3$); (3): [OMIM]Br-AlCl$_3$ + Dowex (0.16 g/g of [OMIM]Br-AlCl$_3$) + 30 ppm H_2O in HC; (4): [OMIM]Br-AlCl$_3$ + ([(HO$_3$SBu)MIM]HSO$_4$ (0.24 g/g of [OMIM]Br-AlCl$_3$).

As described above, water adsorbed on the resin has an additional positive effect. Thus the influence of water was studied in more detail whereby the amount of resin was kept constant. Up to 6 wt% of water (related to the mass of resin) were adsorbed on the resin before it was contacted with the IL. The results are depicted in Fig. 5. For a better comparison with the data shown in Fig. 3, the water content related to the hydrocarbons (in ppm by weight) is also given (bottom scale in Fig. 5).

Using water adsorbed on the resin (Dowex) leads to a higher quality of the alkylate compared to Dowex or water only (Fig. 3). The TMP content rises from 40 wt% (no water) to 60 wt% (3 wt% of water in resin) while the content of heavy products decreases from 40 to 20 wt%, respectively. However, a water content of the resin of more than 3 wt% is unfavourable as the alkylate quality then starts to decrease (Fig. 5). Thus the optimal water content is 3 wt% related to the resin (or 225 ppm related to HC). This content is higher than the optimal value found for water mixed with HC (30 to 90 ppm, Fig. 3). A possible explanation is that a certain amount of water is absorbed inside the resin and therefore kept away from the Lewis acidic ILs. For the optimal water content of 225 ppm (related to HC), an alkylate selectivity of 164% was reached.

The influence of the resin-to-IL ratio is shown in Fig. 6. For these experiments, the content of water was kept constant at the optimal value of 3 wt%. The results show that it is necessary to establish an excess of $[Al_2Cl_7]^-$ to saturate the resin (Fig. 6).

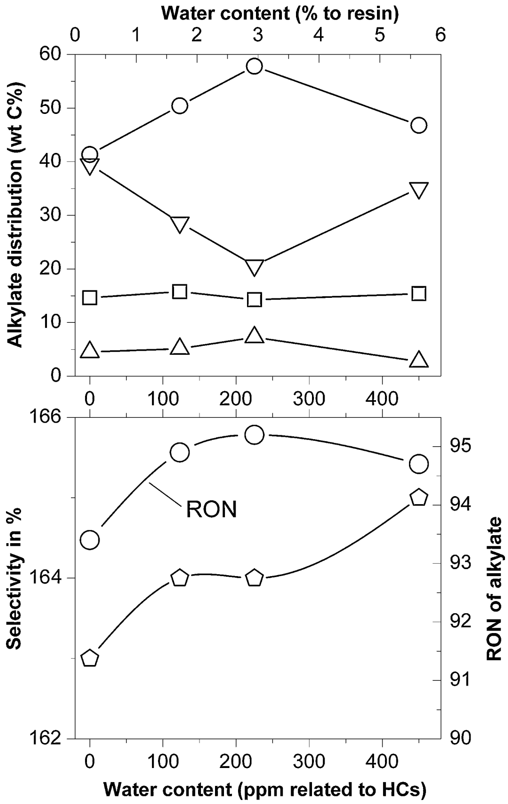


Fig. 5 Influence of resin adsorbed water on alkylation (resin: Dowex (0.16 g/g of IL, other conditions see Fig. 2, □ C_5–C_7, ○ TMPS, △ other C_8, ▽ C_{9+})).

This ensures that free Lewis acidic sites are still present and can react with HCl (liberated from the reaction of resin or water with the IL). The optimum resin-to-IL ratio is 0.15 g/g which corresponds to a molar ratio of SO_3H-groups to $[Al_2Cl_7]^-$ of 0.5.

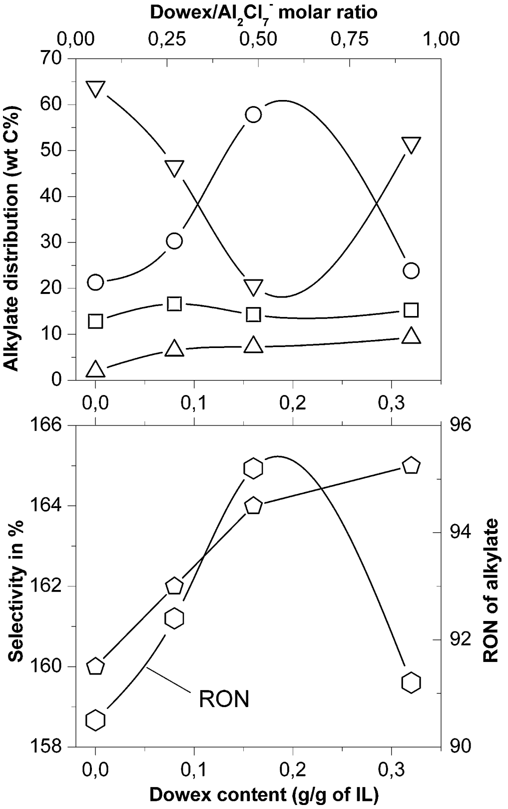


Fig. 6 Influence of Dowex resin content on alkylation of isobutane with 2-butene (Dowex with 3 wt% adsorbed water, other conditions see Fig. 2, □ C_5–C_7, ○ TMPS, △ other C_8, ▽ C_{9+}).

4.4 Reusability of the investigated catalytic systems

Since the reusability of a catalyst is extremely important, this parameter was studied in eleven consecutive runs. The reaction was performed ten times without withdrawing of the product phase. Thus after a reaction time of 15 min (to ensure complete conversion of 2-butene), a new feed was recharged. The product of the eleventh batch was finally analysed. The alkylate distribution and the RON are displayed in Fig. 7 (left) for the system [OMIM]Br-$AlCl_3$ modified by Dowex and water. The composition and RON of the alkylate is only slightly reduced after ten cycles, and the presence of water does not result in the deactivation of the catalyst. This demonstrates the high reusability of this catalyst. Similar reuseability experiments were done with all other catalytic systems investigated in this work ([OMIM]Br-$AlCl_3$ with and without water, and mixtures of [OMIM]Br-$AlCl_3$ and $[(HO_3SBu)MIM]HSO_4$). They all showed no or a very low deactivation rate.

For comparison with an industrially used catalyst, the same experiments were carried out with sulfuric acid (Fig. 7, right).

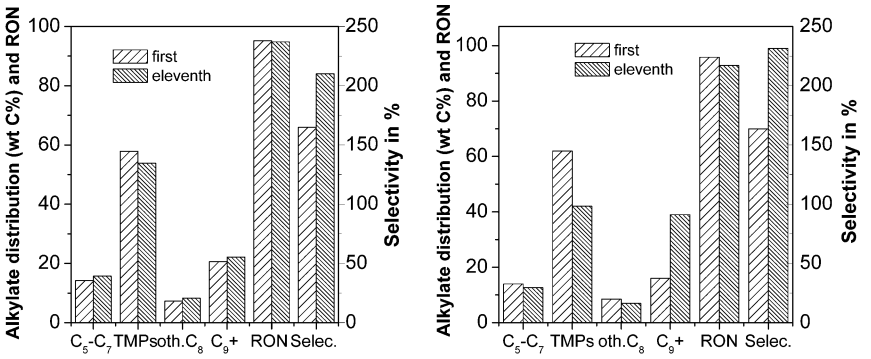


Fig. 7 Comparison of reusability of [OMIM]Br-$AlCl_3$–Dowex–water and of H_2SO_4 as catalyst in isobutane/2-butene-alkylation. Left: IL catalyst (5 °C; 600 kpa; P/O molar ratio = 13; stirring time = 15 min, $x_{AlCl_3} = 0.6$; conditions see Fig. 1); right: experiment with H_2SO_4 (42 vol% of reaction mixture).

Table 1 TMP content and RON of products of the investigated catalyst systems (–5 °C; 600 kPa; P/O ratio (mol) = 13; stirring time = 60 min; $x_{\mathrm{AlCl_3}} = 0.6$; IL/olefin mol ratio = 0.4; amount of water = 30 ppm (in HCs)

	Water content (ppm in HCs)	Content of [(HO$_3$SBu)MIM] HSO$_4$ (g/g [OMIM]Br-AlCl$_3$)	Resin content (g/g IL)	TMPs (% C)	RON	Selectivity ($m_{\mathrm{alkylate}}/m_{\mathrm{2\text{-}butene}}$)
[OMIM]Br-AlCl$_3$	—	—	—	21.3	90.5	160%
[OMIM]Br-AlCl$_3$	30	—	—	47.8	94.4	162%
[OMIM]Br-AlCl$_3$	—	0.5	—	52.7	94.8	161%
[OMIM]Br-AlCl$_3$	225	—	0.15[a]	57.8	95.2	164%
[OMIM]Br-AlCl$_3$	225	—	0.16[b]	63.9	96.2	165%
H$_2$SO$_4$	—	—	—	59.1	94.9	176%

[a] Dowex (surface acid concentration: 0.15 meq) [b] Amberlyst-15 (surface acid conc.: 0.11 meq)

After eleven cycles, the product quality decreases and oligomerisation reactions are favoured. (2-Butene conversion was almost 100%.)

5. Conclusions

A summary of some of the best alkylation results for the various IL systems as well as the result with sulfuric acid is shown in Table 1.

For the three best systems (entries 3, 4 and 5 in Table 1), the yield of TMPs and the RON is comparable or higher than that with H_2SO_4 as the alkylation catalyst. Thus, the approach to control the Brønsted acidity by forming superacidic IL species or superacidic species in ILs *via* protic additives is promising. In all cases, the products were separated simply by decantation, and thus the catalyst can be reused. Moreover, the formation of acid soluble heavy hydrocarbons is minimised.

Abbreviations

[OMIM]Br/AlCl$_3$	1-n-octyl-3-methylimidazolium bromide aluminium chloride
IL	ionic liquid
[(HO$_3$SBu)MIM]	1-methyl-3-(butyl-4-sulfonic)
[HSO$_4$]	imidazolium hydrogensulfate
TMPs	trimethylpentanes
RON	research octane number
[CF$_3$SO$_3$]	triflouromethanesulfonate
[PTSA]	*p*-toluene sulfonate
[CH$_3$SO$_3$]	trifluoroacetate
DMHs	dimethylhexanes
HC	hydrocarbon
P	paraffin
O	olefin

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